Density Functional Theory Study of Aromatic Adsorption on Iron Surfaces



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To the fourteen women who lost their lives at the École Polytechnique massacre in my hometown of Montreal on December 6th, 1989. This dedication follows in my mother's footsteps, as she also dedicated her PhD thesis to this group composed mainly of female engineering students. May they never be forgotten.

Declaration

This dissertation is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text. It is not substantially the same as any that I have submitted, or, is being concurrently submitted for a degree or diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. I further state that no substantial part of my dissertation has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or Similar institution except as declared in the salready been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. It does not exceed the specified length limit of 60,000 words as defined by the Physics and Chemistry Degree Committee.

Signature: _____

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Date: _____

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Abstract

Density Functional Theory Study of Aromatic Adsorption on Iron Surfaces Bianca Provost

This thesis studies the adsorption behaviour of aromatic molecules on iron surfaces using density functional theory (DFT) calculations. The adsorbates studied are benzene (C_6H_6) , naphthalene (C_8H_{10}) and quinolinium $(C_7H_{10}N^+)$ as well as a molecule composed of these fragments known to inhibit acid corrosion on steels used in the oil and gas industry (naphthylmethylquinolinium, $C_{20}H_{16}N^+$ or NMQ+). This work represents an effort towards a mechanistic understanding of acid corrosion inhibition of steel as well the development of a general understanding of aromatic adsorption on iron, which has rarely been studied computationally or experimentally.

First, the results of a DFT study of benzene adsorption on the three most stable surface facets of bcc iron, including flat {110}, kinked {100} and stepped {211} surfaces, are presented. All stable adsorption sites are identified and the most energetically favourable adsorption sites are compared across the three surfaces. In general, sites which appear centered over hollow-like surface sites are preferred. The effect of van der Waals (vdW) corrected DFT on binding site energetics and geometries has also been studied by way of the Tkatchenko-Scheffler (TS) correction. It shows a strong influence on the adsorption energies, some effect on the relative energetic ordering of sites and little to no effect on adsorption geometries.

Second, the adsorption of naphthalene and quinolinium is studied on the most stable surface of bcc iron, Fe{110}, using DFT. Quinolinium and naphthalene differ only by one atom but their electronic structure differences result in significant changes in preferred adsorption site energetics and geometries. Quinolinium tends to adsorb preferentially in geometries which allow its nitrogen atom to bind in an atop position on the Fe{110} surface, in agreement with prior DFT work on NHx adsorbed on Fe{211} showing tetravalent arrangements of adsorbed nitrogen are preferred. The preferred naphthalene adsorption configuration presents the highest overall symmetry of all investigated naphthalene sites. The adsorption energy for the top quinolinium geometry is 1.12 eV stronger than that found for the best naphthalene adsorption geometry.

Finally, the adsorption behaviour of NMQ+ on the Fe{110} surface is studied using DFT. Prior to the DFT adsorption study, a semi-empirical level conformational search on the NMQ+ ion is conducted to identify preferred gas phase conformations of the ion. Energetically favoured structures are optimised using DFT, which further refines the search and identifies two different favourable gas phase NMQ+ conformations. Six different starting NMQ+ geometries on the Fe{110} surface are tested based on the two favourable gas phase conformations, and reveal a strongly favoured site (1.4 eV stronger adsorption than the next best site) which presents double dehydrogenation of the quinolinium moiety. The next best site also presents double dehydrogenation, but on the methyl linker and quinolinium moiety.

Beyond providing insight into the mode of action of molecules intended for corrosion inhibition of steels, this work provides a fundamental understanding of the behaviour of adsorbed aromatic molecules on iron surfaces, which can play a role in a number of industrially relevant applications, including organic solar cells, transistors and LEDs, heterogeneous catalysts and medical implants.

Contents

1	Intro	oductio	on	1
	1.1	Aroma	tic adsorption on metallic surfaces	1
	1.2	Corros	ion	2
		1.2.1	Chemistry of corrosion	3
	1.3	Acid c	orrosion inhibition	6
		1.3.1	Mode of action	8
	1.4	Comp	utational studies of corrosion inhibition	10
		1.4.1	Molecular computational chemistry	11
		1.4.2	Computational surface science	12
	1.5	Object	ive	14
	1.6	Overvi	ew	15
2	The	ory and	l Methods	17
2	The 2.1	ory and The So	l Methods	17 17
2	The 2.1 2.2	o ry and The So Densit	l Methods chrödinger equation	17 17 19
2	The 2.1 2.2	ory and The So Densit 2.2.1	I Methods chrödinger equation	17 17 19 20
2	The 2.1 2.2	The So Densit 2.2.1 2.2.2	I Methods chrödinger equation	 17 17 19 20 21
2	The 2.1 2.2	The So Densit 2.2.1 2.2.2 2.2.3	I Methods chrödinger equation	 17 17 19 20 21 22
2	The 2.1 2.2	The So Densit 2.2.1 2.2.2 2.2.3 2.2.4	I Methods chrödinger equation	 17 17 19 20 21 22 24
2	Theo2.12.22.3	The So Densit 2.2.1 2.2.2 2.2.3 2.2.4 Solid S	I Methods chrödinger equation y Functional Theory Exchange-correlation energy: $E_{xc}[\rho]$ Spin polarisation Dispersion corrections Hybrid functionals State DFT: the CASTEP code	 17 19 20 21 22 24 25
2	Theo 2.1 2.2 2.3	The So Densit 2.2.1 2.2.2 2.2.3 2.2.4 Solid S 2.3.1	I Methods chrödinger equation y Functional Theory Exchange-correlation energy: $E_{xc}[\rho]$ Spin polarisation Dispersion corrections Hybrid functionals State DFT: the CASTEP code Plane wave basis	 17 17 19 20 21 22 24 25 26
2	Theo2.12.22.3	The So Densit 2.2.1 2.2.2 2.2.3 2.2.4 Solid S 2.3.1 2.3.2	I Methods chrödinger equation y Functional Theory Exchange-correlation energy: $E_{xc}[\rho]$ Spin polarisation Dispersion corrections Hybrid functionals State DFT: the CASTEP code Plane wave basis Pseudopotentials	 17 17 19 20 21 22 24 25 26 27

		2.3.3	Electronic energy minimisation	29
		2.3.4	Geometry optimisation	30
	2.4	Surfac	e calculations	30
		2.4.1	Surface properties	31
		2.4.2	Adsorbate-surface system properties	33
	2.5	Molec	ular DFT: the Gaussian code	36
		2.5.1	Atomic basis sets	36
		2.5.2	Solvation	39
		2.5.3	Semi-empirical methods	40
•	п. п			40
3	ге в	Sulk and	d Surface Studies	43
	3.1	Introd	uction	43
	3.2	Bulk b	cc Fe crystal	44
	3.3	bcc Fe	surface slab Studies	46
		3.3.1	Comparison to Literature Values	47
4	Ben	zene A	dsorption on Fe Surfaces	51
4	Ben 4.1	zene A o Introd	dsorption on Fe Surfaces	51 51
4	Ben 4.1	zene A Introd 4.1.1	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces	51 51 51
4	Ben 4.1	zene A Introd 4.1.1 4.1.2	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces	51 51 51 53
4	Ben 4.1 4.2	zene Ad Introd 4.1.1 4.1.2 Benze:	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110}	51 51 51 53 56
4	Ben 4.1 4.2	zene A Introd 4.1.1 4.1.2 Benze 4.2.1	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110} Introduction	51 51 53 56 56
4	Ben 4.1 4.2	zene A Introd 4.1.1 4.1.2 Benze 4.2.1 4.2.2	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110} Introduction Adsorption geometries and energies	51 51 53 56 56 56
4	Ben: 4.1 4.2	zene A Introd 4.1.1 4.1.2 Benze: 4.2.1 4.2.2 4.2.3	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110} Introduction Adsorption geometries and energies Charge density difference	51 51 53 56 56 58 63
4	Ben 4.1 4.2	zene A Introd 4.1.1 4.1.2 Benze: 4.2.1 4.2.2 4.2.3 4.2.3	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110} Introduction Adsorption geometries and energies Charge density difference Spin density	51 51 53 56 56 58 63 63
4	Ben : 4.1 4.2	zene A Introd 4.1.1 4.1.2 Benze: 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110} Introduction Adsorption geometries and energies Charge density difference Spin density Atomic charges and spin	51 51 53 56 56 58 63 63 63
4	Ben : 4.1 4.2	zene A Introd 4.1.1 4.1.2 Benze 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 4.2.5 4.2.6	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110} Introduction Adsorption geometries and energies Charge density difference Spin density Atomic charges and spin DOS and PDOS	51 51 53 56 56 58 63 63 63 63 66
4	Ben 4.1 4.2	zene A Introd 4.1.1 4.1.2 Benzer 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 4.2.6 4.2.7	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110} Introduction Adsorption geometries and energies Charge density difference Spin density Atomic charges and spin DOS and PDOS Workfunction	51 51 53 56 56 58 63 63 63 63 67 71
4	Ben 4.1 4.2	zene A Introd 4.1.1 4.1.2 Benzer 4.2.1 4.2.2 4.2.3 4.2.4 4.2.5 4.2.5 4.2.6 4.2.7 Benzer	dsorption on Fe Surfaces uction Benzene adsorption on metallic surfaces Benzene adsorption on Fe surfaces ne/Fe{110} Introduction Adsorption geometries and energies Charge density difference Spin density DOS and PDOS Workfunction ne/Fe{100}	51 51 53 56 58 63 63 63 66 67 71 73

		4.3.2	Adsorption geometries and energies	74
		4.3.3	Charge density difference	81
		4.3.4	Spin density	82
		4.3.5	Atomic charges and spin	82
		4.3.6	DOS and PDOS	85
	4.4	Benze	ne/Fe{211}	88
		4.4.1	Introduction	88
		4.4.2	Adsorption geometries and energies	89
		4.4.3	Charge density difference	97
		4.4.4	Spin density	97
		4.4.5	Atomic charges and spin	99
		4.4.6	DOS and PDOS	01
		4.4.7	Workfunction	05
	4.5	Discus	sion and conclusions	05
		4.5.1	Benzene on Fe{110}, Fe{100} and Fe{211}	06
		4.5.2	Benzene on other surfaces	11
		4.5.3	Conclusion	12
5	Poly	4.5.3 varoma	Conclusion	12 15
5	Poly 5.1	4.5.3 varoma Introd	Conclusion	12 15 15
5	Poly 5.1	4.5.3 varoma Introd 5.1.1	Conclusion 1 tic and Heteroatomic Hydrocarbon Adsorption on Fe{110} 1 uction 1 PAH adsorption on transition metal surfaces 1	12 15 15 16
5	Poly 5.1 5.2	4.5.3 varoma Introd 5.1.1 Napht	Conclusion 1 tic and Heteroatomic Hydrocarbon Adsorption on Fe{110} 1 uction 1 PAH adsorption on transition metal surfaces 1 halene/Fe{110} 1	12 15 15 16 21
5	Poly 5.1 5.2	4.5.3 xaroma Introd 5.1.1 Napht 5.2.1	Conclusion 1 tic and Heteroatomic Hydrocarbon Adsorption on Fe{110} 1 uction 1 PAH adsorption on transition metal surfaces 1 halene/Fe{110} 1 Introduction 1	12 15 16 21 21
5	Poly 5.1 5.2	4.5.3 aroma Introd 5.1.1 Napht 5.2.1 5.2.2	Conclusion 1 tic and Heteroatomic Hydrocarbon Adsorption on Fe{110} 1 uction 1 PAH adsorption on transition metal surfaces 1 halene/Fe{110} 1 Introduction 1 Gas-phase naphthalene 1	12 15 16 21 21 23
5	Poly 5.1 5.2	4.5.3 aroma Introd 5.1.1 Napht 5.2.1 5.2.2 5.2.3	Conclusion 1 tic and Heteroatomic Hydrocarbon Adsorption on Fe{110} 1 uction 1 PAH adsorption on transition metal surfaces 1 halene/Fe{110} 1 Introduction 1 Gas-phase naphthalene 1 Adsorption geometries and energies 1	12 15 15 21 21 23 23
5	Poly 5.1 5.2	4.5.3 aroma Introd 5.1.1 Napht 5.2.1 5.2.2 5.2.3 5.2.4	Conclusion 1 tic and Heteroatomic Hydrocarbon Adsorption on Fe{110} 1 uction 1 PAH adsorption on transition metal surfaces 1 halene/Fe{110} 1 Introduction 1 Gas-phase naphthalene 1 Adsorption geometries and energies 1 Charge density difference 1	12 15 16 21 23 23 32
5	Poly 5.1 5.2	4.5.3 varoma Introd 5.1.1 Napht 5.2.1 5.2.2 5.2.3 5.2.4 5.2.5	Conclusion	12 15 16 21 23 23 32 36
5	Poly 5.1 5.2	4.5.3 varoma Introd 5.1.1 Napht 5.2.1 5.2.2 5.2.3 5.2.4 5.2.5 5.2.6	Conclusion	12 15 15 21 23 23 32 36 36
5	Poly 5.1 5.2	4.5.3 aroma Introd 5.1.1 Napht 5.2.1 5.2.2 5.2.3 5.2.4 5.2.5 5.2.6 5.2.7	Conclusion 1 tic and Heteroatomic Hydrocarbon Adsorption on Fe{110} 1 uction 1 PAH adsorption on transition metal surfaces 1 halene/Fe{110} 1 Introduction 1 Gas-phase naphthalene 1 Adsorption geometries and energies 1 Charge density difference 1 Spin density 1 Atomic charges and spin 1 DOS and PDOS 1	12 15 16 21 23 23 32 36 36 38
5	Poly 5.1 5.2	4.5.3 aroma Introd 5.1.1 Napht 5.2.1 5.2.2 5.2.3 5.2.4 5.2.5 5.2.6 5.2.7 5.2.8	Conclusion 1 tic and Heteroatomic Hydrocarbon Adsorption on Fe{110} 1 uction 1 PAH adsorption on transition metal surfaces 1 halene/Fe{110} 1 Introduction 1 Gas-phase naphthalene 1 Adsorption geometries and energies 1 Charge density difference 1 Spin density 1 Atomic charges and spin 1 Workfunction 1	12 15 16 21 23 32 36 36 38 38

	5.3	Quino	linium/Fe{110}
		5.3.1	Introduction
		5.3.2	Gas-phase quinolinium
		5.3.3	Adsorption geometries and energies
		5.3.4	Charge density difference
		5.3.5	Spin density
		5.3.6	Atomic charges and spin
		5.3.7	DOS and PDOS
		5.3.8	Workfunction
	5.4	Discus	sion and Conclusions
		5.4.1	Benzene, Naphthalene and Quinolinium on Fe{110}
		5.4.2	Naphthalene and heteroatomics on other surfaces
6	NMO	Q+: Ga	s-phase and Adsorbed on Fe{110} 175
	6.1	Introd	uction
		6.1.1	NMQCl and NMQ+ as ACI
		6.1.2	Related works
	6.2	Gas-Pł	nase NMQ+
		6.2.1	Conformational search
		6.2.2	MO diagram
		6.2.3	Atomic charges
		6.2.4	Solvation
	6.3	NMQ+	-/Fe{110}
		6.3.1	Introduction
		6.3.2	Adsorption geometries and energies
		6.3.3	Charge density difference
		6.3.4	Spin density
		6.3.5	Atomic charges and spin
		6.3.6	DOS and PDOS
		6.3.7	Workfunction

	6.4	Discussi	on and Conclusions	218
		6.4.1 0	Comparison to naphthalene and quinolinium on Fe $\{110\}$	220
		6.4.2 0	Comparison to other systems	222
		6.4.3 (Conclusions	226
7	Con	clusions		229
	7.1	Summar	ry	229
	7.2	Future V	Nork	231
A	Fe S	lab Conv	vergence Testing	235
	A.1	Fe{110}	•	235
		A.1.1 S	Slab layer number	235
		A.1.2 V	Vacuum spacing	236
	A.2	Fe{100}	•••••••••••••••••••••••••••••••••••••••	237
		A.2.1 S	Slab layer number	237
		A.2.2 V	Vacuum spacing	237
	A.3	Fe{211}	•••••••••••••••••••••••••••••••••••••••	238
		A.3.1 S	Slab layer number	238
		A.3.2 V	Vacuum spacing	239
B	Ben	zene/Fe:	Comparisons to Literature	241
	B.1	Benzene	e/Fe{110}	241
	B.2	Benzene	e/Fe{100}	242
Re	feren	ices		243

List of Figures

1.1	Typical chemical reactions and products from acidic steel corrosion	4
1.2	Pourbaix (potential-pH) diagram for iron	6
1.3	Summary of interactions involved in adsorption of ACI at the atomistic scale	8
2.1	Graphical representation of original wavefunction (Ψ), norm-conserving (Ψ_{nc})	
	and ultrasoft (Ψ_{us}) pseudopotentials	27
2.2	Example surface supercell with adsorbate, bulk, top surface and vacuum	
	layers indicated.	31
3.1	k-point sampling convergence tests on bcc Fe conventional cell lattice constant,	
	total energy and magnetic moment at a cutoff energy of 340 eV. \ldots .	45
3.2	Energy cut-off sampling convergence tests on bcc Fe conventional cell lattice	
	constant, total energy and magnetic moment at a k-point Monkhorst-Pack	
	grid of $7 \times 7 \times 7$	45
4.1	Benzene/Fe{110}: simulation cell dimensions	57
4.2	Benzene/Fe{110}: orientations selected for study	58
4.3	Benzene/Fe{110}: 0° rotated PBE-TS optimised benzene binding sites \ldots	59
4.4	Benzene/Fe{110}: 30° rotated PBE-TS optimised benzene binding sites \ldots	60
4.5	Benzene/Fe{110}: charge density difference	64
4.6	Benzene/Fe{110}: spin density	65
4.7	Benzene/Fe{110}: Projected density of states (PDOS) for interacting C-Fe	
	pair within the H-30° site	69

4.8	Benzene/Fe{110}: Projected density of states (PDOS) for interacting C-Fe
	pair within the S-0° site $\ldots \ldots \ldots$
4.9	Benzene/Fe{110}: E_{vac} calculation setup
4.10	Benzene/Fe{100}: simulation cell dimensions
4.11	Benzene/Fe{100}: orientations selected for study 75
4.12	Benzene/Fe{100}: PBE-TS optimised benzene binding sites
4.13	Benzene/Fe{100}: further PBE-TS optimised benzene binding sites 79
4.14	Benzene/Fe{100}: charge density difference
4.15	Benzene/Fe{100}: spin density 84
4.16	Benzene/Fe{100}: Projected density of states (PDOS) for interacting C-Fe
	pair within the H site
4.17	Benzene/Fe{211}: simulation cell dimensions
4.18	Benzene/Fe{211}: orientations selected for study 90
4.19	Benzene/Fe{211}: top three strongest PBE-TS optimised benzene binding sites 94
4.20	Benzene/Fe{211}: further PBE-TS optimised benzene binding sites 95
4.21	Benzene/Fe{211}:PBE-TS optimised atop benzene binding sites
4.22	Benzene/Fe{211}: charge density difference
4.23	Benzene/Fe{211}: spin density
4.24	Benzene/Fe{211}: Projected density of states (PDOS) for interacting C2-Fe40
	pair within BU2 site
4.25	Benzene/Fe{211}: Projected density of states (PDOS) for interacting C1-Fe15
	pair within BU2 site
5.1	Gas-phase naphthalene PBE-TS optimised structure and bond lengths 123
5.2	Naphthalene/Fe{110}: orientations selected for study
5.3	Naphthalene/Fe $\{110\}$: 0° and 120° rotated PBE-TS optimised naphthalene
	binding sites
5.4	Naphthalene/Fe{110}: 150° rotated PBE-TS optimised naphthalene binding
	sites

5.5	Comparison of adsorption energies for all PBE (blue) and PBE-TS (red) opti-
	mised naphthalene/Fe{110} sites
5.6	Naphthalene/Fe{110}: charge density difference
5.7	Naphthalene MO diagram
5.8	Naphthalene/Fe{110}: spin density
5.9	Naphthalene/Fe{110}: Projected density of states (PDOS) for interacting
	C-Fe pair within the LC site
5.10	Gas-phase quinolinium cation: charge-corrected total energy
5.11	Gas-phase quinolinium PBE-TS optimised structure and bond lengths 146
5.12	Quinolinium/Fe{110}: orientations selected for study
5.13	Quinolinium/Fe{110}: 0° and 120° rotated PBE-TS optimised quinolinium
	binding sites
5.14	Quinolinium/Fe{110}: 150° rotated PBE-TS optimised quinolinium binding
	sites
5.15	Quinolinium/Fe $\{110\}$: 125° rotated PBE-TS optimised quinolinium binding site155
5.16	Comparison of adsorption energies for all PBE (blue) and PBE-TS (red) opti-
	mised quinolinium/Fe{110} sites
5.17	Quinolinium/Fe{110}: charge density difference
5.18	Quinolinium MO diagram
5.19	Quinolinium/Fe{110}: spin density
5.20	Quinolinium/Fe{110}: Projected density of states (PDOS) for interacting
	C-Fe pair within the HH-NA site
5.21	Quinolinium/Fe{110}: Projected density of states (PDOS) for interacting
	N-Fe pair within the HH-NA site
5.22	Comparison of Naphthalene HH and Quinolinium HH-NA adsorption sites on
	Fe{110}
6.1	Naphthylmethyl quinolinium chloride (NMQCl) chemical structure 176
6.2	Cinchonidine (CD, $C_{19}H_{22}N_2O$) molecular structure and torsional angles used
	in conformational search

6.3	Coverage-dependant adsorption modes of cinchonidine on $Pt\{111\}$ surface 181
6.4	NMQ+ torsional angles scanned in the conformational search
6.5	Plot of energy differences resulting from conformational study of NMQ+ 184
6.6	Low-energy NMQ+ conformers identified in PM6 conformational scan and
	DFT-optimised structures
6.7	Further representations of DFT-optimised low-energy structures including
	mirror-image rotamer relationships
6.8	Calculated molecular orbital diagram for B and C-type NMQ+ conformers 190
6.9	Gas-phase NMQ+ B conformer calculated Mulliken charges
6.10	Gas-phase quinolinium and naphthalene calculated Mulliken charges 192
6.11	Three possible adsorption models for the interaction of NMQ+ with Fe{110}. 195
6.12	NMQ+/Fe{110}: orientations selected for study 200
6.13	NMQ+/Fe{110}: B conformer PBE-TS optimised NMQ+ binding sites 202
6.14	NMQ+/Fe{110}: C conformer PBE-TS optimised NMQ+ binding sites 203
6.15	NMQ+/Fe{110}: charge density difference
6.16	NMQ+/Fe{110}: spin density 211
6.17	NMQ+/Fe{110}: Projected density of states (PDOS) for interacting C-Fe pair
	within the C-N-HH site

List of Tables

1.1	Common acidising fluid components	7
3.1	Calculated lattice constant, magnetic moment and bulk modulus for bulk bcc Fe	46
3.2	Calculated lattice constant, magnetic moment and bulk modulus for bulk bcc	
	Fe including van der Waals correction	46
3.3	Parameters describing the bcc Fe slabs used throughout this thesis	47
3.4	Interlayer separation prior to surface relaxation (d) and changes $(\%)$ due to	
	surface relaxation for bcc Fe surfaces	48
3.5	Surface energy (γ) and work function (ϕ) for relaxed bcc Fe surfaces	49
3.6	Interlayer separation prior to surface relaxation (d) and changes $(\%)$ in	
	interlayer spacing due to surface relaxation for bcc Fe surfaces with TS van	
	der Waals correction	50
3.7	Surface energy (γ) and work function (ϕ) for relaxed bcc Fe surfaces with	
	TS van der Waals correction	50
4.1	Benzene/Fe{110} simulation parameters	56
4.2	Benzene/Fe{110}: calculated energies	61
4.3	Benzene/Fe{110}: calculated geometric parameters	62
4.4	Benzene/Fe{110}: Hirshfeld charges and spin	66
4.5	Benzene/Fe{110}: Workfunction results	72
4.6	Benzene/Fe{100}: simulation parameters	74
4.7	Benzene/Fe{100}: calculated energies	77
4.8	Benzene/Fe{100}: calculated geometric parameters	80

4.9	Benzene/Fe{100}: Hirshfeld charges and spin 85
4.10	Benzene/Fe{211} simulation parameters
4.11	Benzene/Fe{211}: geometry optimisation outcomes
4.12	Benzene/Fe{211}: calculated energies 91
4.13	Benzene/Fe{211}: calculated geometric parameters
4.14	Benzene/Fe{211}: Hirshfeld charges and spin
4.15	Benzene/Fe{211}: Workfunction results
4.16	Computed and experimental benzene/TM surface workfunctions (ϕ) from
	literature
5.1	Naphthalene/Fe{110}: simulation parameters
5.2	Naphthalene/Fe{110}: Post-optimisation stability
5.3	Naphthalene/Fe{110}: calculated energies
5.4	Naphthalene/Fe{110}: calculated geometric parameters
5.5	Naphthalene/Fe{110}: Hirshfeld charges and spin
5.6	Naphthalene/Fe{110}: Workfunction results
5.7	Quinolinium/Fe{110} simulation parameters
5.8	Quinolinium/Fe{110}: Post-optimisation Stability
5.9	Quinolinium/Fe{110}: calculated energies
5.10	Quinolinium/Fe{110}: calculated geometric C parameters
5.11	Quinolinium/Fe{110}: calculated geometric N parameters
5.12	Quinolinium/Fe{110}: Hirshfeld charges and spin
5.13	Quinolinium/Fe{110}: Workfunction results
5.14	Benzene, Naphthalene and Quinolinium on Fe{110}: Hirshfeld charges 169
5.15	Benzene, Naphthalene and Quinolinium on Fe $\{110\}$: workfunction results 170
6.1	NMQ+ SCRF Solvation energies
6.2	NMQ+/Fe{110}: simulation parameters
6.3	NMQ+/Fe{110}: calculated energies
6.4	NMQ+/Fe{110}: calculated naphthyl-related geometric parameters 206

6.5	NMQ+/Fe{110}: calculated geometric quinolinium C parameters 207
6.6	NMQ+/Fe{110}: calculated geometric quinolinium N parameters 207
6.7	NMQ+/Fe{110}: calculated geometric methyl linker parameters 208
6.8	NMQ+/Fe{110}: Hirshfeld charges and spin
6.9	NMQ+/Fe{110}: Workfunction results
A.1	Spin in top layer, workfunction (ϕ) and surface energy (γ) values according
	to the number of slab layers of bcc Fe{110} used
A.2	Workfunction (ϕ) and surface energy (γ) values as a function of vacuum
	spacing for a 6-layer bcc Fe{110} slab
A.3	Spin in top layer, workfunction (ϕ) and surface energy (γ) values according
	to the number of slab layers of bcc Fe{100} used
A.4	Workfunction (ϕ) and surface energy (γ) values as a function of vacuum
	spacing for an 8-layer bcc Fe{100} slab
A.5	Spin in top layer, workfunction (ϕ) and surface energy (γ) values according
	to the number of slab layers of bcc Fe{211} used
A.6	Workfunction (ϕ) and surface energy (γ) values as a function of vacuum
	spacing for an 8-layer bcc Fe{211} slab
B.1	Comparison of parameters used in work of Hensley et al. and this work on
	Benzene/Fe{110}
B.2	Comparison of parameters used in work of Sun et al. and this work on
	Benzene/Fe{110}

Abbreviations

ACI	Acid Corrosion Inhibitor	2			
ACIP	Acid Corrosion Inhibition Package	7			
AO	Atomic Orbital				
ARUPS	Angle Resolved Ultraviolet Photoelectron Spectroscopy				
ATR-IR	Attenuated Total Reflectance - Infrared 18				
bcc	Body Centred Cubic				
BSSE	Basis Set Superposition Error				
CASTEP	CAmbridge Serial Total Energy Package	25			
CD	Cinchonidine				
CGTO	Contracted Gaussian-Type Orbitals				
DFT	Density Functional Theory	10			
DFTB	Density Functional based Tight Binding	14			
DOS	Density Of States				
DSS	Duplex Stainless Steel	177			
EDX	Energy Dispersive X-Ray	177			
EIS	Electrochemical Impedance Spectroscopy	118			
fcc	Face Centred Cubic				
GGA	Generalised Gradient Approximation				
GTO	Gaussian-Type Orbitals				
hcp	Hexagonal Close Packing				
HIOS	Hybrid Inorganic-Organic Systems	1			
LDA	Local Density Approximation				
LEED	Low Energy Electron Diffraction				
MC	Monte Carlo	14			

MD	Molecular Dynamics	14
МО	Molecular Orbital	
MP	Monkhorst-Pack	57
NEXAFS	Near-edge X-ray Absorption Fine Structure	121
NMQ+	Naphthylmethyl Quinolinium ion	14
NMQC1	Naphthylmethyl Quinolinium Chloride	
PAH	Polyaromatic Hydrocarbon	
PDOS	Projected Density of States	
QSAR	Quantitative Structure-Activity Relationship	11
QSPR	Quantitative Structure-Property Relationship	11
SCAC	Single Crystal Adsorption Calorimetry	
SEM	Scanning Electron Microscopy	
STM	Scanning Tunneling Microscopy	
STO	Slater-Type Orbitals	
TS	Tkatchenko-Scheffler	
UHV	Ultra High Vacuum	2
vdW	van der Waals	13
XPS	X-ray Photoelectron Spectroscopy	195

Chapter 1

Introduction

1.1 Aromatic adsorption on metallic surfaces

Hybrid Inorganic-Organic Systems (HIOS) are central to a large number of industrially and comercially relevant applications, including organic solar cells, ¹ molecular opto-electronics (transistors and LEDs),^{2,3} medical implants,⁴ heterogeneous catalysts,^{5,6} molecular switches and motors⁷ and corrosion protection⁸ among others. An interesting sub-category within HIOS is the aromatic molecule/metal surface combination. The interaction of delocalised aromatic π electrons with the metal surface, which allows for favourable flat-lying molecular adsorption, allows for a number of interesting applications.⁹ For substrates exhibiting magnetism, typically metallic surfaces including Fe, Co, Mn and Ni, further interesting applications apply. One example is organic spintronics, where inexpensive, mechanically flexible electronic devices benefit from spin-resolution, which allows for faster signal transmission and reduced power consumption.¹⁰

The behaviour of small aromatic molecules such as benzene upon metal surfaces provides key guidance in understanding the often much larger aromatic systems deployed in real HIOS-based applications. Fundamental experimental surface science has provided important lessons in this area since the 1970s.^{9,11} A wide variety of experimental techniques have been developed which allow for the study of many different aspects of adsorption, including adsorption strength, heights, geometry, pattern, electronic structure and vibrational proper-

ties.^{9,12,13} These experiments are complemented by computational approaches which can provide a level of detail not easily achieved using experimental techniques.^{14,15} One metal surface which has seldom been studied in this context is iron. Experimental Ultra High Vacuum (UHV) adsorption studies carried out on iron surfaces are complicated by the metal's reactivity and strong tendency to passivate, which result in significant difficulty obtaining a high purity metal surface. Still, iron is deserving of study as it is the major component of steel and catalyses important industrial reactions such as the Fischer-Tropsch and Haber processes.

This thesis aims to provide a fundamental understanding in the area of aromatic adsorption upon iron surfaces. The research in this thesis is a result of a collaboration with Schlumberger Ltd., the world's largest oilfield services company. Specifically, the collaboration is an effort towards understanding the mechanism underlying the protection of steel surfaces found in oil wells from acid corrosion by Acid Corrosion Inhibitor (ACI) molecules. This problem is introduced and discussed in the following sections. The findings from this thesis are anticipated to be of a relatively fundamental nature, and will therefore also apply to a number of other applications.

1.2 Corrosion

Corrosion, the deterioration of a metal/alloy and its properties when exposed to a corrosive environment, costs the world over 3% of its GDP (2.2 trillion US dollars) every year.¹⁶ Although corrosion has serious consequences for a diverse range of products, services and industries, petroleum and crude oil refining are particularly severely affected by the process. Petroleum and natural gas production and processing are affected by corrosion in almost all components and at all stages of production.¹⁷ Oil and natural gas use account for over 50% of all energy consumption worldwide, and the demand for energy is growing each year.¹⁸ Corrosion in the fossil fuel industry will require attention for decades to come. A particularly corrosion-prone fossil fuel industry scenario is oil well drilling. Petroleum is recovered mostly through conventional oil drilling, where a carefully selected borehole is

drilled into the Earth's crust to bring crude oil to the surface. During the life of a well, it may be necessary to use stimulation techniques to enhance the oil production rate. One such technique is matrix acidisation, in which acidising fluids are pumped down the borehole. The acidising fluid is mainly composed of highly concentrated acid.¹⁹ Acidising is used to partially dissolve the rock matrix which improves the flow of oil through existing and new flow channels. However, the injected acid tends to corrode many key steel components used, including the well casing that maintains the shaft's structural integrity, pipelines and drilling equipment. The corrosion susceptibility is magnified due to high operational pressures and temperatures as well as the presence of dissolved gasses including oxygen, carbon dioxide and hydrogen sulphide which are known to promote corrosion (see section 1.2.1). 10 to 30% of the budget attributed to oilfield plant maintenance is spent in some way on corrosion.²⁰ Failure to mitigate corrosive processes can result in economic losses, environmental pollution, negative public perception and, in extreme cases, loss of life.^{8,21}

For these reasons, it is very important to employ a corrosion control strategy to prevent premature degradation of the equipment. Prior to discussing the form and function of protection methods, it is useful to more carefully explore the chemistry of corrosion found in oil wells.

1.2.1 Chemistry of corrosion

The chemistry of corrosion in the context of oil and gas wells is highly complex. Figure 1.1 provides a general picture of a subset of important chemical reactions involved.¹⁷ As mentioned, the complexity arises due to the high pressures and temperatures within the well and the presence of species known to accelerate corrosion such as O_2 , CO_2 (so-called sweet corrosion) and H_2S (so-called sour corrosion). Additional factors which affect the rate of corrosion are the pH conditions present at different processing stages (from basic to highly acidising), the wide array of compounds injected into the borehole for different purposes (see table 1.1 for examples), the types of metal/alloy used throughout the well (carbon steels, austenitic and duplex stainless steels, high-strength steels and other exotic alloys) as well as the micro- and macroscopic surface morphology of the corroding surfaces. In addition to

localised effects, corrosion propagation mechanisms have been observed which take place at greater length and time scales. Mechanical corrosion represents an example of macroscopic length-scale corrosion. This includes corrosion due to high-velocity fluid flow, erosion by abrasive particles, or so-called stress corrosion, where reduced ductility due to hydrogen embrittlement can result in surface cracks forming, especially in low ductility steels. Finally, a very important consideration relates to the electrochemical nature of the corrosion process. Figure 1.1 shows the anodic and cathodic regions which form within the metal surface due to potential difference between dissimilar microstructural islands upon the surface, called galvanic corrosion. At the anode surface, dissolved Fe²⁺ ions react with nearby ions to form corrosion products, while at the cathode, the accumulation of electrons can reduce H⁺ ions to form H₂. This thesis cannot provide an exhaustive overview of corrosion chemistry and mechanisms; other references should be consulted for this purpose.^{17,22–24}



Figure 1.1. Typical chemical reactions and products from acidic steel corrosion. Taken from Ref. 17 (D. Brondel *et al.*, *Oilfield Review*, 1994, **6**, 4-18)

Focusing more on surface structure which is of relevance for this thesis, low-carbon steels have been found to adopt oxide, oxy-hydroxide, hydroxide, sulphide, carbide and carbonate surface structure under different conditions relevant to oil and gas processing.²⁵ Under highlyacidising conditions, bare metal surfaces have been observed.²⁵ This is supported by the Pourbaix diagram for iron (figure 1.2), which provides information on the thermodynamics of iron within the aqueous electrochemical environment. Figure 1.2 shows that, across a wide range of applied potential values, iron can be found in Fe^0 , Fe^{2+} or Fe^{3+} states at $pH \le 2$, which influences the metastable states which can be found at the metal surface.²⁶ The Pourbaix diagram does not account for kinetic effects, and as a result passivity has also been studied within kinetic stability diagrams, which are beyond the scope of this work.²⁶ As another example of surface structure greatly differing from bulk metal/alloy structure, stainless steels containing above 10% Cr are known to have a nanometer-scale Cr₂O₂ top surface layer, which provides improved corrosion resistance.²⁷ Aside from chemical composition, the texture of the surface is also known to affect the corrosion rate significantly. Crevices, pits and other surface imperfections are especially common at drillpipe joints and tubing collars, and usually show oxygen depletion. This results in anodic surfaces which show increased iron cation dissolution, which can in turn be accelerated by the presence of Cl⁻ ions.¹⁷ Finally, the corrosion process itself can dramatically change the surface structure due to reprecipitatation of corrosion products which form thin films upon these surfaces. These examples support the complex nature of metal surface structure in oil and gas wells, as it is highly dependant on temperature, pressure, pH, electrochemical potential, alloy preparation method, solvation and solvated species.¹⁷ A body of work has evolved which studies the surface chemistry of corrosion processes, see the review of Maurice and Marcus²⁸ for surface science techniques, both experimental and computational, applied in this context. The review of Wood and Clarke²⁹ also more specifically outlines the role in situ neutron reflectometry has played in elucidating corrosion-related morphological changes at metal surfaces. Theoretical studies have been carried out to build a complementary understanding of the corrosion process at an atomistic level, see the reviews of Taylor³⁰ and Costa and Marcus³¹ as well as some more recent works in this area.³²

It is difficult to generalise findings in oil well corrosion research because the corrosion mechanisms are highly dependent on a multitude of system-specific conditions, some of



Figure 1.2. Pourbaix (potential-pH) diagram for iron. Diagram shows active dissolution region (A) metastable oxides (B and C) and stable oxide phase (D). Reprinted from Ref.26, *Corrosion Science* **99**, Obot, I.B., Macdonald, D.D., Gasem, Z.M., *Density functional theory (DFT) as a powerful tool for designing new organic corrosion inhibitors. Part 1: An overview*, 30 pages, Copyright (2015), with permission from Elsevier.

which are difficult to reproduce in a laboratory setting. In any case, as mentioned previously, it is of paramount importance to limit the degradation of oil and gas well metallic substrates. There are different ways of achieving this, but the most cost-effective strategy is the coupled use of lower-grade carbon steels and ACI.⁸

1.3 Acid corrosion inhibition

Arsenic salts were in common use as ACI until the 1960s.³³ Once it was discovered these salts could leach into groundwater, the resulting toxic effects on human health served to advance chemical research on safer ACI. Research into organic chemicals as ACI provided many viable candidates for inhibiting the corrosion of well components. Many of the ACI in use today are aromatic molecules containing hetero atoms such as N, S and O.

Component	wt %	Function	Sample Compounds
Acid Inhibitor	10-28 ≼ 5	Acidised oil well stimulation Inhibition of acid corrosion	HCl, organic acids alkenylphenones, derivatives of pyri- dinium & quinolinium salts
Intensifier	0.5-5	Ensures adequate steel protection at high temperature and long exposure times	KI, formic acid
Surfactant	0.5-15	Improve dispersability of ACI, wets metal surface	formic acid
Solvent	-	Reduce viscosity, stabilise formulation for variety of environments, can act as surfactant	methanol, ethanol
Other	-	Prevent formation of ferric iron plug, prevent formation acid-promoted hy- drocarbon sludge, prevent oil-acid emulsions, reduce precipitation of ACI on rocks, increase viscosity of fluid	

Table 1.1. Common acidising fluid components^a

^a Data taken from Ref. 8 (M. Finšgar and J. Jackson, Corrosion Science, 2014, 86, 17-41).

An ACI which is effective in one environment tends not to be as successful in a dissimilar environment. Even small changes in alloy composition, acid concentration, pressure, temperature and exposure time all have been shown to significantly change the effectiveness of a given ACI.^{8,34} Additionally, although ACIs alone do provide corrosion resistance in oil well drilling, they are significantly more effective when combined with a slew of other compounds. Table 1.1 lists commonly included components which forms the acidising fluid or Acid Corrosion Inhibition Package (ACIP). The determination of an effective ACIP composition is very environment-dependant and selection is mostly based on trial and error.

Broadly, ACI being used today can be divided among three different categories: physisorbed cationic molecules, chemisorbed molecules and surface-initiated polymerisation. The choice of method depends on the drilling conditions, such as well temperatures and pressures. In this work, mainly chemisorbed-type systems will be addressed. This is because it is the system most amenable to the type of approach to be carried out in this thesis and may provide insight in the study of other system types. A number of reviews study specific subcategories of compounds which function according to one of the three ACI mechanisms, but broadly speaking this includes surfactants, polymers, ionic liquids and natural products among other compound types.^{8,35–37}

1.3.1 Mode of action



Figure 1.3. Summary of interactions involved in adsorption of ACI at the atomistic scale. Reproduced from Ref. 25 (C. D. Taylor *et al.*, *Faraday Discussions*, 2015, **180**, 459-477) with permission from The Royal Society of Chemistry.

Figure 1.3 shows the numerous interactions which must be accounted for at the atomic scale to fully understand ACI-afforded corrosion inhibition.²⁵ This includes considerations which relate to corrosion chemistry as discussed in section 1.2.1 such as metal surface structure (including surface morphology and solvation) and electrochemical effects. In addition to the specific interaction of ACI with the surface, the interactions of ACI with the solvent/oil as well as solubilised compounds/ions are of critical importance. Figure 1.3 demonstrates that the corrosion inhibition process is a competition between ACI-surface,

ACI-solvent, and surface-solvent interactions (where solvent incorporates oil, water, and solubilised species able to interact with either surface or ACI). Several papers^{25,38,39} advocate for the use of interdisciplinary multiscale and multiphysics models to incorporate the computational and experimental results of different ACI interaction domains and processes. This would require individual contributions from scientists working within domains using atomistic techniques all the way to kilometer-scale methodology, for example techniques in engineering or geosciences.

Focusing more on ACI-surface interactions, the mechanism of corrosion inhibition by organic inhibitors is generally poorly understood. This is due to considerations described prior to this paragraph, including the sensitivity to the environment of ACI function as well as the complexity of the corrosion process itself (see section 1.2.1). Based on experimental evidence, certain hypotheses regarding the mechanism of action of chemisorbed ACI can be drawn. It is generally accepted that ACI of the chemisorbed-type can produce protective films over steel surfaces. This film prevents corrosion through reactive site blockage as well as through disruption of cathodic and anodic reactions at the steel surface (see figure 1.1 for these reactions).³³ Depending on whether an adsorbate inhibits cathodic, anodic or both types of corrosive surface chemistry, it is denoted as being a cathodic, anodic or mixedtype inhibitor respectively. Other plausible effects upon the corrosion rate via ACI include interaction of the ACI with surface-adsorbed corrosion reaction intermediates or adsorptioninduced modification of the surface potential (workfunction).^{40,41} It is also possible that any number of these proposed modes of action could be in effect at once, and different inhibitors which may have very different functionality are unlikely to act in the same way. It has been suggested that the binding strength of an inhibitor to the steel surface could be a measure of its ability to provide corrosion protection, but evidence in recent years suggests a more complex picture, for example that some strongly bound adsorbates could enhance the corrosion rate.³⁹

The focus of this thesis work is on the inhibitor-surface interactions, which as described represent a small fraction of the interactions involved in determining the inhibitory action of ACI and corrosion inhibitors more generally. Decoupling these interactions from the multitude of other interactions present within corrosion inhibition can provide fundamental insight into one aspect of inhibitor action, which in turn can shed light on other aspects.^{42,43} As was also mentioned previously, this thesis work aims to shed more fundamental insight on aromatic adsorption upon metal surfaces which can also be applied to a number of other systems external to the corrosion space.

1.4 Computational studies of corrosion inhibition

Experimental surface chemistry methods can provide sub-nanometer resolution, however it is uncommon to uncover atomic-resolution information. Even when such resolution is achieved, it can often not provide the level of detail which offers insight on mechanisms. Finally, while experiments can provide important insight on realistic systems, the complexity of such systems can make the interpretation of data rather difficult. Atomistic simulation techniques can be used in this context to provide supporting results on model systems.

To date, the study of ACI using atomistic computational methods has been achieved using computational methods within the realm of molecular chemistry and the solid state moleculesurface interface.⁴⁴ Methods within both subcategories rely upon Density Functional Theory (DFT) for results. Within computational chemistry, physics and materials science, DFT has become the most widely used quantum mechanical technique to study the electronic structure of many-body systems.⁴⁵ Indeed, a 2014 account of the top 100 most-cited scientific papers of all time features twelve papers related to DFT.⁴⁶ Several reviews outline the successes of DFT applied to ACI behaviour and corrosion science more generally; these should be consulted for a more thorough overview.^{26,28,30,31,47,48} For more information on the theoretical underpinnings of DFT which is used throughout this thesis, see chapter 2.

The following sections outline the different approaches used to study corrosion inhibition afforded by chemisorbed-ACI. Alongside a general description for each method, the method's strengths and limitations are outlined.

1.4.1 Molecular computational chemistry

An approach which is widespread throughout the computational corrosion inhibition literature is the use of chemoinformatics to correlate molecular properties with corrosion inhibition. Two widely used techniques are Quantitative Structure-Activity Relationship (QSAR) and Quantitative Structure-Property Relationship (QSPR), which differ mainly in their mathematical implementations as well as whether biological (QSAR) or non-biological properties (QSPR) are of interest.⁴⁹ Briefly, the QSPR and QSAR approaches define a mathematical relationship between a desired property (for example, the corrosion rate) and relevant structural and chemical properties of a set of molecules, called molecular descriptors. Once the relationship between the property and molecular descriptors is established, the model can be used to predict the property quantitatively for molecules outside the set used to create the model. Additionally, the model can provide insight into which descriptors are most important in determining the property or activity. The range of molecular descriptors which have been used to generate QSAR/QSPR models is extremely diverse; dipole moment, polarisability, electronegativity, specific atom-atom type distances, atomic charges, HOMO and LUMO energies and band gap energy are but a few. Certain descriptors can be derived from experiment, but many of the descriptors mentioned can only be derived from methods in computational quantum chemistry. The bulk of QSPR studies within the corrosion inhibition space make use of DFT-derived molecular descriptors. The works of Gece⁴⁷ and Obot et al.²⁶ should be consulted for a full overview of the studies in this space.

These studies have received criticism for several reasons.^{49–51} First, from a more technical standpoint, the experimental corrosion rate data sets used in the majority of studies are too small and lacking in chemical diversity to provide statistically valid correlations, discrediting any relationships identified between molecular descriptors and corrosion inhibition.⁴⁹ This is being addressed in more recent works which make use of a combination of robust experimental data sets, machine learning approaches to develop the mathematical model and reduced reliance on quantum chemically-derived molecular descriptors.^{49,52,53} Second, almost all QSPR works fail to account for the role of the solvent and especially the surface in predicting properties relevant to corrosion inhibition. Recent experimental and computational works have shown that traditional QSPR strategies fail to correctly predict corrosion inhibition behaviour due to these omissions.^{50,51} More recent QSPR models have included qualitative solvation effects as well as surface specific parameters,⁵⁴ but a final concern with QSPR approaches more generally is that they provide little to no insight on the actual mechanism of inhibition.⁵⁰ Although QSPR can provide clues as to which molecular features/physicochemical properties are in some way linked to corrosion inhibition, they provide no information on reactivity at the metal interface, or indeed any information on the effect of varying the alloy surface, solvent or co-adsorbing species, all of which are known to affect the corrosion rate. This is why a large part of the work presented in this thesis relies on techniques developed in the area of computational surface science, which is described in the next section.

1.4.2 Computational surface science

The coupling of experimental and computational surface science has led to a wide variety of insights which have made important contributions to fundamental and applied science, from characterising surface structures and dynamics to the development of new, higherefficiency heterogeneous catalysts.^{55,56} Computational surface science incorporates methods developed in computational condensed-matter physics and computational chemistry. Since the 1970s, DFT has been the method of choice for quantum mechanical simulations in the solid-state.⁴⁵ The application of solid state DFT calculations to study corrosion inhibitor action is a more recent development.³⁹ Recent reviews^{28,30} and a book chapter³¹ provide an overview of exisiting studies in this area. Some specific recent examples include works on the adsorption of organic ACI upon pure copper and copper oxide surfaces;, 43,57-61 pure aluminium and aluminium oxides; ^{59,62–64} pure zinc and zinc oxides ^{65,66} and pure iron and iron oxide surfaces.^{59,67-71} Insights these calculations have provided are varied, for example calculations have shown that for stepped surfaces, strong covalent binding of organic inhibitors is responsible for corrosion protection while upon close packed surfaces, homogeneous inhibitor thin films are responsible for inhibiting corrosion.³¹ Recent works aim to include the effects of solvation, co-adsorbed species and variable electrochemical
potential alongside the traditional adsorption studies carried out within DFT.³¹

A major criticism of the existing solid state DFT ACI-surface literature to date has been that its models do not account for realistic surface structure.²⁶ Many of the studies so far have concentrated on pure metallic surfaces, when in reality surface structure in concentrated acid or exposed to solvent and ionic species is likely to differ from a pure metal as already mentioned in section 1.2.1.^{39,72} Additionally, to date corrosion studies have focused mainly on single-inhibitor surface systems, and work including solvents and/or co-adsorbates is still lacking. Finally, most calculations fail to account for the electrochemical nature of the corrosion process, and recent calculations have shown that the applied potential can have an important effect of the adsorption mode of organic molecules upon metal surfaces.⁷³ Some of the aforementioned issues are not unique to computations, and are also concerns within experimental corrosion surface science, see section 1.2.1. These issues are beginning to be addressed as expertise in this area develops, and continuing efforts in this area will enable parallels to be drawn more readily between computational results and real systems.

Aside from the setup of simulations, DFT itself has certain limitations. One of the most important in terms of the adsorption of aromatic molecules upon metal surfaces is that standard DFT lacks description of long-range van der Waals (vdW) interactions due to the local nature of the technique.⁷⁴ This results in significant under-estimates of adsorption strength where vdW interactions dominate. vdW-corrected DFT methods have evolved enormously over the past decade, such that computed results for HIOS are now in excellent agreement with experimental results.⁷⁵ Progress in this important area is reviewed and discussed in this thesis, see chapter 2.

Another DFT-related limitation is the high computational expense of the calculations needed to study typical ACI-surface interactions. Modern computational architectures and state of the art DFT packages allow for treatment of systems containing several hundred atoms. Beyond this, calculations become prohibitively expensive. This is problematic given that many of the high performing ACI are relatively large molecules, and once metal surface, co-adsorbates and solvent molecules are also included within the system, traditional DFT approaches become computationally intractable. More recently, approaches which make use of Density Functional based Tight Binding (DFTB), which allow for much larger system sizes while maintaining treatment of electrons, are being used to study corrosion inhibition.^{76,77}

A final limitation is that standard DFT calculations provide a static, thermodynamic description of a system, but kinetics are likely to play an important role in the corrosion inhibition mechanism. Dynamics can be probed using techniques which propagate a system through time, for example Molecular Dynamics (MD) and Monte Carlo (MC) approaches. It is possible to couple MD/MC with DFT, but these approaches can be prohibitively expensive, though some examples do exist.⁷⁸ More recently MD and MC approaches which rely on inexpensive force field methods to evaluate the total energy and forces of the system have been used to study corrosion inhibitor adsorption and kinetics, see the review of Verma *et al.*⁷⁹ Force field methods make use of inexpensive interatomic potentials to approximate the interactions between atoms. Although their low computational cost makes these methods attractive, charge and spin transfer occurs regularly at the aromatic molecule-metallic surface interface and is not captured using standard force field methods.¹⁴ Unless sophisticated and potentially computationally expensive force fields are used, quantum mechanical techniques such as DFT provide a more accurate picture of surface chemical phenomena.

The study of acid corrosion inhibitor chemistry using solid state DFT calculations is still at a relatively early stage.³⁹ This area of research is expected to grow significantly thanks to the development of more accurate quantum chemical methods, the increased availability of powerful parallel computer networks and further guiding experimental insights into inhibitory phenomena and metal surface structure.

1.5 Objective

This work aims to better understand the mechanism of inhibitory action of a known ACI molecule (Naphthylmethyl Quinolinium ion (NMQ+)) on an iron surface. This is achieved using computational analysis, specifically DFT is used to study the gas-phase inhibitor-surface interaction. The NMQ+ molecule is relatively large on the scale of DFT calculations, therefore studies of the interactions of key components of the molecule (benzene, naphthalene and

quinolinium) will first be carried out to better direct the study. In addition to providing preliminary insight on the mechanism of action of NMQ+ as well as other ACI which share these building blocks, simulation of smaller molecular building blocks will enable validation of the selected models, as surface studies of smaller components have already been carried out. Finally, a secondary aim of the thesis is to provide a fundamental understanding in the area of aromatic adsorption upon iron surfaces, which is currently limited in the computational and experimental surface science literature.

1.6 Overview

Chapter 2 outlines the theory and methods used throughout this work. Chapter 3 presents convergence testing and results for the bulk and surface models of bcc iron used throughout this thesis. Chapter 4 presents the results and accompanying discussions of DFT study of benzene adsorption of the Fe{110}, Fe{100} and Fe{211} surfaces. Chapter 5 compares the results of DFT study of naphthalene and quinolinium adsorption on the Fe{110} surface. Chapter 6 presents DFT results for NMQ+ both gas-phase and surface-adsorbed (on the Fe{110} surface) states, and these results are compared to those obtained previously in chapters 4 and 5. Final conclusions and future work directions are presented in chapter 7.

Chapter 2

Theory and Methods

2.1 The Schrödinger equation

Because electrons have wave-particle duality, they cannot be described by classical mechanics, and instead must be described by quantum mechanics. Central to the study of quantum mechanics is the time-independent many-body Schrödinger equation,

$$\hat{H}(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},...,\mathbf{r}_{N})\Psi(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},...,\mathbf{r}_{N}) = E\Psi(\mathbf{r}_{1},\mathbf{r}_{2},\mathbf{r}_{3},...,\mathbf{r}_{N})$$
(2.1)

where \hat{H} is the Hamiltonian operator, \mathbf{r}_{N} is the three dimensional position vector for particle N, Ψ is the many-electron wavefunction and E is total energy. The Hamiltonian operator \hat{H} represents the sum of kinetic (\hat{T}) and potential (\hat{V}) energy operators, which can each be expressed as,

$$\hat{T} = -\frac{1}{2} \sum_{i} \nabla_{i}^{2} \tag{2.2}$$

where ∇_i^2 is the Laplacian operator for electron *i* in Cartesian coordinates, and

$$\hat{V} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_{i} - \mathbf{r}_{j}|}$$
(2.3)

where t is time, and \hat{V} accounts for Coulomb interactions between electrons i and j. The $\frac{1}{2}$

terms eliminate double counted interactions.

A major difference between classical and quantum mechanics is that quantum mechanics is probabilistic, and only provides a probability of where the particles are located. The probability of finding all *N* particles simultaneously in positions $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N$ is equal to $|\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, ..., \mathbf{r}_N)|^2$. The solution of equation 2.1 provides energy as a function of nuclear coordinates, a relationship of prime importance in the study of physics, chemistry and beyond.

Methods which endeavour to solve the Schrödinger equation are referred to as electronic structure calculations. These require a number of approximations, one of the most important being the Born-Oppenheimer approximation. It states that coupled nuclear and electronic motion can be neglected. This is a valid approximation in many situations because nuclei have comparatively much higher mass than electrons, and therefore have insignificant quantum behaviour. This allows for the Schrödinger equation to be solved only for electrons while nuclei are set as parameters. Once the potential energy surface has been mapped for electrons, it can be used to solve the Schrödinger equation for stationary nuclei. The major computational effort therefore lies in solution of the electronic Schrödinger equation for a set of given nuclei.

Because of the complexity of solving the Schrödinger equation for many-electron systems, it is necessary to make further approximations to facilitate calculations. Hartree-Fock theory represents one of the oldest and most established methods for solving the multi-electron Schrödinger equation. This method is classified as an independent-particle method owing to the main approximation that electron motion is independent of all other electrons, and is accounted for in an average way. Within this method, the total wavefunction Ψ is expressed as a combination of orbitals, each of which describes an electron within a given system.

Electrons, which are fermions, cannot share the same quantum state. This property, known as antisymmetry or Pauli's exclusion principle, must also be incorporated into treatment of the wavefunction which describes the electrons. This is resolved through use of a Slater determinant. The variational theorem states that a trial wavefunction will have an energy eigenvalue greater than or equal to the ground state wavefunction. The wavefunction can therefore self-consistently be tested until the energy is minimised for the single Slater determinant, giving the ground state energy and wavefunction.

A major omission from Hartree-Fock theory is that it neglects to account for electron correlation, i.e. how electron movement is affected by surrounding electrons. This is because of the very nature of the method, which accounts for average electron-electron interactions only. This can result in important underestimates of geometric and energetic parameters compared to experimental results. Although there are solutions to this problem which remain within the realm of Hartree-Fock theory (see section 2.5.3 for example), Density Functional Theory (DFT) is a different method for solving the Schrödinger equation which does include correlation, and represents a very successful improvement over traditional Hartree-Fock theory.

2.2 Density Functional Theory

Density Functional Theory (DFT) has become the most popular quantum mechanical simulation method in physics, chemistry and materials science. Its description of the electronic structure of atomic, molecular, and condensed-matter systems has provided invaluable insights. In this section, DFT's underlying mechanics shall be addressed.

In summary, DFT has two guiding principles: (1) Energy is a function of total electron density and (2) the total energy, wave function and all other molecular electronic properties are *unique* to the ground state electron density. The first point is in stark contrast to the Hartree-Fock method. Similarly to Hartree-Fock, the solution to the Schrödinger equation in DFT approximates the true many-body wavefunction as a combination of one electron densities. Instead of having to solve the Schrödinger equation using the complex and computationally demanding many-electron wavefunction, the only necessary variable is the total electron density, $\rho(\mathbf{r})$, which is expressed as a function of real space coordinates $\mathbf{r} = (x, y, z)$. DFT energy ($E[\rho(\mathbf{r})]$) is a "functional", as it is a function (electron density) of a function (real space coordinates).

What is referred to today as modern DFT is generally Kohn-Sham DFT. In 1965, Kohn

and Sham introduced the following form of the exact energy functional:

$$E[\rho(\mathbf{r})] = T_s + U + V_{nuc} + E_{xc}[\rho]$$
(2.4)

where $E[\rho(\mathbf{r})]$ is the ground-state energy, T_s is the kinetic energy of the non-interacting single-particle Kohn-Sham orbitals, U is the Coulomb energy, V_{nuc} is the nuclear-electron potential and $E_{xc}[\rho]$ is the exchange-correlation energy. U and V_{nuc} are borrowed from Hartree-Fock theory; the real innovations of DFT lie in T_s and $E_{xc}[\rho]$. In Kohn-Sham DFT, it is possible to find the ground state density through self-consistent solution of Equation 2.4. Single particle Kohn-Sham orbitals form a set of solutions to Schrödinger-like equations, and total energy can be minimised with respect to this solution set. For a system containing a number of electrons N, DFT and Hartree-Fock methods scale with N^3 and e^N respectively, resulting in significant computational cost savings overall through use of DFT.

2.2.1 Exchange-correlation energy: $E_{xc}[\rho]$

Although DFT is in theory exact, in practice approximations are made because there is no known analytical solution to the exchange-correlation functional. Exchange and correlation arise from the Pauli principle as well as dynamic Coulomb interactions between electrons, respectively. It is also worth noting that $E_{xc}[\rho]$ additionally corrects for the error made in T_s . This error arises because the kinetic energy for the non-interacting single-particle Kohn-Sham orbitals is not the same as the true kinetic energy.

The two main approximate forms of $E_{xc}[\rho]$ are the Local Density Approximation (LDA) and the Generalised Gradient Approximation (GGA), the latter of which is used throughout this work.

LDA versus GGA

The LDA was quite popular for calculating the electronic structure of solids through the 1970s and 80s.⁸⁰ The LDA relies on computation of $E_{xc}[\rho]$ exclusively from the value of ρ at each point in real space for a uniform electron gas. Mathematically, this can be expressed

as:

$$E_{xc}^{LDA}[\rho] = \int \rho(\mathbf{r})(\epsilon_x[\rho(\mathbf{r})] + \epsilon_c[\rho(\mathbf{r})])dr \qquad (2.5)$$

where $\epsilon_x[\rho(r)]$ and $\epsilon_c[\rho(r)]$ are the exchange and correlation energies per particle, respectively. A major problem with the LDA is that molecules typically will be overbound by around 1 eV/bond. Specifically of relevance for this thesis is that an LDA does not identify the correct ground state for bulk Fe. Computations carried out by Blancá *et al.*⁸¹ show an LDA to predict non-magnetic fcc Fe as the lowest energy phase, while ferromagnetic bcc Fe is known to be the ground state for bulk Fe and is correctly identified with a GGA.

GGAs were popularised in the late 1980s and represent the majority of functionals in use today. GGAs differ from LDAs in that they not only account for ρ at each point in space, but also the gradient $\nabla \rho$. The GGA created by Perdew, Burke and Ernzerhof (PBE) was used for all calculations involving iron throughout this work.⁸²

2.2.2 Spin polarisation

Systems which demonstrate magnetism require additional technical considerations in order to account for spin-polarisation. Typically, this includes metallic systems containing Fe, Co, Mn and Ni as well as transition metal oxides. Spin polarisation is incorporated in the DFT work within this thesis through use of spin-polarised GGAs.⁸³ In essence, separate calculations are carried out on majority spin (or spin up) and minority spin (or spin down) electrons. This therefore requires the use of two separate ρ variables, often denoted ρ^{\uparrow} and ρ^{\downarrow} , where $\rho = \rho^{\uparrow} + \rho^{\downarrow}$. Mathematically,

$$E_{xc}^{GGA}[\rho^{\uparrow},\rho^{\downarrow}] = \int \epsilon_{xc}(\rho^{\uparrow}(\mathbf{r}),\rho^{\downarrow}(\mathbf{r}),\nabla\rho^{\uparrow}(\mathbf{r}),\nabla\rho^{\downarrow}(\mathbf{r}))dr \qquad (2.6)$$

In addition to the two separate calculations, the interaction between ρ^{\uparrow} and ρ^{\downarrow} must also be accounted for. As a result, spin polarised calculations incur significant additional cost to traditional DFT calculations, typically over twice the cost of the non-spin polarised calculation.

2.2.3 Dispersion corrections

Reliable dispersion corrections are a fairly recent addition to the DFT toolbox and are still actively being developed.⁷⁴ The failure to describe long-range electron correlations (electron dispersion forces) occurs due to the approximate nature of exchange-correlation functionals such as LDA and GGA. Specifically, it is because instantaneous density fluctuations are not considered and only local properties are used to calculate the exchange-correlation energy.

The most widely adopted, inexpensive approach to account for vdW forces is the addition of a pairwise additive dispersion correction energy term (E_{disp}) to the computed DFT energy. For two particles which are separated by a distance r, the dispersion scheme should display $-1/r^6$ asymptotic behaviour. A general form for E_{disp} can be expressed as follows:

$$E_{disp} = -\sum_{A,B} C_{AB}^{6} / r_{AB}^{6}$$
(2.7)

where r_{AB}^6 is the distance between atoms A and B and C_{AB}^6 is the dispersion coefficient for atom pair A and B. In this work, the vdW scheme created by Tkatchenko-Scheffler (TS) is used.⁸⁴ This method makes use of reference atomic polarizabilities in addition to reference C_{AB}^6 coefficients. An attractive feature of the TS scheme is the environment-dependent C_{AB}^6 coefficients, which are scaled from reference atomic values based on effective atomic volumes.

The review of Klimes and Michaelides⁷⁴ provides an overview and classification scheme for the wide range of exisiting vdW methodologies. Pairwise schemes such as D2⁸⁵ as well as environment-dependant pairwise TS⁸⁴ and D3⁸⁶ schemes incur the lowest computational cost at the expense of high accuracy. Moderate cost and accuracy are achieved through use of the vdw-DF functionals,⁸⁷ which instead of applying pairwise corrections make use of a new functional form which includes long-range interactions. The random phase approximation (RPA)⁸⁸ and many body dispersion (MBD)⁸⁹ schemes represent approaches which go beyond the pairwise approximation, and are of the highest accuracy and computational cost.

Hybrid inorganic-organic junctions (HIOS)

An understanding of the electronic structure of industrially relevant HIOS is key to tuning their properties (see chapter 1 for applications). As a result, electronic structure calculations aiming to provide an understanding of these systems at the atomistic level are popular. Significant efforts have been invested in studying the effect of DFT vdW corrections upon HIOS with an emphasis on molecular adsorption on metal and semiconductor surfaces, see for example the reviews of Liu *et al.*¹⁵ and Tkatchenko *et al.*⁹⁰ Many studies have shown significant changes in adsorption energies, relative energetic ordering of adsorption configurations as well as geometric parameters when dispersion corrections are included for aromatic molecules adsorbed on metal and semi-conductor surfaces.^{57,91–105} Typically, the most important effect is seen for adsorption energies, which have been estimated to increase on average by 5.5 kJ/mol (0.06 eV) per carbon-sized atom.⁷⁴ The impact has been shown to vary from that estimate, and is dependent on a large number of factors including the vdW correction/functional used, the adsorbate identity, the surface composition, the strength of the adsorbate-surface interactions and the type and roughness of surface facet.

In terms of the method used to account for vdW interactions, schemes which make use of a pairwise additive dispersion correction energy term tend to over-estimate the impact of the interactions.^{74,92} Generally, more sophisticated vdW-including implementations tend to produce results more in line with experimental results, but there certainly are exceptions to this. For example, use of the vdW-DF functional underestimates the experimental adsorption energy of benzene/Cu{111} (vdW-DF $E_{ads} = 0.55 \text{ eV}$,⁹³ experimental $E_{ads} = 0.68 \text{ eV}-0.81 \text{ eV}$,¹⁰⁶ PBE-TS $E_{ads} = 1.05 \text{ eV}^{92}$). This is particularly important given that use of vdW-DF and other sophisticated schemes increases the cost of the calculation by at least 50%, while the additional cost of pairwise additive corrections is minimal.⁷⁴ New vdW schemes continue to be developed to incorporate the realistic effect of vdW interactions within DFT.

Systems containing aromatic molecules can show especially strong changes upon addition of vdW corrections due to dispersion interactions of the aromatic π -electron system with the surface.¹⁴ This is why benzene, being the simplest small aromatic molecule, has been intensely studied in this context upon metal and semi-conducting surfaces.^{91–95,97–99,102–106} As for the metal identity, adsorption upon more noble metals, which tend to show less reactivity, are usually strongly impacted by vdW corrections, as shown for example in the work of McNellis *et al.*⁹² on azobenzene adsorption on three coinage metal (Au{111}, Ag{111} and Cu{111}) surfaces. Conversely, in cases where strong chemisorption occurs, for example for 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane on Cu{111} ($E_{ads} = -2.60 \text{ eV}$),¹⁰⁷ excellent agreement with experiment is achieved without the use of vdW corrections. In some cases, a given vdW correction can provide better agreement with experiment for adsorption on one surface facet (Cu{111}) than another (Cu{100}), showing that this can also have an effect on the approach.^{108,109} A further effect which has infrequently been discussed in the literature is the impact the chosen vdW scheme has on the metal surface's properties. Particularly, in cases where a functional which has been shown to produce good agreement for bulk/surface properties with experiment (i.e. PBE), the *ad hoc* addition of pairwise vdW corrections to such functionals can lead to poorer agreement.¹¹⁰

In more recent years, an approach (called DFT+vdW^{surf})¹⁰⁶ to incorporate vdW interactions specifically for HIOS systems has emerged. It has shown results in excellent agreement with experiment for a number of aromatic/metal surface systems.⁷⁵ Although this scheme has not been employed for the work in this thesis (its implementation within the CASTEP code we use is at present incomplete), its use represents an interesting future work direction.

It is clear there are a number of important considerations within the DFT treatment of HIOS. This thesis does not aim to ascertain or employ the ideal vdW-DFT method for the adsorption of aromatic molecules on Fe surfaces; this would not be possible to determine given the lack of experimental data for such systems. Instead, the work presented in this thesis aims to ascertain more generally the effect of addition of vdW interactions to DFT upon Fe surface adsorption energies and geometries. This is why the TS correction has been selected for our work.

2.2.4 Hybrid functionals

Hybrid functionals include a range of functionals which mix Hartree-Fock and DFT. They aim to improve the expression for exchange-correlation energy by incorporating a portion of Hartree-Fock-derived exact exchange.

The B3LYP functional^{111,112} is used for the gas-phase molecular DFT work in this thesis. This is one of the most popular hybrid functionals and has been in use for DFT calculations for decades. The paper describing the method is among the ten most cited scientific papers of all time.⁴⁶ B3LYP references the Becke 88 exchange functional, its three parameters and the correlation functional of Lee, Yang and Parr. The B3LYP exchange-correlation functional has the following form:

$$E_{xc}^{B3LYP} = E_x^{LDA} + 0.20(E_x^{HF} - E_x^{LDA}) + 0.72(E_x^{GGA} - E_x^{LDA}) + E_c^{LDA} + 0.81(E_c^{GGA} - E_c^{LDA})$$
(2.8)

where *x* represents exchange, *c* represents correlation, *HF* is Hartree-Fock. As can be seen in equation 2.8, B3LYP also includes a mixture of both LDA and GGA exchange and correlation contributions.

The combination of B3LYP/6-31G(d,p) has been shown to produce a mean average error of 2.5 kcal/mol (0.11 eV) for both heats of formation and isomerisation energies for 622 organic compounds containing C, H, N and O.¹¹³

2.3 Solid State DFT: the CASTEP code

CAmbridge Serial Total Energy Package (CASTEP) is one of many implementations of a DFT simulation package. Its focus is on solid-state condensed matter, which generally presents different features compared to DFT implementations which focus on molecular species (see section 2.5 for details of molecular DFT codes). Since the conception of CASTEP in 1986, many authors have contributed to create a very robust electronic structure code.^{114,115}

Many solid-state DFT codes such as CASTEP share common features, including a plane wave basis to represent the wavefunction, pseudopotentials and total-energy minimisation (to identify the ground-state). In the following sections, these key concepts as well as certain CASTEP-specific features shall be discussed. Throughout all thesis work, version 17.2.1 of the CASTEP code is used.

2.3.1 Plane wave basis

Bloch's theorem

Bloch's theorem is stated as follows:

$$\psi_{\vec{k}}(\vec{r}) = u_{\vec{k}}(\vec{r})e^{ik\cdot\vec{r}}$$
(2.9)

where $\psi_{\vec{k}}(\vec{r})$ is the Bloch wave, $u_{\vec{k}}$ is a periodic function with the same periodicity as the crystal under study (also known as the Bloch function), \vec{r} is the position vector and \vec{k} is a vector of real numbers (also called the crystal wave vector). A suitable mathematical basis must be selected for the Bloch function, and for crystal systems this is generally plane waves. For mathematical convenience, this can be expressed in reciprocal space:

$$\psi_{\vec{k}}(\vec{r}) = \sum_{\vec{G}} u_{\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}}$$
(2.10)

where \vec{G} is the reciprocal lattice vector. In order to represent any $\psi_{\vec{k}}(\vec{r})$, the basis set should in theory be complete and therefore contain an infinite number of plane waves. In practice this is not possible, so a cut-off energy is introduced, and only plane waves with a kinetic energy below the following cut-off are used:

$$\frac{\hbar^2 |\vec{G} + \vec{k}|^2}{2m} < E_{\text{cut-off}}$$
(2.11)

The change of $\psi_{\vec{k}}(\vec{r})$ with \vec{k} becomes negligible for close k-points. This implies that a finite number of k-points can be used to study a system. The number of k-points selected to approximate infinite \vec{k} is referred to as k-point sampling and is one of the basis set parameters which must be tested for convergence with respect to a particular property, usually the total energy of the system. This work makes use of the common Monkhorst-Pack (MP) grid sampling scheme, which is a regular, homogeneous user-defined grid of k-points.

A plane wave basis presents many advantages over an atom-centered one. It is mathematically complete and simple, does not depend on atomic positions, has a single convergence criterion, treats all space the same and readily incorporates periodic boundary conditions, which are necessary for solid-state calculations. Atom-centered basis sets are still in use for study of solid-state systems to overcome certain plane wave-related disadvantages (more discussion of this in section 2.5.1). One such disadvantage is that the number of necessary plane waves is determined by the greatest curvature of the wavefunction. A solution to this problem is through use of pseudopotentials.

2.3.2 Pseudopotentials

A pseudopotential replaces the real potential, originating from both the core electrons and ionic cores, with an effective potential. More specifically, the true wavefunction is replaced with a smoothed pseudo-wave function within a core radius R_c . Figure 2.1 provides a visual depiction of three of the most important requirements for a valid pseudopotential. First, the real and pseudo-wavefunction must agree below distances of R_c . Second, the real and pseudo-potential must agree beyond R_c . Finally, the eigenvalues must be the same whether real potentials or pseudopotentials are used. When appropriate pseudopotentials are used, they significantly lower the computational cost due to a reduced number of electrons to be treated explicitly and a smaller basis set.



Figure 2.1. Graphical representation of original wavefunction (Ψ), norm-conserving (Ψ_{nc}) and ultrasoft (Ψ_{us}) pseudopotentials.

Norm-conserving-type pseudopotentials, which were proposed in the late 1970s, were the first to become routine in use within plane-wave DFT codes. A norm-conserving pseudopotential has the requirement that the charge in the core region should be the same for the all-atom wavefunction as for the pseudo-wavefunction. To ensure transferability of pseudopotentials, a suitable R_c should be chosen. The larger the R_c value, the smaller $E_{\text{cut-off}}$ can be, but it also makes it more difficult to preserve norm-conservation and the pseudopotential becomes less transferable.

Ultrasoft nonlinear core corrections

In practice, norm-conserving pseudopotentials can be prohibitively expensive for first-row and transition metal elements as large basis sets and high $E_{cut-off}$ values are usually required.¹¹⁵ Vanderbilt's ultrasoft pseudopotentials address these issues by relaxing the normconserving requirement.¹¹⁶ This allows for a much smoother pseudo-wavefunction region below R_c , which allows for a smaller number of plane waves to be used. Typically, this translates to $E_{cut-off}$ values around two times smaller than with norm-conservation resulting in less than a third of the number of plane waves.¹¹⁵ A problem which arises due to not reproducing the all-electron core charge with the ultrasoft pseudopotential is that scattering properties may become incorrect due to a generalised eigenvalue problem.¹¹⁶ In CASTEP, this is amended by using two or three reference energies each having their own set of projectors for the valence electrons. This results in ultrasoft pseudopotentials being generally much more transferable than their norm-conserving counterparts.¹¹⁵ The additional cost incurred by solving the generalised eigenvalue problem is more than offset by the computational time savings afforded by a reduced number of plane waves. Ultrasoft pseudopotentials are therefore inexpensive in addition to being highly transferable.

It can be difficult to determine which electrons should be classified as core or valence for transition metals. These so-called semi-core states can be treated as valence electrons to err on the side of caution, but treating more electrons explicitly results in a more costly calculation. Nonlinear core corrections (NLCC) provide a solution to this problem.¹¹⁷ These corrections, which explicitly treat the exchange and correlation interactions between core and valence charge densities, tend to be of a much lower cost and highly transferable at the expense of accuracy. NLCC have been shown to be particularly important for magnetic

materials, because spin density is more localised around the atomic core than charge density.¹¹⁸

2.3.3 Electronic energy minimisation

Electronic energy minimisation is where all the previously described DFT calculation occurs. Initial wavefunctions and densities are input and modified in some way to generate new output wavefunctions and electron densities.

Electronic energy minimisation in CASTEP makes use of a preconditioned conjugate gradient method.¹¹⁵ The conjugate gradient method is a variant on the steepest descent search method. Steepest descent is characterised by a cycle through the following steps:

- 1. A trial wavefunction is provided;
- 2. Energy is computed;
- 3. The energy gradient is computed;
- The coefficients used for subtracting the gradient from the trial wavefunction are adjusted;
- 5. An improved trial wavefunction is generated;
- 6. Steps 2-5 are repeated until the ground-state is identified.

CASTEP offers two iterative minimisation schemes, namely density mixing and ensemble DFT (EDFT).¹¹⁸ These schemes differ mainly in whether $E[\rho(\vec{r})]$ is recomputed at each step. In this work, density mixing is used, where $E[\rho(\vec{r})]$ is not recomputed at each step, which denotes it as non-self-consistent. Charge density at the end of a minimisation step is "mixed" with the initial charge density for the next step until convergence is reached. This mixing of density results in a robust and efficient minimisation scheme for most metallic systems and surfaces. This technique is however non-variational, meaning energy is not always lowered during the steepest descent search. This can sometimes result in difficulty converging the ionic forces. An additional concern arises for spin-polarised calculations,

where spin is also mixed-in separately from the charge density mixing. EDFT does also work well for metallic systems and is variational, but as $E[\rho(\vec{r})]$ is recomputed at each step it is prohibitively expensive. In cases where charge sloshing occurs or the steepest descent search is otherwise unstable, EDFT can prove useful.

For all calculations described in this thesis, only density mixing is used. The electronic tolerances used are 1×10^{-8} eV for energies and 1×10^{-5} eV/Å for forces.

2.3.4 Geometry optimisation

Geometry optimisation calculations involve iteration over a series of inner and outer loops. The outer loop, called the ionic or geometric loop, makes use of the converged result of the inner loop, i.e. electronic energy minimisation, to obtain the forces on the ionic coordinates. These provide an indication as to how the atomic positions should be changed in order to get closer to the ground-state configuration. The ground-state is considered to have been reached once further ionic steps do not significantly change user-defined force, energy and ionic displacement tolerances. Within this thesis, the tolerances used are 0.01 eV/Å (forces), 1×10^{-5} eV (energy) and 0.01 Å (ionic displacement).

Geometric convergence is achieved through use of the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimisation algorithm, where first and second derivatives of the energy are both used to identify minima. This results in much faster convergence than with only the first derivative being used, as is done for example when using steepest descent minimisation.

2.4 Surface calculations

Two dimensional surfaces do not have natural three dimensional periodicity, so generation of a three dimensional periodic supercell is not possible by default. The periodic nature of the two dimensional plane of a surface is appropriate for this task, so a unit cell can be built through inclusion of artificial periodicity in the direction normal to the surface. This is accomplished through use of a finite vacuum space above the surface. Usually, the vacuum selected will be of at least 10 Å to prevent non-physical interaction of the surfaces separated



Figure 2.2. Example surface supercell with adsorbate, bulk, top surface and vacuum layers indicated.

by the vacuum spacing. Additionally, bulk and surface regions of the two dimensional material are introduced. A sufficient number of bulk and surface layers must be selected to ensure realistic behaviour, which can be verified by comparing against characteristic surface properties. Generally, the bulk surface atom coordinates are frozen while the surface layers are allowed to relax along with any species being adsorbed on the surface. A representative diagram of a surface supercell is shown in figure 2.2.

2.4.1 Surface properties

Surface energy

Surface energy quantifies the energy required to cut a crystal along a given surface plane to form two halves. A first form often seen in the computational literature which we will refer to as ς , can be expressed according to the following equation:

$$\varsigma = \frac{1}{2}E_{slab} - nE_{bulk} \tag{2.12}$$

where E_{slab} is the total energy of the slab, *n* is the number of slab atoms and E_{bulk} is the total energy of the bulk material per atom. the $\frac{1}{2}$ factor accounts for the formation of two surfaces upon cleavage of a crystal.

Of experimental relevance is the surface energy per unit area (γ) which is expressed as follows:

$$\gamma = \frac{E_{slab} - nE_{bulk}}{2A} \tag{2.13}$$

where *A* is the surface area of the slab. A correction must however be applied to equation 2.13 because γ does not converge with increasing slab thickness.^{119–121} As documented in works from literature, this is a result of the well-converged bulk energy (E_{bulk}) differing from the bulk energy associated with the lower portion of the surface slab. A number of methods have been proposed to correct this error. This work makes use of the method developed by Boettger¹¹⁹, which employs incrementally thicker slab energies to ascertain the slab-derived bulk energy. This can be expressed as,

$$E_{bulk} = E_{slab}^{i} - E_{slab}^{i-1} = \frac{\Delta E_{slab}}{\Delta N}$$
(2.14)

where *i* is the slab thickness. Making use of an average of several ΔE_{slab} values for different *i* increments results in improved predictions. The ranges of *i* used for these averages are described where surface energies are calculated throughout this work.

Workfunction

The workfunction (ϕ) is defined as the minimum energy needed to move a surface electron to a point just outside the solid surface. It is calculated according to the following equation:

$$\phi = E_{vac} - E_F \tag{2.15}$$

Where E_{vac} is the vacuum energy and E_F is the Fermi energy. E_F is provided directly in the output of geometry optimisation or single point calculations. E_{vac} can be calculated from the local potential, which must be extracted from the CASTEP binary check file. This is accomplished using the pot1d CASTEP tool, which makes use of the macroscopic averages method presented by Fall *et al.*¹²²

2.4.2 Adsorbate-surface system properties

In addition to properties which describe the clean surface, there are a number of properties suited to the study of a coupled adsorbate-surface system. These properties can reveal interesting information about the interactions between adsorbate and surface, and are discussed in the following sections.

Adsorption energy

The adsorption energy (E_{ads}) provides a measure of the strength of the interaction between the surface and adsorbate. More specifically,

$$E_{ads} = E_{surf+molec} - (E_{surf} + E_{molec})$$
(2.16)

where $E_{surf+molec}$ is the energy of the adsorbed molecule and surface, E_{surf} is the energy of the bare, geometry-optimised surface slab and E_{molec} is the energy of the geometryoptimised gas-phase molecule. This measure can provide insight into whether the species is chemisorbed or physisorbed, with a minimum E_{ads} of -0.5 eV per molecule typically characterising chemisorption. Throughout the literature, both positive and negative values are used to describe E_{ads} . In this thesis, negative values are used for exothermic adsorption processes, where a more negative value is indicative of stronger adsorption.

Distortion energy

There is often a change in the conformation adopted by a molecule when adsorbed on a surface compared to its optimal isolated configuration in the gas-phase. The distortion energy

 (E_{dist}) serves to quantify the deformation of the molecule's adsorbed configuration away from its isolated gas-phase optimised configuration. All E_{dist} values presented throughout this work are positive owing to the energy gain upon distortion away from the isolated gas-phase molecule's configuration. The distortion energy, particularly when coupled with other data such as E_{ads} , can provide complementary insight into the underlying mechanism for adsorption. For example, molecular distortion at the metal surface can result if it provides improved overlap of adsorbate orbitals with surface orbitals.

Charge density difference

The distribution of charge density (ρ) within the adsorbate-surface system can be studied, but a potentially more useful metric is the charge density difference ($\Delta \rho$) which is calculated similarly to the adsorption energy, i.e.

$$\Delta \rho = \rho_{surf+molec} - (\rho_{surf} + \rho_{molec}) \tag{2.17}$$

where $\rho_{surf+molec}$ is the charge density of the combined adsorbate-surface system, ρ_{surf} is the charge density associated with the clean surface in its adsorbed configuration and ρ_{molec} is the charge density associated with the isolated gas-phase adsorbate in the adsorbed configuration. Because $\Delta \rho$ aims to analyse the differences in density between adsorbate and surface, it is important to make use of the charge densities for adsorbed configurations as opposed to the isolated gas-phase optimised charge densities. The adsorbed and isolated gas-phase configurations will have slight differences in their distribution of density, and subtracting the wrong ρ_{surf} and ρ_{molec} will result in erroneous $\Delta \rho$.

The charge density difference is most useful as a visual representation of the charge transfer interactions between the adsorbate and surface. Regions of decreased (increased) electron density can usually be correlated with the HOMO (LUMO) orbitals of the adsorbate which can donate (back-donate) electron density.

Spin density

The spin density provides an insight into the distribution of spin within the adsorbate-surface system. This is particularly interesting for adsorption upon iron surfaces, as adsorbates without spin-polarisation can become spin-polarised as a result of interaction with the ferromagnetic surface.

As with the charge density difference, the spin density is most helpful when visually represented. Throughout this thesis, blue (yellow) regions denote minority (majority) spin. Unlike the charge density difference, it is of most use to directly represent the spin density as opposed to the spin density difference. Because none of the adsorbates studied carry spin in the gas-phase, the spin density already naturally provides the "difference" compared to the gas-phase molecule.

All spin and charge density data is prepared using the c2x utility¹²³, which extracts and reformats the desired densities from the CASTEP binary checkpoint file.

Density of states

The Density Of States (DOS) provides information on the number of occupied states at a range of energy levels. A study of the DOS for the adsorbate-surface components prior to, as well as after, adsorption can provide important insights on changes in electronic structure for both adsorbate and surface. Of special relevance for this thesis is the Projected Density of States (PDOS), where the DOS can be projected upon a specific atom, orbital(s) (i.e. s, p or d) or some combination of both. Projection upon specific atoms and their orbitals can be useful in cases where it is expected that a certain atom or orbital plays an active role in the adsorption process, and would therefore show a shift in occupation of energy levels. In terms of molecules, specific DOS bands can be assigned to specific molecular orbitals; their change upon adsorption can be indicative of those orbitals which have favourable alignment and therefore interact favourably with the surface orbitals.

All DOS and PDOS data shown throughout this thesis are calculated using the OptaDOS program in conjunction with CASTEP.¹²⁴

2.5 Molecular DFT: the Gaussian code

From a technical standpoint, it is possible to treat gas-phase molecular systems using a plane wave-basis DFT implementation such as CASTEP. This would require placing the molecule of interest in a periodic vacuum large enough to prevent unphysical self-interactions. In doing so, a large region of vacuum is treated with the same level of accuracy as the gas-phase molecule, resulting in high computational cost. Because molecular systems are finite, they do not typically benefit from use periodic boundary conditions, rendering the plane wave approach unnecessarily expensive.

In certain cases found throughout this thesis, it is necessary to make use of the approach described above in order to make direct comparisons between the gas-phase and adsorbed states of a molecule. In all other cases, molecular systems have been studied using a separate DFT implementation, which relies on a localised basis set, called Gaussian.¹²⁵ The distinguishing features of this code which are used in this thesis are described in the following sections.

2.5.1 Atomic basis sets

The plane wave basis is one of many which can be used to represent the electronic wave function and solve the Kohn-Sham equation (equation 2.4). As explained previously, such basis sets tend to be favoured for problems in materials science where periodic boundary conditions are convenient. As for gas-phase molecular systems, they are often better suited to other basis sets. Specifically, one such category is the Atomic Orbital (AO) basis.

In the same way that the plane wave basis is a linear combination, the AO basis is made up of a linear combination of atomic orbitals (also called LCAO). There are two main ways in which the atomic orbital basis is implemented: Slater-Type Orbitals (STO) and Gaussian-Type Orbitals (GTO). Mathematically, the GTO takes the form:

$$\Phi^{nlm\zeta}(r,\theta,\phi) = \alpha Y_{lm}(\theta,\phi) r^{2n-n-l} e^{-\zeta r^2}$$
(2.18)

Where $\Phi^{nlm\zeta}(r,\theta,\phi)$ is the GTO expressed in spherical coordinates, l, m and n are

quantum numbers which determine the type of orbital (l = 0 is an s orbital, l = 1 is a p orbital, etc.), ζ determines the width of the orbital (a small ζ results in a more diffuse function), r is distance from the nuclear positions, α is a normalisation constant and $Y_{lm}(\theta, \phi)$ is a spherical harmonic. The main difference between STO and GTO lies in the $e^{\zeta r^2}$ term; in the case of STO, the dependence is of the form $e^{-\zeta r}$. The r power provides a better description of the orbital compared to r^2 at the expense of very high computational cost (the r power requires square root calculations which are time-consuming). Although GTOs describe the orbital less accurately, they are of such a reduced computational cost compared to STO (even with the minimum three times more GTO functions required for a description as good as STO) that they tend to be preferred.

The dependence on quantum numbers and atomic positions results in a chemically intuitive basis set as well as basis sets of small size which give decent results. This approach does have some disadvantages, one of the most important being Basis Set Superposition Error (BSSE). These errors result from the finite nature of the AO-basis set. When two molecules are in close proximity to each other, their basis functions will overlap, which can result in an overall improvement in computed energies for example compared to when the two molecules are distanced. In other words, computed properties will differ according to the distance between two molecules due to BSSE. There are a number of approaches to resolve this issue, including increasing the number of basis functions used or the so-called counterpoise correction, where calculations are carried out with the new "mixed" basis set and the associated error is subtracted from the original basis set.

Aside from the increase in computational cost due to treatment of a large vacuum with plane waves in the molecular case, distinguishing features between the plane wave and GTO approaches include: core electrons not being treated explicitly for plane wave DFT when pseudopotentials are used; the plane wave approach does not suffer from BSSE; the plane wave basis is orthogonal while the AO basis is non-orthogonal; exact exchange is more readily calculated within an atomic orbital basis which allows for trivial use of high-accuracy hybrid functionals (see section 2.2.4 for a description of these methods) while calculation of exact exchange in the plane wave basis comes at very high computational cost, limiting their coupled use with hybrid functionals. There are a number of other differences between these methods; for a good overview the paper of Tosoni *et al.*¹²⁶ is recommended. The paper also provides evidence that structures, interaction energies and vibrational modes are identical for plane wave and atomic orbital approaches as long as high-quality basis sets are employed.¹²⁶ It is also worth mentioning that periodic DFT codes can and have been implemented which rely on atomic basis, such as for example the SIESTA code.¹²⁷

Pople basis

The basis set used within this work is one of those developed by John Pople, which were popularised by the Gaussian DFT package. As mentioned previously, a combination of several GTO must be used to provide the same accuracy as the STO approach. The so-called Contracted Gaussian-Type Orbitals (CGTO) is just that; a sum over a combination of n GTO, as shown in equation 2.18. This is the approach employed by Pople basis sets.

The naming scheme employed by the Pople basis sets (i.e. X-YZG) explains the construction of the basis set. The first character (X) is the number of GTO which make up the CGTO which describe the core atomic orbitals. Y and Z relate to the description of valence orbitals. Specifically, Y and Z refer to the use of what is a called a split-valence type basis set, more specifically of the double zeta type. Because valence electrons are of central importance in describing reactivity, the description of each AO with more than one CGTO (which in turn can be made up of several GTO) results in a better overall description of the valence.

Throughout this work, the 6-31G(d,p) basis set within Gaussian 09 is used.¹²⁵ 6-31G(d,p) offers a good level of accuracy alongside a reasonable computational cost.¹¹³ It makes use of a 6-GTO CGTO in describing the core AO and a double zeta basis set for the valence, where one CGTO is composed of a single Gaussian, while the other is described by the combined use of three GTO. As for the (d,p) term (which is used interchangeably with ** in the literature), this relates to the use of polarisation functions. Specifically, d refers to the use of additional d polarisation functions on non-hydrogen atoms and p refers to use of additional p polarisation functions on hydrogen. Polarisation functions help to account for changes in the shape of orbitals when other orbitals with higher angular momentum (*l*) are

in their vicinity. This is the reason why hydrogen atoms have p polarisation functions (l + 1) and the valence p-orbitals found in common organic molecule atoms have d polarisation functions.

2.5.2 Solvation

Solvation is accounted for in this work using the self-consistent reaction field (SCRF) model coupled with the polarisable continuum model (PCM) as implemented in Gaussian.^{125,128} This method places the molecule, which is contained within a cavity of overlapping spheres, in a polarisable medium with a dielectric constant ϵ . The sphere radii are determined by atomic van der Waals radii which are scaled by an empirically-derived factor. The free energy of solvation (ΔG_{solv}) is defined as:

$$\Delta G_{solv} = \Delta G_{cavity} + \Delta G_{dispersion} + \Delta G_{elec}$$
(2.19)

where ΔG_{cavity} represents the energy cost associated with formation of a hole in the continuum, $\Delta G_{dispersion}$ represents the stabilising dispersion interactions between solvent and solute and ΔG_{elec} accounts for the electrostatic stabilisation which arises from the electric charge on the solute (this polarises the medium which in turn changes the dipole moment of the solute). The effect described for ΔG_{elec} explains why the reactive field solvent must be treated self-consistently; an iterative computational procedure ensures that the description of both solvent and solute accounts for their interactions with each other. The dielectric constant ϵ is constant and is the only parameter which characterises the solvent. As water is of interest throughout this thesis, ϵ is set to 78.3553.

It should be stressed that the SCRF PCM solvation scheme provides only a qualitative picture of solvation. Reaction field models cannot simulate the effect of solvation within the first solvation sphere due to cavitation.

2.5.3 Semi-empirical methods

The purpose of semi-empirical methods is to speed up the expensive *ab initio* Hartree-Fock method through empirical parameterisation.¹²⁸ An overview of Hartree-Fock theory is provided in section 2.1.

A first source of simplification is in treating only valence electrons explicitly. Depending on the semi-empirical method, different techniques are used to account for the core electrons, including reduction of the nuclear charge or use of effective core potentials which account for the repulsion arising from the nuclei and core electrons. This, coupled with the use of minimal STO basis sets (only *s*- and *p*-functions), results in a first cost-reduction compared to the Hartree-Fock method.

The second and most important source for reduction of computational cost lies in the computation of expensive two-electron integrals. The number of these integrals can be reduced because products of basis functions of the same type on different atoms are set to zero. This assumption is referred to as Zero Differential Overlap (ZDO). This results in all two-electron integrals with two-center charge distributions being neglected. The remaining integrals are assigned parametric values which are based on experimental or high-quality computed data. The number of neglected integrals as well as the parametrisation procedure distinguishes different semi-empirical methods.

PM6

The parametric method number 6 (PM6) method¹²⁹ is used within this work to conduct otherwise computationally expensive conformational analysis. This method relies on the Modified Neglect of Differential Diatomic Overlap (MNDO) integral approximation, which effectively is the same as ZDO described above *except* that parameters are optimised to reproduce molecular properties (as opposed to atomic properties). The original MNDO parameterisation procedure was first improved upon in the AM1 method (1985) followed by PM3 method and its various extensions (1989-2004). The PM6 method (2007) evolved from deficiencies in the MNDO/AM1/PM3 methods. Namely, it applies a number of different modifications to the core-core approximations, provides better coverage of main group elements (with an emphasis on biochemical compounds), and provides a set of restricted optimised parameters for transition elements, allowing for treatment of 70 different elements. For a test set of 1373 compounds which includes the elements treated in this thesis, the PM6 method offers an average unsigned error of 4.4 kcal mol⁻¹ (0.19 eV), a slight improvement over certain significantly more expensive DFT methods i.e. B3LYP 6-31G*: 5.2 kcal mol⁻¹ (0.23 eV).¹²⁹

Chapter 3

Fe Bulk and Surface Studies

3.1 Introduction

In order to study adsorption on iron surfaces, it is first necessary to ensure that suitable models for bulk iron and iron surface slabs are selected. The following section includes results of convergence testing for Body Centred Cubic (bcc)-type iron, both in bulk and slab forms, which are compared to analogous computational and experimental values from the literature. The goal of this exercise is to identify the highest accuracy parameters at the lowest computational cost. This is important, as some of the adsorbates used in future chapters are large, meaning large metallic slabs will be required to accurately simulate the adsorption process. Efficiency gains made on the expensive metallic portion of the system therefore have a significant impact on our ability to carry out the work in future chapters.

Another factor which has been tested is the effect of the chosen van der Waals correction (TS⁸⁴) on these parameters. As discussed in chapter 2, van der Waals corrections have been shown to be of great importance for correctly capturing the adsorption behaviour of aromatic molecules on transition metal surfaces. Given their necessity for following chapters, it is prudent to study their impact on bulk and metal surface properties, particularly since other studies have shown vdW correction schemes can have a significant impact of the properties of the metal, including a study on the Fe{110} surface.¹¹⁰

3.2 Bulk bcc Fe crystal

The search for suitable Fe surface models begins with studying the bulk phase. Body centered cubic (bcc) Fe (also called ferrite or α -Fe) is the stable pure Fe phase at standard pressure and temperature conditions. At a temperature of around 1185 K, Fe undergoes phase transition to form the Face Centred Cubic (fcc) Fe phase, also referred to as γ -Fe or austenite. For this thesis, only bcc Fe will be studied, however fcc type surfaces are also of great interest for future work given the often high pressure and/or temperature conditions present in oil wells, the presence of microstructural islands on steel surfaces which have austenitic-type structure and the complex and interesting magnetic behaviour of fcc Fe bulk and derived surfaces.^{130,131} This is discussed more in chapter 7. In terms of bcc Fe, its magnetic behaviour is far less complex, and has a ferromagnetic configuration in the ground state.

In terms of some general guidelines regarding the computational treatment of Fe, spin polarisation is necessary to account for the strong magnetic behaviour of bcc Fe. A GGA method (specifically we use PBE as implemented in the CASTEP code) has been shown to correctly capture the ground magnetic state of bcc Fe.⁸¹ Finally, as a result of the magnetic nature of Fe, we make use of ultrasoft pseudopotentials with additional nonlinear core corrections (NLCC) due to the tendency for spin density to localise near the atomic core. These issues and accompanying methods are discussed in more detail in chapter 2.

Convergence of the bulk lattice constant, total energy and magnetic moment are tested with respect to k-point sampling at a cutoff energy of 340 eV for the bcc Fe conventional cell. The conventional cell is chosen as opposed to the primitive cell because it is the unit used to construct surface slabs in this thesis. Results of these convergence tests are shown in figure 3.1. The plot of free energy as a function of k-point sampling shows that energy has converged for a $7 \times 7 \times 7$ Monkhorst-Pack (MP) grid of k-points. For results shown from chapter 4 onwards, sampling equivalent to a k-point mesh of $8 \times 8 \times 8$ or higher is used. Therefore, values obtained at $8 \times 8 \times 8$ MP sampling are shown in table 3.1. The computed lattice constant and magnetic moment at the $8 \times 8 \times 8$ MP sampling are within 1.7 % and 1.8 % of experimental values respectively. The bulk modulus, which was measured through fitting to the Murnaghan equation of state, ¹³² is within the range of theoretically determined

bulk moduli, albeit at the higher end, as shown in table 3.1. When comparing to another CASTEP-derived study of bcc Fe, good agreement is achieved, which demonstrates that the CASTEP-derived bulk modulus is slightly higher than that identified using other codes.¹³³ Overall, excellent agreement is achieved.



Figure 3.1. k-point sampling convergence tests on bcc Fe conventional cell lattice constant, total energy and magnetic moment at a cutoff energy of 340 eV.



Figure 3.2. Energy cut-off sampling convergence tests on bcc Fe conventional cell lattice constant, total energy and magnetic moment at a k-point Monkhorst-Pack grid of $7 \times 7 \times 7$.

van der Waals corrected bcc results

The addition of empirical TS van der Waals corrections on the bcc bulk lattice constant, magnetic moment and bulk modulus were studied and are reported in table 3.2. The lattice constant and magnetic moment are slightly smaller (-2% and -3% respectively) compared to

Study	Lattice constant	Magnetic moment (u_{ij})	Bulk modulus
	(Л)	(μ_B)	(01a)
This work	2.82	2.17	192
Theory	$2.79 - 2.89^{134}$	$2.17 - 2.32^{135}$	144-215 ¹³⁴
Theory (CASTEP) ¹³³	2.81	2.21	219
Experiment ¹³⁶	2.87	2.22	166-173

Table 3.1. Calculated lattice constant, magnetic moment and bulk modulus for bulkbcc Fe.

Table 3.2. Calculated lattice constant, magnetic moment and bulk modulus for bulk bcc Fe including van der Waals correction^a

Method	Lattice constant	ce constant Magnetic moment	
	(Å)	(μ_B)	(GPa)
PBE-TS (This work)	2.76	2.10	242
PBE-D2 ¹¹⁰	2.80	2.15	176
optB86b-vdW ¹¹⁰	2.81	2.12	199

 a The work of Chiter et al. 110 makes use of VASP with PAW, k-point sampling mesh of 18 \times 18 \times 18 and cutoff energy of 400 eV.

the pure PBE DFT calculation while the bulk modulus is higher (+27%). The decreased lattice constant result is unsurprising given that the purpose of adding van der Waals corrections is to provide the pure DFT result with attractive dispersion forces, meaning that Fe atoms would prefer to lie closer together. Aside from the bulk modulus, the work of Chiter *et al.*¹¹⁰ show similar trends going from PBE to different vdW-corrected methods. The paper mentions that the effect of the chosen vdW scheme on bulk modulus can vary significantly, and that the D2 and optB86b-vdW methods resulted in decreased and increased values compared to their PBE result (186 GPa), respectively.

3.3 bcc Fe surface slab Studies

It is important to study adsorption phenomena on the most stable, lowest energy surfaces (for Fe, these are the flat bcc {110} followed by the kinked bcc {100}) as they are most likely

Surface	No. Layers	No. Fixed layers	Vacuum spacing (Å)
{110}	6	3	10
{100}	8	4	10
{211}	8	4	10

Table 3.3. Parameters describing the bcc Fe slabs used throughout this thesis

to be the predominantly exposed crystal faces in a realistic system. However, the study of adsorption on a higher energy stepped surface such as Fe{211} is also valuable. The Fe{211} surface is of special interest as it is the most symmetric stepped Fe surface structure and is slightly lower in energy than the Fe{111} surface.^{137,138} Many research works show that metal surfaces have high vulnerability to corrosion where there are defects, steps or edges as the surface atoms will be under-coordinated and thereby more reactive.³⁹ It is for this reason that a range of surfaces will be studied throughout this thesis.

Below, the results of convergence testing for the bcc Fe{110}, Fe{100} and Fe{211} are shown and compared to values found in the literature. The detailed survey of all convergence testing carried out in order to identify the best number of metallic layers and vacuum spacing to represent the slab are shown in Appendix A.

3.3.1 Comparison to Literature Values

Using the computed bulk lattice constant found in 3.2 and the same DFT parameters which were used in that section, the models selected to best represent the three studied surfaces facets are described in table 3.3.

Changes in interlayer spacings upon surface relaxation for the {100}, {110} and {211} surfaces are shown in table 3.4. Values for the {100} and {211} compare very well with other theoretical and experimental values, particularly considering this work makes use of eight surface layers while the work of Błoński and Kiejna makes use of fifteen surface layers.¹⁴⁰ As for the Fe{110} surface, the trends in computed distances are inconsistent across two different studies, ^{139,140} and experimental data is limited only to the Δ_{12} value.¹⁴¹

Surface	Study	d (Å)	Δ_{12}	Δ_{23}	Δ_{34}
{110}	This work	2.002	-0.82	-0.66	-0.59
	Yu et al. ¹³⁹	-	-0.35	0.17	-0.031
	Błoński and Kiejna ¹⁴⁰	-	-0.1	0.3	-0.5
	Experiment (LEED) ¹⁴¹	2.03	0.5 ± 2	-	-
{100}	This work	1.416	-3.31	1.81	-0.52
	Yu et al. ¹³⁹	-	-3.09	0.89	-0.12
	Błoński and Kiejna ¹⁴⁰	-	-3.6	2.3	0.4
	Experiment (LEED) ¹⁴²	1.433	-5 ± 2	5 ± 2	-
{211}	This work	1.156	-9.20	5.25	-0.91
	Błoński and Kiejna ¹⁴⁰	-	-9.1	3.7	-0.5
	Experiment (LEED) ¹⁴³	1.17	-10.4 ± 2.6	5.4 ± 2.6	-1.3 ± 3.4

Table 3.4. Interlayer separation prior to surface relaxation (*d*) and changes (%) due to surface relaxation for bcc Fe surfaces

With this in mind, the spacing changes we achieve are reasonable despite Δ_{23} being negative while other studies find it to be positive. It should be stressed that the values are expressed in %, so the difference in Δ_{23} of a fraction of a percent is negligible.

Calculated surface energies and work functions for the studied bcc surfaces are shown in table 3.5, and values are compared to calculated and experimental values from the literature. As described in chapter 2, the method of Boettger¹¹⁹ is used to calculate all surface energies. Specifically, an average of the slab-derived bulk energies for 6-10 layer slabs is used to calculate surface energies for the {110}, {100} and {211} slabs respectively. A similar approach is used in the work of Błoński and Kiejna¹⁴⁰ to which this work is compared, however their work makes use of an average of slab-derived bulk energies for 10-15 layer slabs.

For all surface energies and work function values, the results of this work compare favourably to those from literature. This work's γ values are slightly higher than others, which is in part due to the slightly smaller CASTEP-derived lattice constant. The ς values, which do not include the effect of the smaller surface area, compare well with other computed ς values, and are within 15% of other computed results from the literature.
Surface	Study	ς (eV)	$\gamma~(J/m^2)$	ϕ (eV)
{110}	This work	0.97	2.73	4.87
	Radilla et al. ⁶⁸	-	2.06	4.84
	Błoński and Kiejna ¹⁴⁰	0.85	2.37	4.76
	Experiment ¹⁴⁴	-	-	4.80
{100}	This work	1.40	2.81	3.95
	Radilla et al. ⁶⁸	-	2.43	3.95
	Błoński and Kiejna ¹⁴⁰	1.25	2.47	3.91
	Experiment ¹⁴⁵	-	-	4.27
$\{211\}$	This work	1.81	2.95	4.23
	Błoński and Kiejna ¹⁴⁰	1.57	2.50	4.12

Table 3.5. Surface energy (γ) and work function (ϕ) for relaxed bcc Fe surfaces

van der Waals corrected bcc results

The addition of empirical TS van der Waals corrections has a non-negligible impact on the surface structure of the bcc surfaces, as can be seen in table 3.6. In all cases, the contraction of the first surface layer is greater than without van der Waals corrections. For all three surfaces studied using van der Waals corrections, only one interlayer spacing (Fe {211} spacing 2-3) experienced an expansion with respect to the bulk. This is due to the attractive long range forces introduced through use of the TS correction.

As for the PBE-TS surface energies (shown in table 3.7), significant increases are observed in all cases. Again, this is partly correlated with the smaller PBE-TS-derived lattice constant in the case of γ values. This is in agreement with the work of Chiter *et al.*¹¹⁰ on the Fe{110} surface. As for workfunction values, PBE-TS has relatively little effect on them. The work of Chiter *et al.* on Fe{110} shows PBE-D2 to also have a minimal effect on the workfunction. As the D2 correction shares certain similar features with the TS scheme, the similar trend in workfunction change is expected.

Surface	Study	d (Å)	Δ_{12}	Δ_{23}	Δ_{34}
{110}	This work	2.002	-0.82	-0.66	-0.59
	This work PBE+TS	2.002	-2.46	-1.79	-
	PBE-D2 ¹¹⁰	-	1.01	0.80	-0.34
	optB86b-vdW ¹¹⁰	-	-0.18	0.54	-0.36
{100}	This work	1.416	-3.31	1.81	-0.52
	This work PBE+TS	1.416	-4.65	-0.42	-3.65
{211}	This work	1.156	-9.20	5.25	-0.91
	This work PBE+TS	1.156	-9.44	2.66	-2.43

Table 3.6. Interlayer separation prior to surface relaxation (d) and changes (%) in interlayer spacing due to surface relaxation for bcc Fe surfaces with TS van der Waals correction

Table 3.7. Surface energy (γ) and work function (ϕ) for relaxed bcc Fe surfaces with TS van der Waals correction

Surface	Study	ς (eV)	$\gamma~(J/m^2)$	ϕ (eV)
{110}	This work	0.97	2.73	4.87
	This work PBE+TS	1.60	4.51	4.86
	PBE-D2 ¹¹⁰	-	3.02	4.78
	optB86b-vdW ¹¹⁰	-	2.89	5.00
{100}	This work	1.40	2.81	3.95
	This work PBE+TS	2.28	4.56	3.93
{211}	This work	1.81	2.95	4.23
	This work PBE+TS	2.84	4.64	4.28

Chapter 4

Benzene Adsorption on Fe Surfaces

4.1 Introduction

This chapter presents and compares the results of DFT study of adsorption of benzene on three different iron surface facets.

Section 4.1.1 introduces the motivations and current research efforts made on benzene adsorption on metallic surfaces. Section 4.1.2 presents progress made in the study of benzene adsorption on iron and iron-like surfaces.

This work's results are presented for benzene adsorption on the flat Fe{110} surface in section 4.2, followed by benzene adsorption on the kinked Fe{100} surface in section 4.3 and, finally, results for benzene adsorption on the stepped Fe{211} surface are shown in section 4.4. A discussion of the similarities and differences in trends observed for benzene adsorption on the Fe{110}, Fe{100} and Fe{211} surface facets is presented in section 4.5. Concluding remarks are made at the end of the section.

4.1.1 Benzene adsorption on metallic surfaces

Because benzene is the simplest, most accessible aromatic building unit, it has featured heavily in experimental surface science research as a model system to probe fundamental surface-adsorbate interactions as well as to better understand more complicated aromatic adsorption phenomena. For this reason, the adsorption of benzene on catalytically relevant surfaces has been studied rigorously since the 1970s.

A comprehensive review of experimental efforts and corresponding results for benzene adsorption on a number of transition metal surfaces is included in the book chapter of Steinrück and Held.¹¹ One of the earliest papers in this area, which studies the adsorption of benzene upon Pt{111} and {100} surfaces through use of Low Energy Electron Diffraction (LEED) and workfunction change, is presented in the 1973 paper of the Somorjai research group.¹⁴⁶ Somorjai *et al.* have continued to study aromatic adsorption experimentally using a wide variety of surface science techniques, and have had a major influence on this research area.¹⁴⁷ Other important contributors to this area include the groups of Steinrück^{11,148} and Netzer.^{149–151} The 1991 paper of Netzer also provides a perspective on trends in adsorption of benzene on transition metal surfaces based on experimental data which had been collected up to that time.¹⁵⁰ Benzene adsorption on transition metals does continue to be of current interest, as evidenced for example by the very recent paper of Carey *et al.* which makes use of Single Crystal Adsorption Calorimetry (SCAC) to study heat of adsorption and sticking probability of benzene on Pt{111} and Ni{111}.¹⁵²

Theory has been an important tool in furthering the understanding of the electronic structure of organic-inorganic junctions, and this is certainly no exception in the area of benzene adsorption on many different types of surfaces. DFT work prior to 2009 on benzene adsorption on transition metal surfaces is thoroughly covered in the review of Jenkins.¹⁴ As is mentioned in this review, effectively all studies presented there fail to account for the effect of van der Waals which is neglected within DFT. Such effects are particularly important for aromatic adsorption on metal surfaces due to the tendency for these molecules to maximise their van der Waals interaction with the surface. In 2009, the inclusion of such corrections to DFT was not yet routine. Over the course of the past decade, new formalisms to account for van der Waals corrections and their implementation in popular DFT packages has resulted in a renewed interest in the study of benzene and aromatic molecule adsorption on transition metal surfaces. As with DFT functionals, there is now a wide range of correction schemes, including cost-effective but lower accuracy pairwise schemes (D2⁸⁵), environment-dependant pairwise schemes (D3,⁸⁶ TS⁸⁴ and long-range

density functionals (vdw-DF denoted functionals⁸⁷) which are of moderate cost and accuracy, all the way up to the very accurate, high-cost many body schemes (RPA⁸⁸). An excellent perspective on progress in this area, classification of existing schemes and a comparison of them is presented in the paper of Klimes and Michaelides.⁷⁴

In recent years, computational research works have focussed heavily on the suitability of various DFT van der Waals correction schemes by probing the nature of aromatic adsorption on transition metal surfaces. Such works include: the recent thorough study of benzene adsorption on the {111} surfaces of Pt, Pd, Rh, Ir, Ni and Ag, the {110} surfaces of Mo, W and the {0001} surface of Ru by Lakshmikanth *et al.*¹⁰³ as well as a study by the same group on Pt{111}, {110} and {100};¹⁰⁴ the combined experimental-computational study of benzene adsorption on Cu{111} of Sacchi *et al.*¹⁰⁹; the combined experimental-computational work of Liu *et al.*¹⁰¹ on benzene adsorption on {111} facets of Cu, Ag and Au; the study of Matos et al.¹⁰² of benzene adsorption on {110} facets of Ag, Au, Cu, Pd, Rh and Ni; benzene on {111} surfaces of Cu, Ag, Au, Rh, Pd, Ir and Pt using a number of different van der Waals correction methods by Carrasco *et al.*⁹⁷; benzene on Cu{111} using a local orbital DFT code with various van der Waals correction schemes (as opposed to the plane-wave codes employed by all previously listed studies).⁹⁸ A study conducted by Canduela-Rodriguez *et al.* using the vdW-DF method and the optPBE-vdW functional on the adsorption of benzene on fcc Pd{100} showed an average increase in binding strength of around 0.5 eV compared with uncorrected DFT (PBE).^{99,153} There is also a recent study of benzene as well as toluene, phenol and *m*-cresol adsorption on a variety of Fe, Co, Ni, Cu, Ru, Rh, Pd and Pt surfaces using the optB88-vdW functional (all adsorbates are studied within the same adsorption site across all surfaces).¹⁰⁵ The absence of Fe from this series of papers (but one) exploring benzene adsorption on transition metal surfaces is noteworthy.

4.1.2 Benzene adsorption on Fe surfaces

There is a limited body of research regarding the adsorption of aromatic molecules on Fe surfaces. Experimentally, UHV Fe adsorption experiments are highly challenging due to the difficulty in obtaining clean Fe surfaces because of the tendency for passivation/reaction of Fe single crystals. For this reason, there is an extremely limited number of studies on benzene or any aromatic molecule adsorption on Fe surface facets. To the best of our knowledge, there is a single study on adsorption of benzene on an iron surface in UHV, specifically benzene adsorption on a thin film of Fe(110) on a W support.¹⁵⁴ Angle and spin-resolved ultra-violet photoelectron spectroscopy (A/SRUPS) experiments at saturation pressure at 200 and 300 K reveal benzene adsorbs molecularly and flat on the Fe{110} film with pseudo- C_{3v} symmetry. There is also the less traditional surface science study of Sun *et al.*¹⁵⁵ which studies the spinpolarised electronic structure of benzene adsorbed upon a thin film of Fe{100} (mounted on a MgO{100} single crystal) using spin-polarised metastable-atom deexcitation spectroscopy (SPMDS). We are unaware of any aromatic adsorption studies on an Fe single crystal under UHV conditions.

As for computational studies of benzene on Fe surfaces, there are a few, however several fail to account for van der Waals interactions in their DFT calculations, mostly due to these corrections not being readily accessible at the time these papers were published. This includes the study of perpendicular and parallel-adsorbed benzene on Fe(100) by Goumri-Said *et al.*¹⁵⁶ which makes use of a combination of molecular mechanics and DFT and the studies of Sun *et al.* on benzene adsorption on Fe{100}.^{155,157} Such results are still interesting, however should be regarded as potentially inaccurate due to the lack of correction to account for non-local interactions.

As for DFT studies of aromatic adsorption on iron which do account for van der Waals corrections, the only one we are aware of is a study of benzene adsorption on the Fe{110} surface in the context of a wider study on the interaction of benzene with PdFe bimetallic surfaces by Hensley *et al.* ⁹⁶ The inclusion of van der Waals interactions is achieved through use of the optB88-vdW functional in this work. ¹⁵³ Its use shows a significant change in adsorption energy compared to the results using PBE, with adsorption energies on average 0.74 eV stronger when van der Waals effects are included. There is also the recent study of Jia and An ¹⁰⁵ which analyses the effect of three different forms of van der Waals-corrected DFT upon the adsorption energetics and geometries of benzene on Fe{110}. An important detail to mention within the study of Jia and An is that they only study adsorption of benzene

centered upon a Fe{110} bridge site, while hollow-centered sites have been shown to be preferred both on Fe{100} and Fe{110} whether or not van der Waals-corrected DFT is used.^{96,155} To the best of our knowledge, there has been no van der Waals-corrected DFT study of benzene adsorption on either Fe{100} or Fe{211}, the latter of which has not been studied at all for aromatic adsorption.

In terms of Fe-like or related surfaces, there is a growing body of DFT work on iron oxide, sulphide, nitride and carbide type surfaces. The very recent DFT work of Muñoz Ramo and Jenkins on benzene and naphthalene adsorption on θ -Fe₃C{010} (among other adsorbates) represents a good example of such efforts.¹⁵⁸ There are also a number of studies carried out by the group of Professor Nora de Leeuw on such surfaces, namely one which probes benzene adsorption on hematite (α -Fe₂O₃)surfaces as well as on one of the smallest heteroatomic aromatics, thiophene, on layered FeS {001}, {011} and {111}.^{159,160} There is a paper by Zhang *et al.* which studies the benzene/Fe₄N interface and identifies an interesting antiferromagnetic spin state for the Fe atoms lying just below the benzene molecule.¹⁶¹ We expect this body of work to continue growing given the relevance of this type of surface in many industrially relevant applications including oil and gas processing, pigments, catalysis, semiconductors and organic coatings.

It becomes clear that study of the adsorption of benzene on iron surfaces is rather incomplete, both experimentally and computationally. Studies in this area using van der Waals-corrected DFT allow for important insights to be gathered on a system for which experimental studies are challenging. In this chapter, we describe results on the study of benzene adsorbed on Fe{110}, Fe{100} and Fe{211} surfaces. These three surfaces were selected on the basis that they represent the three energetically most stable surfaces for bcc Fe, as well as presenting three different roughnesses, with Fe{110} being the only flat bcc facet, Fe{100} showing a kinked structure and Fe{211} having stepped structure. The choice of Fe{211} is also relevant in the context of our focus on corrosion inhibition due to corrosion being shown to take place at more reactive sites such as step edges, defects sites and roughened surfaces.³⁰

4.2 Benzene/Fe{110}

4.2.1 Introduction

The Fe{110} surface is a sensible choice for our study of benzene adsorption for several reasons. First, it is the only existing flat bcc surface, is energetically favoured and therefore likely to be predominantly present on a real iron crystal.¹³⁷ Second, there is existing DFT work on the benzene/Fe{110} system which also includes important vdW corrections, so provides an opportunity for comparison to the results presented here.⁹⁶ Comparing our own DFT results to those derived from an analogous study will improve confidence in our results for benzene adsorption on the Fe{100} (section 4.3) and Fe{211} (section 4.4) surfaces, for which other DFT studies are either incomplete or missing from the literature.

 Table 4.1. Simulation details and parameters

 specific to the benzene/Fe{110} calculations

Parameter	Value
Vacuum spacing (Å)	10
Cell size (c \times c)	(4 × 4)
Number of slab layers	6
Number of fixed slab layers	3
MP K-point sampling	$2 \times 2 \times 1$

Detailed information on the computational methods and general simulation parameters used throughout this chapter is presented in chapter 2. Results of convergence testing carried out on the bcc Fe bulk and Fe $\{110\}$ slab system are presented in chapter 3. Results from the aforementioned section are used in determining the simulation parameters such as cell dimensions and k-point sampling for our benzene/Fe $\{110\}$ model system.

As the packing of benzene on the Fe $\{110\}$ surface is not known experimentally, we have opted for a packing arrangement which minimizes intermolecular interactions. For the purposes of studying the interaction of benzene with the Fe $\{110\}$ surface, we make use of a (4 × 4) unit supercell (made up of four by four units of the conventional bcc Fe cell). The chosen supercell, alongside its dimensions, is shown in figure 4.1. As can be seen,



Figure 4.1. Surface structure, simulation cell and relevant PBE-optimised distances for the (4×4) Fe $\{110\}$ simulation cell. All distances in Å.

the {110} conventional cell has a parallelepiped shape, which is why the simulation cell also has this shape. It should be noted that this is larger than what is necessary to prevent intermolecular interactions between periodic copies of benzene. We have chosen these cell dimensions in order to directly compare our findings for benzene/Fe{110} with results presented in chapter 5 for naphthalene and quinolinium adsorption on the Fe{110} surface, which require at minimum a (4×4) simulation cell. The smallest possible cell size which would limit interactions between periodic copy images would be a (3×3) unit simulation cell, which is what is used in the benzene/Fe{110} DFT work of Hensley et al.⁹⁶ There are a number of other differences between the cited work and this work which could result in different results; see the table in the Appendix (section B) as well as the discussion in section 4.5. A six layered slab with three fixed layers was used as this system produced a well converged surface workfunction (see chapter 3). Finally, the chosen Monkhorst-Pack (MP) k-point sampling of $2 \times 2 \times 1$ has a density comparable to an $8 \times 8 \times 8$ k-point sampling of the conventional bcc cell. This produces distances converged to within 0.002 Å, energies within 0.01 eV and spin within 0.03 μ_{β} . A full list of simulation parameters used for the benzene/Fe{110} system can be found in table 4.1.

4.2.2 Adsorption geometries and energies



Figure 4.2. Benzene orientations selected for study on Fe{110}. Hydrogen atoms omitted for clarity.

Figure 4.2 shows the eight high symmetry benzene binding sites on the Fe{110} surface which are tested alongside the naming convention used throughout this section. The eight sites are selected because they represent the points of highest symmetry on the bcc{110} surface. The bcc{110} facet is the lowest energy surface for iron, however unlike the usual lowest energy fcc{111} surface which is also flat (fcc being the structure more commonly adopted by catalytically-relevant transition metals), bcc{110} presents lower symmetry. The bcc{110} surface is close-packed only in two directions, while the fcc{111} is close-packed in all three directions. As a result, there is a greater number of unique high symmetry points and therefore possible binding sites on the bcc{110} surface than on the fcc{111} surface.

All eight adsorption sites are first geometry-optimised using the PBE functional. Out of the eight tested binding sites, five are stable and three (A-0°, A-30° and S-30°) are unstable, and shift towards one of the five favoured geometries. This is in agreement with the results of Hensley *et al.* for benzene adsorption on the Fe{110} surface, as they also find the two atop sites and short bridge site to be unstable.⁹⁶



Figure 4.3. Images of 0° rotated PBE-TS optimised benzene binding sites. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).



Figure 4.4. Images of 30° rotated PBE-TS optimised benzene binding sites. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).

Figures 4.3 and 4.4 depict all PBE-TS optimised geometries of benzene on Fe{110}. The PBE-optimised geometries are not shown for brevity because they are essentially identical to the PBE-TS optimised ones; this is discussed in section 4.2.2. In all cases, the benzene molecule C-H bonds flip up and away from the surface. For all stable binding sites on the Fe{110} surface, the benzene molecular plane buckles slightly. The adsorbed geometry of benzene across all five adsorption sites is similar, and this is reflected in the similar binding energies, distortion energies and geometric parameters as shown in tables 4.2 and 4.3. The largest difference in binding energy is between the H sites (-1.62 eV) and the stable L-30° site (-1.56 eV) and is 0.06 eV. The small difference in energy between the different adsorption

sites indicates a flat potential energy landscape for benzene adsorption on Fe{110}, and is indicative of difficulty in distinguishing different sites in UHV experiments. Additionally, it would not be possible to observe the least stable of the adsorption sites (L-30°) below temperatures of 80 K. This is because the Arrhenius equation reveals that the probability of finding a system at energy E is proportional to $e^{-\Delta E/k_BT}$, and $k_BT = 0.07$ eV at 80 K.

There is an interesting but subtle change in Fe{110} surface structure seen for the S-30° binding site: stability is afforded by the gap between the short bridge atoms opening up. In other words, the increased space between the bridging atoms makes the site resemble more of a stable long bridge geometry.

vdW-corrected adsorption geometries and energies

Table 4.2. Calculated optimised energies for stable benzene adsorption sites on $Fe{110}^a$

	E_{ac}	_{ls} (eV)	E_{dist} (eV)		
site	This work	Hensley <i>et al</i> . ⁹⁶	This work	Hensley <i>et al</i> . ⁹⁶	
S-0°	-1.59 (-3.45)	-1.11 (-1.82)	1.25 (1.36)	1.20 (1.14)	
H-30°	-1.62 (-3.43)	-1.21 (-1.97)	1.41 (1.48)	1.16 (1.08)	
H-0°	-1.62 (-3.42)	-1.20 (-1.95)	1.60 (1.44)	1.19 (1.12)	
$L-0^{\circ}$	-1.58 (-3.35)	-1.17 (-1.88)	1.23 (1.33)	1.13 (1.07)	
$L-30^{\circ}$	-1.56 (-3.33)	-1.16 (-1.91)	1.20 (1.32)	1.19 (1.12)	

^{*a*} E_{ads} represents the adsorption energy and E_{dist} represents the distortion energy upon adsorption. Data in brackets represents a van der Waals corrected result. In the case of this work, the TS correction is used,⁸⁴ while in the DFT work of Hensley *et al.*,⁹⁶ the optB88-vdW functional is used.¹⁵³ All non-bracketed results were calculated using PBE.

Figures 4.3 and 4.4 show all PBE-TS optimised geometries of benzene on Fe{110} and tables 4.2 and 4.3 show the PBE-TS derived energetics and geometric parameters. The most obvious change is the strong increase in adsorption energy strength of on average 1.80 eV. The increase in adsorption strength upon addition of a vdW correction scheme is expected for this system given that benzene binds parallel to the metallic surface in an effort to maximise its vdW interaction with the surface. Another interesting change is found in the

site	$d_{C-C}(\text{\AA})$	$d_{C-H}(\text{\AA})$	$\theta_{C-H}(^{\circ})$	$\theta_{C-C}(^{\circ})$	$d_{C-Fe}(\text{\AA})$
free benzene	1.39 (1.40)	1.09 (1.09)	0(0)	120 (120)	-
S-0°	1.45 (1.45)	1.10 (1.10)	20 (21)	119 (119)	2.11 (2.09)
H-30°	1.46 (1.45)	1.10 (1.10)	25 (24)	119 (120)	2.11 (2.10)
H-0°	1.46 (1.45)	1.10 (1.10)	24 (23)	120 (120)	2.11 (2.12)
L-0°	1.45 (1.45)	1.09 (1.09)	22 (24)	120 (120)	2.16 (2.09)
L-30°	1.45 (1.45)	1.09 (1.09)	23 (23)	120 (120)	2.11 (2.14)

Table 4.3. Calculated optimised geometric parameters for benzene on $Fe{110}^a$

^{*a*} d_{C-C} represents the average C-C bond length in benzene, d_{C-H} the average C-H bond length, θ_{C-H} the average CH tilt angle (dihedral) with respect to the molecular plane, θ_{C-C} the average angle between carbon atoms in the molecule and d_{C-Fe} () represents the average C-Fe distance. Data in brackets represents a van der Waals corrected result. All non-bracketed results were calculated using PBE. The free benzene results were extracted from a GGA-PBE (PBE-TS) geometry optimisation using a cubic 20 Å box to prevent benzene self-interactions.

relative energetic ordering of the five sites. In particular, a new geometry has become the most favourable adsorption site, namely the S-0° site. It is worth noting that it isn't much stronger binding than the top PBE-optimised H-0° and H-30° sites (energy difference of 0.03 eV). This is again due to the flat potential energy landscape for benzene adsorption on Fe{110}, which results in minimal energetic distinction between the stable adsorption geometries.

The TS vdW correction used throughout this work, though simple, environment-dependant and cost-effective, has been observed to overbind certain aromatic systems on metal surfaces.⁹² Table 4.2, which compares this work's vdW-corrected energy results to those of Hensley *et al.*⁹⁶, demonstrates this to be the case. Their work makes use of a more sophisticated vdW scheme (optB88-vdW¹⁵³) which is less prone to overbinding, and as a result the optB88-vdW results are only around 0.70 eV stronger than the PBE results. With the exception of the S-0° site, despite the discrepancy in numbers due to different vdW correction schemes, PBE-vdW trends are similar for this work and that of Hensley *et al.* See section 4.5 for discussion of the S-0° site energetics.

Table 4.3 lists the PBE-TS geometric parameters alongside analogous PBE-derived data. The results show clearly that PBE adsorption geometries are minimally affected by the addition of the TS correction. The largest discrepancies lie in the C-Fe distances. While they are not very big differences (the biggest difference between PBE and PBE-TS data is for the L-0° site and is on the order of 0.07 Å), it is no great surprise to see a change in this data given that the TS correction captures benzene-Fe interactions which do not exist using pure PBE.

4.2.3 Charge density difference

Contour plots of charge density difference for the five stable PBE-TS optimised adsorption sites of benzene on Fe{110} are shown in figure 4.5. As a reminder, the calculation method and purpose of charge density difference analysis is explained in chapter 2. The five density distributions show more similarities than they do differences. This can be attributed to the similarity in binding energy and adsorption geometry of the five identified stable sites. In all cases, regions surrounding the carbon atoms are yellow which indicates increased local charge density, while the region between the surface and adsorbate is blue, indicating a reduction in the electronic density. This area of reduced charge density follows the benzene molecule, extending to the hydrogen atoms. Some configurations show particularly strong decrease of electron density below the center of the benzene ring, namely L-0° and L-30°. Just below the region of electron depletion, yellow regions of charge density increase extend out from the metal surface. These findings are discussed in section 4.5.

4.2.4 Spin density

Spin density plots are shown for the five stable benzene/Fe{110} sites in figure 4.6 (see chapter 2 for more information on spin density studies and calculation method). The overall look of the plotted densities for different sites is similar (minority spin (yellow) regions above carbon atoms, majority spin (blue) regions below carbon atoms and majority spin (blue) regions on hydrogen atoms). As with the charge density difference, this is consistent with the fact that the different sites were found to be similar in energy. It is however interesting to note that the distribution of minority spin around the carbon atoms seems quite different even for sites which were found to be identical in terms of binding strength. This is seen for



Figure 4.5. Images of optimised benzene binding site charge density difference. View shown from above the Fe{110} surface. Blue (yellow) regions denote a decrease (increase) in electron density on the order of 2×10^{-2} electrons/Å³.

H-0° and H-30° sites for example, where in one case the minority spin (blue) distribution roughly follows the C-ring shape, whereas for H-30°, the minority spin (blue) region extends over the top of one of the C-H bonds. The same can be said for L-0° and L-30°, which have quite different minority spin distribution above the carbon atoms.



Figure 4.6. Images of optimised benzene binding site spin densities. View shown from above the Fe{110} surface. Blue (yellow) regions denote minority (majority) spin regions on the order of 3×10^{-3} electrons/Å³.

4.2.5 Atomic charges and spin

Charge and spin density contour plots provide a qualitative picture of the distribution of charge and spin. Hirshfeld charges and atom-resolved spin can provide complimentary quantitative results. Hirshfeld charges have been calculated for the PBE and PBE-TS optimised S-0° conformation of benzene on the Fe{110} surface. These are presented alongside spin measured on different groups of atoms in table 4.4.

Atom group	charge (e) PBE	charge (e) PBE-TS	spin (μ _β) PBE	spin (μ_{β}) PBE-TS
C ₆ H ₆ sum	0.13	0.13	-0.32	-0.32
C sum	-0.22	-0.22	-0.32	-0.34
H sum	0.35	0.35	0	0.02
Metal slab sum	-0.25	-0.21	165.74	164.72

Table 4.4. Calculated Hirshfeld charges and atomic spin results for S-0° benzene on Fe{110}

First, the results show that charges derived from PBE and PBE-TS methodologies are essentially identical. The benzene molecule carries a small partial positive charge (+0.13), which results from the sum of a negatively charged ring of carbon atoms (-0.22) and positively charged H atoms (+0.35). This charge is balanced by a negatively charged metal slab (-0.25). It is also worth noting here that the sum of Hirshfeld charges is non-zero, i.e. there is an excess negative charge of -0.08 in the PBE-TS case. The results shown in table 4.4 are derived from a single point calculation using $4 \times 4 \times 1$ MP sampling of the (4 × 4) simulation cell. Even with a k-point mesh two times finer than that used for all other calculations studying benzene/Fe{110}, the sum of charges does not add up to zero. Studying the metal slab charges more closely, there are several atoms with -0.01 e charge. Within the CASTEP output file, Hirshfeld charge values are included with rounding to two decimal places. Given that the simulation cell includes 96 Fe atoms alongside the presence of ± 0.01 charges resulting from rounding, it is plausible that a slight negative excess charge should appear. This finding is corroborated by the +0.13 e on benzene being identical whether $2 \times 2 \times 1$ or $4 \times 4 \times 1$ MP sampling is used. Finally, the numerical values match the

trends seen in the charge density difference diagram (figure 4.5), where electronic density increases on C atoms (therefore they carry negative charge) and decreases on H atoms (where positive charges are seen).

As for spin, again PBE and PBE-TS derived results are effectively identical, and show negative values (minority spin) for both the carbon atoms and entire molecule. The H atoms show very little majority spin polarisation, the same direction of spin as the Fe atoms. These results are consistent with what is seen in the spin density diagrams, see figure 4.6.

It is worth commenting on the small but noticeable difference between PBE and PBE-TS derived charges and spins on the Fe slab. This is because the optimised coordinates for PBE and PBE-TS slabs is different; in the case of PBE-TS, the upper surface slab layers are more tightly bound to each other and the bulk-like slab layers, which results in slightly more strongly-bound Fe atoms, ie. the upper surface layers of Fe have slightly more bulk character. Given that iron surfaces are known to have higher surface spin polarisation than their bulk,¹⁶² it therefore isn't surprising that PBE-TS spin (164.72) is slightly reduced compared to PBE spin (165.74).

4.2.6 DOS and PDOS

The PDOS for a carbon atom and an Fe atom from the PBE-preferred H-30° adsorption site is shown in figure 4.7 (for more general information on PDOS calculations and the information they reveal, see chapter 2). These atoms are selected for PDOS analysis because they are in close contact within the H-30° adsorption geometry. Previous DFT work on benzene/Ni{111}¹⁶³ shows the PDOS antibonding and bonding orbitals lie above and below the Fermi energy, respectively. As for the precise assignment of gas-phase PDOS peaks to benzene orbitals, the paper of Mittendorfer and Hafner¹⁶³ provides a detailed account of their assignment. Quantitative agreement of DOS peaks with experimental Angle Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS) data cannot be expected given that calculations neglect many-body effects, but the ordering of unoccupied and occupied levels is reproduced when compared to ARUPS data acquired for benzene.¹⁶⁴ We are not aware of any benzene/iron experimental ARUPS data, so it is not possible to compare the

adsorbed benzene/Fe{110} PDOS data to analogous experimental results.

Looking first at the carbon peaks in figure 4.7, the adsorbed-benzene peaks show a shift to higher (i.e. more negative) binding energies. This is also observed for benzene/Ni{111}.¹⁶³ The higher energy carbon peaks $(3a_{1g}, 2b_{1u} \text{ and } 1b_{2u})$ remain sharp and well-defined, whereas the orbitals which lie closer to the Fermi energy are broadened or disappear. The latter effect is a result of interaction with Fe 3*d* orbitals. The highest occupied molecular orbitals $(1e_{1g}, 3e_{2g} \text{ and } 1a_{2u})$ are those which overlap most significantly with the iron PDOS, and as a result these peaks are no longer well defined in the adsorbed-state PDOS plot. This behaviour is in agreement with the H-30° benzene/Fe{110} PDOS of Hensley *et al.*⁹⁶

The adsorption process also has an effect upon the distribution of states for Fe interacting with C. Specifically, there is an increase in the number of majority spin states just before the Fermi level, while there is an increase in minority spin states at binding energy higher than the Fermi level as well as a reduction of minority spin states above the Fermi level. New states for Fe in the adsorbed benzene case can also be seen at binding energies lower than -6 eV, which correspond to the PDOS peaks of shifted $3e_{1u}$ and $1a_{2u}$ benzene orbitals.

The plot overall supports the strong electronic interaction of benzene with the Fe $\{110\}$ surface. The trends and general appearance of the PDOS are in near perfect agreement with those for the analogous study of benzene adsorption on Fe $\{110\}$ of Hensley *et al.*⁹⁶

In addition to the H-30° site-derived PDOS, a plot of the PDOS for the PBE-TS-preferred S-0° site is included in figure 4.8. Overall, the S-0° has similar features to the H-30° plot. The main differences include a more significant shift of the minority spin Fe states to higher binding energies, almost no change in the majority spin Fe distribution of states as well as different changes in the shape and shifts of the $1b_{2u}$, $3e_{1u}$ and $1a_{2u}$ carbon peaks. These changes show that the preferred benzene orbital-Fe 3*d* interactions are different for different adsorption sites.



Figure 4.7. Projected density of states (PDOS) for benzene on Fe{110} in the H-30° adsorption geometry. The upper plot shows the majority spin and minority spin PDOS for Fe atom 87 before (black) and after adsorption (red). The lower plot shows C atom 3 within benzene in the gas-phase (black) and after adsorption (red, majority spin and minority spin shown). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase benzene DOS has been aligned with the C(2s) peak for the adsorbed benzene, as this level is not expected to be involved in the adsorption process.



Figure 4.8. Projected density of states (PDOS) for benzene on Fe{110} in the S-0° adsorption geometry. The upper plot shows the majority spin and minority spin PDOS for Fe atom 91 before (black) and after adsorption (red). The lower plot shows C atom 1 within benzene in the gas-phase (black) and after adsorption (red, majority spin and minority spin shown). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase benzene DOS has been aligned with the C(2s) peak for the adsorbed benzene, as this level is not expected to be involved in the adsorption process.

4.2.7 Workfunction



Figure 4.9. Plot of the calculated potentials used for calculating the vacuum energy (E_{vac}) needed to calculate the workfunction (top) alongside the cell used for the calculation (below). The plot and configuration are aligned so that what is plotted matches atomic coordinates below it. Results shown for PBE optimised geometry.

Prior to presenting the workfunction results for benzene/Fe{110}, it is useful to review the procedure used to obtain these results. As discussed in chapter 2, workfunction (ϕ) is calculated by subtracting the Fermi energy (E_F) from the vacuum energy (E_{vac}). As explained previously, E_F is obtained directly through geometry optimisation/single point calculations, but E_{vac} needs to be calculated from the density stored in the binary CASTEP .check file. This is achieved using the pot1d utility. Figure 4.9 depicts the behaviour of the pot1d-calculated potentials for a double-sided bcc Fe{110} surface slab with benzene (in the H-30° adsorption site) adsorbed on both sides. In figure 4.9, the vacuum region is depicted from around

Table 4.5. Calculated Workfunction (ϕ) results for 3-fold-hollow-30° benzene on Fe{110}^{*a*}

Method	$E_{vac}(eV)$	$E_F(eV)$	Fe{110} φ (eV)	$C_6H_6/Fe{110} \phi$ (eV)	$\Delta \phi$ (eV)
PBE	-3.19	-6.90	4.90	3.71	-1.19
PBE-TS	-3.19	-6.89	4.86	3.70	-1.16

^{*a*} E_{vac} represents the vacuum energy, E_F represents the Fermi energy and $\Delta \phi$ represents the difference between the C₆H₆/Fe{110} ϕ and bare Fe{110} ϕ . Bare Fe{110} ϕ values are calculated using the 6-layer (4 × 4) slab.

0-0.17 and also 0.83-1.0 fractional coordinate units. The pot1d guidelines recommend use of the value for the electrostatic potential (V_{elec}) within the vacuum region as the value for E_{vac} if the potential has gone flat within the vacuum region. If the total potential (V_{loc} , which is the sum of V_{elec} and the exchange correlation potential, V_{xc}) has gone flat within the vacuum region, its value in the vacuum can also be used as the vacuum potential, but it tends to require larger vacuum spacings to go flat because V_{xc} has a longer decay length. Figure 4.9 also demonstrates that for a spin-polarised system such as benzene/Fe{110}, the calculated potentials can differ for majority and minority spin electrons.

For the surface slab alone, a single-sided slab (one bulk, one surface and one vacuum region in the simulation cell) can serve as a good enough approximation to achieve a reasonable workfunction value. For slab systems which include an adsorbate or more complex surfaces, it becomes necessary to make use of double-sided slabs (two surface and vacuum regions and one bulk region sandwiched between the two surface regions) where the potentials will be symmetric with respect to the unit cell. This is because there is an unphysical effect associated with the potentials derived from a unit cell containing a "fixed" surface, which arises from the termination of the bulk section of the metal slab. In such cases, it becomes awkward to define E_{vac} due to the sloping potential in the vacuum region.

Workfunction data for the H-30° benzene geometry on Fe{110} is presented in table 4.5. Data has been calculated using both PBE and PBE-TS optimised geometries. The PBE-TS bezene/Fe{110} ϕ result (3.70 eV) is very slightly smaller than the PBE result (3.71 eV).

Despite the slight changes in PBE-TS and PBE optimised slab geometry, the PBE and PBE-TS optimised benzene/Fe{110} workfunctions differ only by 0.01 eV. As for the change in workfunction compared to the bare slab ($\Delta \phi$), both PBE and PBE-TS show a decrease of just over 1 eV. Again, there is a slight difference between the two calculation methods, but it is very small (0.03 eV). Adsorption-induced workfunction decrease is common for benzene adsorption on transition metals: this effect, as well as a comparison of these results to other transition metal surface ϕ values, is presented and discussed in section 4.5.

4.3 Benzene/Fe{100}

4.3.1 Introduction

The second most stable bcc Fe surface, Fe{100}, is studied in this section for its interaction with benzene. Given its relative stability and therefore potential to be exposed on a real crystal, it is an interesting surface to study. It is also particulary interesting to compare results obtained on this surface to those on Fe{110}; on the Fe{110} surface, as mentioned previously in section 4.2, atoms assume the most close-packed arrangement for a bcc surface, ie. in two directions. As can be seen in figure 4.10, the top surface layer of Fe{100} is now no longer close-packed in any dimension. The practical outcome of this is that the layer directly underlying the uppermost one becomes exposed, and can have more of an effect on stabilising adsorption geometries. The Fe{100} surface presents a high level of symmetry which is also interesting in terms of the adsorption behaviour upon it. Finally, the benzene/Fe{100} case is also of interest because there is existing DFT work on this system in the literature.¹⁵⁵ The work of Sun *et al.*¹⁵⁵ on the benzene/Fe{100} system does not make use of vdW corrections, so it is relevant to study the impact these may have in this work.

Table 4.6 lists the simulation parameters used for the benzene/Fe{100} system. Of particular note is the increased number of slab layers (8) compared to that used for Fe{110} (6). The kinked structure of the Fe{100} surface is more open than the flat Fe{110} top layer, which, as mentioned previously, can result in the Fe{100} underlying layer playing a more active role in the adsorption process. It is therefore prudent to include a greater number

of slab layers to increase the distinction between surface and bulk layers. Additionally, it was necessary to use 8 layers to achieve convergence of slab parameters (see Appendix section A). Geometry optimisation calculations allowed for relaxation of the top four surface layers as well as the benzene molecule. The bottom four slab layers, which are meant to represent the bulk, are kept fixed. The dimensions of the (3 × 3) simulation cell chosen for study, as well as relevant interatomic Fe-Fe distances, are shown in figure 4.10. The chosen MP k-point sampling grid (4 × 4 × 1) is equivalent to a 12 × 12 × 1 sampling of the conventional cell, which should be sufficient to produce results with high accuracy (slightly better than distances converged to within 0.002 Å, energies within 0.01 eV and spin within 0.03 μ_{β} .) Chapter 3 offers more details on matters related to convergence testing of the bulk and bare bcc Fe{100} surface.

Table 4.6. Simulation details and parametersspecific to the benzene/Fe{100} calculations

Parameter	Value
Vacuum spacing (Å)	10
Cell size (c \times c)	(3 × 3)
Number of slab layers	8
Number of fixed slab layers	4
MP K-point sampling	$4 \times 4 \times 1$

4.3.2 Adsorption geometries and energies

Adsorption is studied at six different high symmetry adsorption sites as depicted in figure 4.11. These sites have been studied in a previous work on the Pd{100} surface (note: although this is a fcc {100} surface, the fcc {100} surface has a similar appearance to the bcc {100} surface).⁹⁹ The hollow (H), atop (A), bridge1 (B1) and bridge2 (B2) benzene/Fe{100} sites have been studied in work published by Sun *et al.*¹⁵⁵ To the best of our knowledge, there has been no published DFT study on benzene on Fe{100} binding sites H-15° and A-15°. Binding sites H-15° and A-15° are related to the H and A sites by a 15° rotation, so that the C-C bonds are parallel to the [011] direction. Unlike the Fe{110} surface, 30°



Figure 4.10. Surface structure, simulation cell and relevant PBE-optimised distances for the (3×3) Fe $\{100\}$ simulation cell. All distances in Å.



Figure 4.11. Benzene orientations selected for study on Fe{100}. Hydrogen atoms omitted for clarity.

rotation of a site results in an identical conformation on the surface.

Upon geometry optimisation, all six studied sites produced unique, stable adsorption geometries. Adsorption and deformation energies are presented in table 4.7, where they are also compared to those from the analogous work of Sun *et al.* Optimised geometric

parameters are included in table 4.8. Images of all optimised configurations are shown in figures 4.12 and 4.13. Although all initial configurations produced unique optimised geometries, in all but one case the optimised geometry is very similar to the starting geometry. Upon geometry optimisation of the initial B2 binding site, it was found to drift in the [001] direction to a different, highly favourable binding site. We refer to this new geometry as double atop (DA) due to its alignment of two C atoms with two Fe atoms.

In all cases, the benzene C-C distances have expanded somewhat, which indicates that C-C bonds have less double bond character as a result of interaction of the π -electron system with the metal surface. The data shown in table 4.8 demonstrates the upwards flip away from the surface of the hydrogen atoms, also seen for $Fe{110}$, to a greater extent in certain cases (H and B1) than others (A). As discussed in section 4.2, this has been seen in many other DFT studies of benzene on transition metal systems.¹⁶⁵ The closest approach for benzene to the surface is achieved by the B1 binding site, which is also the case for the work by Sun et al. The adsorption energies identified in this work are compared to those identified by Sun et al. in table 4.7. Although the relative ordering of different sites is matched, the PBE energies from this work are in all cases approximately 0.3 eV stronger in energy than those identified in the work of Sun et al. The differences between the simulation parameters in this work and the work Sun et al. are presented and further discussed in section 4.5, alongside the comparison of this work's benzene/Fe{110} results and analogous work by Hensley et al. The difference in adsorption energy between strongest adsorption site (H, -1.41 eV) and weakest adsorption site (A, -0.21 eV) shows a difference of 1.27 eV, therefore there is a fairly significant energetic distinction between the studied sites, and certain sites (A and A-15°) would be expected to not be observed as easily experimentally at 298 K, as explained in section 4.2 because $k_B T = 0.26$ eV. As for distortion energies, the values show that they roughly scale with adsorption energy, where the most favourable adsorption sites show stronger distortion than those which adsorb weakly to the Fe{100} surface. The exception to this rule is the B1 site, which as shown by this work and that of Sun et al., has the strongest distortion energy but the fourth strongest adsorption energy on Fe{100}. This can also be seen through observation of its configuration at the surface (shown in figure

	E_{ads}	(eV)	E_{dist} (eV)		
site	This work	Sun <i>et al</i> . ¹⁵⁵	This work	Sun <i>et al</i> . ¹⁵⁵	
Н	-1.41 (-3.02)	-1.07	1.12 (0.92)	0.957	
H-15°	-1.35 (-3.02)	-	1.06 (1.04)	-	
DA	-1.35 (-2.98)	-	1.06 (1.07)	-	
B1	-1.09 (-2.84)	-0.74	1.70 (1.70)	1.433	
А	-0.21 (-1.82)	-0.04	0.28 (0.42)	0.251	
$A-15^{\circ}$	-0.22 (-1.81)	-	0.18 (0.23)	-	

Table 4.7. Calculated optimised energies for stable benzene adsorption sites on $Fe\{100\}^a$

^{*a*} E_{ads} represents the adsorption energy and E_{dist} represents the distortion energy upon adsorption. Data in brackets represents a van der Waals corrected result. In the case of this work, the TS correction is used.⁸⁴ The DFT work of Sun *et al.* makes use of the PBE functional only. All non-bracketed results are calculated using PBE.

4.12) where it displays a cyclohexane-boat like geometry at the surface. This similarity to a saturated hydrocarbon can also be seen in the B1 average C-C bond of 1.46 Å, which is much longer than a typical C-C double bond, as seen in table 4.8. This demonstrates that benzene deformation does not necessarily always scale directly with its adsorption strength on a metal surface.

Images of configurations not studied by Sun *et al.* are shown in figure 4.13 and relevant energy and geometric data is shown in tables 4.7 and 4.8. The H-15° site presents an optimised configuration which is slightly tilted with respect to the surface. The work of Sun *et al.* only presents data for two sets of benzene carbon (two C^2 atoms and four C^4 atoms), which suggests that additional symmetry could have been imposed in their DFT calculations, which could result in such tilted configurations being missed. In any case, although the H-15° binding site is among the most energetically favourable which feature in this study, it is still weaker than the original hollow site, on the order of 0.06 eV. The A-15° is only 0.01 eV more strongly binding than the A site.

As mentioned previously, the DA site is obtained from geometry optimisation of the B2 initial configuration. It presents a binding energy which is an order of magnitude stronger



Figure 4.12. Images of PBE-TS optimised benzene binding sites. Views shown above the Fe{100} surface (a) to the side (b) as well as an alternate side view (c).



Figure 4.13. Images of PBE-TS optimised benzene binding sites which are not studied in the work of Sun *et al.* (Ref. 155) Views shown above the Fe{100} surface (a) to the side (b) as well as an alternate side view (c).

site	$d_{C-C}(\text{\AA})$	$d_{C-H}(\text{\AA})$	$\theta_{C-H}(^{\circ})$	$\theta_{C-C}(^{\circ})$	$d_{C-Fe}(\text{\AA})$
free benzene	1.39 (1.40)	1.09 (1.09)	0 (0)	120 (120)	-
Н	1.45 (1.44)	1.09 (1.09)	23(21)	120 (120)	2.12 (2.15)
H-15°	1.45 (1.44)	1.09 (1.09)	21 (21)	120 (120)	2.14 (2.14)
DA	1.44 (1.44)	1.09 (1.09)	21 (20)	120 (120)	2.17 (2.15)
B1	1.46 (1.46)	1.10 (1.10)	21 (21)	118 (118)	2.12 (2.11)
А	1.42 (1.42)	1.10 (1.10)	7 (7)	120 (120)	2.24 (2.25)
A-15°	1.42 (1.42)	1.10 (1.10)	6 (6)	120 (120)	2.23 (2.22)

Table 4.8. Calculated optimised geometric parameters for benzene on $Fe{100}^a$

^{*a*} d_{C-C} represents the average C-C bond length in benzene, d_{C-H} the average C-H bond length, θ_{C-H} the average CH tilt angle (dihedral) with respect to the molecular plane, θ_{C-C} the average angle between carbon atoms in the molecule and d_{C-Fe} represents the average C-Fe distance. Data in brackets represents a van der Waals corrected result. All non-bracketed results were calculated using PBE. The free benzene results were extracted from a GGA-PBE (PBE-TS) geometry optimisation using a cubic 20 Å box to prevent benzene self-interactions.

than the the original B2 site identified by Sun *et al.* This is a binding site which we believe would not have been identified if additional symmetry constraints were imposed upon benzene as may have been done in the existing DFT work from the literature. As shown in the side-view offered in figure 4.13, the double atop localised portion of the adsorbate is raised from the surface while the other side of the molecule has moved closer to the surface. The DA site is only 0.06 eV weaker than the hollow site, making it to be one of the most stable adsorption sites on Fe{100}. The starting B2 structure identified by Sun *et al.* is decidedly less stable.

vdW-corrected adsorption geometries and energies

The work of Sun *et al.* on benzene/Fe{100} does not consider the effect of vdW corrections on DFT calculations. Dispersion corrections are known to play a significant role in the binding strength of aromatic molecules on metallic surfaces, therefore a vdW-corrected DFT study is a necessary step towards understanding the adsorption of benzene on Fe{100}. Tables 4.7 and 4.8 show the PBE-TS benzene/Fe $\{100\}$ energy and geometric data. A large decrease in binding energy of on average 1.64 eV is observed across all binding sites. As mentioned previously, existing literature shows that PBE-TS tends to result in overbinding of aromatic molecules on metal surfaces, resulting in artificially high binding energies. Aside from the large change in adsorption energy, only minor changes in the adsorption geometries can be observed, as with benzene/Fe{110} in section 4.2. The relative ordering of the binding site strengths is effectively the same as with pure PBE, although the H-15° has increased in relative strength to be as strong as the top H site. This finding is in itself interesting, as other studies (including the benzene/Fe{110} work shown in section 4.2 previously) have shown that the relative binding strength of different aromatic binding sites may change from pure PBE when using dispersion correction schemes for metallic systems.⁵⁷ This suggests that vdW corrections have less impact on adsorption energies upon more open, reactive or kinked surfaces compared to close-packed surfaces. This is discussed further in section 4.5.

4.3.3 Charge density difference

The charge density difference for the most favourable binding sites has been calculated and studied. Images of the distribution of charge are shown for the four strongest binding sites (H, H-15°, DA and B1) in figure 4.14. In all cases, charge density increases on the carbon atoms and decreases immediately below them. The way in which the charge density is distributed across the benzene molecule however is not the same even for relatively similar binding sites. For example, comparing the H and H-15° sites, the increased charge density is seen to spread across a C-C bond in the rotated case whereas for the regular H site, the charge increase remains localised over carbon atoms only. Even more dramatic is the significantly weaker B1 site which shows delocalisation of increased charge over the entire

benzene ring. This is likely related to the comments made in preceding section 4.3.2, which is that the B1 benzene conformation shows strong distortion, and bears a resemblance to a cyclohexane boat conformation. The DA site also shows some differences as a result of the tilted geometry of the adsorbate. The four charge density plots do show other similarities, namely that the charge density distribution near the hydrogen atoms decreases and there is an increase in charge density directly above the Fe surface. The B1 site has an interesting lack of change in charge density in the center of the benzene ring directly above the Fe surface, while all the other binding sites show decrease in density in the same region. Tilted and strongly deformed geometries aside, all of the features described here are similar to those observed for benzene/Fe{110}.

4.3.4 Spin density

Figure 4.15 shows the the spin densities for four benzene/Fe{100} binding sites (H, H-15°, DA and B1). Minority spin is seen around all of the benzene carbon atoms. Hydrogen atoms are of majority spin, matching the spin of Fe slab atoms. Certain C-H bonds, for example in the DA site in figure 4.6, present more minority spin character than others. The DA site, which shows more benzene distortion/tilting, has distinctly lower symmetry contours. As for B1, although benzene also distorts in this adsorption site, it does so symmetrically and as a result shows a high-symmetry spin density structure which looks quite different to the other sites.

4.3.5 Atomic charges and spin

Hirshfeld charges are calculated for the PBE and PBE-TS optimised H conformation of benzene on the Fe{100} surface. These are presented in table 4.9 alongside atom-resolved spin on different atom groups.

As with the Hirshfeld charges for benzene/Fe{110} (section 4.2.5), the sum of all atom charges for the simulation cell is non-zero (+0.02 e). The charges shown in table 4.9 are derived using a $8 \times 8 \times 1$ MP mesh, double the density of k-points used to study benzene/Fe{100} adsorption energies and geometries. The slight excess positive charge



Figure 4.14. Charge density difference shown for the four strongest benzene/Fe{100} binding sites. Views shown from above the Fe{100} surface (a) as well as from the side (b). Blue (yellow) regions denote a decrease (increase) in electron density on the order of 2×10^{-2} electrons/Å³.



Figure 4.15. Spin density for optimised geometries of benzene bound to Fe{100}. Views shown from above the Fe{100} surface (a) as well as from the side (b). Blue (yellow) regions denote minority (majority) spin regions on the order of 3×10^{-3} electrons/Å³.
Atom group	charges (e) PBE	charges (e) PBE-TS	spin (μ_{β}) PBE	spin (μ_{eta}) PBE-TS
C ₆ H ₆ sum	-0.08	-0.02	-0.4	-0.4
C sum	-0.36	-0.32	-0.44	-0.44
H sum	0.28	0.30	0.04	0.04
Entire slab sum	0.10	0.03	180.44	178.77

Table 4.9. Calculated Hirshfeld charges and atomic spin results for preferred H benzene adsorption site on Fe{100}

is likely to arise from rounding errors for small charges within the $Fe\{100\}$ slab. As the slab contains fewer atoms (72) than the $Fe\{110\}$ model (96), it is to be expected that the rounding error should be of a lower magnitude than for the $\{110\}$ slab.

The charge and spin values confirm the qualitative observations in the spin and charge density difference plots shown in figures 4.15 and 4.14, which is that C atoms show minority spin/decrease in charge density and hydrogen atoms show slight majority spin/increase in charge density. The changes between PBE and PBE-TS methodology are minor for both Hirshfeld charges and spin. The biggest change related to charge is seen in the reduction of charge in the Fe slab using PBE-TS compared to PBE. A reduction in spin is also observed using PBE-TS compared to PBE. As discussed in section 4.2.5 for Fe{110}, this is most likely due to changes in the lattice parameter going from PBE to PBE-TS (i.e. Fe atoms prefer to lie slightly closer together using PBE-TS).

4.3.6 DOS and PDOS

The PDOS for a C-Fe pair within the preferred H site for benzene/Fe $\{100\}$ is shown in figure 4.16. As with the PDOS for benzene/Fe $\{110\}$ (see section 4.2.6), the chosen carbon and iron atoms are in close contact within the benzene/Fe $\{100\}$ adsorption site.

The PDOS for the Fe atom in the bare Fe{100} shows a different distribution of states owing to the different surface structure. Specifically, it shows an increase in more strongly bound majority spin states and a significant increase in minority spin states just above the Fermi level. The carbon-C1 peaks show very similar shifts to higher binding energies compared to the H-30° site on Fe{110}; an unsurprising finding given that both sites are centered above hollow-like sites. The orbital closest to the Fermi energy $(1e_{1g})$ disappears due to favourable overlap with the Fe 3*d* states. As for the Fe PDOS, aside from the new peaks at high binding energies (arising due to the high binding energy C orbitals) as well as a slight reduction in the number of minority spin and majority spin states, the Fe atom in the benzene-adsorbed and bare slab cases are very similar. This implies that the electronic structure of the surface is not affected as strongly for the benzene/Fe{100} case as for example benzene/Fe{110}. All trends are in good agreement with the H site benzene/Fe{100} PDOS of Sun *et al.* ¹⁵⁵ Given that the work of Sun *et al.* does not employ any vdW correction, the similar PDOS plots support the claim often made in the literature that the application of vdW corrections minimally affects electronic structure.



Figure 4.16. Projected density of states (PDOS) for benzene on Fe{100} in the H adsorption geometry. The upper plot shows the majority spin and minority spin PDOS for Fe atom 8 before (black) and after adsorption (red). The lower plot shows C atom 1 within benzene in the gas-phase (black) and after adsorption (red, majority spin and minority spin shown). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase benzene DOS has been aligned with the C(2s) peak for the adsorbed benzene, as this level is not expected to be involved in the adsorption process.

4.4 Benzene/Fe{211}

4.4.1 Introduction

The final surface studied in the context of benzene adsorption in this chapter is the stepped Fe{211} surface. As shown in figure 4.17, the bcc {211} surface features rows of single-atom thickness, close-packed atoms separated by troughs which expose an underlying layer of close-packed atoms.

ParameterValueVacuum spacing (Å)10Cell size $(c \times c)$ (2×3) Number of slab layers8Number of fixed slab layers4MP K-point sampling $6 \times 4 \times 1$

Table 4.10. Simulation details and parametersspecific to the benzene/Fe{211} calculations

There are several reasons for studying adsorption upon Fe{211}. Fe{111}, which might be the logical low Miller index surface for study after Fe{110} and Fe{100}, is known to be a high-reactivity facet (for example it is the most active facet in ammonia synthesis) and as a result is relatively unstable.^{166,167} Field-ion microscopy experiments show that pyramidal bcc{211} facets, which have been shown to be the second most active in certain catalytic reactions, grow on bcc crystals preferentially over bcc{111}, particularly when adsorbates are involved.^{168–171} Prior work shows the Fe{211} facet has surface energy above that of Fe{110} and Fe{100} but below Fe{111}.¹³⁸ It is also relevant for this particular thesis to study aromatic adsorption on a higher reactivity, open surface because corrosion inhibition has been said to take place within surface crevices and pits, which typically feature stepped, terraced and defective surfaces.³⁰ Finally, to the best of our knowledge there has been no study (experimental or theoretical) of the adsorption behaviour of benzene on Fe{211}, which provides additional motivation to carry out such a study.

In this section, the results of DFT calculations probing the adsorption of benzene on

the Fe{211} surface are presented and analysed. All simulation details and parameters used specifically for the benzene/Fe{211} calculations can be found in table 4.10. The conventional cell of Fe{211} is rectangular, therefore the (2 × 3) dimensions are chosen for the simulation cell both to accommodate the benzene molecule as well as to produce a nearly square simulation cell so each periodic copy of benzene is approximately equidistant across the four edges of the cell. As with Fe{110}, it is sensible to use a high number of surface layers (eight) to account for the potential for underlying layers to interact with the adsorbate. This is also why four of the eight layers are allowed to relax during geometry optimisation. Finally, a MP sampling of 6 × 4 × 1 k-points is used, which produces sampling equivalent to 12 × 12 × 12 k-points for the convental bcc Fe cell, which as mentioned before, produces results converged to within 0.002 Å (distances), 0.01 eV (energies) and 0.03 μ_{β} (spin).



Figure 4.17. Surface structure, simulation cell and relevant PBE-optimised distances for the (2×3) Fe $\{211\}$ simulation cell. All distances in Å.

4.4.2 Adsorption geometries and energies

Figure 4.18 shows the sixteen high-symmetry benzene adsorption sites at the Fe{211} surface. The Fe{211} surface presents the lowest symmetry of the three surfaces investigated thus far, which is why it has the highest number of unique high-symmetry binding sites where benzene is likely to be found in a local energy minimum. Upon geometry optimisation, eight adsorption sites were stable while eight were unstable. The unstable sites all migrated towards one of the eight stable structures identified. Table 4.11 provides an account of these results for all sixteen tested sites.

Tables 4.12 and 4.13 show the adsorption energies and geometric data collected for all eight stable adsorption benzene sites on the Fe{211} surface. Correspondingly, optimised geometries are represented in figures 4.19, 4.20 and 4.21.



Figure 4.18. Benzene orientations selected for study on Fe{211}. Hydrogen atoms omitted for clarity.

The three strongest binding sites (in descending order, these are BU2, AU2 and H3) all sit in hollow or hollow-like geometries on the surface. The two most favourable sites BU2 and AU2 sit in the troughs formed by the Fe{211} stepped surface. It is interesting to note the strong distortion of the benzene molecule in the case of BU2 in figure 4.19 which shows it adopting a cyclohexane-like boat conformation. The second strongest site (AU2 in figure 4.19) which is shifted along the trough to sit centered atop an Fe atom, shows very little

Benzene binding site	Stable	Unstable
H1		х
H2		Х
H3	х	
H4		Х
A1	Х	
A2	Х	
BT1		Х
BT2		Х
B1		Х
B2		Х
B3	Х	
B4		Х
AU1	Х	
AU2	Х	
BU1	Х	
BU2	х	

Table 4.11. Outcome of geometry optimisation for the 16 high-symmetry benzene binding sites on the Fe{211} surface

Table 4.12.	Calculated	optimised	energies	for st	able
benzene ads	sorption site	es on Fe{2	$11\}^{a}$		

Adsorption site	$E_{ads}(eV)$	E_{dist} (eV)
BU2	-1.55 (-3.44)	2.97 (3.22)
H3	-1.34 (-3.14)	2.85 (3.08)
AU2	-1.41 (-3.08)	2.25 (2.51)
BU1	-1.29 (-2.96)	1.43 (1.58)
AU1	-1.13 (-2.78)	1.39 (1.50)
A2	-0.59 (-2.33)	0.11 (0.17)
A1	-0.64 (-2.28)	0.17 (0.28)
B3	-0.61 (-2.21)	0.79 (0.76)

^{*a*} E_{ads} represents the adsorption energy and E_{dist} represents the distortion energy upon adsorption. Data in brackets represents a van der Waals corrected result, for which the TS correction is used.⁸⁴ All non-bracketed results were calculated using PBE.

site	$d_{C-C}(\text{\AA})$	$d_{C-H}(\text{\AA})$	$\theta_{C-H}(^{\circ})$	$\theta_{C-C}(°)$	$d_{C-Fe}(\text{\AA})$
free benzene	1.39 (1.40)	1.09 (1.09)	0 (0)	120 (120)	-
BU2	1.47 (1.48)	1.11 (1.11)	29 (29)	116 (116)	2.11 (2.11)
H3	1.47 (1.48)	1.10 (1.10)	31 (31)	119 (118)	2.11 (2.09)
AU2	1.47 (1.47)	1.10 (1.10)	32 (34)	120 (120)	2.10 (2.08)
BU1	1.45 (1.45)	1.10 (1.10)	24 (27)	120 (120)	2.33 (2.30)
AU1	1.45 (1.45)	1.10 (1.10)	23 (26)	120 (120)	2.32 (2.30)
A2	1.42 (1.42)	1.09 (1.10)	3 (4)	120 (120)	2.23 (2.21)
A1	1.42 (1.42)	1.10 (1.10)	3 (3)	120 (120)	2.23 (2.25)
B3	1.43 (1.43)	1.09 (1.09)	16 (15)	120 (120)	2.40 (2.42)

Table 4.13. Calculated optimised geometric parameters for benzene on $Fe{211}^a$

^{*a*} d_{C-C} represents the average C-C bond length in benzene, d_{C-H} the average C-H bond length, θ_{C-H} the average CH tilt angle (dihedral) with respect to the molecular plane, θ_{C-C} the average angle between carbon atoms in the molecule and d_{C-Fe} represents the average C-Fe distance. Data in brackets represents a van der Waals corrected result. In the case of this work, the TS correction⁸⁴ is used. All non-bracketed results were calculated using PBE. The free benzene results were extracted from a GGA-PBE (PBE-TS) geometry optimisation using a cubic 20 Å box to prevent benzene self-interactions.

ring deformation in comparison. The third strongest site (H3 in figure 4.19) once again shows strong ring deformation in its optimised geometry at the hollow position, however it does not deform symmetrically like the strongest site. The binding sites found within the trough with 0 degree rotation (BU1, AU1, see figure 4.20) show much lower stability in comparison to the strongest 30 degree rotated trough sites BU2 and AU2. This shows that the 30 degree molecular rotation provides a particularly favourable adsorbate alignment with the uppermost layer Fe{211} atoms. The PBE energetic separation between the top site (BU2, $E_{ads} = -1.55$ eV) and weakest adsorbing site (A2 $E_{ads} = -0.59$ eV) is 0.96 eV, which is significantly larger than any energy difference found on Fe{110} or {100}. It is likely atop-centered sites would not readily be observed under experimental conditions based on the computed adsorption energies, because at 298 K, $k_BT = 0.26$ eV.

The strong adsorption sites show upward-tilt of the C-H bonds with respect to the benzene molecular plane as has been seen in preceding sections. In the case of Fe{211}, the greatest C-H bond tilts yet are observed, with the best sites showing average tilt angles upwards

of 30°. Benzene/Fe{211} also shows the strongest distortion energies of all three surfaces studied, in some cases (BU2 for example) just shy of 3 eV. Additionally, the lengths of C-C bonds in benzene adsorbed on Fe{211} are the highest of all three Fe surfaces, which again hints at the benzene adopting a conformation closer to cyclohexane which is consistent with the boat-like geometry found in the strongest adsorption site. Even for the strongest adsorbing site BU2, the C-C bond lengths are still shorter than those found for a cyclohexane molecule (1.50 Å). Finally, an interesting phenomenon unique to the Fe{211} surface is that lateral movement of slab layers is observed quite far away from the uppermost movable slab layers. In other words, the adsorption of benzene on the top slab layers provokes changes even several layers deep below the top layer. This is not entirely surprising given that the Fe{211} surface is stepped, therefore far more open than the surfaces studied up until this section.

vdW-corrected adsorption geometries and energies

PBE-TS derived benzene/Fe{211} adsorption energies and geometric parameters are shown in tables 4.12 and 4.13. All geometries look essentially identical to those identified with PBE, which is supported by data in table 4.13. As for adsorption energies, unsurprisingly a significant increase in strength is observed, between 1.60 - 1.90 eV for all binding sites. As for the relative ordering of adsorption sites, some changes are seen, mainly shuffles amongst the best and the worst sites. This includes swapping of H3 and AU2 in second and third place as well as new ordering of weakest three sites (A2 switches to sixth place from eighth place, A1 moves from sixth to seventh place and B3 is the weakest site). The distortion energies also increase non-negligibly for the strongest adsorption sites (around 0.25 eV increase for the top three sites) but minimally for weaker sites.



Figure 4.19. Images of the three strongest PBE-TS optimised benzene binding sites. Views shown above the Fe{211} surface (a) to the side (b) as well as an alternate side view (c).



Figure 4.20. Further images of PBE-TS optimised benzene binding sites. Views shown above the Fe{211} surface (a) to the side (b) as well as an alternate side view (c).



Figure 4.21. Images of PBE-TS optimised atop-like benzene binding sites. Views shown above the Fe{211} surface (a) to the side (b) as well as an alternate side view (c).

4.4.3 Charge density difference

PBE-derived charge density difference plots are shown for the top three benzene/Fe{211} binding sites (BU2, AU2 and H3) in figure 4.22. Of the three density distributions, the H3 site charge density is the most dissimilar to any benzene/Fe charge density seen before, owing to the strong asymmetric deformation of benzene in this site. Another stand-out feature is the appearance of a region of increase in electronic density (yellow) within the top surface Fe atoms for the BU2 site. Specifically, this occurs between atoms in the uppermost row of atoms, not the trough layer, and in a region some distance away from the adsorbate. This is noteworthy as changes in the charge density of Fe surface atoms has not yet featured in an important way in any other charge density difference plot. For the BU2 and AU2 site density plots, there is a decrease in electronic density in the trough under benzene formed on the surface, while there is an increase just above the uppermost Fe atoms. This is also observed for the H3 site, albeit a little less clearly due to the site having features of adsorption both above and within the trough.

Aside from the differences highlighted above, the charge density difference plots for benzene on Fe{211} are certainly reminiscent of those seen for benzene adsorption on Fe{100} and Fe{110}, where charge density has increased around the carbon atoms, decreased just below the plane of the benzene molecule and increased just above the uppermost Fe atoms. The density near H atoms has in most cases decreased but in one case (H3) it does increase on certain H atoms.

4.4.4 Spin density

The spin density for the top three benzene adsorption sites on Fe{211} is shown in figure 4.23. Given the important differences in adsorption energy and structure for the three most favourable binding sites, the spin polarisation is not expected to be the same in all three cases at the surface. This is indeed the case, as there are important differences between the three density plots shown in figure 4.23. Comparing the spin density for the strongest site (BU2) to that of the other two (AU2 and H3), the most notable difference is the reduction of majority spin regions (yellow regions) at the surface and increase in minority spin areas (blue regions)



Figure 4.22. Images of most favourable optimised benzene binding site charge density difference. Views shown from above the Fe{211} surface (a) as well as from the side (b). Blue (yellow) regions denote a decrease (increase) in electron density on the order of 2×10^{-2} electrons/Å³.

at the surface. This shows that the adsorption of the strongly distorted benzene molecule seen in BU2 induces more minority spin regions within the Fe{211} surface, specifically in the trough regions. The spatial regions above the carbon atoms in the benzene ring are of minority spin (blue), similarly to all other benzene-C atoms within adsorption geometries studied on iron surfaces. Also, the contours surrounding the hydrogen atoms are of majority spin (yellow) except in the case of the third strongest site H3, where one of the hydrogen atoms is distinctly polarised with minority spin. Referring back to figure 4.20, it is clear that the molecule deforms in such a way that one hydrogen atom is much further above the slab surface than all others, which is the same hydrogen atom which has become surrounded by a region of minority spin. The region of minority spin along the H3 benzene-ring connects with the region of minority spin above the hydrogen atom, and the full minority spin contour does not match the benzene ring as in other cases, as it has a node along one C-C bond.

4.4.5 Atomic charges and spin

Hirshfeld charges are calculated for the BU2 benzene/Fe{211} site at the PBE and PBE-TS levels. The data is presented in table 4.14 alongside spin measured on different groups of atoms.

Atom group	charges (e) PBE	charges (e) PBE-TS	spin (μ_{β}) PBE	spin (μ_{β}) PBE-TS
C ₆ H ₆ sum	0.02	0.04	-0.36	-0.34
C sum	-0.26	-0.26	-0.38	-0.36
H sum	0.28	0.30	0.02	0.02
Entire slab sum	-0.05	-0.05	116.12	113.37

Table 4.14. Calculated Hirshfeld charges and atomic spin results for BU2 benzene adsorption site on Fe{211}

Firstly, the distinction between PBE and PBE-TS results for charge is minimal. The non-zero charge sum, i.e. -0.01 e for PBE-TS, which has been observed for Fe{110} and and Fe{100} is seen again. As explained, this is the result of rounding in the CASTEP output file. There is also little distinction between PBE and PBE-TS derived spin, aside from a



Figure 4.23. Images of three most favourable optimised benzene binding site spin densities. Views shown from above the Fe{211} surface (a) as well as from the side (b). Blue (yellow) regions denote spin minority (majority) regions on the order of 3×10^{-3} electrons/Å³.

decrease of 2.75 μ_{β} for PBE-TS compared to PBE. This type of difference has been observed for both Fe{100} and Fe{110} and can be attributed to the changes in surface structure upon application of vdW corrections, which shorten Fe-Fe distances slightly. This effect is slightly stronger than on Fe{110} and Fe{100}, which can be attributed to the more under-coordinated stepped structure experiencing stronger changes upon application of vdW-corrected DFT.

The Hirshfeld charges match the trends seen in the charge density difference plots from section 4.22, showing negative charge on carbon atoms (therefore increased charge density on carbon atoms) and positive charge on hydrogen atoms (therefore reduced charge density on hydrogen atoms). The slab carries a minimal negative charge of -0.05 e and the adsorbate as a whole carries a charge between 0.02-0.04 e dependant on whether PBE or PBE-TS is used. The molecule as a whole shows distinct minority spin polarisation (-0.36 μ_{β}) which arises from the spin polarisation on C atoms.

4.4.6 DOS and PDOS

The PDOS for the benzene/Fe{211} BU2 adsorption site are shown for two sets of interacting C-Fe atom pairs in figure 4.24 and 4.25. The Fe15-C1 pair (figure 4.25) represents the pairing of an underlying-layer Fe atom and nearby C atom (i.e. within the surface trough) while the Fe40-C2 pair (figure 4.24) represents a C atom above the surface trough interacting with an uppermost-layer Fe atom. These two different interaction types are achieved through strong deformation of benzene within the BU2 site - see section 4.4.2 for visualisations and quantification of this effect.

Certain trends in peak shifts are similar to those observed for benzene/Fe{110} in section 4.2.6. This includes a shift of orbital binding energies to more negative values compared to the gas-phase; a disappearance of the adsorbed-C peaks near the Fermi level due to interaction with Fe 3*d* orbitals and the appearance of new high binding energy peaks in the Fe PDOS due to the adsorbate-C orbitals. It is also worth noting that the Fe{211} PDOS do not resemble that of Fe{110} or {100} because of different surface coordination. Additionally, the PDOS plots for Fe15 and Fe40, both within the Fe{211} surface, are different. Differences

are found mainly near the Fermi level, where the underlying layer atom (Fe15) shows an increase in spin-up states in the Fermi level's vicinity while the uppermost layer atom (Fe40) shows an increase in spin-down states in this region. Given the different coordination of these two atoms, such minor differences are to be expected.

One difference between the benzene/Fe{211} PDOS and previous benzene/Fe{110} and Fe{100} plots is found in the adsorbed C PDOS peaks. The high binding energy $3a_{1g}$ and $2b_{1u}$ orbitals have shifted to higher binding energies, but have additionally split into pairs of peaks. This is undoubtedly related to the strong deformation of benzene at the surface, which experiences changes in its electronic structure thanks to its structural resemblance to the boat cyclohexane conformation.

Comparing figures 4.24 and 4.25, there are some differences between the C peaks for C1 and C2, namely the shifted $1b_{2u}$ and $3e_{1u}$ are of significantly different shapes. The most striking difference is the change in the Fe states for Fe40 (figure 4.24). This iron atom shows a shift of majority spin states towards the Fermi level, i.e. to lower binding energies. There is also an increase in minority spin states at higher binding energies accompanied by a decrease in states at lower binding energies, above the Fermi level. Fe15 in the underlying layer is in relatively close contact with C1, but it shows minimal change compared to the bare slab. As the underlying surface layer has higher coordination to neighbouring Fe atoms, the Fe PDOS is less affected by the vicinal benzene-C atom.



Figure 4.24. Projected density of states (PDOS) for benzene on Fe{211} in the BU2 adsorption geometry. The upper plot shows the majority spin and minority spin PDOS for Fe atom 40 before (black) and after adsorption (red). The lower plot shows C atom 2 within benzene in the gas-phase (black) and after adsorption (red, majority spin and minority spin shown). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase benzene DOS has been aligned with the C(2s) peak for the adsorbed benzene, as this level is not expected to be involved in the adsorption process.



Figure 4.25. Projected density of states (PDOS) for benzene on Fe{211} in the BU2 adsorption geometry. The upper plot shows the majority spin and minority spin PDOS for Fe atom 15 before (black) and after adsorption (red). The lower plot shows C atom 1 within benzene in the gas-phase (black) and after adsorption (red, majority spin and minority spin shown). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase benzene DOS has been aligned with the C(2s) peak for the adsorbed benzene, as this level is not expected to be involved in the adsorption process.

4.4.7 Workfunction

The results of workfunction calculation on the preferred benzene/Fe{211} BU2 adsorption site are shown in table 4.15. The calculation procedure is as described for benzene/Fe{110} in section 4.2.7. In comparing PBE and PBE-TS derived quantitites, there are very small differences between them, at most on the order of 0.03 eV. The workfunction of the bare Fe{211} slab is reduced (by -1.04 eV using PBE-TS) upon adsorption of benzene, which is the trend which was also observed for benzene/Fe{110}. This is discussed further in section 4.5.

Method	$E_{vac}(eV)$	$E_F(eV)$	Fe{211}	C ₆ H ₆ /Fe{211}	$\Delta\phi$ (eV)
			ϕ (eV)	ϕ (eV)	
PBE	-2.40	-5.59	4.23	3.19	-1.04
PBE-TS	-2.40	-5.60	4.20	3.20	-1.01

Table 4.15. Calculated Workfunction (ϕ) results for BU2 benzene adsorption site on Fe{211}^{*a*}

^{*a*} E_{vac} represents the vacuum energy, E_F represents the Fermi energy and $\Delta \phi$ represents the difference between the C₆H₆/Fe{211} ϕ and bare Fe{211} ϕ . Bare Fe{211} ϕ values are calculated using the 8-layer (2 × 3) slab.

4.5 Discussion and conclusions

Herein, a discussion and comparison of the trends observed for benzene adsorption across Fe{110}, Fe{100} and Fe{211} surfaces is presented. Comparisons between results developed in this thesis are also compared to other transition metal surfaces and Fe-containing surfaces. Conclusions are drawn at the end of the section.

4.5.1 Benzene on Fe{110}, Fe{100} and Fe{211}

Certain trends can be identified across all three surfaces. Firstly, hollow or hollow-like geometries tend to be preferred across all surfaces; this often enables at least a portion of the C atoms to lie in close contact with one or several Fe atoms. Looking at the top adsorption sites identified using PBE-TS on Fe{110}, Fe{100} and Fe{211}, benzene adsorption is strongest on Fe{110} (-3.45 eV), very closely followed by Fe{211} (-3.44 eV) and finally is weakest on Fe{100} (-3.02 eV). Using PBE, the ordering for benzene adsorption strength across all three surfaces is exactly the same as with PBE-TS; Fe{110} (-1.62 eV), Fe{211} (-1.55 eV) and Fe{100} (-1.41). It is worth noting that the identity of the strongest adsorption site does change from PBE to PBE-TS for Fe{110} (the H-30° is preferred using PBE while S-0° is preferred with PBE-TS), but the same site is preferred whether PBE and PBE-TS are used for Fe{100} (H) and Fe{211} (BU2). Aside from preferred adsorption sites, it is clear the inclusion of vdW corrections can affect the relative energetic ordering of sites, given that with PBE-TS Fe{110} and {211} differ only by 0.01 eV, whereas with PBE they differ by 0.07 eV, just shy of an order of magnitude higher. Interestingly, the trend is reversed with respect to Fe{100}, which is 0.14 eV weaker than Fe{211} with PBE but 0.36 eV weaker with PBE-TS. This is an indication that vdW corrections play an important role for benzene adsorption on the Fe{211} surface. This observation was also made within section 4.4.2 for Fe{211}, because the energies for the most strongly adsorbed conformations have noticeably stronger adsorption strengths upon switching from PBE to PBE-TS methodology. More generally, use of PBE-TS increases the strength of adsorption compared to use of PBE, but minimally affects the geometry of adsorption. Studying average vdW-corrected adsorption strengths over all sites per surface, the increases compared to PBE are of 1.80 eV for benzene/Fe{110}, 1.64 eV for benzene/Fe{100} and 1.75 eV for benzene/Fe{211}. It is worth stressing here again that several works have found that use of PBE-TS results in overbinding of aromatic molecules on metal surfaces.^{57,92} Other recent works however have found that TS performs suitably for aromatic adsorption when compared to experiment, for example on Cu surfaces.¹⁰⁹

As for adsorption geometries, some deformation is observed for benzene in all cases. In all cases, the C-H bonds flip up and away from the metal surface. This is related to the so-

called cushion effect.¹⁷² The cushion effect describes the region of depleted electron density commonly found between aromatic adsorbates and metal surfaces, which is observed within all charge density difference plots shown in this chapter. This is a result of the squashing of metal *d* orbitals by Pauli repulsion with the aromatic π electrons. This results in a decrease in the surface dipole. The adsorbed "dished" conformation of benzene generates an internal dipole which further reduces the surface dipole. This effect is separate from charge tranfer interactions, and in the case of benzene results in the observed decrease in workfunction compared to the clean surface. As mentioned previously, the flip of aromatic C-H bonds up and away from the metal surface has been observed in numerous other calculations.^{163,165,172,173} One of these works¹⁶³ finds rehybridisation of C-p_z states with Ni-*d* states results in more favourable orbital overlap for benzene/Ni{111}, and the extent to which this occurs is correlated with C-H tilt angles.

For the flat and relatively flat Fe{110} and Fe{100} surfaces, some buckling of the benzene molecular plane is observed, so PBE-TS deformation energies are the order of 1.39 eV (Fe{110}) and 0.90 eV (Fe{100}). For benzene/Fe{211} however, very strong deformation of the molecular plane of benzene is observed, with deformation energies of over 3 eV. Strong deformation of benzene is a feature of favoured adsorption sites on Fe{211}, with the top site showing a cyclohexane boat-like geometry. A similar type of benzene deformation has also been observed in the inorganic complex Fe₂(C₆H₆).¹⁷⁴ The lengthening of C-C bonds of benzene for the top adsorption sites on Fe{211} to 1.47 are reflective of a strong reduction of benzene's aromaticity. The reduced aromaticity and strong deformation of benzene can explain why the preferred benzene adsorption site (BU2) on the most under-coordinated and therefore most reactive Fe{211} surface is not stronger than the preferred adsorption site on the more stable Fe{110} surface. The adsorption energy is a balance between strength of adsorbate-surface interactions as well as the extent of molecular (and surface) deformation.¹⁷³

In comparing the PBE benzene/Fe{110} results to the analogous results of Hensley *et al.*, although the same trends are observed, the adsorption energy results presented in this thesis are around 0.4 eV stronger than those from the published work.⁹⁶ This difference may be

arise for a number of reasons. One source is the differing calculation setup; in particular, the smaller simulation cell (3×3) and smaller number of slab layers (4) could result in nonnegligeable differences. All known differences between this work and the work of Hensley et al. have been summarised in section B in the Appendix. Special consideration should also be accorded to the choice of DFT code. The Δ -value metric developed by Lejaeghere et al. ¹⁷⁵ quantifies the root-mean-square energy difference between the equations of state averaged over all elemental crystals for two different DFT codes. The paper of De Waele *et al.* ¹⁷⁶ uses the Δ -value to provide a scale with which to compare energies derived from a large number of electronic structure calculation codes. Depending on the version of VASP which was used in the work of Hensley *et al.*⁹⁶, the standard deviation Δ value compared to CASTEP for benzene/Fe{110} adsorption energies is anywhere from 0.25 ev to 0.68 eV, which is on the order of the differences observed. The Δ -value increases for larger systems and is particularly significant for iron in comparing CASTEP and VASP. As for the comparison to the vdW-corrected benzene/Fe{110} work of Hensley et al., as the chosen scheme isn't the same as the one used in this work (optB88-vdW), there is no expectation that the results should match. The results show that the TS scheme used in this work strongly overbinds benzene compared to optB88-vdW. It is however interesting to note the trends are relatively similar, aside from the S-0° binding site. Our work identifies an interesting but subtle change in Fe{110} surface structure for this site only: it appears additional stability is afforded to this particular binding site by formation of a larger gap between the iron atoms involved in binding the S-0° site. The increased space between the bridging atoms makes the site resemble more of a stable long bridge geometry. Because Hensley *et al.* make use of a smaller simulation cell dimensions, it is possible that the cell size restricts such changes in Fe-Fe distance. This is a plausible reason for the differing S-0° stability.

As for benzene/Fe{100} which is also studied at the PBE level by Sun *et al.*¹⁵⁵, this thesis presents adsorption energies which are between 0.2 - 0.3 eV stronger than those from the analogous work. Similarly to the comparison of this work to that of Hensley *et al.*, we believe this is a combined result of differing simulation parameters (see section B in the Appendix for a full summary of differing simulation parameters) as well as the Δ value

contribution. It should be noted that no vdW-corrected work was produced in the work of Sun *et al.*, therefore only PBE results can be compared. The trends we find are the same as those in the analogous work, however it is also worth noting that this work identifies additional stable adsorption sites, and that the B2 starting point shifts to the DA site. It is unclear from the text, but there is a possibility addition symmetry was imposed in the work of Sun *et al.*, which may prevent the DA site from being identified.

In studying charge density difference for benzene across all surfaces, generally the regions surrounding the carbon atoms in benzene show an increase in charge, while the hydrogen atoms show either a decrease or little change. The region just below the adsorbate demonstrates the cushion effect, where there is a decrease in electronic density due to the π -orbitals squashing the iron 3*d* orbitals which point up and away from the surface. There are also cases where charge density decrease regions appear above the plane of the molecule, showing up as lobes on C-C bonds. This is reflective of the molecular orbitals of benzene involved in charge transfer. This is seen particularly strongly for the top three Fe{211} sites, see figure 4.22. An interesting difference between the charge densities for Fe{110} and Fe{100} is that the decrease in electron density (blue) just above the Fe surface extends out further away from the benzene ring than it does for benzene on Fe{100}. This suggests that charge transfer is redistributed more easily across the flat surface than on the kinked {100} surface. As for spin density, the same trends can generally also be seen across all surfaces; the area around carbon atoms show spin opposite to that of the surface while the hydrogen atoms almost all show spin polarisation to match the majority spin of the surface. There are a few cases where a carbon atom shows spin majority, for example the Fe{100} DA site. With respect to Hirshfeld charges and atom-resolved spin, all data agreed with the corresponding charge density differences and spin densities. What is interesting is the difference in charge and spin polarisation acquired by benzene on different surfaces. Benzene carries a positive charge on $Fe\{110\}$ and $Fe\{211\}$ but a slight negative charge on $Fe\{100\}$. Across all surfaces, benzene polarises to be of minority spin, owing mostly to the carbon atom minority spin polarisation.

In general, the results presented here show adsorption of benzene on Fe surfaces results

Surface	ϕ_{exp} (eV)	$\phi_{\scriptscriptstyle DFT}$ (eV)	$\Delta\phi$ (eV)
Pd{100} ⁹⁹	-	3.87	-1.28
$Co\{0001\}^{177}$	4.25	-	-1.30
$Cu\{111\}^{172,178}$	3.85	(4.07)	(-0.78)
Ag{111} ^{178,179}	3.80	(3.73)	(-0.73)
Au{111} ^{172,178}	4.25	(4.49)	(-0.79)
Fe{110} (This work)	-	3.71 (3.70)	-1.19 (-1.16)
Fe{211} (This work)	-	3.19 (3.20)	-1.04 (-1.01)

Table 4.16. Computed and experimental benzene/TM surface work-functions (ϕ) from literature^{*a*}

^{*a*} ϕ_{exp} represents an experimental result for the value of workfunction of the benzene adsorbed on transition metal surface system while ϕ_{DFT} represents an analogous result derived using DFT. $\Delta \phi$ represents the change in work function compared to the bare metal slab (unless a DFT result is unavailable, this is given for a DFT result). For ϕ_{DFT} , data in brackets represents a vdw-corrected result, and all non-bracketed results are derived using non-vdw corrected DFT. The van der Waals correction used for the results in Ref. 178 is Becke and Johnson's XDM method coupled with the RPBE functional.

in a reduced workfunction compared to the bare slab. This is a fairly consistent trend for benzene adsorption across a number of metal surfaces. See table 4.16 for a comparison of workfunction values with those derived from other calculations.

Finally, the PDOS across all three surfaces show certain similar trends: a shift of benzene orbital peaks to higher binding energies, disappearance of benzene orbital peaks near the Fermi level due to hybridisation with d orbitals, when shifts appear in the Fe PDOS, spin-up states tend to shift to lower binding energies (closer to the Fermi level) and spin-down states tend to shift to higher binding energies (away from the Fermi level). These trends are in good agreement with analogous benzene/Fe DFT works.^{96,155}

4.5.2 Benzene on other surfaces

As many fcc metals are used as industrial catalysts, they feature heavily in the experimental literature on benzene adsorption upon metal surfaces. This is in contrast to relatively few experimental studies of benzene adsorption on bcc surfaces.^{154,180} Across fcc surfaces, experiments and calculations reveal preferred benzene adsorption sites are flat-lying (except on stepped or more corrugated surfaces, i.e. fcc {110} where benzene can show tilting at the metal surface), show C-C bond lengthening compared to the benzene gas-phase bond lengths, and show higher adsorption strength on more reactive metals.^{11,150} This agrees with what is seen in this thesis for benzene on the flat bcc Fe{110} and kinked bcc Fe{100}. Aside from these trends however, there is a wide variety of possible preferred adsorption sites, orientations and ordering of benzene at different fcc metal surfaces. As a result, it is not straightforward to extend other findings from fcc surface adsorption as a whole to the results from this thesis. In terms of calculations, the DFT work of Lakshmikanth et al.¹⁰³ investigates the preferred adsorption site for benzene on flat surfaces for nine different metals including fcc, bcc and Hexagonal Close Packing (hcp) surfaces. The work of Lakshmikanth et al. makes use of vdW-corrected DFT across all surfaces, so any potentially important vdW-related effects on adsorption energy have been accounted for. A bridge-centered site is preferred upon most fcc {111} surfaces (the exception is Rh, for which the bridge site is as favourable as the hcp hollow site) while upon hcp Ru{0001}, a hcp hollow site with 30° rotation is preferred. As for the two bcc{110} surfaces (Mo and W), long bridge and hollow sites are equally preferred in both cases. Interestingly, our work also identifies the hollow site as favourable on the Fe{110} in addition to the short bridge site, in contrast to other results on bcc {110} surfaces. As discussed in section 4.2, this could be related to the chosen cell size, which allowed the short bridge to expand slightly, making the final S-0° site resemble a long bridge type site. There could also be a change due to the relatively different lattice parameters for these bcc metals, allowing for better orbital overlap in the long bridge site on Mo and W (Mo: 3.15 Å, W: 3.17 Å) than on Fe (Fe: 2.87 Å). Finally, the strong spin polarisation of iron could also play a role in determining the preferred adsorption site on the bcc{110} surface. In summary, it is unsurprising to see differences in preferred adsorption modes for differently packed flat metal fcc, bcc and hcp surfaces, as the surface symmetry is different upon these surfaces (i.e. close packing in three directions on the fcc {111} surface in contrast with close packing in two directions for the bcc{110} surface) and packing distances vary depending on the lattice parameter.

The experimental LEED work of Pussi *et al.*¹⁸¹ on benzene adsorption on Co $\{10\overline{1}0\}$ is particularly interesting to compare to the benzene/Fe{211} results from this thesis, as the stepped surface structure of hcp $\{10\overline{1}0\}$ is quite similar to bcc $\{211\}$. At 300 K saturation of the Co{1010} surface with benzene, a p(3 \times 1) monolayer of benzene is favoured, where the preferred adsorption site is analogous to either H1 or H3 sites on the Fe{211} surface (see figure 4.18 in section 4.4). Their quantitative LEED(I-V) analyses indicate that the adsorbed benzene molecule is not flat on the surface; it may either be flat within the surface trough or deforming quite heavily in a similar site. Our DFT result for benzene/Fe{211} would support the proposal that benzene should deform when adsorbed within the trough, though adsorption behaviour could be different upon the hcp $\{10\overline{1}0\}$. As for the preferred adsorption site, the work from this thesis does identify H3 as being a strong adsorption site, albeit not as strong as the BU2 site, which is centered about the surface trough. The work presented in this thesis neglects to account for the effect of higher surface coverage, in which case it is reasonable that the H3 adsorption site could provide a favourable positioning at the surface, as it allows for hydrogen bonding between adsorbates more readily than the BU2 site. Work on higher surface coverage is planned for the future; see chapter 7 for more information.

4.5.3 Conclusion

The adsorption of benzene has been studied using DFT and vdW-corrected DFT upon three different surface facets; the bcc Fe{110}, Fe{100} and Fe{211} surfaces. These three surfaces were chosen as they each represent a different type of stable surface (flat, kinked or stepped) which has the highest chance of being present on a real iron crystal.

The DFT-PBE findings reveal that hollow or hollow-like adsorption sites are preferred across all surfaces: the H-30° and H-0° sites on Fe{110} ($E_{ads} = -1.62 \text{ eV}$); the H site on

Fe{100} ($E_{ads} = -1.41 \text{ eV}$) and the surface-trough bridge centered BU2 site on Fe{211} ($E_{ads} = -1.55 \text{ eV}$). Once vdW corrections are accounted for by way of the TS correction scheme, the relative energetics are shifted and adsorption energies are overall stronger. As a result, the S-0° site is preferred on Fe{110} ($E_{ads}^{vdW} = -3.45 \text{ eV}$) while the H site on Fe{100} ($E_{ads}^{vdW} = -3.02 \text{ eV}$) and BU2 site on Fe{211} ($E_{ads}^{vdW} = -3.44 \text{ eV}$) remain strongest. The use of PBE-TS minimally affects PBE-optimised adsorption geometries. Geometries vary depending on the adsorption site and surface, but show the strongest deformation on the Fe{211}, followed by the kinked Fe{100} and flat Fe{110}. The Fe{211} shows particularly interesting strong deformation in its preferred adsorption site BU2, where the adopted benzene conformation bears a strong resemblance to the boat form of cyclohexane. Across sites and iron surface facets studied, the C-H bonds flip up and away from the metal surface. This behaviour is related to hybridisation of C-p orbitals with Fe 3*d* orbitals as well as what is known as the cushion effect, arising from π and surface electron Pauli repulsion.

Analysis of Hirshfeld charges and differential charge density reveal increase of electron density around carbon atoms while the regions surrounding H atoms show a decrease of charge density. The H-0° site on Fe{110} carries an overall positive charge (+0.09 e) as well as the BU2 site on Fe{211} (+0.04 e) while the H site on Fe{100} carries a negative charge (-0.02 e). As for spin, across all surfaces benzene is spin-polarised as a result of adsorption; carbon atoms are of minority spin while hydrogen atoms are of majority spin except in a few cases. Finally, the surface workfunction is reduced due to the adsorption of benzene across all surfaces (Fe{110} $\Delta \phi = -1.16$ eV and Fe{211} = -1.01 eV) in line with results seen for benzene on many other metal surfaces.

Chapter 5

Polyaromatic and Heteroatomic Hydrocarbon Adsorption on Fe{110}

5.1 Introduction

In this chapter, the adsorption of two Polyaromatic Hydrocarbon (PAH) species (naphthalene and quinolinium) on the bcc Fe{110} facet is presented. The adsorption of PAH on transition metal surfaces, whether purely containing C-H bonds or including heteroatoms, is central to many technologies. Research on HIOS relevant to this work is reviewed in section 5.1.1. Research which employs iron as the inorganic component within HIOS is highlighted in this section, alongside literature featuring adsorption of relevant PAH molecules on other metal surfaces.

The results for adsorption of naphthalene of the Fe $\{110\}$ surface are presented in section 5.2. This is followed by the results for quinolinium adsorption on the Fe $\{110\}$ in section 5.3. A comparative discussion of the adsorption behaviour of structurally similar naphthalene and quinolinium molecules on the Fe $\{110\}$ surface is presented in section 5.4, alongside comparisons to the benzene/Fe $\{110\}$ data presented in chapter 4 as well as other related systems.

5.1.1 PAH adsorption on transition metal surfaces

There is a large body of experimental and computational research on the adsorption of PAH on transition metal surfaces, which has been reviewed previously.^{2,12–14} This is because such systems are of central relevance in a large number of applications, including (but not limited to) heterogeneous catalysis, lubrication and coatings, chemical sensing, organic opto-electronic devices, dye-sensitised solar cells, batteries, and of particular focus for this thesis, corrosion inhibition. Because of this wide spectrum of potential applications, the amount of work is too vast to review in any comprehensive way in this thesis. The following introductory material carries a focus on simulations related to the application of interest, corrosion inhibition. In this first section, a review of efforts towards the study of corrosion inhibition in general are presented. It should be noted that there are reviews on this topic which should certainly be consulted, particularly for a more thorough overview of all calculations and experiments done in this context.^{28,30,31}

Aside from steel and iron, corrosion is a problem requiring study for many other metallic substrates which feature in different applications. A particularly popular choice for study by the surface science community is copper. Copper is widely used industrially and commercially and is prone to acid corrosion, so a number of corrosion inhibitor molecules have been developed to protect such surfaces. Benzotriazole (BTAH) as well as its derivatives are one of the most popular choices in this context, and have been studied on a number of different copper and copper oxide surfaces.^{39,50,57,58,182} Azole-type inhibitors, including imidazoles and triazoles, have also been studied rigorously in this context. ^{43,60,61,183,184} When discussing the adsorption of heteroatomic PAH upon transition metal surfaces using DFT with a special emphasis on corrosion inhibition, it is necessary to mention Kokalj et al., ^{39,42–44,50,58–61,185,186} who have established themselves as authorities in this area. Their group have studied a number of molecular systems on a number of different surfaces, as well as a review on the methods used and calculations carried out in this area. Generally, their studies take place on Cu and Cu oxide surfaces, however other surfaces have also been studied. Marcus et al. have also made important contributions in the DFT study of corrosion inhibition alongside corrosion mechanisms more generally, especially on oxide surfaces as well as zinc corrosion inhibition.^{24,31,39,48,65,66,187–191} Finally, Taylor *et al.* have made key insights related to corrosion and corrosion inhibition from a computational standpoint, with an emphasis on how atomistic calculations fit into the multiple length and timescales present within the corrosion process.^{25,30,31,39,192,193} Outside the corrosion inhibition space, the adsorption of large PAH systems on Cu has been studied using DFT, for example in a study of a polyimide, which has shown promise as a polymeric substrate for flexible printed circuit boards, on Cu{111}.¹⁹⁴ Another popular metal for study in the context of corrosion has been aluminium. The DFT study of 8-hydroxyquinoline and related molecules on Al{111} has been carried out.^{62,64} Also, a DFT study of gallic acid, which is known to have an inhibitory effect on Al, has been conducted on the Al{111} surface.⁶³

DFT work in recent years has focussed on more nuanced analyses, for example the work of Wang *et al.*¹⁸⁴ which studies the adsorption of imidazole, benzotriazole and 2-mercaptobenzoxazole on the Cu{100} grain boundary. Larger systems are also now being treated in this context, for example in the study of surfactants used as corrosion inhibitors.⁷⁰ Methods beyond DFT are also being used, such as DFTB which has allowed for the study of adsorption of large aromatic systems which are expensive to study using DFT.⁷⁷ Hybrid DFT methods have also been used to better quantify charge transfer at the organic-metal interface.¹⁹⁵ There has also been work done to try to build predictive models for aromatic adsorption behaviour and energetics on the Pt{111} surface.¹⁹⁶ There is an important emerging research area in the DFT study of corrosion inhibitor adsorption on Metal surfaces under potential bias, as demonstrated in one paper in the study of pyridine on Au{111}.⁷³ Such studies are expected to develop and play an important role in the future study of corrosion inhibition research; this is discussed more in chapter 7.

PAH adsorption on iron surfaces

Given the importance of steel, it is unsurprising that steel and steel-like iron surfaces should be of interest in the context of acid corrosion inhibition research. There is an enormous body of work on experimental adsorption of corrosion inhibitor and small aromatic molecules on different steel and iron oxide surfaces at a wide variety of experimental conditions (temperature, solvent, pressure, within an electrochemical cell, etc.) A review of such work falls outside the scope of this thesis, so only the relevant computational studies conducted to date are presented here.

Significant work has been invested towards correlation of the experimental corrosion inhibition properties of known corrosion inhibitors to molecular descriptors, such as the energy of the HOMO and LUMO, dipole moment, and atomic charges, extracted from molecular DFT studies.^{26,47} Although trends linking corrosion inhibition efficiency to ACI structural and electronic properties have been identified, the use of such QSAR and QSPR approaches has received criticism in the literature. A number of studies^{49–51} have shown that these methods do not work well to predict the experimental inhibitory action for all systems, which is in large part because the effectiveness of ACI molecules depends not only on molecular properties, but additionally on the interplay of molecule-surface, water-surface, and molecule–water interactions. In saying this, there have been a number of studies which attempt to incorporate the surface-molecule interactions into QSAR models, typically using cluster models to represent the metallic surface.⁵⁴ These studies have issues of their own, as the clusters used tend to be small and may therefore not be representative of the true nature of a metallic surface. There is a small number of studies which do attempt to study the effectiveness from many different angles, including periodic DFT studies, such as the study of Camacho-Mendoza et al. which in addition to building their DFT QSAR model around imidazole-based compounds also perform Electrochemical Impedance Spectroscopy (EIS) to study experimental corrosion inhibition as well as periodic DFT studies of benzimidazole and imidazole adsorption on Fe{110}.⁶⁹ Finally, the QSAR and QSPR approaches can be useful when robust experimental data sets and machine learning models are used, for example in the work of Winkler et al. ⁵² which identifies molecular descriptors (not derived from quantum chemical calculations) that can be used to quantitatively predict corrosion inhibition properties of organic molecules upon aerospace alloys.

Perhaps in part as a response to criticism of QSAR and QSPR approaches, the past decade has resulted in a growing body of published work which features force-field based MD and MC simulation techniques to probe the adsorption of an aromatic ACI, typically

on an iron surface facet to represent the steel surface, most often alongside experimental electrochemical experiments. These efforts are reviewed comprehensively in the recent work of Verma et al.⁷⁹ Some examples from this class of work which are of relevance to this work include the work of Zheng *et al.* on two oxadiazole derivatives on the Fe{100} surface, ¹⁹⁷ quinazolinone derivatives on the Fe{110} surface (in the context of lubricating oils),¹⁹⁸ three thiourea derivatives adsorbed on the Fe{110} surface in water¹⁹⁹ and the study of five bis-azo dyes on the Fe{110} surface.²⁰⁰ This work can provide helpful clues on how the adsorption takes place, and compared to uncorrected DFT, such approaches do better capture important vdW interactions which play a significant role in the binding of aromatic systems. Because such methods are relatively inexpensive, they also readily allow for the inclusion of solvent (water) or even other components of interest. A major flaw of the typical force field-based approaches, as other works rightly point out,²⁰¹ is that they fail to capture reactivity such as charge transfer that may occur on the surface. Such effects may play a key role in the activity of corrosion inhibitors. Additionally, the metallic character of a pure iron slab is described poorly by a general purpose force field, which is the solution most often used in existing works. There has been a very limited number of ab initio MD studies of corrosion inhibitor/surface systems, see for example the work of Allal *et al.*⁷⁸ on thiophene adsorption on Al{111}. Such studies are rare because of the high computational expense involved to propagate a relatively large hybrid organic-inorganic system through time at the DFT level.

There is a number of DFT works in the literature which probe molecule-iron surface interactions under UHV conditions. In terms of molecules around the size of benzene which include heteroatoms, this includes guaiacol and phenol on Fe{110}, 202,203 pyridine on Fe{100}, 204 m-cresol on Fe{110}, 205 anisole on Fe{110}, 206 thiophene, pyrrole and furan on Fe{110}, 201 2-mercaptoimidazole on Fe{100}, 68 phenylalanine and methionine on Fe{110} and imidazole on Fe{100}. 186 It is worth highlighting the work of Guo *et al.* 201 which provides interesting insight into the study of corrosion inhibitor molecules through comparative study of cyclic molecules containing N, O and S atoms on the Fe{110} surface. As for molecules adsorbed on iron surfaces more similar in size to naphthalene and quinolinium, a recent work

by Kumar *et al.*⁷¹ employs periodic DFT calculations to study the adsorption mechanism of henna extracts, which are known to have anticorrosive properties, on the Fe{100} surface.⁷¹ The three adsorbates studied (lawsone (2-hydroxy-1,4-naphthoquinone), gallic acid and α -D-glucose) share similar features with both naphthalene and quinolinium. The work of Sun et al.²⁰⁷ on DFT adsorption of pentacene on the Fe{100} surface represents an impressive computational effort, particularly at the time it was published. A very recent work by Murmu *et al.*⁷⁶ studies the adsorption of 1-phenoxybenzene and 1,4-diphenoxybenzene on the Fe{110} surface using DFTB to better understand the adsorption mode of much larger azomethine-derived Schiff bases which have some corrosion inhibitory action on mild steel surfaces. There is also the study of Camacho-Mendoza et al. as mentioned previously, which studies the adsorption of benzimidazole and imidazole on Fe{110} including the effect of solvation through use of a periodic implicit solvation model.⁶⁹ A recent study by Gouron et al. also looks at adsorption of imidazole derivatives in the context of corrosion inhibition using DFT, but with an emphasis of self-assembled monolayer behaviour (close packing) upon the Fe₂O₂ {0001} surface.²⁰⁸ It is worth mentioning that a significant proportion of the listed studies neglect to use vdW-corrected DFT, which as discussed previously can result in failure to adequately describe the adsorption process.

It becomes apparent that studies of ACI subunits on iron surfaces has not been systematic. It is particularly noteworthy that the choice of surface upon which adsorption is studied seems arbitrarily decided in certain works. Additionally, it isn't always made clear in these works how/whether different adsorption configurations were tested. Rigorously studying the adsorption behaviour of simple, moderately-sized ACI scaffolds such as naphthalene and quinolinium on the most stable surface facet (Fe{110}) is therefore worthwhile.

Naphthalene and quinoline adsorption on metal surfaces

Studies of naphthalene adsorption on metal surfaces are not uncommon given that it is a logical second step in the study of simple aromatics after benzene. Naphthalene adsorption has been studied using DFT on Pt{111}, ^{173,209} Pd{111} and Rh{111}²⁰⁹ and more recently using the PBE+vdW^{surf} approach upon Ag{111}, Cu{111} and Pt{111}.⁷⁵ As for UHV ex-
periments, the adsorption behaviour of naphthalene been studied on Pt{111}, ^{146,210,211} Pt{100},¹⁴⁶ Cu{100},²¹² Cu{111},^{213,214} Ag{111},^{215,216} Ag{100}²¹⁷ and Rh{111}²¹⁸ by way of a wide variety of surface science techniques, including LEED, SCAC, Scanning Tunneling Microscopy (STM), and Near-edge X-ray Absorption Fine Structure (NEXAFS) among others. Findings vary depending on the surface facet and metal identity, but in all cases naphthalene adsorbs in a flat-lying (or slightly tilted) configuration to maximise its vdW interaction with the metal surface. On fcc $\{111\}$ surfaces, the longer C₂ naphthalene axis aligns with a primitive surface lattice direction, and on several fcc {111} surfaces, LEED reveals naphthalene occupies a threefold 120° rotated (3 × 3) overlayer structure which does not show long-range ordering.^{210,218} DFT calculations reveal the preferred naphthalene adsorption site on Pt{111} features benzyl rings centered on bridge sites found on the fcc{111} surface, where the central C-C bond sits above an atop site.^{75,173} In the preferred adsorption geometry, the naphthalene molecule distorts, which enables better overlap of the molecular orbitals with the surface d orbitals.¹⁷³ The picture is quite different for Ag{111} and Cu{111}, which were studied using vdW-corrected DFT by Maurer et al.⁷⁵: the benzyl rings prefer to lie centered above hollow sites. To the best of our knowledge, there are no UHV experiments or calculations for naphthalene adsorption on bcc metal surfaces.

As for the adsorption of quinolinium, to the best of our knowledge this has not been studied; the fact that it is a charged species and would therefore adsorb with a counter ion under experimental conditions is likely to complicate UHV experiments. The adsorption behaviour of a number of related molecules on metal surfaces have however been studied, namely pyridine and quinoline.^{209,219,220} The differences between these molecules is discussed more carefully in section 5.3.

5.2 Naphthalene/Fe{110}

5.2.1 Introduction

Naphthalene $(C_{10}H_8)$ is a logical next step in the study of aromatic adsorption on iron after benzene. Naphthalene also features heavily in the corrosion inhibition literature as a scaffold

for known effective inhibitors. Understanding the way this simplified system interacts with the Fe{110} surface, which is the most stable bcc iron surface, is sure to help rationalise the interaction mode of more complex adsorbates with the same surface.

In this section, the results of DFT calculations probing the adsorption of naphthalene upon the Fe{110} surface are presented. Simulation parameters can be found in table 5.1. The parameters used are essentially identical to those used for benzene adsorption on the Fe{110} surface. See chapter 4 for a more detailed description and rationalisation for the choice of parameters as well as a visualisation of the chosen simulation cell. The naphthalene/Fe{110} simulation parameters are identical to those used to study the adsorption of benzene/Fe{110} so that results for benzene and naphthalene adsorption on Fe{110} can be directly compared to each other.

Table 5.1. Simulation details and parametersspecific to the naphthalene/Fe{110} calculations

Parameter	Value
Vacuum spacing (Å)	10
Cell size (c \times c)	(4 × 4)
Number of slab layers	6
Number of fixed slab layers	3
MP K-point sampling	$2 \times 2 \times 1$

5.2.2 Gas-phase naphthalene

The PBE-TS-optimised gas-phase structure of naphthalene is shown in figure 5.2.2 alongside its optimised C-C and C-H bond lengths (the same distances are found using PBE). Geometry optimisation was conducted using a 20 Å box to prevent interaction with periodic copies of naphthalene. As can be seen in figure 5.2.2, there are four types of C-C bond within naphthalene: four short C-C bonds (1.38 Å) (1) four longer C-C bonds (1.42 Å) (2) two outer C-C bonds (1.41 Å) (3) and the longest C-C bond which connects the two cycles (1.43 Å)(4). The C-H bonds are all of the same length (1.09 Å). The lengths observed are in excellent agreement with other theoretical results^{173,221,222} ((1): 1.38 Å, (2) and (3): 1.41 Å, (4): 1.43 Å) and experimental results^{223–225} ((1): 1.37 Å, (2) and (3): 1.42 Å, (4): 1.43 Å).



Figure 5.1. Gas-phase naphthalene PBE-TS optimised structure and bond lengths.

5.2.3 Adsorption geometries and energies

In order to systematically study the various possible adsorption sites of naphthalene on $Fe\{110\}$, a sensible starting point is to align one of naphthalene's benzyl groups on one of the five known possible high symmetry sites as identified in chapter 4 for benzene on $Fe\{110\}$. Namely, these are the first and second short bridge sites, which are treated as distinct due to the positioning of the second benzyl ring with respect to the first as well as the long bridge site, the 3-fold hollow site and the atop site. After positioning the benzyl

ring upon one of the five identified sites, the entire naphthalene molecule is rotated by 30° increments about the benzyl-centered portion. The 30° increment was chosen owing to our previous finding that benzene may adopt a 0 or 30° non-symmetrically equivalent version of each of the five aforementioned binding sites. In doing this, we end up with thirty possible adsorption sites (six rotations × five unique sites).

From this initial survey of possible binding sites, it is possible to narrow down the number of binding sites for DFT study. First, certain rotations produced identical sites to other rotation angles. On this basis, ten of the thirty sites could be discarded. Of the twenty remaining sites, we identify nine sites which have very high symmetry and therefore stand the best chance of high stability after DFT optimisation. These sites, which form the basis of our starting point for DFT calculations, are shown in figure 5.2. The 11 discarded sites are not studied due to low symmetry, most often due to the second benzyl group not occupying a high-symmetry site. Results for a DFT study of the similar naphthalene/Pt{111} system from the literature support the hypothesis of higher symmetry generally being favoured.¹⁷³

The nine naphthalene/Fe{110} geometries chosen for study include sites where the benzyl ring on naphthalene is rotated along one of three distinct angles. There are five different 150° rotated geometries, three 120° rotated geometries and one 0° rotated geometry. All chosen sites feature high-symmetry benzene/Fe{110} sites for the positioning of the two aromatic rings. The naming conventions used throughout this chapter are based on the benzene/Fe{110} adsorption site names, where each benzyl ring's position is part of the final name. The rotation angle is omitted for clarity, but has been indicated in figure 5.2. The following abbreviations are used throughout the chapter: "H" for 3-fold-hollow site, "S" for short bridge site, "L" for long bridge site and "A" for atop site. This shortens the 150°-3-fold-hollow-3-fold-hollow centered binding site for example to HH.

A summary of the outcome of DFT optimisation is shown in table 5.2. Of the nine adsorption sites studied, four are unstable upon DFT optimisation. In such cases, the initial geometry converted to one of the other five stable sites. The final geometry achieved is not the same one for the four unstable starting configurations, and has been indicated in table 5.2.



Figure 5.2. Naphthalene orientations selected for study on Fe{110}. Hydrogen atoms have been omitted for clarity.

Tables 5.3 and 5.4 list the energy results and geometric parameters for the five stable PBE-optimised naphthalene/Fe{110} adsorption sites. Representations of the corresponding PBE-TS optimised adsorption geometries are included in figures 5.3 and 5.4. There are minimal changes between the adsorption geometries calculated using PBE and PBE-TS; only the PBE-TS geometries are therefore shown. As can be seen from the adsorption energies in table 5.3, the most favourable configuration is the HH arrangement closely followed by the LL site. These two adsorption sites are relatively similar geometrically (see figure 5.4) and as a result are only separated by 0.02 eV. In decreasing order of energetic stability are a long bridge centered-type site (LC, for which the starting geometry was a short bridge centered site, SS3), long bridge - short bridge type site (LS) and finally a different short bridge - short bridge site (SS1). These predictions are mostly as expected, as the most favourable PBE-optimised benzene/Fe{110} site was a 3-fold-hollow-centered site followed

Configuration Name	Stable	Unstable
SS1	Х	
SS2		Х
LL	Х	
HH	Х	
AA		Х
LS	Х	
AS		Х
HA		Х
SS3	X^*	

Table 5.2. Stability of different tested naph-thalene/Fe{110} configurations

* In this case, the geometry of the initial configuration changed upon optimisation. The new optimised geometry is referred to as LC.

relatively closely in energy by a long bridge-centered site (see chapter 4). The difference in energy between the best (HH) and worst (SS1) sites is 0.33 eV, which is an indicator that a significant proportion of the more favourable proposed adsorption sites would be observed under UHV conditions thanks to thermal motion (again, because E is proportional to $e^{-\Delta E/k_BT}$, and $k_BT = 0.26$ eV at 298 K). As for the distortion of naphthalene, as with benzene/Fe{110} in all cases the C-H bonds flip up and away from the surface while the aromatic rings undergo some degree of buckling depending on the adsorption site. This is reflected in the E_{dist} values (table 5.3) which are all above 1.60 eV.

One unexpected result is the change in adsorbate geometry for the SS3 starting geometry (see figure 5.3 for a representation of the final geometry). The optimised geometry no longer features benzyl rings centered about short bridges, but instead features very high overall symmetry without the benzyl rings being centered about high symmetry sites. The new site, which will be referred to as LC (Long bridge Centered), features the central C-C bond of naphthalene centered above the long bridge site on the Fe{110} surface. The LC conformation features two pairs of carbon atoms each interacting with a single iron atom, as well as the two central carbon atoms interacting with an iron atom each. This new site

Adsorption site	$E_{ads}(eV)$	$E_{dist}(eV)$
LC	-2.59 (-5.68)	2.15 (2.36)
HH	-2.66 (-5.59)	1.95 (2.04)
LL	-2.64 (-5.58)	1.84 (1.98)
LS	-2.40 (-5.32)	1.74 (1.81)
SS1	-2.33 (-5.25)	1.67 (1.89)

Table 5.3. Calculated optimised energies for stable naphthalene adsorption sites on $Fe{110}^a$

^{*a*} E_{ads} represents the adsorption energy and E_{dist} represents the distortion energy upon adsorption. Data in brackets represents a vdW-TS corrected result.⁸⁴ All non-bracketed results were calculated using PBE.

presents an adsorption energy which is 0.07 eV less stable than the strongest HH site, which puts it in third place compared to all other binding sites. This demonstrates that there may be favoured naphthalene/Fe $\{110\}$ sites where the benzyl rings are not necessarily centered on high-symmetry benzene/Fe{110} sites. This is quite interesting in comparing to the DFT work of others on naphthalene adsorption on flat transition metal surfaces, where all the most stable adsorption sites feature centering of naphthalene's benzyl rings on high symmetry benzene/metal{111} adsorption sites.^{173,209} One site which is identified and moderately favoured on Pt{111} (referred to as "butadiene-like") features strong deformation of the naphthalene molecule in order that it may bind to the surface through four C-Pt bonds (Four carbon atoms and three Pt atoms) instead of the entire molecule, which allows for the other half of the molecule to maintain aromaticity as it is relatively far away from the surface. This is quite a different case to the LC site observed here, as the butadiene-like geometry demonstrates poor overall symmetry with respect to the surface, whether laterally or in the direction perpendicular to the surface. Additionally, because of the difference in symmetry between the studied fcc {111} surfaces and the bcc {110} surface presented in this thesis, a butadiene-like arrangement of naphthalene on Fe{110} appears to either be unstable or not produce a lifting of the other portion of the molecule, as some of the configurations tested feature this type of arrangement and this has not been observed on Fe{110}. Finally, the

difference in reactivity between previously tested Pt, Pd and Rh and Fe could also explain the differences observed. These comparisons will be considered more carefully in section 5.4.

site	$d_{C-C}(\text{\AA})$	$d_{C-H}(\text{\AA})$	$\theta_{C-H}(^{\circ})$	$\theta_{C-C}(^{\circ})$	$d_{C-Fe}(\text{\AA})$
free naphthalene	1.40 (1.40)	1.09 (1.09)	0 (0)	121 (121)	-
LC	1.46 (1.46)	1.10 (1.10)	22 (22)	120 (120)	2.12 (2.10)
HH	1.45 (1.45)	1.10 (1.10)	21 (21)	120 (120)	2.13 (2.12)
LL	1.45 (1.45)	1.09 (1.09)	23 (23)	120 (120)	2.11 (2.10)
LS	1.45 (1.45)	1.09 (1.09)	21 (21)	120 (120)	2.16 (2.15)
SS1	1.44 (1.45)	1.10 (1.10)	20 (21)	120 (119)	2.12 (2.11)

Table 5.4. Calculated optimised geometric parameters for naphthalene on $Fe{110}^a$

^{*a*} d_{C-C} represents the average C-C bond length in benzene, d_{C-H} the average C-H bond length, θ_{C-H} the average CH tilt angle (dihedral) with respect to the molecular plane, θ_{C-C} the average angle between carbon atoms in the molecule and d_{C-Fe} represents the average C-Fe distance. Data in brackets represents a vdW-TS corrected result.⁸⁴ All non-bracketed results were calculated using PBE. The free naphthalene results were extracted from geometry optimisation using a cubic 20 Å box to prevent naphthalene self-interactions.



Figure 5.3. Images of 0° and 120° rotated optimised naphthalene binding sites. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).



Figure 5.4. Images of 150° rotated optimised naphthalene binding sites. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).

Vdw-corrected adsorption geometries and energies



Figure 5.5. Comparison of adsorption energies for all PBE (blue) and PBE-TS (red) optimised naphthalene/Fe{110} sites.

The PBE-TS optimised structures are shown in figures 5.3 and 5.4, and accompanying PBE-TS energetics and geometric data are shown in tables 5.3 and 5.4 respectively. As seen from previous benzene/Fe{110} studies, accounting for the effect of important vdW corrections can impact the surface adsorption energies. This is also the finding from this work for naphthalene/Fe{110}, as seen in the significantly stronger energies in table 5.3. For all sites studied, the adsorption energy strength increase is on the order of 3 eV. This is a larger change than for PBE vs PBE-TS for benzene/Fe{110} which is in line with the fact that naphthalene is a larger molecule containing a larger extent of aromaticity, which makes it capable of further vdW interactions compared to benzene with the metal surface. Another finding of great interest is the change in the relative energetic ordering of the stable adsorption conformations. The change in relative energetics is shown in figure 5.5. The

clear outlier is the LC adsorption site, which as mentioned previously is the third most stable of all sites with PBE, but is the preferred adsorption site with PBE-TS. There is no significant change in geometry observed between any of the PBE and PBE-TS optimised structures as can be seen from the geometric PBE-TS parameters listed in table 5.4, so this relative increase in adsorption strength for LC compared to the other sites is a purely electronic effect. LC is significantly stronger (by 0.09 eV) than the next best site, HH. This is interesting as it is very similar to the PBE-optimised energy difference between LC and HH sites (0.07 eV), where HH is instead preferred. Distortion energies shows the strongest distortion for LC (2.36 eV) followed by HH (2.04 eV) which matches the trend seen in adsorption strength. Similar changes in relative energetic ordering due to the use of a vdW correction have been observed in other works, and will be discussed in section 5.4.

5.2.4 Charge density difference

Charge density difference plots for the stable naphthalene/Fe{110} adsorption sites are shown in figure 5.6. From upper left to bottom right, the density plots shown are ordered by decreasing adsorption strength. Across all sites, it is clear that electron density tends to increase on C atoms while there are regions of decreased electron density 1) below the adsorbate plane 2) around H atoms and 3) above the molecular plane, often appearing as "nodes" separating the positive charge density regions. Comparing different structures, the most striking/interesting contours appear for the LC site which, as explained in section 5.2.3, is a long bridge-centred site with overall high symmetry but low-symmetry positioning of the benzyl rings. The overall charge density difference plot for this adsorption site also appears to be very symmetrical, particularly when compared to the others.

The contour shapes of the charge density diagrams can be rationalised by studying the Molecular Orbital (MO) diagram for a given adsorbate, see the work of Yamagishi *et al.*¹⁶⁵ for example. The naphthalene MO diagram has been computed using molecular DFT calculations and is represented in figure 5.7. In studying the high symmetry top PBE-TS site (LC in figure 5.6), the region of charge density increase (yellow) is effectively identical to the structure of the MO corresponding to LUMO+2, so it is likely this orbital plays a role

in accepting electron density from the iron surface in the given configuration. However, looking at the yellow regions for all other adsorption sites, they do not clearly resemble a single MO, but do present features of LUMO, LUMO+1, LUMO+2 and LUMO+3. The orbital(s) which provide the best overlap with the underlying metal's *d* (or *s* or *p*) orbitals will feature most significantly in the charge density diagram plot. From our plots, it appears that all configurations aside from LC provide their maximal interaction with the surface through a mixture of unoccupied and occupied orbitals. As for the electron density depletion regions (blue), above the plane of the LC site adsorbate again quite clearly presents what seems to correspond to the HOMO contour plot. This seems to be the case also for the blue regions above the LS site, although it seems the lobes aren't all equivalent, so there may be contributions from other orbitals. Finally, electron density decrease above the SS1 site plane presents features of the HOMO-3 orbital, but also has traces of other orbitals being involved in the adsorption process. It's also worth noting that the appearance of occupied and unoccupied orbital-like charge density contours is a clear indicator that the adsorbate is capable of both forward and back-donation of electron density with the metal surface.

The most important conclusions to draw from the combined charge density difference - MO analysis is that regions of electron increase for naphthalene roughly correspond to LUMO (or higher order LUMO)-like MO configurations, while regions of electron depletion seen above the plane of the molecule correspond to HOMO (or lower order HOMO)-like MO configurations. Of further importance is that it isn't necessarily just the HOMO and LUMO involved in the adsorption process; it seems the involved orbitals are highly adsorption configuration-dependant, and therefore that HOMO-1, HOMO-2 etc. and LUMO-1, LUMO-2 etc. can become involved in the electron exchange process if it improves orbital overlap at the surface. The nature of such findings has been discussed extensively in other papers, for example for benzene/Ni{111}.¹⁶⁵



Figure 5.6. Images of optimised naphthalene binding site charge density density. View shown from above the Fe{110} surface. Blue (yellow) regions denote a decrease (increase) in electron density on the order of 1.5×10^{-2} electrons/Å³.



Figure 5.7. Calculated molecular orbital diagram for naphthalene. The calculated energies and MOs were obtained using DFT (B3LYP/6-31G(d,p)) as implemented in Gaussian09.¹²⁵ HOMO, LUMO and other MOs are indicated on the diagram.

5.2.5 Spin density

The spin densities for all naphthalene/Fe{110} adsorption sites are shown in figure 5.8. Surface-induced spin polarisation can be seen on the adsorbate, which carries no spin in the gas-phase, for all geometries. Across all adsorption configurations, H atoms are of majority spin while C atoms are all of minority spin. All the configurations show slightly different spin density distribution, but probably the most unique-looking of all is the LS site. It features C-related minority spin which is distorted compared to other adsorption configurations. This may have something to do with LS being the only site which presents benzyl rings centred on different high symmetry sites (a long bridge and short bridge type site). As with the charge density difference, the LC site shows the highest symmetry spin density contours. This again supports the comments made for charge density difference that this adsorption configuration must allow for particularly good overlap of its MOs with the underlying surface orbitals.

5.2.6 Atomic charges and spin

Table 5.5 lists the PBE and PBE-TS-derived Hirshfeld charges and atom-resolved spin for relevant atom groupings from the top adsorption site (LC). Values for the top PBE-optimised site (HH) are also presented later in section 5.4 as they compare more closely to the quinolinium/Fe{110} results.

The Hirshfeld charges derived for the LC site using PBE and PBE-TS methodologies are effectively identical, save for the negligible 0.01 change for the iron slab. As discussed previously for benzene/Fe{110} in chapter 4, charges have been produced using an increased k-point sampling $(4 \times 4 \times 1 \text{ mesh})$, therefore the small non-zero sum of charges (for PBE-TS, the sum is -0.02 e) is likely related to rounding in the CASTEP output. Also similarly to benzene/Fe{110}, the LC site overall acquires a positive charge (+0.16 e) while the iron slab overall carries a counter-balancing negative charge (-0.18 e). The carbon atoms within the LC site overall carry a negative charge (-0.28 e) while the H atoms overall carry a larger positive charge (+0.44 e). This is in good agreement with the charge density difference plot as shown in figure 5.6, where increased electron density appears around the C atoms while regions of decreased charge density occupy the regions surrounding H atoms.



Figure 5.8. Images of the optimised naphthalene binding site spin densities. View shown from above the Fe{110} surface. Blue (yellow) regions denote minority (majority) spin regions on the order of 3×10^{-3} electrons/Å³.

The spin values show negative spin polarisation on the C atoms and no polarisation on the H atoms. The C result agrees well with the spin density shown in section 5.2.5 where blue minority spin regions are observed above the C atoms. As for H, spin majority regions are observed about the H atoms in the spin density plot in contrast with the zero spin polarisation. A reasonable explanation for the discrepancy would be that, given the scale of the contours shown in figure 5.8, $(3 \times 10^{-3} \text{ electrons/Å})$, perhaps these values are below 0.01 μ_{β} per atom. The PBE-TS spin values observed for benzene/Fe{110} (0.02 μ_{β}) are very small, so the naphthalene/Fe{110} result is also sensible in comparison. The PBE and PBE-TS results are in perfect agreement for H and C atom spin, but as has previously been seen for benzene adsorption, there is a slight decrease in the metal slab spin sum. This difference is likely to result from additional relaxation of the surface when the TS correction is applied.

Atom group	charges (e)	charges (e)	spin (μ_{eta})	spin (μ_{β})
	PBE	PBE-TS	PBE	PBE-TS
C ₁₀ H ₈ sum C sum H sum Motel clob cum	0.16 -0.28 0.44	0.16 -0.28 0.44	-0.52 -0.52 0.00	-0.52 -0.52 0.00

Table 5.5. Calculated Hirshfeld charges and atomic spin results for LC on Fe{110}

5.2.7 DOS and PDOS

Figure 5.9 shows the PDOS for one surface iron atom and the nearest carbon with which it directly interacts in the LC naphthalene/Fe{110} adsorption site. The carbon plot shows a significantly larger number of gas-phase orbital peaks compared to benzene/Fe{110} from chapter 4. The assignment of these peaks to isolated gas-phase naphthalene orbitals can be done, but will form part of a future work. Given that the gas-phase naphthalene PDOS has been aligned with the adsorbed naphthalene PDOS, the difference between the two shows the same trend as for benzene/Fe{110}, namely that the orbital peaks are shifted to higher

binding energies. The Fe PDOS plot shows the usual new peaks in the high binding energy region which correspond to the high binding energy carbon orbitals. The most notable change in the Fe PDOS plot is a significant shift in the minority spin densities to higher binding energies, both below and above the Fermi level. This results in a reduction of the number of spin-down states at the Fermi level. As for the majority spin Fe PDOS, they remain relatively unaffected by the adsorption process.

5.2.8 Workfunction

The change in workfunction upon adsorption has been studied for the preferred PBE-TS optimised adsorption geometry (LC). The computed results are listed in table 5.6. The methodology used to obtain these results is identical to that used to study benzene/Fe{110} in chapter 4.

As per the findings for benzene on Fe{110}, there are negligible differences between the PBE and PBE-TS energies used to calculate the workfunction. A decrease in the pure iron surface workfunction of 1.51 eV is observed using PBE-TS. This shows that naphthalene decreases the Fe{110} surface workfunction more than the most favourable benzene adsorption site does (-1.16 eV). This is in line with all results seen throughout this section, where naphthalene tends to show similar trends to benzene only on a greater scale owing to naphthalene's larger size and increased aromaticity.

Method	$E_{vac}(eV)$	$E_F(eV)$	Fe{110} φ (eV)	$C_{10}H_8/Fe{110} \phi$ (eV)	$\Delta \phi$ (eV)
PBE	-3.19	-6.59	4.90	3.40	-1.50
PBE-TS	-3.18	-6.53	4.86	3.35	-1.51

Table 5.6. Calculated Workfunction (ϕ) results for best site for naphthalene on Fe{110}^{*a*}

^{*a*} E_{vac} represents the vacuum energy, E_F represents the Fermi energy and $\Delta \phi$ represents the difference between the C₁₀H₈/Fe{110} ϕ and bare Fe{110} ϕ . Bare Fe{110} ϕ values are calculated using the 6-layer (4 × 4) slab.



Figure 5.9. Projected density of states (PDOS) for naphthalene on Fe{110} in the LC adsorption geometry. The upper plot shows the majority spin and minority spin PDOS for Fe atom 91 before (black) and after adsorption (red). The lower plot shows C atom 2 within naphthalene in the gas-phase (black) and after adsorption (red, majority spin and minority spin shown). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase naphthalene DOS has been aligned with the lowest energy C(2s) orbital for adsorbed naphthalene, as this level is not expected to be involved in the adsorption process.

5.3 Quinolinium/Fe{110}

5.3.1 Introduction

In this section, the adsorption behaviour of quinolinium $(C_9H_8N^+)$ on the Fe{110} surface is studied. There are several compelling reasons to study the adsorption behaviour of quinolinium on iron which will be discussed here. As before, the reason for the choice of the Fe{110} facet is that it has been shown to be the most stable of all bcc iron facets, which implies that it should predominantly be exposed on a realistic iron single crystal.

Quinolinium has the same structure and connectivity as naphthalene, with the only difference being that it has a nitrogen atom in place of one of the carbon atoms. As a result, quinolinium carries a +1 charge. The study of structurally similar molecules which have different electronic structure is interesting in its own right, as it can be used to ascertain the effect of different heteroatom substitutions in aromatic rings upon adsorption. This is of particular relevance in the study of ACI adsorption upon steels because it is known that heteroatom-substituted aromatic molecules are effective whereas aromatic hydrocarbons, which most often are insoluble in the acidising fluids used, are unable to provide corrosion protection. The choice of quinolinium is motivated by the fact that it (and closely related compounds) are known to have acid corrosion inhibition activity on a variety of metal surfaces including steel.^{8,19,226–229} It should be noted at this stage that there are DFT studies of the adsorption of quinoline (C₉H₇N) and quinoline-derived molecules on metal surfaces.^{62,209,230} It is expected that only limited comparisons can be drawn between quinoline and quinolinium adsorption, because the N-H functionality in quinolinium is expected to act quite differently than the bare, aromatic N present in quinoline. In particular, other studies have shown quinoline to be able to adsorb tilted on a metallic surface, similarly to pyridine, by binding to the surface partly through the nitrogen - metal bond.²³¹ An obvious further difference is the presence of positive charge on quinolinium, which we expect would lead to important differences in adsorption geometry compared to neutral quinoline.

In the following sections, the results of quinolinium adsorption on Fe{110} surface will be presented. Prior to showcasing the work, it is necessary to outline technical considerations

Table 5.7. Simulation details and parametersspecific to the quinolinium/Fe{110} calculations

Parameter	Value
Vacuum spacing (Å)	10
Cell size (c \times c)	(4 × 4)
Number of slab layers	6
Number of fixed slab layers	3
MP K-point sampling	$2 \times 2 \times 1$

which affect the DFT calculations for charged species. These considerations are discussed in this section. All simulation details and parameters can be found in table 5.7. These simulation parameters are identical to those used to study the adsorption of benzene/Fe{110} and naphthalene/Fe{110}, meaning our results for benzene, naphthalene and quinolinium adsorption on Fe can be directly compared to each other. For rationalisation of the selected parameters as well as a visual representation of the chosen unit cell, chapter 4 should be consulted. The results of quinolinium/Fe{110} DFT calculations are presented from section 5.3.3 onwards.

Periodic DFT for charged systems

Charged systems can be studied using DFT, but there are a number of issues which do not apply to neutral calculations which must be addressed to ensure a correct answer is being produced from the calculation.²³² These considerations are presented and discussed here, and the solutions and workarounds used throughout this chapter are presented.

The first issue which must be considered arises from treating a charged simulation cell with periodic boundary conditions using DFT. Because the cell is infinitely repeated in three dimensions, so then is also the charge applied to the system. Clearly this is problematic, as finite charge is needed to accurately represent the system being studied. One technical solution to this problem is to apply a homogeneous counter-charge to the entire cell to balance the charge added into the system. This type of correction is used for calculating the properties of periodic systems containing ions and charge defects for example.²³³ For

quinolinium adsorption on an iron surface, it may therefore be sensible to apply a +1 charge (charge on the quinolinium ion) as well as a counter-balancing homogeneous -1 charge on the entire cell. We have however opted to treat the quinolinium/Fe{110} as neutral throughout the DFT calculations presented in this chapter. This is a sensible approach thanks to the nature of the real system our simulations are meant to emulate. We are interested in the adsorption of quinolinium on a steel-like slab, which is meant to represent the steel piping used in oil well applications. In this sort of application, the metal slab would be grounded or earthed, meaning that electrons from earth can be provided to the slab or donated from the slab to earth as necessary to equilibrate the additional charge coming from the adsorbate. Using a sufficiently large slab (ie. having enough layers for there to be a bulk-like phase of iron) ensures there are sufficient electrons in the bulk metal to act as an electron sink, able to provide or remove additional electron density as a grounded metal would. It should however be noted that for applications where the real system of interest would not be grounded, for example a nanoparticle in solution, this neutral cell approach could be problematic.

The problematic infinite charge for the quinolinium/Fe{110} system is therefore resolved thanks to making use of a neutral cell. A second issue in the same vein arises in the calculation of adsorption energy. This is because it is not possible to make any simplifications to prevent quinolinium in the gas phase from being positively charged. In other words, in the DFT optimisation of quinolinium alone, it is necessary to apply a +1 charge as well as the homogeneous neutralising -1 background charge as mentioned above. This results in a new issue; the total energy of the simulation cell converges very slowly with increasing cell size. Convergence is challenging, to the extent that it isn't realistic to achieve convergence by simply increasing the size of the simulation cell. This results in the energy of the gas phase ion quinolinium being ill-defined, as it is dependent on the size of the artificial box it is placed in. It is therefore necessary to identify the ion's "true" total energy which can be used in the adsorption energy calculations.

This can be resolved in different ways. The first method is to plot a number of DFT total energies for the same system as a function of varying cubic cell length (L), where the

intercept at 1/L = 0 is used as the converged total energy. The second method makes use of the so-called Leslie-Gillan correction scheme.²³⁴ The Leslie-Gillan correction takes the following form:

$$E_{int} = \frac{q^2 \alpha}{2L\epsilon_0} \tag{5.1}$$

where E_{int} is the corrected total electrostatic energy of the charged species, q is the total charge on the charged species (for quinolinium: $+1.603 \times 10^{-19}$ C), α is the lattice-dependant Madelung constant (for quinolinium: 2.8373 for simple cubic arrangement of point charges), L is the linear dimension of the supercell and ϵ_0 is the vacuum permittivity (for quinolinium: 8.854 $\times 10^{-12}$ F/m). This energy correction should be subtracted from the total energy for every different cell dimension used (E_{int} depends on L) to give a converged energy. It should be noted there are other correction methods, such as the Makov-Payne extension which has additional dependance on the quadrupole moment and L^3 cubic term.²³⁵

The result of the application of the two correction methods, alongside the original divergent total energies, is shown in figure 5.10. The two methods predict quite a similar converged total energy. The intercept of the Leslie-Gillan-derived curve has a negligible difference of 6×10^{-6} eV compared to the 1/L intercept method total energy, so we have opted to use the 1/L method intercept-derived value for our calculations (-1787.74646 eV).

Thanks to the 1/L intercept method, the charged quinolinium total energy is no longer ill-defined. At this stage, all that remains is to calculate adsorption energies, but a new problem arises. This third issue relates to our usual adsorption energy calculation equation. As a reminder;

$$E_{ads} = E_{surf+molec} - (E_{surf} + E_{molec})$$
(5.2)

If equation 5.2 is used as is, the energy associated with the adsorbate (E_{molec}) represents a +1 charged system while the bare metal surface energy (E_{surf}) represents a neutral system. This is problematic because we know the combined surface and adsorbate system energy $(E_{surf+molec})$ is neutral while in its current form, equation 5.2 has the sum of separate gas



Figure 5.10. Total energy (eV) for quinolinium in a cubic box plotted as a function of 1/L (Å). The red curve shows the lack of convergence of total energy as a function of simulation cell size, even up to very large cell size. The total energies after application of the Leslie-Gillan correction (blue) and 1/L intercept-derived total energy (green) are also shown.

phase components $(E_{surf} + E_{molec})$ as +1.

The solution we have developed for this issue is to include the workfunction (ϕ) in the adsorption energy equation. This is shown in equation 5.3:

$$E_{ads} = E_{surf+molec} - (E_{surf} + E_{molec} - \phi)$$
(5.3)

Where ϕ is the bare metal workfunction. As the workfunction represents the energy necessary to remove one electron from the surface into the vacuum, subtracting it from the surface energy E_{surf} results in a good approximation for the total energy of the -1 charged surface slab. In the limit of low surface coverage, the workfunction of the slab covered with adsorbate will be equal to that of the bare slab, therefore we can make use of the computed bare Fe{110} value for these calculations. For higher coverage cases, it would be necessary to make use of the workfunction value for the adsorbate/Fe{110} system.

Finally, it is also worth noting that the procedure described here is repeated for both PBE and vdW-corrected PBE-TS calculations. The inclusion of the TS correction shifts all energy results to more negative values.

5.3.2 Gas-phase quinolinium

The PBE-TS-optimised structure of quinolinium is shown alongside all bond lengths in figure 5.3.2 (the same distances are found using PBE). As with naphthalene, geometry optimisation was conducted using a 20 Å box to prevent interaction with periodic copies of quinolinium. In comparing to the gas-phase naphthalene data (see section 5.2.2), there is a wider variety of bond lengths due to the N atom. In particular, DFT geometry optimisation reveals there is a longer (1.38 Å) and shorter (1.34 Å) C-N bond within quinolinium. This is in good agreement with an experimental crystal structure for quinolinium perchlorate (1.37 Å and 1.33 Å).^{236,237} The calculated C-N-C angle (124°) is also in excellent agreement with the experimental value (123°). As for the C-C bond lengths, a range of experimental C-C bond lengths is observed within quinolinium, from 1.37 Å to 1.42 Å, in excellent agreement with the range observed using DFT. The N-H bond (1.03 Å) is shorter than the C-H bond (1.09 Å).



Figure 5.11. Gas-phase quinolinium PBE-TS optimised structure and bond lengths.



Figure 5.12. Quinolinium orientations selected for study on Fe{110}. Hydrogen atoms have been omitted for clarity. The nitrogen atom is indicated in blue.

5.3.3 Adsorption geometries and energies

On the basis of the similarity of quinolinium to naphthalene, the optimised naphthalene/Fe{110} sites (see section 5.2.3) form the basis for the starting structures chosen for study of quinolinium adsorption on the Fe{110} surface. As a result of the nitrogen atom in quinolinium in place of naphthalene's carbon, quinolinium has reduced symmetry compared to naphthalene. The result of this is that the number of quinolinium/Fe{110} sites selected for study is greater than the five stable naphthalene/Fe{110} configurations. Within a given high-symmetry naphthalene adsorption site on Fe{110}, there can be different arrangements of the quinolinium molecule depending on the location of the N atom with respect to the surface. This is illustrated in figure 5.12, for example for the HH-NA and HH-NS sites. As with naphthalene/Fe{110}, H is used to represent the centering of a benzyl ring over a 3-fold-hollow site, so the HH notation indicates that both benzyl rings are centered above

Adsorption site	Stable	Unstable
LC-NH	Х	
LS-NH	Х	
LS-NA	Х	
HH-NA	Х	
HH-NS	Х	
LL-NS		Х
LL-NA		Х
SS2-NA	Х	
AS-NA		Х
SS1-NA		Х
LA-NA	Х	

Table 5.8. Stability of different testedquinolinium/Fe{110} configurations

such sites. The additional "-NX" notation indicates the arrangement X of the nitrogen atom within high-symmetry surface sites. As a result, HH-NA indicates two 3-fold-hollow centered aromatic rings alongside nitrogen in the atop (A) position, while HH-NS represents the same site but with the N atom in the short bridge (S) position.

DFT optimisation of the naphthalene/Fe{110}-based starting configurations showed sites in which the N atom was positioned atop of an Fe atom (i.e. -NA denoted configurations) were favoured. To ensure all sites featuring nitrogen in an atop arrangement had been studied, a further three relatively high-symmetry starting configurations are identified through rotation of quinolinium about a NA-centered axis. The three further quinolinium/Fe{110} sites (LA-NA, SS1-NA and AS-NA, see figure 5.12 feature high symmetry and therefore the strongest likelihood of favourable adsorption. As a result, a total of eleven quinolinium/Fe{110} starting configurations are studied throughout this section.

The general results of DFT optimisation for all eleven sites studied is listed in table 5.8. As can be seen, seven of the the eleven sites are unique, stable adsorption geometries while the other four are unstable. The nitrogen atom has a strong directing effect upon quinolinium adsorption, such that the LL sites optimise to HH type sites, where the N atom has a higher symmetry arrangement with respect to the Fe{110} surface. As for the

AS-NA and SS1-NA sites, the preference for N to be in an atop arrangement is insufficient to stabilise the lower symmetry arrangement of the molecule. Tables 5.9, 5.10 and 5.11 list the adsorption energies, bond lengths and angles of interest for the seven stable PBE-optimised quinolinium/Fe{110} adsorption sites. Images of the PBE-TS optimised adsorption geometries are included in figures 5.13, 5.14 and 5.15. As with naphthalene/Fe{110}, the optimised PBE and PBE-TS adsorption geometries have very similar appearance; as a result, only the PBE-TS geometries are shown.

The preferred PBE-optimised adsorption site is the HH-NA site ($E_{ad} = -3.73$ eV) and is significantly stronger than the next strongest site (LS-NA, $E_{ad} = -3.50$ eV). The difference in energy is 0.23 eV, nearly an order of magnitude higher than the separation between the top two naphthalene/{110} configurations. The strongest three adsorption sites (HH-NA, LS-NA and LA-NA) all feature the aromatic N atom in the atop position. It is interesting to note however that nitrogen being in the atop site is not a guarantee of favourable adsorption, as demonstrated by the SS2-NA site, which is among the weakest of the stable adsorption sites. This is also true of the two unstable sites (AS-NA and SS1-NA) which were chosen specifically to orient the N to an atop orientation. The preferred tetravalent atop orientation of the nitrogen atom has been observed in prior work on sp^3 hybridised NH₃ adsorption on the Fe{211} surface.²³⁸ The energetic separation between strongest (HH-NA) and weakest (LS-NH) sites is 0.57 eV, which indicates that several of the less favoured sites are likely not to be observed under standard conditions in UHV experimental surface science experiments (because $k_B T = 0.26$ eV at 298 K, see chapter 4 for further discussion of this). For cases where N is not in an atop position (LC-NH, LS-NH and HH-NS configurations), the N atom is found to be out of the plane of the quinolinium molecule into the vacuum. This is demonstrated for example for the LS-NH site (see figure 5.13).

Quinolinium distortion energies show that there is moderate deformation for all sites compared to the ideal, flat gas-phase quinolinium molecule. It also shows that deformation energy is uncorrelated with adsorption energy. As an example, LA-NA shows the strongest deformation energy (1.54 eV), which is most likely due to the fact that it shows the highest average C-H tilt angle (27°) of all the adsorption sites. It is also interesting to note that despite

Adsorption site	$E_{ads}(eV)$	$E_{dist}(eV)$
HH-NA	-3.73 (-6.71)	1.45 (1.46)
LS-NA	-3.50 (-6.51)	1.27 (1.30)
LA-NA	-3.49 (-6.49)	1.54 (1.62)
SS2-NA	-3.29 (-6.43)	1.10 (1.41)
LS-NH	-3.16 (-6.41)	1.13 (1.31)
HH-NS	-3.38 (-6.29)	1.15 (1.11)
LC-NH	-3.24 (-6.29)	1.48 (1.52)

Table 5.9. Calculated optimised energies for stable quinolinium adsorption sites on $Fe\{110\}^a$

^{*a*} E_{ads} represents the adsorption energy and E_{dist} represents the distortion energy upon adsorption. Data in brackets represents a vdW-TS corrected result.⁸⁴ All non-bracketed results were calculated using PBE.

this, LA-NA is not the preferred adsorption site, although among the strongest sites. The second strongest distortion energy (1.48 eV) is observed for one of the weakest adsorption sites, LC-NH. Table 5.11 shows that it features one of the longest N-Fe distances (2.69 Å), and figure 5.13 shows the N atom shifted above the plane of the quinolinium molecule, which would contribute significantly to the strong distortion energy. Comparing E_{dist} among adsorption sites provides certain interesting trends, however the absolute value for E_{dist} should be treated as approximate. This is because the deformed quinolinium geometry which is found on the Fe{110} surface has participated in charge transfer interactions with the metal surface. The adsorbed geometry therefore no longer carries the +1 charge found on the ideal gas-phase quinolinium molecule to which it is being compared.

The C-C and C-Fe distances are of comparable dimensions to those obtained for naphthalene (explicit comparisons are made in section 5.4). It is therefore more interesting to discuss the nitrogen-related metrics here (see table 5.11). First, it is evident from the N-Fe distances and N-H angle data that the data broadly falls under two categories: cases where N is in the atop configuration (N-Fe distance around 2 Å and N-H tilt angle around 5°) and cases where N is not in the atop configuration (N-Fe distances above 2.55 Å and N-H tilt angles of 20° or more). It seems if N cannot bind in a tetravalent arrangement with a single underlying Fe atom, the loss of aromaticity in the pyridinyl ring results in the ejection of N from the plane to form the familiar trigonal pyramidal shape associated with sp^3 hybridization of NH₃ for example, where a lone pair of electrons points up from N and away from the surface.

site	$d_{C-C}(\text{\AA})$	$d_{C-H}(\text{\AA})$	$\theta_{C-H}(^{\circ})$	$\theta_{C-C}(°)$	$d_{C-Fe}(\text{\AA})$
free quinolinium	1.40 (1.40)	1.09 (1.09)	0 (0)	121 (121)	-
HH-NA	1.45 (1.45)	1.10 (1.10)	25 (24)	119 (119)	2.13 (2.11)
LS-NA	1.45 (1.45)	1.10 (1.10)	23 (21)	120 (120)	2.12 (2.10)
LA-NA	1.46 (1.45)	1.09 (1.09)	27 (27)	120 (120)	2.12 (2.11)
SS2-NA	1.45 (1.45)	1.10 (1.10)	23 (20)	120 (119)	2.12 (2.11)
LS-NH	1.45 (1.45)	1.09 (1.10)	22 (24)	120 (120)	2.14 (2.12)
HH-NS	1.45 (1.45)	1.10 (1.10)	23 (23)	120 (120)	2.11 (2.09)
LC-NH	1.46 (1.46)	1.10 (1.10)	22 (22)	119 (119)	2.11 (2.10)

Table 5.10. Calculated optimised geometric parameters for C in quinolinium on $Fe{110}^a$

^{*a*} d_{C-C} represents the average C-C bond length in quinolinium, d_{C-H} the average C-H bond length, θ_{C-H} the average CH tilt angle (dihedral) with respect to the molecular plane, θ_{C-C} the average angle between carbon atoms in the molecule and d_{C-Fe} represents the average C-Fe distance. Data in brackets represents a vdW-TS corrected result.⁸⁴ All non-bracketed results were calculated using PBE. The free quinolinium results were extracted from geometry optimisation using a cubic 20 Å box to prevent quinolinium self-interactions.

site	$d_{N-C}(\text{\AA})$	$d_{N-H}(\text{\AA})$	$\theta_{N-H}(°)$	$\theta_{C-N-C}(°)$	$d_{N-Fe}(\text{\AA})$
free quinolinium	1.34, 1.38	1.03 (1.03)	0 (0)	121 (122)	-
	(1.34, 1.38)				
HH-NA	1.43, 1.45	1.03 (1.03)	20 (29)	120 (120)	2.03 (2.02)
	(1.43, 1.45)				
LS-NA	1.41, 1.45	1.03 (1.03)	19 (31)	121 (121)	2.03 (2.03)
	(1.41, 1.45)				
LA-NA	1.43, 1.45	1.03 (1.03)	33 (37)	120 (121)	2.00 (2.00)
	(1.44, 1.45)				
SS2-NA	1.42, 1.43	1.03 (1.03)	27 (37)	122 (122)	2.01 (2.13)
	(1.42, 1.46)				
LS-NH	1.40, 1.42	1.03 (1.03)	4 (6)	120 (119)	2.76 (2.88)
	(1.39, 1.42)				
HH-NS	1.39, 1.42	1.03 (1.03)	6 (7)	123 (124)	2.56 (2.52)
	(1.39, 1.43)				
LC-NH	1.40, 1.43	1.03 (1.03)	4 (4)	119 (119)	2.69 (2.65)
	(1.41, 1.43)				

Table 5.11. Calculated optimised geometric parameters for N in quinolinium on $Fe{110}^a$

^{*a*} d_{N-C} represents the average N-C bond length in quinolinium, d_{N-H} the N-H bond length, θ_{N-H} the NH tilt angle (dihedral) with respect to the molecular plane, θ_{C-N-C} the angle between C, N and C in the molecule and d_{N-Fe} represents the N-Fe distance. Data in brackets represents a vdW-TS corrected result.⁸⁴ All non-bracketed results were calculated using PBE. The free quinolinium results were extracted from geometry optimisation using a cubic 20 Å box to prevent quinolinium self-interactions.



Figure 5.13. Images of 0° and 120° rotated PBE-TS optimised quinolinium binding sites. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).



Figure 5.14. Images of 150° rotated PBE-TS optimised quinolinium binding sites. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).



Figure 5.15. Image of the 125° rotated, N-atop position PBE-TS optimised quinolinium binding site. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).

Vdw-corrected adsorption geometries and energies



Figure 5.16. Comparison of adsorption energies for all PBE (blue) and PBE-TS (red) optimised quinolinium/Fe{110} sites.

The energies and accompanying geometric data for vdW-corrected DFT optimisation of all stable quinolinium/Fe{110} sites are summarised in tables 5.9, 5.10 and 5.11. Figures 5.13, 5.14 and 5.15 show the PBE-TS optimised structures. All seven starting structures are stable after PBE-TS optimisation and showed minor geometric changes with respect to their respective starting configuration. As for the adsorption energies all adsorption sites show a strong increase in adsorption strength, on the order of around 3 eV. The increase is on the same order as for naphthalene/Fe{110}, a sensible finding given the similar dimensions of the two adsorbates. The PBE-preferred site (HH-NA) remains the best adsorption site using PBE-TS, with a 0.2 eV stronger adsorption energy than the second best site. The second and third best sites also remain in the same relative energetic ordering, however there are changes in the relative energetic ordering of the weaker sites. This is shown in figure 5.16
which provides a comparison of the adsorption energies for all PBE and PBE-TS optimised quinolinium/Fe{110} configurations. Comparisons of PBE-TS changes in relative energetic ordering observed here for quinolinium will be compared to those seen for benzene and naphthalene in section 5.4.

5.3.4 Charge density difference

Charge density difference analysis for quinolinium adsorbed on Fe{110} is not as straightforward as for neutral molecules. This is because these analyses rely on the difference between the charge density of adsorbed and isolated gas-phase components. Simply applying a +1charge to the gas-phase adsorbate in its adsorbed configuration is not representative of the charge density of the adsorbed ion, as it no longer carries the full +1 charge due to the transfer of charge with the surface. Additionally, the surface becomes charged in the adsorption process, and should therefore carry charge somewhere between 0 and -1. This is problematic, as applying a portion of charge to the clean Fe surface will result in it localising quite differently compared to a situation where an adsorbate is present. Specifically, the charge will distribute uniformly across the surface, whereas in the case of quinolinium adsorption, it would be rather localised in the upper layer beneath the adsorbate. Figure 5.17 shows the effect the charge applied to the adsorbate has upon the charge density difference plot. The neutral (0) and +1 charge cases are shown for comparison alongside the +0.26 charge case, where the charge is applied only to the isolated adsorbed configuration of quinolinium. The +0.26 charge value is extracted from Hirshfeld charge calculation, see section 5.3.6. The +0.26 configuration quite closely resembles the 0 charge configuration, which is sensible given that the +0.26 charge is closer to 0 than +1. The +1 charge density difference shows a notable overall increase in charge density on the adsorbate, namely extending out on to the H atoms and slightly beyond the molecule. There are arguments for use of either of the positively charged charge densities, but in order to better represent the actual charge on the adsorbed species, the +0.26 case will be used for further study throughout this section.

As with the naphthalene/Fe{110} charge density, the differential charge density distri-

bution can be compared to the MO diagram for quinolinium, which has been calculated and is shown in figure 5.18. Compared to the naphthalene MO diagram, it shares more resemblances than differences, but it is clear the N atom has an effect on the size and shape of the orbitals. Comparing the computed MOs to the +0.26 plot of charge density difference, the region of increased electron density (yellow) has a distinct resemblance to the LUMO, which is sensible given the increase in electronic density. As for the regions of decreased electron density (blue) which lie above the plane of the molecule, they are less pronounced but do resemble the HOMO most of all the MOs. These findings are in line with what would be expected, though it is interesting that for this adsorption configuration, it is less clear that orbitals aside from the HOMO and LUMO are contributing to stabilising the favoured adsorption geometry.



Figure 5.17. Comparison of charge density difference as a function of charge applied to gas phase adsorbate for the HH-NA adsorption site. Configurations are viewed from above the Fe{110} surface (above) and the side (below). Blue (yellow) regions denote a decrease (increase) in electron density on the order of 2×10^{-2} electrons/Å³. The position of the nitrogen atom is indicated (N).



Figure 5.18. Calculated molecular orbital diagram for quinolinium. The calculated energies and MOs were obtained using DFT (B3LYP/6-31G(d,p)) as implemented in Gaussian09.¹²⁵ The HOMO, LUMO and other MOs are indicated on the diagram. The position of nitrogen is indicated for all MOs.

5.3.5 Spin density

The spin densities for the strongest three quinolinium/Fe{110} adsorption sites, which all feature N in the atop position, are shown in figure 5.19. As is observed for naphthalene, the surface induces spin polarisation in quinolinium, which is not normally spin polarised in the gas-phase. Regions of minority spin can be seen following the C-C and C-N bonds, and in all cases the N-H group appears to be of minority spin. Beneath the adsorbate, regions of spin majority can be observed, and most of the H atoms associated with aromatic C atoms are of majority spin. There are insignificant differences between the spin density plots for the top three adsorbates, which is perhaps a further hint that the N plays a significant role in the adsorption mode of the molecule upon the surface, i.e. only the quinolinium MOs which favour N-Fe alignment participate in charge transfer at the surface.

5.3.6 Atomic charges and spin

Hirshfeld charges and spin for the preferred HH-NA quinolinium adsorption geometry on Fe{110} are presented in table 5.12.

Regarding charges, the same comment which has been made for benzene and naphthalene/Fe{110} must again be made; a higher k-point sampling $(4 \times 4 \times 1 \text{ MP mesh})$ has been employed for charge calculation, so the non-zero sum of charges (-0.07 e) is most likely due to rounding in the CASTEP-derived Hirshfeld charge output. The charges show an overall positive charge on the molecule, which results as a combination of negative charge on C and N atoms and larger positive charge on the H atoms. This behaviour is overall consistent with the picture provided by the charge density difference plot in section 5.3.4, which shows regions of increased charge density above C and N atoms, and regions of charge density decrease in the vicinity of H atoms. The slab carries a negative charge which is expected given the positive charge on the adsorbate. Similarly to benzene and naphthalene, the PBE and PBE-TS-derived Hirshfeld charges show only minor differences. A small negative charge (-0.03) appears on the quinolinium N atom. This is due to the stronger electronegativity of N compared to C, which draws electron density away from surrounding C atoms. This behaviour has been observed for other similar aromatic system



Figure 5.19. Images of top three PBE-TS optimised quinolinium binding site spin densities. View from above the Fe{110} surface. Blue (yellow) regions denote minority (majority) spin minority regions on the order of 3×10^{-3} electrons/Å³. The position of the nitrogen atom is indicated (N).

with N-heteroatoms.²³⁹

As for spin, the C and N atoms all are minority spin polarised, while the H atom grouping is only very slightly majority spin polarised $(0.01 \,\mu_{\beta})$. This is consistent with the spin density plot shown in 5.3.5. The very low majority spin contribution of the H atoms is consistent with that seen for naphthalene on Fe{110}. The slight difference between the metal slab sum for PBE and PBE-TS is also observed for quinolinium/Fe{110}, and relates to additional attractive interactions between Fe atoms which results in more strongly coordinated upper layers, and thereby reduced spin. Aside from this difference, PBE and PBE-TS spin show only minor differences.

Atom group	charges (e) PBE	charges (e) PBE-TS	spin (μ_{β}) PBE	spin (μ_{β}) PBE-TS
C ₉ NH ₈ ⁺ sum	0.26	0.25	-0.51	-0.50
C sum	-0.22	-0.23	-0.49	-0.48
H sum	0.51	0.51	0.01	0.01
Ν	-0.03	-0.03	-0.03	-0.03
Metal slab sum	-0.36	-0.32	221.88	220.30

Table 5.12. Calculated Hirshfeld charges and atomic spin results for HH-NA quinolinium site on Fe{110}

5.3.7 DOS and PDOS

The PDOS for the HH-NA quinolinium/Fe{110} adsorption site in figure 5.20 (C-Fe pair) and figure 5.21 (N-Fe pair). As with all other PDOS plots shown, the atom pairs are chosen because they feature surface and adsorbate atoms in very close contact, therefore having the highest probability of showing electronic structure changes. As with naphthalene/Fe{110} PDOS (section 5.2.7), the assignment of orbital identities to peaks in the C and N spectra is challenging, and shall feature in a future work.

Looking first to the C-Fe PDOS shown in figure 5.20, the usual shift of adsorbate orbital peaks to stronger binding energies can be seen, although the shifts are less significant than for naphthalene/Fe{110}. This is also reflected generally in the Fe PDOS, where a minor

shift towards stronger binding energies of minority spin states can be observed. This results in a reduction of the number of minority spin states at the Fermi level. The majority spin Fe PDOS remains relatively unchanged compared to the clean Fe{110} surface.

The N-Fe pair PDOS plot shown in figure 5.21 shows several of the same trends as the C-Fe PDOS. Namely, the shift of minority spin Fe states to higher binding energies resulting in fewer minority spin states at the Fermi level. The Fe PDOS shows new peaks at binding energies between -6 eV to -8 eV compared to the clean Fe{110} surface which arise from the N orbitals, as can be seen from the match between the two plots. As for the comparison of gas-phase N and adsorbed N, the peaks at low energies show relatively good a match from -10 eV to -8 eV, after which point they have shifted towards stronger binding energies or broadened due to their interaction with the Fe 3*d* states. The disappearance of adsorbed-N orbital PDOS peaks occurs slightly earlier than for the C-Fe pair.



Figure 5.20. Projected density of states (PDOS) for quinolinium on Fe{110} in the HH-NA adsorption geometry. The upper plot shows the majority spin and minority spin PDOS for Fe atom 91 before (black) and after adsorption (red). The lower plot shows C atom 4 within quinolinium in the gas-phase (black) and after adsorption (red, majority spin and minority spin shown). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase quinolinium DOS has been aligned with the lowest energy C(2s) peak for adsorbed quinolinium, as this level is not expected to be involved in the adsorption process.



Figure 5.21. Projected density of states (PDOS) for quinolinium on Fe{110} in the HH-NA adsorption geometry. The upper plot shows the majority spin and minority spin PDOS for Fe atom 90 before (black) and after adsorption (blue). The lower plot shows the N atom within quinolinium in the gas-phase (black) and after adsorption (blue, majority spin and minority spin shown). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase quinolinium DOS has been aligned with the lowest energy N(2s) peak for adsorbed quinolinium, as this level is not expected to be involved in the adsorption process.

5.3.8 Workfunction

The change in workfunction upon adsorption has been studied for the top PBE-TS optimised adsorption geometry, the HH-NA site. The results are listed in table 5.13. The methodology used to obtain these results is identical to that used to study benzene and naphthalene/Fe{110}, see chapter 4 for more details.

There is a difference of 0.02 eV between the PBE and PBE-TS quinolinium/Fe{110} ϕ and also $\Delta \phi$. This difference is similar to that found for benzene/Fe{110} and naph-thalene/Fe{110}. The workfunction for the adsorbate/metal slab system has been reduced by 1.82 eV (PBE-TS) compared to the pure metal surface. This result is also in line with other results in this thesis, however it appears the presence of the nitrogen reduced the workfunction more than the C and H containing naphthalene (-1.51 eV). The significance of these differences is considered and discussed in section 5.4.

Table 5.13. Calculated Workfunction (ϕ) results for quinolinium on Fe{110} (HH-NA site)^{*a*}

Method	$E_{vac}(eV)$	$E_F(eV)$	Fe{110}	C ₉ NH ₈ ⁺ /Fe{110}	$\Delta\phi$ (eV)
			ϕ (eV)	ϕ (eV)	
PBE	-3.38	-6.44	4.90	3.06	-1.84
PBE-TS	-3.38	-6.42	4.86	3.04	-1.82

^{*a*} E_{vac} represents the vacuum energy, E_F represents the Fermi energy and $\Delta \phi$ represents the difference between the C₉NH₈⁺/Fe{110} ϕ and bare Fe{110} ϕ .

5.4 Discussion and Conclusions

In this section, the results of sections 5.2 and 5.3 on naphthalene and quinolinium adsorption on the Fe $\{110\}$ surface are compared and discussed. It is useful to make comparisons between naphthalene, quinolinium and benzene adsorption on Fe $\{110\}$ given that benzene is a subunit in both naphthalene and quinolinium. The naphthalene and quinolinium comparisons are for this reason extended to the results of benzene/Fe $\{110\}$ calculations from chapter 4. Following this, the results of naphthalene adsorption on Fe{110} are compared to results for naphthalene adsorption on other flat transition metal surfaces. Conclusions follow this final discussion section.

5.4.1 Benzene, Naphthalene and Quinolinium on Fe{110}

Overall, the results show quinolinium adsorbs more strongly to the Fe{110} surface than naphthalene, with or without the inclusion of the TS correction. PBE (PBE-TS) results show a difference of 1.07 eV (1.03 eV) between the most strongly bound quinolinium and naphthalene adsorption sites. It is also interesting that the preferred adsorption geometry is equivalent using PBE (HH for naphthalene and HH-NA for quinolinium) while with PBE-TS, a shift in relative adsorption energetics results in naphthalene preferring to adopt the very high symmetry LC site while the HH-NA quinolinium geometry remains the preferred site for quinolinium. As discussed, there are also changes in relative energetics for quinolinium/Fe{110} adsorption geometries, but only among the less favourable adsorption geometries. The top quinolinium adsorption sites all share the common feature of N adsorbing in a tetravalent orientation above an Fe atom, which demonstrates that this is an important feature in providing strong adsorption of quinolinium on the surface. It also explains why PBE-TS does not impact the relative energetic ordering of top adsorption sites, as vdW interactions play a less important role than for naphthalene, where such interactions dominate. Clearly, vdW interactions still play an important role in the adsorption behaviour of quinolinium; indeed, this can be seen in the strong effect the TS correction has on all the quinolinium adsorption energies. It does, however, appear that these interactions do not play the dominant role in the determination of best adsorption geometries for quinolinium on Fe{110}. As for benzene/Fe{110}, the change in PBE-preferred (H-type sites) and PBE-TS-preferred (S- 0°) provides a similar picture to the change in preferred adsorption site for naphthalene/Fe{110}. As expected, PBE-TS adsorption energies for naphthalene (-5.68 eV) and quinolinium (-6.71 eV) are significantly stronger than for benzene (-3.45 eV). It is also of little surprise to see the naphthalene and quinolinium energies just under double that of benzene, as there are 40% more atoms (C and N) which participate in direct surface binding

interactions.

To better quantify the difference in adsorption energy offered by substitution of a C atom (in naphathalene) with a N atom (in quinolinium), additional calculations have been carried out (results shown in figure 5.22). In these calculations, the preferred quinolinium adsorption geometry (HH-NA) has had its N atom substituted by a C atom, and the energy of this new adsorbate/surface system has been evaluated (without relaxation). The approximation which is made in this case is that the quinolinium structure is identical to that of optimised naphthalene, which in reality is not the case (for example, the C-N bond lengths are different to C-C bond lengths, and also are slightly different on either side of the pyridinyl ring). If the structure were relaxed, the naphthalene configuration would likely convert to the HH site, which has slight structural differences to the HH-NA site geometry. The geometric and energetic differences between the HH-NA quinolinium geometry, HH-NAderived naphthalene geometry and the HH naphthalene geometry are shown in figure 5.22. The energy differences show that the N atom contributes just over 1 eV to the PBE-TS adsorption energy. There is a difference of 0.09 eV between the HH and HH-NA-type naphthalene adsorption sites, which confirms a slight difference in preferred adsorption geometry for naphthalene compared to quinolinium.



Figure 5.22. Side views of quinolinium HH-NA site, naphthalene in the identical HH-NA geometry and naphthalene in the optimised HH geometry. These are shown alongside the differences in adsorption energy (ΔE_{ads}) between the three adsorption geometries.

The charge density difference gives clues as to the MOs involved in the adsorption process. In comparing the charge density differences across the HH and HH-NA sites for naphthalene and quinolinium respectively, it is little surprise to see similar charge density plots. In observing figures 5.7 and 5.18 which show the MO diagram for naphthalene and quinolinium, N does have an effect on the energies and overall shape of the orbitals, but

there is still a strong similarity to the naphthalene MO diagram. Other notable differences between the MO diagrams lie in the HOMO-LUMO gap energies, where naphthalene ($\Delta E =$ 4.80 eV) has a larger gap than quinolinium ($\Delta E = 4.29$ eV). The smaller gap for quinolinium offers further insight as to why it has stronger adsorption energy compared to naphthalene; a smaller HOMO-LUMO gap is indicative of higher reactivity. In comparing the naphthalene-LC and quinolinium-HH-NA charge density difference plots, few comparisons can be drawn. The LC density distribution shape is quite dissimilar to any other shown in this chapter, demonstrating that a different set of orbitals are involved in stabilising the LC site. The same can be said of the spin density shown in figure 5.8. The PDOS analysis will be key to ascertaining the exact orbitals which hybridise with iron 3*d* orbitals to stabilise adsorption geometries; this assignment and analysis is planned for a future work.

Charges (e)	C ₆ H ₆ (H)	$C_{10}H_{8}$ (HH)	$C_9H_8N^+$ (HH-NA)
Charge on molecule	0.10	0.14	0.26
Charge on C	-0.23	-0.29	-0.22
Charge on H	0.33	0.43	0.51
Charge on N	-	-	-0.03
Charge on slab	-0.19	-0.22	-0.36

Table 5.14. PBE-TS Hirshfeld charges for benzene (H-0 $^{\circ}$ site), naphthalene (HH site) and quinolinium (HH-NA site) adsorption geometries on Fe{110}

Table 5.14 summarises the Hirshfeld charges of interest for the H-0° site of benzene/Fe{110}, HH site for naphthalene/Fe{110} and HH-NA site for quinolinium/Fe{110}. It is worth mentioning that HH is not the preferred PBE-TS geometry for naphthalene on Fe{110}, but in order to compare the charges on structurally similar benzene and quinolinium adsorption geometries, it was selected over the preferred LC geometry for this analysis. Table 5.14 shows that across all adsorbate/surface systems, the adsorbate carries an overall positive charge while the metal slab carries a negative charge. In all cases, the carbon atoms carry negative charge while H atoms carry positive charge. This is in line with charge density difference plots for naphthalene and quinolinium (figure 5.6) showing electron density increase on C atoms and decrease on H atoms. As for the charge on the slab, it is negative.

Table 5.15. PBE-TS calculated workfunction (ϕ) results for best sites of benzene, naphthalene and quinolinium adsorption on Fe{110}^{*a*}

Adsorbate/Fe{110}	ϕ (eV)	$\Delta \phi$ (eV)
Benzene	3.70	-1.16
Naphthalene	3.35	-1.51
Quinolinium	3.04	-1.82

^{*a*} ϕ represents the adsorbate/Fe{110} workfunction and $\Delta \phi$ represents the difference between the adsorbate/Fe{110} ϕ and bare Fe{110} ϕ (4.86 eV).

for all adsorbates, and counters the positive charge which appears on the molecule. Across the three adsorbates and metal slabs, in general the magnitude of charge increases from benzene to naphthalene and finally is largest for quinolinium.

Workfunction values for quinolinium, naphthalene and benzene adsorbed on Fe{110} are compared in table 5.15. As with the trend in adsorption energies, the strongest workfunction change is observed for quinolinium, followed by naphthalene and benzene. Again, the N atom in quinolinium has a significant effect in further reducing the workfunction (on the order of -0.31 eV) compared to naphthalene.

5.4.2 Naphthalene and heteroatomics on other surfaces

DFT studies of naphthalene adsorption on metal surfaces are surprisingly uncommon; as of writing this, there are the studies of Morin *et al.*¹⁷³ on Pt{111}, Santarossa *et al.*²⁰⁹ on Pt{111}, Pd{111} and Rh{111} and that of Maurer *et al.*⁷⁵ on Ag{111}, Cu{111} and Pt{111} using PBE+vdW^{surf}. The three studies are conducted on flat fcc metal surfaces, and the two first studies neglect to use vdW-corrected DFT. As mentioned in chapter 4, limited comparisons can be made between the flat fcc{111} and bcc{110} because the coordination number (CN) of atoms at either surface is different (surface fcc atom CN = 9, surface bcc atom CN = 6). The work of Santarossa *et al.*²⁰⁹ mentions that the influence of vdW occurs between the adsorbate and metal surface. Based on the results in this thesis, it is true that many properties are not substantially affected by the application of the TS correction (the geometry of adsorption, charge and spin density distributions and the workfunction for example), but the application of PBE-TS has a non-negligible effect on the relative stability of naphthalene adsorption sites. Specifically, the use of PBE-TS stabilises the highly symmetric naphthalene LC site such that it is favoured over the PBE-preferred adsorption site, HH. There is the possibility that the use of PBE-TS overly stabilises the LC site compared to other vdW correction schemes given its tendency for overbinding, but even the more sophisticated optB88-vdW functional used by Hensley *et al.*⁹⁶ to study benzene/Fe{110} shows changes in relative energetic ordering of benzene adsorption sites. The conclusion which should be drawn from this evidence is that the influence of vdW-corrected DFT cannot be ignored to provide an accurate representation of the behaviour of naphthalene adsorbed on metal surfaces. Disregarding the effect of vdW-corrected DFT, the works on naphthalene adsorption on more reactive fcc metal surfaces (i.e. Pt, Pd and Rh) show preferential adsorption at di-bridge sites, where both benzyl rings are centered on bridge sites.^{173,209} The emphasis on reactive fcc metals should not be understated, as the work of Maurer et al.⁷⁵ shows adsorption on flat coinage metal surfaces to occur with benzyl rings centered above hollow sites. The findings for reactive fcc metal surfaces are in line with results for benzene adsorption on the same fcc surfaces, which shows preferential adsorption centered on the bridge site. According to the same logic, it makes sense to see naphthalene/Fe{110} in the HH site using PBE given that the H-0° and H-30° benzene/Fe $\{110\}$ are preferred using PBE. Upon application of the TS correction, in both cases bridge-centered sites are preferred; the S-0° for benzene and the new LC site for naphthalene.

In closer relation to the motivation for the work in this thesis, it is relevant to compare our results to those of similar corrosion inhibitor fragments on iron surfaces. DFT calculations have been carried out on a series of cyclic molecules containing N (pyrrole), O (furan) and S (thiophene) atoms on Fe{110} by Guo *et al.*²⁰¹ Across the three adsorbates studied, all prefer to adsorb in flat-lying adsorption geometries on the Fe{110} surface and also tend to donate electron density to the surface to an extent which correlates with observed experimental

inhibition efficiency trends (O < N < S). This also is in line with the finding from this thesis, which is that an aromatic adsorbate without heteroatoms donates less electron density (+0.16 e) to the surface than a heteroatom-containing version (+0.24 e). As the authors of the paper make use of Hirshfeld charges to describe charge transfer, those can also be directly compared to data from this thesis. The charges they derive (furan: 0.09e, pyrrole: 0.15e, thiophene: 0.17e) demonstrate they are all of lower electron donating ability than quinolinium.

There is also the work of Kumar *et al.*⁷¹ which studies the adsorption behaviour of henna extract, including lawsone (2-hydroxy-1,4-naphtoquinone) which has the best inhibition efficiency of all henna extract molecules and bears some resemblance to both naphthalene and quinolinium. Aside from the fact that they study adsorption on the Fe{100} facet as opposed to the flat Fe{110} surface studied in this work, certain interesting comparisons can be made. First, compared to the other two molecules studied (gallic acid and α -D-glucose), the preferred adsorption geometry for lawsone is much more flat-lying and has a far stronger adsorption energy upon the $Fe\{100\}$ surface. Gallic acid in particular is of a similar planarity to lawsone and contains almost the same number of atoms, albeit two more oxygen atoms and lesser aromaticity (substituted benzene ring). A comparison of the results of Kumar et al. and from this thesis demonstrate that in addition to heteroatom substitution, the choice of aromatic inhibitor scaffold is also an important element found within excellent corrosion inhibitors. In particular, naphthalene-type scaffolds tend to result in improved corrosion inhibition compared to benzene-type scaffold. This is supported by the results of Schmitt and Bedbur²²⁸, where the application of compounds containing naphthalene scaffolds exhibited far lower steel corrosion rates compared to molecules containing one or even multiple benzene groups instead.

Conclusion

In this chapter, the adsorption behaviour of naphthalene $(C_{10}H_8)$ and quinolinium $(C_9H_8N^+)$ on the flat Fe{110} surface are studied using DFT. The results reveal significant differences between the adsorption mode of these two molecules, particularly when vdW-corrections

are applied to the calculations. First, the PBE adsorption energy for naphthalene in the preferred HH site ($E_{ads} = -2.66$ eV) is weaker than that for quinolinium in its preferred site which is analogous to HH (called HH-NA) ($E_{ads} = -3.73$ eV). This is also true of the PBE-TS case, where the preferred naphthalene adsorption site (LC) ($E_{ads} = -5.68$ eV) is still significantly weaker than the preferred quinolinium adsorption site HH-NA ($E_{ads} = -6.71 \text{ eV}$). In both cases, there are changes in relative energetic ordering of the adsorption sites; in the case of quinolinium, this is mainly for the less favourable sites while for naphthalene, a less favourable PBE-optimised site becomes the most stable adsorption geometry using PBE-TS. In all preferred quinolinium adsorption sites, the N atom is found in an atop site on the surface; prior DFT work on NH₃ adsorption on Fe{211} supports this finding, as it enables nitrogen to adopt a favourable tetravalent arrangement.²³⁸ The PBE-TS preferred naphthalene site LC exhibits high symmetry at the surface, and the charge density difference suggests the naphthalene MOs involved in adsorption are unlike those seen for any of the other naphthalene/Fe{110} adsorption sites. Quinolinium adsorption is found to decrease the Fe{110} workfunction ($\Delta \phi = -1.82$ eV) to a greater extent than naphthalene ($\Delta \phi$ = -1.51 eV), again demonstrating the strong effect the N heteroatom has upon the metal surface. Parallels can readily be drawn to the benzene/Fe{110} system studied in using DFT in this thesis as well as in prior published work,⁹⁶ including similar adsorption geometries both with and without the application of the TS vdW correction.

Chapter 6

NMQ+: Gas-phase and Adsorbed on Fe{110}

6.1 Introduction

A highly effective ACI, offering protection to a wide range of steel surfaces under the acidic conditions and elevated temperatures present in oilfields, is Naphthylmethyl Quinolinium Chloride (NMQCI).²²⁸ The adsorption mechanism of cationic NMQ+ is not known, although it is suspected to be driven by electrostatic forces and chemisorption.

In this introduction, the NMQCl and NMQ+ species are introduced alongside research on their known effectiveness as ACI (section 6.1.1). Some of the research on ACI presented in this chapter has already been presented in chapter 5, but particularly relevant works are highlighted again here in section 6.1.2, with an emphasis on molecules similar to the gas phase NMQ+ species.

In section 6.2, the results of the molecular DFT study of the gas-phase and solvated NMQ+ cation are presented. This includes conformational study of the ion, a closer look at its gas-phase properties as well as the impact of solvation effects. In section 6.3, the adsorption behaviour of the NMQ+ ion on the Fe{110} surface is presented. All results are discussed in section 6.4 and compared to the Fe{110} adsorption results for benzene, naphthalene and quinolinium presented in chapters 4 and 5.

6.1.1 NMQCl and NMQ+ as ACI

Figure 6.1 shows the structure of NMQCl. NMQCl has the formula $C_{20}H_{16}NCl$ and the ionic form of the molecule has the formula $C_{20}H_{16}N^+$. The ion carries a charge of +1. It contains a naphthyl moiety and quinolinium moiety which are linked through the quinolinium N atom and one of the naphthalene C atoms by a methyl C. A reported synthesis of NMQCl requires dissolution of quinoline and 1-chloromethyl-naphthalene in isopropyl alcohol, where the mixture is allowed to reflux at 95°C for 6 hours.²⁴⁰ A search of the NMQCl structure within the literature reveals it features exclusively within corrosion inhibition papers, with a large portion of these publications comprising patents on novel acid corrosion inhibitor package formulations in the oil and gas industry.^{19,34,40,41,228,240–242}



Figure 6.1. Naphthylmethyl quinolinium chloride (NMQCl) chemical structure

The earliest published work on the effectiveness of NMQCl in corrosion inhibition comes from Schmitt and Bedbur²²⁸, who studied the anti-corrosion properties of eleven quaternary ammonium compounds in a 10% HCl solution on high purity iron and mild steel surfaces. The work shows NMQCl to produce the lowest corrosion rate among all eleven compounds investigated by an order of magnitude. This finding is indicative of the special anti-corrosive properties of NMQCl, as certain other compounds investigated in the work of Schmitt and Bedbur have very similar structure. Within the work, improved inhibition

efficiency is found to be correlated with increasing number of aromatic cycles in the inhibitor molecule. Patents published a few years later detail the ACI package in use by Schlumberger Ltd. which features the NMQCl molecule, alongside salts which further improve corrosion inhibition at oilfield conditions.^{19,241} A more recent paper also provides further evidence of good corrosion resistance upon application of NMQCl to steel surfaces.²⁴⁰ Other papers demonstrate that certain molecules which bear structural resemblances to NMQCl also have corrosion resistance on steel, other metal surfaces and immersed in other solvents, such as benzyl quinolinium chloride on nickel immersed in HClO₄ for example.^{228,229,243}

A study of the interaction of NMQCl with a Duplex Stainless Steel (DSS) surface has recently been published.³⁴ DSS surfaces have a heterogeneous microstructure composed of ferritic (Fe with bcc crystal structure) and austenitic (Fe with fcc crystal structure) steel phases. They include a slew of alloying elements including Cr, Ni, Mo, Mn and N. These elements tend not to distribute equally between the austenite and ferrite phases. As DSS materials present a combination of favourable ferritic and austenitic steel characteristics, they have found extensive application in the production of oil and gas. During acid-mediated active corrosion of DSS materials, differences in the elemental composition of the austenite and ferrite phases promote galvanic corrosion, resulting in significant differences between the dissolution rate of the two phases.^{34,244,245} A highly effective ACIP for DSS under these acidic conditions as well as at the elevated temperatures present in oilfields contains NMQCl.^{34,228} Scanning Electron Microscopy (SEM)-Energy Dispersive X-Ray (EDX) results shown in the paper of Ho *et al.*³⁴ demonstrate a marked preference by NMQCl for the ferritic phase. The reason for this selectivity is not well understood.

In solution, NMQCl dissociates to form cationic NMQ+ ions alongside the chloride counter-ions. Adsorption of the cationic ACI NMQ+ has been suggested to be driven by electrostatic forces (via ionic interaction with the charged metal surface or higher concentration of ions in the vicinity) and chemisorption (via interaction of the naphthyl group with the metal surface).^{40,41} Although a chemically intuitive proposal, little evidence has been provided to directly support this mechanism. Investigations of any kind to validate adsorption mechanisms are complicated by a number of considerations. This includes (but

is not limited to) the poorly understood nature of the steel surface under varied and often intense oil well conditions, the presence of a multitude of other compounds in the acidising fluid, some of which are known to enhance the corrosion inhibition of ACI molecules, and the coupling of results determined at the various time and length scales which determine corrosion inhibitory action. See chapter 1 for further general discussion of the mode of action of corrosion inhibitors.

A wide variety of surface structures can be found on steels found within oil wells.²⁵ As discussed in chapter 1, the corrosion process itself may significantly modify the surface through dissolution of the protective oxide layer, redeposition of solubilised oxide layer components (including Cr and Mo found in stainless steels) as well as redeposition of corrosion byproducts, the nature of which depend on the corrosion environment.⁷² Redeposition aside, steels such as DSS present different microstructural islands at the surface, which also can differ significantly from the bulk alloy due to segregation of certain alloying elements to the surface. In order to validate our models and to study the effect of ACI on the major component of steels i.e. iron, we have opted to simulate adsorbates on a pure bcc Fe surface. For reasons outlined above, this is a relatively common approach in the periodic DFT corrosion inhibitor literature to date. We plan to work on different surface structures in the future, see chapter 7 for more detailed information on such research directions.

6.1.2 Related works

Gas Phase NMQ+

Cinchona alkaloids are a class of molecules which occur in the bark of *Cinchona* genus trees. This class of molecules has been of interest given their application as anti-malarial drugs, but in more recent times have been intensely studied for their application within heterogeneous and homogeneous enantioselective organocatalysis. One of the more heavily studied cinchona alkaloids which bears a structural resemblance to NMQ+ is Cinchonidine (CD). CD (chemical formula: $C_{19}H_{22}N_2O$, see figure 6.2) enhances the rate of enantionselective hydrogenation of α -ketoesters (Orito reaction) by 1-2 orders of magnitude. It is formed of two different moieties, namely the heteroatomic aromatic quinoline ring as well as the

quinuclidine ring. The two groups are connected by a methanol group. The consensus view in terms of the role CD plays in asymmetric synthesis is that CD orients the reactant molecule (an activated ketone) in a special way on a platinum surface which favours one of two enantiopure alcohols.^{5,246} The CD structure is highly reminiscent of the NMQ+ scaffold, although CD is charge neutral, which could result in some significant differences in reactivity.



Figure 6.2. Cinchonidine (CD, $C_{19}H_{22}N_2O$) molecule with different moieties indicated. The torsional angles τ_1 and τ_2 are also shown, which are used to describe the results of conformational search. Figure adapted with permission from Ref. 5 (A. Baiker, *Chem. Soc. Rev.*, 2015, **44**, 7449) - Published by The Royal Society of Chemistry.

Given the important role CD plays in enantioselectivity, there have been a number of experimental and quantum chemical studies to determine the preferred gas-phase geometry of the CD molecule, see the review of Baiker⁵ as well the more computationally-focussed review of Tanriver *et al.*²⁴⁷ In particular, the flexible methanol linker allows for a rich conformational space, where the quinuclidine and quinoline ring systems can be positioned in various favourable orientations with respect to each other. Typically, these orientations are described by torsional angles τ_1 and τ_2 (see figure 6.2) but can also depend on other factors, such as the orientation of the methanol linker for example. The study of Dijkstra

*et al.*²⁴⁸ reports the first X-ray structure of a cinchona alkaloid alongside combined NMR and molecular mechanics level calculations to probe a number of different molecules' conformational space. They identify four low-energy conformers for each molecule studied, which differ in energy by up to around 5 kcal/mol (0.22 eV). As for cinchonidine specifically, a combined 2D NMR-DFT study by Urakawa *et al.* reveals eleven low-energy structures which differ at most by around 7 kcal/mol (0.30 eV).²⁴⁹ The later DFT conformational study of Kristyan²⁵⁰ should also be noted, as it additionally studies the interaction of various CD conformations with the reactant, methyl pyruvate. Cinchona alkaloid conformers are categorised either by being closed or open, which refers to the positioning of the quinuclidine nitrogen; if it is oriented toward the aromatic quinoline rings then it is considered to be a closed conformer, and if it is pointing away from the quinoline then it is considered to be an open structure.²⁵¹ Other studies show that the preferred conformations are impacted by a number of factors including solvent, solutes, temperature, self-interactions, protonation as well as the surface in cases of adsorption.^{5,249,250,252} All these considerations support the complexity of the conformational landscape of cinchona alkaloids.

Adsorbed NMQ+

There are a few experimental studies of the corrosion inhibition behaviour of NMQCl. ^{34,228,240} There is, however, a large number of experimental corrosion inhibition studies which employ structurally similar molecules to NMQ+ as ACI. The study of Abboud *et al.* ²⁵³ of 5naphthylazo-8-hydroxyquinoline in contact with 1M HCl-immersed mild steel via weight loss, potentiodynamic polarisation, FT-IR, XRD and UV-VIS spectroscopy provides a representative example. As these studies include the effects of solvent (including acid), corrosion product redeposition as well as limited characterisation of surface structure at the atomisitic level, only limited comparisons can be made between the results from this thesis and such literature. It is more useful to compare the results from this thesis to those from more closely related and/or simplified studies.

One of the closest research papers in terms of motivation and research methods to the study of NMQ+/Fe{110} presented in this chapter can be found in the recent publication

of Guo *et al.*⁷⁷, where the anticorrosive properties of three chalcone derivatives (aromatic ketones found in biological systems) are studied on the Fe{110} surface using DFTB. The DFTB approach enables high-quality computational study of much larger corrosion inhibitor systems with relative ease, particularly when compared with DFT. An interesting periodic DFT study conducted by Özcan *et al.*²⁵⁴ studies the adsorption of 2-((3-Methylpyridine-2-imino)methyl)phenol (MPIMP) on Fe{110}, however it should be noted this study is carried out without the influence of potentially important vdW corrections.²⁵⁴ The results of these studies are presented and compared to those from this thesis in section 6.4. DFT aside, as discussed in chapters 1 and 5 there are a number of computational studies of acid corrosion inhibition which make use of force field-based MD or MC simulation. As mentioned, these studies typically lack any description of charge or spin transfer which can be critical to correctly describe the adsorption process. As a result, only limited or qualitative comparisons should be made to such studies. A recent review⁷⁹ provides a comprehensive collection of such studies.



Figure 6.3. Coverage-dependant adsorption modes of cinchonidine on Pt{111} surface. Coverage increases from left to right. Figure used with permission from Ref. 5 (A. Baiker, *Chem. Soc. Rev.*, 2015, **44**, 7449) - Published by The Royal Society of Chemistry.

Outside the corrosion inhibition research area, the CD molecule which bears structural similarity to NMQ+ has been scrutinised with respect to its adsorption behaviour on platinum surfaces, including use of DFT studies. The most relevant experiments, calculations and their results for the CD/Pt system are listed in the following paragraph.

Experimental work by Ferri and Bürgi using Attenuated Total Reflectance - Infrared

(ATR-IR) shows that the interaction of cinchonidine in CH₂Cl₂ solutions with the Pt surface is dependant on surface coverage (see figure 6.3 for a schematic depiction of the different adsorption modes).²³¹ In their work, shifts in the CD IR signals show direct interaction of CD with the metallic surface. At low coverages of CD, the molecule prefers to maximise its vdW interaction with the surface by binding through the π electrons of the quinoline ring. At moderate coverages, the H atom bound to the C atom next to the nitrogen atom (α -H) is abstracted from the molecule, which allows both the α carbon on quinoline and nitrogen to bind directly to the Pt surface. Finally, at the highest coverages, the CD packs more tightly by foregoing binding the α carbon atom to the surface and binds instead solely through nitrogen, giving way to a more upright adsorption geometry of quinoline with respect to the surface. This is in contrast to the moderate coverage (α -H abstracted CD), in which quinoline is notably tilted with respect to the surface. In all cases, the quinuclidine group does not interact with the surface, which is why quinoline is said to act as the anchoring group in the literature. These results are supported by computational work by Vargas and Baiker, where the adsorption behaviour of CD on Pt{111} is studied using DFT calculations.²³⁰ There have been many other computational works on this and related systems, to study ion and molecule co-adsorption, ^{255–257} dynamic effects, ²⁵⁸ bimetallic surfaces ²⁵⁹ and different chiral modifier molecules^{260–262} in addition to the studies on the conformational behaviour of the isolated molecule in the gas phase.^{248–250} A number of reviews, some of which cover chiral adsorption and catalysis more generally, provide a more thorough overview of progress in this field. 6,246,263

6.2 Gas-Phase NMQ+

In this first section of results, the behaviour of isolated NMQ+ in the gas phase is studied using computational methods. A conformational search for the NMQ+ molecule is first conducted in order to identify the most energetically favourable conformers, see section 6.2.1. As discussed in section 6.1.2, studies of the similar CD system reveal a relatively complex conformational landscape with multiple local energy minima, which supports the

need for conformational search studies of NMQ+.

The conformational search is followed by geometry optimisation using a higher level of theory. These results are also described in section 6.2.1, and further results derived specifically for the lowest energy conformers, namely an overview of the MO diagram, atomic charges and behaviour in aqueous solution are covered in sections 6.2.2, 6.2.3 and 6.2.4 respectively.

The findings from this section serve to guide the DFT study of adsorption of NMQ+ on the Fe{110} surface, which is presented in section 6.3. The understanding of the gas-phase behaviour of isolated NMQ+ also serves as a starting point for future work on the behaviour of solvated NMQ+.

6.2.1 Conformational search



Figure 6.4. The NMQ+ ion with the two torsional angles τ_1 and τ_2 which are scanned in the conformational search.

The conformational search of NMQ+ is performed similarly to work described in prior publications^{248–250} on gas-phase conformational search on the CD molecule, where the change in energy is computed as a function of varying two torsional angles which we refer to as τ_1 (centered on the quinolinium group) and τ_2 (centered on the naphthyl group). The

torsional angles τ_1 and τ_2 on NMQ+ are represented in figure 6.4.

The scan is performed at the semi-empirical level, specifically using the PM6 method within the Gaussian 09 program.^{125,129} The torsional angles τ_1 and τ_2 are varied by 15 degree increments which produces 625 NMQ+ conformers which all undergo PM6-level constrained geometry optimisation, i.e. geometry optimisation whilst keeping the τ_1 and τ_2 torsional angles fixed. Using a semi-empirical method allows for a relatively inexpensive scan with a good level of accuracy, and scan regions of interest can be further refined through subsequent unconstrained geometry optimisation using a more accurate level of theory.



Figure 6.5. Plot of energy differences (ΔE , in eV) resulting from conformational study of NMQ+. Results are shown for 625 NMQ+ conformers, produced by incremental 15 degree rotation of torsional angles τ_1 and τ_2 , which are geometry-optimised at the PM6 level. The letters A-C and A'-C' shown on the plot indicate regions of lowest energy which are studied throughout this section. D and D' are indicated for use further in this section. A DFT-optimised NMQ+ configuration is used as the starting point for the scan, where $\tau_1 = 75^\circ$ and $\tau_2 = -157^\circ$.

The conformational scan results are shown in figure 6.5. Dark blue regions indicate the lowest energy conformers while the orange and red regions indicate highest energy conformers. The scan reveals several regions of minimum energy, some of which are of relatively similar energy. There are four different regions of minimal energy: The region including the letters A and B (1), a region of similar shape and size including letters A' and B' (2), the region denoted C (3) and the region denoted C' (4). As for the region of overall lowest energy, there are two such points: points B and B' on figure 6.5. The highest energy red areas are indicative of NMQ+ conformers where the naphthyl and quinolinium portions of the molecule are in unfavourably close contact due to the constrained torsional angles τ_1 and τ_2 . This confirms what is chemically intuitive, which is that the most favourable conformations of NMQ+ appear when the napthyl and quinolinium groups are in a staggered conformation.

The low-energy region which includes A' and B' and that including C ' can be seen to connect by a shallow barrier. Because the plot wraps three dimensionally, regions including A, B and C are connected in a similar way. A higher energy barrier splits regions A, B and A', B' of minimal energy, however there are lower energy pathways connecting these regions, which feature conformations on the order of 0.4 eV higher in energy. The scan overall presents a high level of symmetry, an unsurprising finding given that the molecule itself presents relatively high symmetry.

The low-energy conformers A-C and A'-C', along with their PM6 computed energies, are illustrated in the top of figure 6.6. The labels shown in figure 6.6 correspond to the labels as shown in the conformational search (figure 6.5). The lowest energy conformers of all are conformers B ($\tau_1 = 165^\circ$ and $\tau_2 = -98^\circ$) and B' ($\tau_1 = 135^\circ$ and $\tau_2 = 98^\circ$). Conformers A and A' are very close in energy to B and B', with less than 0.01 eV separating them. C and C' are within 0.05 eV of the lowest energy conformers, which indicates that these could be easily accessed at room temperature (given that $k_BT = 0.26$ eV at 298K).

The semi-empirical PM6 analysis provides a useful starting point for analysis, but to better understand the energy landscape of NMQ+, the conformations require unconstrained relaxation, i.e. All degrees of freedom (including the τ_1 and τ_2 torsional angles) should



Figure 6.6. Low-energy NMQ+ conformers (A-C and A'-C') identified by a PM6 coordinate scan as well as the resulting DFT-optimised structures. Energies are shown in reference to the lowest energy structure for PM6 and DFT-optimised cases, respectively. The PM6 structures correspond to the labelled regions on figure 6.5.

be allowed to relax to their preferred orientation. Full DFT-level geometry optimisation is performed on the low-energy structures A-C and A'-C' and the resulting optimised geometries and energies are presented in the lower portion of figure 6.6. DFT optimisation is carried out using the B3LYP functional and 6-31G(d, p) basis set.

The DFT-level optimisation results in structural changes compared to the PM6-level constrained optimisation conformers. As a result, the energy differences between different conformers change and three minima emerge; the lowest-energy B and A' structures ($\Delta E = 0$), the moderately low energy C structure ($\Delta E = +0.10$) and finally the highest energy A, B' and C' structures ($\Delta E = +0.17$). A selection of PM6-derived conformers aside from those shown in figure 6.6 have also been geometry optimised using DFT and all converted to one of these three structures.

The differences between the three DFT-optimised conformers are illustrated in figure 6.7. Looking first at the lowest energy conformer (hereafter referred to as "B-type"), it can be further separated into two categories, distinguished by the sign of the τ_2 angle (80° or -80°). These structures are mirror-image rotamers: this is illustrated in figure 6.7. This finding has important implications, for example for adsorption on chiral surfaces. As for the C-type conformer, no mirror-image rotamer is identified through the PM6-search, and it features τ_1 (75°) and τ_2 (-157°) angles which are nearly "swapped" compared to the B-type conformer $(\tau_1 = 177° \text{ and } \tau_2 = -80°)$.

In studying the highest energy conformers, i.e. DFT-optimised C', A and B', the τ_1 and τ_2 angles they adopt are quite different to their starting values. According to the adopted angles ($\tau_1 = -62$ or 62 and $\tau_2 = -63$ or 63), this corresponds to the regions labelled D and D' in figure 6.5. The PM6 scan correctly identifies this conformer as being less favourable, on the order of +0.2 eV higher in energy than the B-type conformer, which compares well with the +0.17 eV difference identified with DFT optimisation. D and D' conformers are also mirror-image rotamers, which are again distinguished by the sign of the τ_1 and τ_2 dihedral angles.

For the rest of the section as well as for the study of adsorption behaviour upon Fe{110}, the B-type and C-type conformers only are studied. Although interesting, the D-type con-



Figure 6.7. Three distinct conformers identified from full DFT relaxation of PM6-level conformer scan. All conformers shown with the naphthyl group perpendicular to the plane of the page. The relationship between mirror-image B-type and D-type rotamers is shown. Energy differences shown are in eV.

former is significantly higher in energy ($\Delta E = +0.17 \text{ eV}$) as it features a more "closed" structure compared to the other two conformer types. A full study of the potential energy landscape, including the study of high energy conformers, transition states as well as the D-type conformer is planned for future work; see chapter 7.

6.2.2 MO diagram

To better understand the differences between the B and C-type conformers, the molecular orbitals of these two optimised conformers are studied. Figure 6.8 shows the five highest occupied and five lowest unoccupied orbital representations alongside their energetics for conformers B and C. Despite the structural and energetic differences between B and C, these conformers show the same HOMO and LUMO spatial separation onto naphthyl and quinolinium moeities, respectively. The DFT-optimised HOMO and LUMO energies are, however, quite different; the HOMO-LUMO gap for the B-type structure (2.70 eV) is 0.36 eV larger than for the less favourable C structure (2.34 eV). This results due to the B-HOMO energy being lower and B-LUMO energy being higher than the C-HOMO and C-LUMO energies respectively. Again, pre-empting the study of the NMQ+/Fe{110} system, this could have important implications for the preferred NMQ+ conformer when adsorbed on the surface. As for orbitals above and below the LUMO and HOMO respectively, there are some differences between B and C; namely, certain C MOs (LUMO+2, LUMO+3) show more spreading of orbital density across the entire molecule compared to B and the structure of C HOMO-2 and HOMO-3 switch compared to the ordering B HOMO-2 and HOMO-3. The switch is not overly surprising given that HOMO-2 and HOMO-3 are very close in energy. Otherwise, trends are largely the same for conformers B and C.

Common to both conformers is the localisation of HOMO-1 and LUMO+1 on the same portions of the molecule as the HOMO and LUMO respectively, while the HOMO-2 and LUMO+2 localise on opposite portions of the molecule to the previous two MOs. The HOMO-3 MO (and LUMO+2 and LUMO+3 MOs for conformer C) shows the most spreading of its MO density across the entire molecule, whereas most other MOs localise more on one of the two main portions of the molecule. In some cases, the MO extends from one portion



Figure 6.8. Calculated molecular orbital diagram for B (left) and C (right) type NMQ+ conformers. The calculated energies and MOs were obtained using DFT (B3LYP/6-31G(d,p)). The HOMO, LUMO and other MOs are indicated on the diagram. The same view of each MO is shown, where the quinolinium portion (Q) is on the left side of the structure and naphthyl (N) on the right. The HOMO-LUMO gap energy (ΔE) is indicated.

of the molecule onto the methyl linker atoms, for example the LUMO.

6.2.3 Atomic charges



Figure 6.9. Gas-phase NMQ+ molecule with accompanying calculated B conformer Mulliken charges. Charges on carbon atoms are indicated in grey, charge on nitrogen atoms are indicated in blue, and charges on hydrogen atoms are indicated in black.

The computed Mulliken charges on the B3LYP-optimised NMQ+ B conformer are shown alongside the NMQ+ structure with accompanying labels in figure 6.9. In the calculation, a +1 charge is applied to the entire molecule. The Mulliken charges demonstrate that the N atom carries negative charge (-0.54 e) while two of the three surrounding C atoms each carry a positive charge. This is because nitrogen is more electronegative than the surrounding C atoms. This is in line with the results found for Mulliken charge distribution near N on quinolinium as shown in figure 6.10 as well as with results from other work on other N-heterocycles.²³⁹

In comparing the NMQ+ charge distribution to that of quinolinium (see figure 6.10), the



Figure 6.10. Quinolinium (top) and naphthalene (bottom-right) molecules with computed Mulliken charges. Charges on carbon atoms are indicated in grey, charge on nitrogen atoms are indicated in blue, and charges on hydrogen atoms are indicated in black.

H atom connected to N also carries a positive charge (+0.32 e) which is greater than all other H atoms. However, the methyl-C in the same position in NMQ+ carries a negative charge (-0.13 e). There are several reasons why this behaviour is observed. Firstly, the methyl-C is not a part of the aromatic cycle, and therefore charge may be less readily withdrawn from it by N. Second, C is more electronegative than H, and therefore has a stronger tendency to retain its charge compared to H in an equivalent position. Third, the C atom on the naphthyl group which connect with the methyl-C has less negative charge (-0.03 e) than all other negatively charged C atoms within the naphthyl linker. This demonstrates that the methyl-C is more electron withdrawing than the naphthyl-C, which likely is due to its proximity to the highly electron withdrawing N atom. Finally, the charge on C in methane using 6-31G(d,p) has been calculated to be -0.47 e, which is significantly more negative than the methyl-C value within NMQ+.²⁶⁴ As for the charges on NMQ+-naphthyl, they compare very well with
the charges on isolated naphthalene (see figure 6.10), and show the greatest differences nearer to the methyl linker.

6.2.4 Solvation

The solvation energy of both B and C conformers has been calculated using the polarisable continuum model (PCM) within the Solvent Cavity Reaction Field (SCRF) method implemented in Gaussian 09.^{125,128} The result is shown in table 6.1 below. Interestingly, the energetic separation of conformers B and C is reduced from 0.10 eV to 0.03 eV, meaning that once in aqueous solution the conformers are much closer in energy. This is also an indicator more generally that a high energy conformer in the gas phase won't necessarily be the preferred conformer in solution and/or at the metal surface, which is what has been observed previously for the similar CD system in solution and on the platinum surface.^{230,249} It is important to note here that the SCRF approach simply studies the B or C-type structures within a polarisable medium without allowing for any structural changes to the molecule (see chapter 2 for more detailed information about the SCRF methodology). It is expected that the structure could change significantly under aqueous conditions, as well as for explicit water molecules to react with NMQ+. Further solvation studies of the NMQ+ ion, including interaction of NMQ+ with explicit molecules, form part of planned future work; see chapter 7 for further details.

Calculation Method	Energy of B (eV)	Energy of C (eV)
B3LYP/6-31G(d,p)	0.00	+0.10
B3LYP/6-31G(d,p) + PCM	0.00	+0.03

Table 6.1. Relative energies (given with respect to B) of B and C-type structures as a function of PCM implicit solvation.

6.3 NMQ+/Fe{110}

In this section, the results of DFT study of the adsorption of NMQ+ on the Fe{110} surface are presented. The topic is introduced in section 6.3.1 with a particular emphasis on the models used to guide the selection of starting configurations for adsorption on the Fe{110} surface. The optimised adsorption configurations for NMQ+ on Fe{110} and accompanying analyses are presented from section 6.3.2 onwards.

6.3.1 Introduction

A number of different hypotheses for the preferred interaction mode of NMQ+ with a metal surface have evolved over the course of this research project based on existing surface science and corrosion science literature. The following section presents the arguments which support and challenge certain proposed adsorption models. The models selected for study help ascertain the simulation parameters, which are presented and discussed later in this section.

NMQ+/Fe{110} Adsorption: Models

There are a number of ways in which NMQ+ can plausibly interact with a metal surface. In order to simplify studies of this model system, the steel surfaces of industrial relevance will throughout this work be approximated with bcc iron. Steels are principally composed of iron, and ferritic steels in particular have bcc-like structure. Alloying elements which provide steels with their favourable properties will almost certainly have an impact on the steel's surface structure and therefore adsorption behaviour. As there have been few studies of aromatic adsorption on iron more generally, it is sensible to build upon the adsorption studies in chapter 5 presented on the flat, most energetically stable Fe{110} surface. Future work is planned for other steel-like, roughened and/or defective surfaces. Chapter 7 provides more detailed overview of such research directions.

Figure 6.11 shows three proposed adsorption modes for NMQ+ on an iron surface. Within all three models, chloride counter-anions play some role in the adsorption process



Figure 6.11. Three possible adsorption models for the interaction of NMQ+ with Fe{110}.

(note: other anions may be substituted, chloride is mentioned specifically because (1) steel acid corrosion found in gas and oil wells often takes place in concentrated HCl solutions and (2) it is the counter-ion found within the NMQCl ACI). The study of Morales-Gil et al. ²⁶⁵ shows that, for a carbon steel substrate immersed in 1M HCl, the oxide/hydroxide film found on the polished sample dissolves and is replaced by an iron chloride salt film. The absence of a metal oxide or hydroxide layer in the models shown in figure 6.11 is deliberate; the Pourbaix diagram (a plot of electrochemical potential against pH for a given material, see chapter 1) indicates iron is likeliest to be found in the Fe^0 , Fe^{2+} or Fe^{3+} states at the pH values characteristic of the strongly acidising environments employed in oil wells. The precise oxidation state is dependant on the applied voltage potential, which is dependant on the alloy used, chemical species in the vicinity of the electrochemical cell and the extent of galvanic corrosion among other factors.²⁶ Further X-ray Photoelectron Spectroscopy (XPS) experiments by Morales-Gil et al.²⁶⁵ reveal that in the presence of a sufficient concentration of a known ACI molecule (2-mercaptobenzimidazole), the chloride salt film dissolves and the inhibitor takes its place, binding directly to the steel surface. The inhibitor used in the work of Morales-Gil et al. differs from NMQ+ in that it is a N and S-containing heteroaromatic inhibitor while NMQ+ has only the N heteroatom in the quinolinium group. Despite these differences, the results of Morales-Gil et al. provide convincing evidence that under acidising conditions and with a high enough concentration of ACI included, ACI can interact directly with the metal surface. As for the CD/Pt system, which has already been discussed in section 6.1.2 due to its resemblance to the NMQ+/Fe system, ATR-IR spectroscopy experiments show that it directly interacts with the Pt surface, and it is generally accepted that enantiodifferentiation occurs thanks to the direct modifier-platinum interaction.^{5,231}

Model 3 presents a situation where NMQ+ interacts through its quinolinium group with the chloride salt layer formed on top of the metal surface. Although such a situation is likely to exist at some stage, the evidence presented above points toward direct adsorbatemetal binding being especially important in corrosion inhibition. From the perspective of computational feasibility, Model 3 presents a more demanding problem, as it first requires evaluation of the optimal model for the iron chloride surface. Some DFT work does exist in this area, specifically on the Fe{100} surface^{266,267} as well as the Fe{110} surface which also includes the effect of the electrode potential.¹⁹² For the two reasons cited, only Models 1 and 2 will be investigated by way of DFT studies in this thesis. The merits and evidence which supports the existence of these two models is presented in the following text.

Model 1 features adsorption of NMQ+ through direct interaction of the naphthyl group with the iron surface. Given the strong interaction of naphthalene and quinolinium with the Fe{110} surface (chapter 5), it is tempting to put forward a model which features both naphthyl and quinolinium groups on NMQ+ interacting with the surface directly. Based on the conformational search presented in section 6.2, all favoured conformers of NMQ+ feature staggered naphthyl and quinolinium groups, so it is improbable for both naphthyl and quinolinium to interact with the iron surface in their respective preferred configurations. Within Model 1, the charged quinolinium group is stabilised through interaction with nearby chloride anions in solution. There has been general support for this mechanism in the literature, though little evidence has been provided to support it.^{40,41} Some recent experimental evidence which supports Model 1 is provided in the work of Ho *et al.*,³⁴ which studies the corrosion protection of a DSS surface by NMQ+. DSS presents ferritic (bcc-type) and austenitic (fcc-type) islands due to the segregation of elements added to the steel to one of two phases. The adsorption of NMQ+, which was monitored via the carbon concentration in SEM-EDX, was observed to appear selectively on the lower potential ferrite phase. In other

terms, NMQ+ selectively adsorbs on the anodic regions of the employed DSS. Because the quinolinium portion of the NMQ+ molecule carries a significant amount of positive charge, adsorption to the bare metal surface could preferentially proceed through direct interaction of the naphthyl group with the metal surface. The publication of Ho *et al.* also notes that because the ferrite dissolves more rapidly than the austenitic phase even with NMQ+ present, there is the possibility that higher local surface area promotes preferential adsorption of NMQ+. Furthermore, the highest carbon concentrations are observed in crevices and grain boundaries separating bcc and fcc phases. These findings weaken arguments made for this first model, as they imply that NMQ+ is drawn to the ferritic phases of DSS because it presents a larger number of under-coordinated, reactive sites compared to the austenitic phases.

As for Model 2, it presents an opposite proposal to the Model 1; instead of interacting with the metal surface through its naphthyl group, NMQ+ adsorbs to the metal surface via the quinolinium moiety. Initial support for this model is provided by the results presented in chapter 5, which identify the most stable quinolinium adsorption site on Fe{110} as having stronger adsorption energy than the most stable naphthalene site on the Fe{110} surface. The interaction of quinolinium with the metal surface would also be favoured in the presence of co-adsorbed chloride anions. The adsorption of anionic Cl⁻ on the metal surface generates localised regions of charge depletion (i.e. image charges) in the metal surface. This would produce a neutralising area of charge density increase in the metal, which could favour the adsorption of NMQ+ via its positively charged quinolinium group. These changes in charge density are illustrated in figure 6.11 Finally, Model 2 is supported by quinolinium and smaller quinolinium-derivatives presenting corrosion inhibitory action on their own (although of reduced effectiveness compared to NMQ+).²⁴¹ In spite of these supporting arguments, the second model fails to explain why NMQ+ is more strongly attracted to positively-charged regions of DSS as shown in the work of Ho *et al.*³⁴ Additionally, although solvation is not explicitly being considered in these models, theoretical results from the literature reveal that the solvation energy of quinolinium is over an order of magnitude larger (-2.34 \pm 0.13 eV) than for naphthalene (-0.105 eV).^{268,269} This is not an unexpected

finding given that quinolinium is ionic while naphthalene is not. Although quinolinium may adsorb more strongly on the iron surface, the strong solvation energy of quinolinium translates into a higher energy cost to displace its surrounding solvation shell so it may interact directly with the metal surface.

In the next sections, adsorption configurations which place either naphthalene or quinolinium in an anchoring position on the surface are studied using DFT. This is done in order to study proposed Models 1 and 2. Calculations will be guided by the results of our studies of naphthalene and quinolinium adsorption on the Fe{110} surface (chapter 5) as well as work done on the conformational stability of NMQ+ in the gas phase (see section 6.2). It is important to stress that the adsorption studies presented in the following sections do not include the effect of water, acid, electrochemical potential or any additional ionic species upon the preferred adsorption geometries of NMQ+ on the Fe{110} surface. The combination of all these factors is likely to contribute significantly to the real preferred adsorption mode. The results presented from section 6.3.2 onwards represent an effort towards studying the isolated ACI-metal interactions. The results of this work can be coupled with all the other components involved in this complex system in the future, for example using a multiphysics modelling framework.²⁵ A more detailed discussion of these considerations is provided in chapter 7.

Simulation details and parameters

The simulation parameters used in the study of NMQ+ adsorption on the Fe{110} surface are included in table 6.2. To accommodate the large size of the NMQ+ adsorbate and prevent intermolecular interactions, it is necessary to make use of larger cell dimensions than have been used so far throughout this thesis. The minimal cell dimensions which can be used are (5×5) , which results in 150 Fe atoms being used to represent the metal slab. The total system is composed of 187 atoms including the C, N and H atoms of NMQ+. Due to the large size of the system (note also the increased vacuum spacing of 18 Å to prevent unphysical interactions of the NMQ+ molecule with the bulk Fe layers), initial geometry optimisation is carried out using only the Γ point. Once sufficient convergence is achieved

at this level, geometry optimisation is carried out at a 2 × 2 × 1 MP mesh until convergence is achieved. This k-point sampling provides density comparable to an 10 × 10 × 10 k-point mesh sampling of the conventional bcc cell, which produces distances converged to better than 0.002 Å, energies slightly lower than 0.01 eV and spin around 0.03 μ_{β} .

Table 6.2. Simulation details and parametersspecific to the NMQ+/Fe{110} calculations

Parameter	Value
Vacuum spacing (Å)	18
Cell size $(c \times c)$	(5 × 5)
Number of slab layers	6
Number of fixed slab layers	3
MP K-point sampling	$2 \times 2 \times 1$

6.3.2 Adsorption geometries and energies

Figure 6.12 shows the six NMQ+/Fe{110} configurations chosen for DFT optimisation. Three configurations are based on the DFT-optimised lowest energy gas-phase NMQ+ B conformer and a further three configurations are based on the second low-energy gas-phase NMQ+ conformer C. The structural differences between these two conformers is shown in the upper section of figure 6.12. Further discussion of these differences can be found in section 6.2 where conformational search is carried out. Given the relatively small energetic separation between low-energy NMQ+ conformers B and C (0.10 eV), it is sensible to study the adsorption behaviour of both conformers on the Fe{110} surface. This is further justified given findings from previous works on a similar system (CD/Pt{111}) which demonstrate that conformers which are of lesser stability in the gas phase can be stabilised on the surface.²³⁰

For each NMQ+ conformer, three unique adsorption sites are studied. For each of the conformers B and C, two adsorption configurations are based on having the naphthyl group lying flat on the surface while the other features the quinolinium acting as the anchor for NMQ+ to the Fe{110} surface. A single flat-lying quinolinium configuration (HH-NA, see



Figure 6.12. Six starting configurations for NMQ+ binding sites on the Fe{110} surface. The corresponding anchoring NMQ+ group and its adsorption site is shown on the left. The two NMQ+ conformers (B and C) used in the adsorption studies are shown at the top.

chapter 5) per conformer is sufficient given that the PBE and PBE-TS methods both identify it as the strongly favoured adsorption site on Fe{110}. As for the naphthyl group, the favoured PBE and PBE-TS-optimised naphthalene/Fe{110} adsorption geometries are not the same. PBE identifies the HH site as being preferred while PBE-TS identifies the LC site as being most favourable. In either case, the energetic separation between HH and LC sites is not large (around 0.05 eV). It is therefore prudent to study NMQ+ adsorption configurations in which the naphthyl group serves to anchor the molecule to the surface in different ways, i.e. HH and LC naphthalene adsorption sites.

The naming scheme used throughout this chapter to describe the six different adsorption sites accounts for the factors mentioned above and is included within figure 6.12. The first character, which is either B or C, distinguishes the NMQ+ conformer selected for adsorption. The second character, either Q or N, depicts how the NMQ+ adsorption site is anchored to the iron surface, i.e. through the quinolinium (Q) or naphthyl (N) moiety respectively. The final portion of the adsorption site name depicts the adsorption site of the anchoring moiety. There are two possibilities here as well: either HH (a 3-fold-hollow-3-fold-hollow arrangement of either naphthyl or quinolinium) or LC (the long bridge-centred site for naphthyl which is preferred when the TS correction is applied).

Figures 6.13 and 6.14 provide visual representations of the geometry optimised B and C conformers on Fe{110}, respectively. Energetic data, including adsoption energies and distortion energies, are provided in table 6.3. Geometric data is provided in tables 6.4, 6.5, 6.6 and 6.7, which are organised as such to easily compare with prior results for naphthalene and quinolinium adsorption on Fe{110}. Data unique to the NMQ+ system, mainly regarding the methyl linker and torsional angles, is included in table 6.7.

In terms of the calculation of adsorption energies, it is first worth noting that as with quinolinium/Fe{110}, the entire NMQ+/Fe{110} system is treated as being neutral. This is a valid simplification, as for the purposes of the intended application the iron slab is earthed, and as a result charge can flow to and from the slab without explicitly including a charge in the calculation. The energy of gas-phase NMQ+ is necessary for the adsorption energy calculations and must carry the +1 charge. This is problematic because (1) the



Figure 6.13. Images of B conformer NMQ+ binding sites. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).



Figure 6.14. Images of C conformer NMQ+ binding sites. Views shown above the Fe{110} surface (a) to the side (b) as well as an alternate side view (c).

energy converges impractically slowly with increasing cell size and (2) adjustments must be made to the usual calculation method of adsorption energy to balance the charges for adsorbed and gas-phase components. These issues and their solutions are identical to those faced for quinolinium/Fe{110}, so are described in more detail in chapter 5. In essence, the solution to (1) lies in making use of the intercept value as the gas-phase energy when 1/L =0, while (2) is resolved by incorporating the bare Fe{110} surface workfunction value in the adsorption energy calculation.

NMQ+ Adsorption site $E_{ads}(eV)$ E_{dist} (eV) C-N-HH -9.85 C-N-LC -8.73 B-Q-HH -7.23 3.24 C-Q-HH -7.03 2.80**B-N-HH** -7.00 2.06 **B-N-LC** -6.85 2.13

Table 6.3. Calculated optimised energies for NMQ+ adsorption sites on $Fe{110}^a$

^{*a*} E_{ads} represents the adsorption energy and E_{dist} represents the distortion energy upon adsorption. All data calculated using PBE-TS.⁸⁴ Distortion energies are calculated with respect to the most favourable gas-phase NMQ+ conformer, B.

In studying the adsorption energies in table 6.3, it is obvious there are some important differences between the C-N sites, which feature anchoring of the C conformer through the naphthyl group, and the B-N, C-Q and B-Q sites. The C-N-HH site in particular is very strongly favoured, with an adsorption energy more than 1 eV stronger than the second best site, C-N-LC. This is impressive given that even C-N-LC is strongly favoured compared to the other four adsorption sites, on the order of 1.38 eV stronger than the strongest of the other sites ($E_{ads} = -7.23$ eV for B-Q-HH). Figure 6.14 reveals the reason for these high energy differences: both C-N-HH and C-N-LC show dissociation of two hydrogen atoms, which allow for the direct interaction of the quinolinium group with the iron surface. To clarify, the hydrogen atoms dissociate from NMQ+ spontaneously in the geometry optimisation

process; this is not imposed nor is the system biased for this process to take place in any way. Another point of interest is that the hydrogen atoms which dissociate are not the same for C-N-HH and C-N-LC. On C-N-HH, the two hydrogen atoms dissociate from the quinolinium group, which allows two quinolinium C atoms to interact directly with the iron surface, each positioned in 3-fold-hollow sites, with the C-C bond centred on the long bridge between iron atoms. On C-N-LC however, one dissociated H atom derives from the analogous C atoms associated with the quinolinium group, but the other dissociated H atom is originally associated with the methyl linker which connects the quinolinium and naphthyl groups. As a result, the C-N-LC site shows interaction of its methyl-C and one quinolinium-C with the iron surface. The quinolinium group shows a very similar orientation with respect to the metal surface, with the quinolinium-C bound to the surface positioned in a 3-fold-hollow site. The methyl-C is positioned in an atop position, which is unlike the C-N-HH configuration, where the methyl-C favours a short bridge site, though this is likely influenced by the positioning of the quinolinium C atoms binding directly to the metal surface. The adsorption energies of more weakly bound conformations (all with E_{ads} around -7 eV) are only slightly higher than the adsorption energies for the strongest PBE-TS naphthalene/Fe{110} site (-5.68 eV) and quinolinium/Fe{110} site (-6.71 eV) (values taken from chapter 5). This slight increase is sensible given that the additional methyl group, which is quite close to the metal surface in all configurations, has some favourable interaction with the surface. This trend does also reveal what is represented in figures 6.13 and 6.14, which is that conformations which fail to orient the group which does not interact in a flat-lying geometry with the surface instead places them up and away from the metal surface as much as possible. This is evidenced in the longer C-Fe distances in tables 6.4 (for B-Q-HH and C-Q-HH) and 6.5 (for B-N-HH and B-N-LC).

As for the distortion energies, they reveal significant deformation occurs at the surface compared to the gas-phase conformer. This is corroborated by the τ_1 and τ_2 dihedral angles listed in table 6.7, which show conformations with a range of τ_1 and τ_2 values. This is not a result of the difference between B and C conformers, as certain angles differ significantly from either B or C dihedral angles. These findings confirm the assertion that

site	$d_{C-C}(\text{\AA})$	$d_{C-H}(\text{\AA})$	$\theta_{C-H}(^{\circ})$	$\theta_{C-C}(°)$	$d_{C-Fe}(\text{\AA})$
free NMQ+-naphthyl	1.40	1.09	0	121	-
C-N-HH	1.45	1.10	21	120	2.12
C-N-LC	1.45	1.10	24	120	2.13
B-Q-HH	1.41	1.10	0	121	4.05
C-Q-HH	1.40	1.09	0	121	4.88
B-N-HH	1.45	1.10	22	120	2.10
B-N-LC	1.46	1.10	20	120	2.11

Table 6.4. Calculated optimised geometric parameters for naphthyl group on NMQ+ adsorbed on the Fe $\{110\}$ surface^{*a*}

^{*a*} d_{C-C} represents the average C-C bond length in the naphthyl portion of NMQ+, d_{C-H} the average C-H bond length, θ_{C-H} the average CH tilt angle (dihedral) with respect to the molecular plane, θ_{C-C} the average angle between carbon atoms in the molecule and d_{C-Fe} represents the average C-Fe distance. All data calculated using PBE-TS. The free NMQ+ results were extracted from a PBE-TS geometry optimisation of the NMQ+ B conformer using a cubic 40 Å box to prevent NMQ+ self-interactions.

surface adsorption can stabilise conformers which are of lesser stability in the gas phase.

There are a number of unexpected results in this section, but the most surprising of all is the identity of the most favourable adsorption geometry (C-N-HH) as well as the spontaneous dissociative adsorption mode. The C-N-HH adsorption site changes very little from its starting geometry aside from the dissociation of hydrogen atoms. It is the most stable adsorption site despite featuring the worst of the two naphthalene/Fe{110} adsorption sites (HH), the worst of the two anchoring groups (naphthalene) in terms of adsorption strength *as well as* the higher energy conformer (C). Based on those considerations alone, it might be reasonable to guess that C-N-HH would be the worst of all adsorption geometries tested, however geometry optimisation reveals it allows for a particularly favourable orientation of the non-flat-lying quinolinium group, which can then bind directly to the iron surface through loss of two H atoms. In order to better understand this adsorption configuration, the charge density difference, spin density, atomic charge and spin values, workfunction and PDOS are studied exclusively for the preferred C-N-HH adsorption site throughout the following sections (6.3.3 to 6.3.7).

site	$d_{C-C}(\text{\AA})$	$d_{C-H}(\text{\AA})$	$\theta_{C-H}(°)$	$\theta_{C-C}(°)$	$d_{C-Fe}(\text{\AA})$
free NMQ-quinolinium	1.40	1.09	0	120	-
C-N-HH	1.41	1.51	0	121	4.16
C-N-LC	1.40	1.36	0	121	4.39
B-Q-HH	1.45	1.10	22	119	2.12
C-Q-HH	1.45	1.10	24	119	2.14
B-N-HH	1.40	1.09	0	121	4.88
B-N-LC	1.40	1.09	0	121	5.16

Table 6.5. Calculated optimised geometric parameters for carbon in the quinolinium portion of NMQ+ on Fe $\{110\}^a$

^{*a*} d_{C-C} represents the average C-C bond length in the quinolinium portion of NMQ+, d_{C-H} the average C-H bond length, θ_{C-H} the average CH tilt angle (dihedral) with respect to the molecular plane, θ_{C-C} the average angle between carbon atoms in the molecule and d_{C-Fe} represents the average C-Fe distance. All data calculated using PBE-TS. The free NMQ+ results were extracted from a PBE-TS geometry optimisation of the NMQ+ B conformer using a cubic 40 Å box to prevent NMQ+ self-interactions.

site	$d_{N-C}(\text{\AA})$	$\theta_{C-N-C}(^{\circ})$	$d_{N-Fe}(\text{\AA})$
free NMQ-quinolinium	1.39, 1.34	121	-
C-N-HH	1.39, 1.40	121	2.86
C-N-LC	1.40, 1.40	119	2.67
B-Q-HH	1.45, 1.46	119	2.00
C-Q-HH	1.44, 1.44	120	2.06
B-N-HH	1.40, 1.36	121	3.89
B-N-LC	1.40, 1.36	121	3.95

Table 6.6. Calculated optimised geometric parameters for nitrogen in the quinolinium portion of NMQ+ on Fe $\{110\}^a$

^{*a*} d_{N-C} represents the average N-C bond length in NMQ+, d_{N-H} the N-H bond length, θ_{N-H} the NH tilt angle (dihedral) with respect to the molecular plane, θ_{C-N-C} the angle between C, N and C in the molecule and d_{N-Fe} represents the N-Fe distance. All data calculated using PBE-TS. The free NMQ+ results were extracted from a PBE-TS geometry optimisation of the NMQ+ B conformer using a cubic 40 Å box to prevent NMQ+ self-interactions.

16(110)						
site	$d_{C-C}(\text{\AA})$	$d_{C-N}(\text{\AA})$	$\theta_{C-C-N}(^{\circ})$	$d_{C-H}(\text{\AA})$	$\tau_1(^\circ)$	$\tau_2(^\circ)$
free NMQ-methyl (B)	1.49	1.51	115	1.10	80	176
free NMQ-methyl (C)	1.52	1.49	114	1.09	157	75
C-N-HH	1.52	1.46	115	1.10	175	109
C-N-LC	1.49	1.46	116	1.85	155	71
В-О-НН	1.49	1.50	116	1.10	93	177

1.47

1.49

1.47

122

120

119

1.11

1.12

1.12

73

168

180

161

57

80

1.50

1.50

1.50

Table 6.7. Calculated optimised geometric parameters for the methyl linker in NMQ+ on $Fe{110}^a$

^{*a*} d_{C-C} represents the C-C bond length in the NMQ+ methyl linker, d_{C-N} the C-N bond length, θ_{C-C-N} the angle between C, C and N in the molecule, and d_{C-H} represents the average C-H bond length on the methyl group. τ_1 and τ_2 indicate the optimised torsional angles within NMQ+, and are used identically to the conformer search in section 6.2.1. All data calculated using PBE-TS. The free NMQ+ B and C results are extracted from a PBE-TS geometry optimisation of the NMQ+ B and C conformers using a cubic 40 Å box to prevent NMQ+ self-interactions.

6.3.3 Charge density difference

C-Q-HH

B-N-HH

B-N-LC

Charge density difference plots for the C-N-HH site are shown in figure 6.15. Charge density is shown for two different contour isovalues, i.e. scales at which charge transfer is shown. This is because the isovalue used throughout this thesis (2×10^{-2} electrons/Å³) fails to show any change in the electron density on the NMQ+ quinolinium group. This is of special relevance for the following section 6.3.4 on spin density.

As was done for the charge density difference for quinolinium on the Fe{110} surface (see chapter 5), the charge on the geometry-optimised configuration of the adsorbate (+0.07 e) is used in the charge density difference calculations. The plots show regions of charge increase surrounding both dissociated hydrogen atoms. There are also some regions showing charge density decrease above and surrounding these regions of increased density. This supports the fact that H is binding directly to surface Fe atoms which as a result modifies the surrounding surface charge density. As for the NMQ+ scaffold, it is helpful to separate it into its different components and analyse them separately. First, the naphthyl moeity charge density can



Figure 6.15. Comparison of charge density difference as a function of contour isovalue (values shown on figure). Charge applied to gas-phase NMQ+ is +0.07 e, the Hirshfeld-derived charge identified on adsorbed C-N-HH. Configurations are viewed from above the Fe{110} surface (top) alternate rotated view from above (middle) and from the side (below). Blue (yellow) regions denote a decrease (increase) in electron density on the order shown on the figure.

be independantly studied. Given that it interacts with the surface very similarly to the naphthalene HH site on Fe{110}, it is unsurprising that the charge density difference should distribute in quite a similar way, with charge density increasing upon the carbon atoms and decreasing around the hydrogen atoms. The pattern shown, which as discussed previously indicates the naphthalene MO which is involved in adsorption at the metal surface, is also very similar to that seen for HH-naphthalene/Fe{110}. As for the NMQ+ quinolinium group, it is clear that the portion of the quinolinium which points away from the surface experiences far less variation in its charge density than the portion which interacts directly with the surface. Even at the alternative 3 \times 10⁻³ electrons/Å³ scale shown, the charge density is minimally changed, particularly when compared to the anchoring naphthyl group. The carbon atoms which bind directly to the metal surface show the greatest differences in their charge density compared to the isolated gas-phase NMQ+; they show increase in electron density with an accompanying decrease in electron density in the area just above the surface upon quinolinium, with some of that electron density decrease found on the N atom. The region of decreased electron density on N is sandwiched by regions of electron density increase on either side of quinolinium. Finally, the methyl linker which connects the naphthyl and quinolinium portions shows effectively no change in its charge density compared to the gas phase at the 2 $\,\times\,10^{-2}$ electrons/Å 3 scale. At the 3 $\,\times\,10^{-3}$ electrons/Å 3 scale, the hydrogen which points away from the surface shows an increase in electron density, while the other methyl component densities are obscured by changes in the metal surface charge density distribution.

6.3.4 Spin density

The contour of spin density at the level of 3×10^{-3} electrons/Å³ is shown for the preferred C-N-HH adsorption site in figure 6.16. The naphthyl portion, which adsorbs flat on the metal surface, displays spin distribution similar to what has been seen previously for naphthalene/Fe{110}, where the hydrogen atoms show majority spin polarisation, while the regions above the carbon atoms are minority spin polarised. The methyl linking the naphthyl and quinolinium show the opposite trend; the linking carbon atom is of majority spin while the hydrogen atoms are of minority spin. The quinolinium portion shows unusual behaviour compared to what has been seen so far. Given its unique adsorption configuration on the surface as well as the loss of 2 H atoms, different behaviour is somewhat expected. The two carbon atoms which bind directly to the iron surface are surrounded by regions of minority spin, but are separated by a region which is majority spin polarised centered between the two carbon atoms. Most of the hydrogen atoms on the quinolinium group show minimal spin polarisation at the given scale, but the distribution of spin on the rest of the molecule is strongly reminiscent of the HOMO-4 orbital for quinolinium (see chapter 5). The nitrogen is polarised to be of minority spin. As for the hydrogen atoms which have dissociated from the quinolinium group, they are of minority spin, and appear to have only a limited effect on the surrounding spin density.



Figure 6.16. Images of the top C-N-HH PBE-TS optimised NMQ+ binding site spin density. Views are from above the Fe{110} surface (top) as well as to the side (bottom). Blue (yellow) regions denote minority (majority) spin regions on the order of 3×10^{-3} electrons/Å³.

In order to better understand the unusual spin polarisation observed on the portion of quinolinium which points away from the metal surface, the charge density difference on the same portion was studied more carefully. The plot shown in figure 6.15 at the 3×10^{-3} electrons/Å³ scale shows poorly defined, minimal changes in the electron density on quinolinium far away from the surface. Therefore, the well-defined spin polarisation on quinolinium is not associated with a significant transfer of electronic density to the quinolinium atoms. The spin polarisation may therefore be a result of the direct bonding pairs of carbon and iron. Finally, reducing the spin density isovalue scale (in the same way as is done for charge density difference) does not reduce the intensity of spin-polarisation on quinolinium any more than on the methyl or naphthyl groups, showing that the acquired spin is on the same order as that observed on the rest of the adsorbed molecule.

6.3.5 Atomic charges and spin

The Hirshfeld charges and atom-resolved spin have been evaluated and grouped by relevant portion within table 6.8 for the C-N-HH NMQ+/Fe{110} adsorption site. In studying the Hirshfeld charges, whether or not the two dissociated hydrogen atoms are included as part of the adsorbate, the adsorbate overall carries a positive charge while the iron surface carries a negative charge. This is in agreement with what has been seen for previous aromatic adsorbates studied in chapters 4 and 5. Including the two dissociated hydrogen atoms on the surface, the adsorbate charge is of +0.07 e while if they are removed from the sum of adsorbate charge of -0.06 e (for a total of -0.12 e). This is in contrast to the charges found on on aromatic-H and methyl-H atoms, which all carry positive charges. All carbon atoms carry a negative charge and the nitrogen atom carries a slight positive charge, which is in agreement with the results of the charge density difference analysis shown in figure 6.15.

The naphthyl moiety has very similar behaviour with respect to charge to the HHnaphthalene/Fe{110}, which is also supported by the charge density difference result. As for the quinolinium portion, unlike any aromatic adsorbate so far, it shows an overall negative

Atom group	charges (e)	spin (μ_{β})
NMQ+		
C sum	-0.55	-0.60
H sum	0.60	-0.12
Dissociated 2H	-0.12	-0.13
Ν	0.02	-0.02
NMQ+ -2H	0.19	-0.61
Full sum (NMQ+ +2H)	0.07	-0.74
Naphthyl		
C sum	-0.30	-0.54
H sum	0.37	0.03
Full sum	0.07	-0.51
Quinolinium		
C sum	-0.24	-0.07
2 C bound to surface sum	-0.10	-0.24
H sum	0.14	-0.14
Dissociated 2H	-0.12	-0.13
Ν	0.02	-0.02
Full sum	-0.08	-0.23
Methyl linker		
С	-0.01	0.01
H sum	0.09	-0.01
Full sum	0.08	0.00
Metal slab		
sum	-0.28	351.23

Table 6.8. Calculated Hirshfeld charges and atomic spinresults for C-N-HH NMQ+ site on Fe{110}

charge (-0.08 e). This is a result of a significant negative charge associated with the C atoms (-0.24 e). Just under half of this negative charge is contributed solely by the two C atoms binding directly to the iron surface, which together contribute -0.10 e. This is consistent with the regions of increased electron density around the C atoms closest to the iron surface. The overall negative charge on the quinolinium portion (-0.08 e) is exactly balanced by the overall positive charge on the methyl linker (+0.08 e), which results from positive charge on the H atoms and a slight negative charge on the C atom. As a final note regarding charges, NMQ+/Fe{110} Hirshfeld charge is calculated using a finer k-point mesh $(4 \times 4 \times 1)$ than for geometry optimisation, and the non-zero sum of charges (-0.21 e) is

likely due to rounding in the CASTEP-derived Hirshfeld output, particularly for metal atoms. This is the largest system studied throughout this thesis, so it is plausible that the error for NMQ+/Fe{110} should also be the largest.

In terms of spin, the overall polarisation of NMQ+ is of minority spin (-0.74 μ_{β}) even if the dissociated hydrogen atoms are excluded (-0.61 μ_{β}). This is unsurprising given that most atom groups are of minority spin, except the H atoms included in the naphthyl group (0.03 μ_{β}) as well as the C atom in the methyl linker (0.01 μ_{β}). This is consistent with the picture provided by the spin density in section 6.3.4. The spin density plot reveals there are additional regions of spin majority on several of the C atoms on the quinolinium portion of NMQ+, but it is evident from the sum of spin on quinolinium C atoms (-0.07 μ_{β}) that these are of lesser magnitude than the minority spin contributed by the two C atoms bound directly to the iron surface (-0.24 μ_{β}). The methyl linker shows overall no spin polarisation, as it is balanced by spin polarisation of equal value on the C and H atoms. The overall spin polarisation of the NMQ+ scaffold is mainly contributed by the naphthyl linker, on the order of 84%.

6.3.6 DOS and PDOS

The PDOS for a C-Fe pair within the optimised C-N-HH NMQ+/Fe{110} site is shown in figure 6.17. Specifically, the C-Fe pair chosen is where dehydrogenation behaviour occurs, i.e. one of the quinolinium-C atoms which loses its hydrogen and binds directly to an iron surface atom.

Because NMQ+ has lost two hydrogen atoms in the preferred C-N-HH adsorbed configuration, the adsorbed state C orbitals are expected to show differences compared to the isolated gas-phase NMQ+ PDOS. This is indeed the case, as there is no obvious relationship between the isolated and adsorbed C5 peaks shown in figure 6.17. As with naphthalene and quinolinium, future work will aim to correlate the isolated NMQ+ PDOS peaks with NMQ+ molecular orbitals, which may assist in understanding the adsorbed C5 peaks. Additionally, a study of the isolated doubly dehydrogenated NMQ+ species in its own right is planned for the future, see section 7. An interesting finding from the plot of adsorbed C5 PDOS is that there is a notably larger number of minority spin states than majority spin states between the -6 eV to -3 eV energy range. Carbon states starting at around -6 eV are the first to significantly overlap with iron states, so this demonstrates that the hybridisation of high energy molecular orbitals with high energy iron orbitals results in an uneven distribution of spin within carbon. This has not been observed for any other PDOS plot produced throughout this thesis. The interesting spin behaviour may provide some support for the unusually well-resolved distribution of spin on the NMQ+ quinolinium group which persists far away from the surface. Perhaps there is a molecular orbital within the -6 eV to -3 eV energy range which provides particularly good overlap with the surface orbitals, which also results in unusual spin polarisation behaviour. This interesting behaviour will be studied more deeply in a future work.

As for the plot of Fe PDOS, similarly to naphthalene/Fe{110} and quinolinium/Fe{110}, the majority spin states show minimal changes while the minority spin states show a shift to higher binding energies, which results in a reduction in the number of states in the vicinity of the Fermi level. Two of the previously discussed prominent minority spin peaks found in the C PDOS appear clearly in the Fe PDOS at a binding energy between -4 eV and -5 eV.



Figure 6.17. Projected density of states (PDOS) for NMQ+ on Fe{110} in the C-N-HH adsorption geometry. The upper plot shows the majority and minority spin PDOS for Fe atom 143 before (black) and after adsorption (red). The lower plot shows the C atom 5 within NMQ+ majority and minority spin PDOS in the gas-phase (black) and after adsorption (red). The Fermi energy (E_F) has been set to zero and is indicated by a black dashed line. The gas-phase NMQ+ DOS has been aligned with the C(2s) peak for the adsorbed NMQ+, as this level is not expected to be involved in the adsorption process.

6.3.7 Workfunction

The change in Fe{110} workfunction upon adsorption of NMQ+ in the C-N-HH has been studied. Results are presented in table 6.9. The same workfunction calculation procedure was used as for benzene, naphthalene and quinolinium on the Fe{110} surface; chapter 4 should be consulted for a detailed summary of the calculation method. The only difference for the NMQ+/Fe{110} system is an increased vacuum spacing (36 Å in the double-sided slab) compared to the benzene, naphthalene and quinolinium setup (20 Å in the double-sided slab). This is done because a large portion of the C-N-HH adsorption site points into the vacuum, and a larger spacing avoids unphysical interaction of the adsorbate with its periodic copy.

As with all other aromatic adsorbates studied in this thesis, adsorption of NMQ+ in the preferred adsorption configuration results in a reduction of the surface workfunction, on the order of -1.63 eV. This value sits between those found for naphthalene ($\Delta \phi = -1.51 \text{ eV}$) and quinolinium ($\Delta \phi = -1.82 \text{ eV}$). The fact that it is closer to that found for naphthalene is also unsurprising given that naphthyl acts as the anchoring site in C-N-HH alongside an additional contribution from the dehydrogenated quinolinium moiety.

Table 6.9. Calculated Workfunction (ϕ) results for C-N-HH NMQ+ adsorption site on Fe{110}^{*a*}

Method	$E_{vac}(eV)$	$E_F(eV)$	Fe{110}	C-N-HH/Fe{110}	$\Delta \phi$ (eV)
			ϕ (eV)	ϕ (eV)	
PBE-TS	-2.34	-5.56	4.86	3.22	-1.63

 a E_{vac} represents the vacuum energy, E_F represents the Fermi energy and $\Delta\phi$ represents the difference between the C_{10}H_8/Fe{110} ϕ and bare Fe{110} ϕ .

6.4 Discussion and Conclusions

In this section, different results are brought together to build an understanding of NMQ+ in both isolated and Fe{110} adsorbed gas-phase states. A discussion of the adsorbed behaviour of NMQ+ on Fe{110} would be incomplete without a comparison to the adsorption behaviour of its building blocks naphthalene and quinolinium on the same surface. This is included in section 6.4.1. Finally, section 6.4.2 compares the gas-phase and adsorbed behaviour of NMQ+ to similar systems, namely CD and CD/Pt{111} alongside other ACI/metal surface adsorption studies.

Prior to comparison with other systems, it is worth discussing certain NMQ+ and NMQ+/Fe{110} results more carefully. Regarding the isolated gas-phase NMQ+ study, unconstrained DFT optimisation of certain PM6 low-energy structures (B') resulted in less favourable structures found within the constrained PM6 scan, i.e. the D-type conformer. This may occur for several reasons. First, this may be a result of shallow energy barriers separating the different energy minima. These barriers are likely to differ at least somewhat within DFT/PM6 and constrained/unconstrained geometry optimisation. Second, this result could at least partly be due to the choice of conformational analysis parameters. The 15° increment used to generate conformations is relatively coarse and could explain why it is easy for PM6 structures to convert from one to another upon unconstrained DFT-level geometry optimisation. Another parameter worthy of consideration in this context is the starting structure used as the basis for the conformer search. As indicated, a DFT-optimised NMQ+ configuration is used as the starting point for the scan, where $\tau_1 = 75^\circ$ and $\tau_2 = -157^\circ$. In other words, 15° increments are added to these starting angles, which results in slightly asymmetric constrained geometries. This procedure still provides a good overview of the NMQ+ conformational space, but it may be wise to conduct a future conformational analysis with identical initial torsional angles (e.g. $\tau_1 = \tau_2 = 0$). Finally, given the changes between constrained PM6 conformational scan and unconstrained DFT-level optimisation, it would be good practice to conduct a separate, refined (perhaps with 1° increment on τ_1 and τ_2) conformational scan at the DFT level. Finally, it would also be necessary to conduct such studies in the presence of solvent; in the first instance, the PCM model used in section 6.2.4

would be a reasonable choice.

As for the NMQ+/Fe{110} results, it is helpful to compare the findings to relevant experimental literature. The experiments of Ho *et al.*³⁴ identify preferential adsorption of NMQ+ on the lower potential anodic ferrite/bcc islands found on a DSS surface, which as a reminder features islands of bcc and fcc (austenitic) steel. The paper mentions that preferential adsorption could be due to higher local surface area on the bcc-type islands, however another consideration may also play a role; namely, the electric potential. An approach to limiting galvanic corrosion reactions would be to halt the flow of electrons within the electrochemical cell by equalising the electric potentials of microstructural metal surface islands. Modification of electrode potentials can be achieved through adsorption of inhibitor on anodic regions, cathodic regions or both.

A concept at the atomistic level which closely relates to the electrode potential is the workfunction. Specifically, that which mostly closely relates to the workfunction within the electrochemical environment is the absolute electrode potential.²⁷⁰ These two quantities represent the work required to withdraw an electron from the metal surface (E_F) into a vacuum. In the case of the absolute electrode potential, the electron must also pass through metal-electrolyte and electrolyte-vacuum interfaces, so additional dipole interactions are present compared to the gas-phase workfunction. These additional contributions are referred to as the Volta potential. Because the absolute electrode potential is difficult to determine in practice, typically electrode potentials are defined with respect to the standard hydrogen electrode (SHE), which features a platinum electrode exposed to an acidic solution containing H_2 gas. As a result of these similarities, a change in the metal workfunction in the gas-phase is related to a change in the metal electrode potential.

The DFT work of Kokalj⁵⁸ finds a significant adsorption-induced reduction of the workfunction ($\Delta \phi = -2.25 \text{ eV}$) in their study of corrosion inhibitor BTAH on Cu{111}. The paper states this should limit reactions which donate electrons to the metal, i.e. corrosive Cl⁻ adsorption, metal dissolution and metal oxidation. Because NMQ+ also reduces the metal workfunction ($\Delta \phi = -1.63 \text{ eV}$), it should also inhibit anodic reactions, perhaps through adsorption upon the anodic ferrite islands found in DSS. However, given the positive charge on NMQ+, this explanation fails to explain why a positively charged inhibitor should adsorb on a positively charged surface. An additional failure of the explanation is why NMQ+ should adsorb upon the lower potential ferritic phase. Drawing parallels between electrode potential and workfunction, the implication is that NMQ+ would further lower the electrode potential at the anode, which would increase the rate of corrosion reactions. The computed Hirshfeld charge on adsorbed dehydrogenated NMQ+ (+0.19 e) on the neutral metal surface is indicative of covalent binding, which could be extended to explain why a positively charged adsorbate interacts favourably with a positively charged surface. The paper of Guo *et al.*²⁷¹ provides answers to the queries raised from a different perspective. Their work studies the differences in workfunction between ferrite and austenite islands found in DSS by way of scanning force microscopy and DFT calculations. Their calculations reveal that the most stable fcc iron surface (fcc Fe{111}) has a higher workfunction than the most stable bcc iron surface (bcc $Fe{110}$). However, their calculations also reveal that the bcc Fe{110} workfunction is higher than those of the two next most stable fcc Fe surfaces (fcc Fe{100} and fcc Fe{110}). Given that many different facets will be exposed at a real crystal surface, this finding may be the key to explaining the selective adsorption of NMQ+ at the anode, where the workfunction is reduced to equalise the lower workfunction i.e. lower electrode potential associated with non-flat fcc surfaces. Future work on studying NMQ+ adsorption at fcc Fe surfaces will be beneficial towards validating these proposals.

6.4.1 Comparison to naphthalene and quinolinium on Fe{110}

The preferred adsorption geometry for NMQ+/Fe{110} (C-N-HH) is interesting to compare to the studies of adsorption of naphthalene and quinolinium upon Fe{110}. The results from calculations on naphthalene and quinolinium adsorption on the Fe{110} surface are insufficient to explain the observed preferred geometry; indeed, this is partly down to the ability for the quinolinium moiety to lose two hydrogen atoms, thereby allowing for additional stabilisation when the naphthyl group acts as the anchor on the metal surface. An interesting finding aside from this is that the NMQ+ naphthyl group adsorbs in a slightly less favoured adsorption site than what was identified to be most favourable for naphthalene using the PBE-TS method, i.e. the HH site is preferred for NMQ+ naphthyl while the LC site is preferred for naphthalene/Fe{110}. There are a number of factors which may explain why this difference is observed; first, and likely to play an important role, is the directing effect of the dehydrogenation of the quinolinium group. For the second best $NMQ+/Fe{110}$ site (C-N-LC), an interesting route is revealed over the course of DFT optimisation; first, the quinolinium group loses one H atom. Next, the methyl linker loses the second H atom. Once this process has occured, it seems a new, stronger anchor point via the methyl group is created at the surface, which in turn allows the naphthyl-LC site to drift to the HH site. Although the optimised C-N-LC site is not the strongest adsorption site, this provides strong support for the HH-naphthyl site being preferred. Another factor which may explain why the HH site is preferred is that the adsorption behaviour of 1-methylnaphthalene, which is in reality what interacts with the surface within NMQ+, may be different to naphthalene/Fe{110}. Naphthalene and 1-methylnaphthalene adsorption energies and geometries have been shown to be very similar on Fe-containing θ -Fe₃C{010}, which suggests there would not be important differences between these adsorbates on Fe{110}.¹⁵⁸ Finally, both the PBE and PBE-TS energetic separation between LC and HH naphthalene/Fe{110} sites is relatively small, on the order of 0.09 eV at the PBE-TS level.

Other comparisons are made to quinolinium and naphthalene/Fe{110} throughout the chapter, but the other main points of interest are: aside from C-N-HH and C-N-LC sites, the preferred adsorption anchor geometries and energies are consistent with results found for naphthalene and quinolinium adsorption on Fe{110}; the charge and spin density distributions found for the naphthyl anchor within C-N-HH are very similar to those found for naphthalene/Fe{110}; the workfunction reduction afforded by C-N-HH (-1.63 eV) is between those found for naphthalene ($\Delta \phi = -1.51$ eV) and quinolinium ($\Delta \phi = -1.82$ eV) which is reasonable given the adsorption mode.

Clearly, hypothesis Models 1 and 2 presented in section 6.3.1 are invalidated by the appearance of a novel adsorption mode which features interaction with the surface by both naphthyl and quinolinium portions of NMQ+, enabled by spontaneous double dehydrogenation of the adsorbate. If the special C-N-HH and C-N-LC sites are not considered,

the adsorption energies show that quinolinium-grafted NMQ+ adsorption sites (B-Q-HH, C-Q-HH) are energetically favoured compared to naphthyl-grafted NMQ+ adsorption sites (B-N-HH, B-N-LC) which is in line with the findings from chapter 5.

6.4.2 Comparison to other systems

As mentioned previously, isolated gas-phase NMQ+ shares similar features with the CD molecule, which has been intensely scrutinised both experimentally and computationally given its important role in enantionselective catalysis. The results of CD conformational study,^{247,249} which is carried out in a near identical way to the conformational scan described in this chapter, bear little resemblance to those for NMQ+. While our NMQ+ studies identify three truly unique conformers, CD conformational search identifies up to eleven unique favourable conformations at the DFT level. Potential energy surfaces resulting from varying au_1 and au_2 for CD (analogous to figure 6.5 in section 6.2.1) show far less symmetry than the plot presented in this thesis. This comes as no surprise given that the CD molecule presents a chiral center where NMQ+ instead presents a non-chiral methyl group. Additionally, the quinuclidine moiety in CD bears no resemblance to its quinoline group, whilst in the case of NMQ+ the naphthyl and quinolinium groups differ only in the N atom. A further distinction is in the vinyl group found on the CD quinuclidine moiety. The vinyl group participates in additional steric interactions with the quinoline ring, and therefore produces a larger energetic separation between structures. In any event, the preferred CD conformer called Open(3) features $\tau_1 = 99^\circ$ and $\tau_2 = 150^\circ$. This spatial distribution is not dissimilar to both B $(\tau_1 = 80^\circ \text{ and } \tau_2 = 176^\circ)$ and $C(\tau_1 = 157^\circ \text{ and } \tau_2 = 75^\circ)$. The next best conformer, which differs depending on the DFT functional used, is either Closed(1) which is 1.11 kcal/mol (0.05 eV) higher in energy or Open(10) which is 1.09 kcal/mol (0.05 eV) higher in energy. This energy difference is lower than the difference between B and C (0.10 eV), in line with the finding that there are more energy minima for CD than NMQ+.

Given the significant differences between the conformational space between CD and NMQ+, it should come as little surprise that DFT studies of adsorption of CD upon Pt{111} reveal a far more complex range of adsorption modes compared to those produced in this the-

sis for NMQ+ on Fe{110}.²³⁰ In addition to the relatively different conformational spectrum, Pt{111} is a flat fcc surface, which presents a smoother surface compared to the less closepacked flat bcc surface as discussed in previous chapters. The work of Vargas and Baiker²³⁰ studies the adsorption mode of CD on a 38 atom Pt{111} cluster. The preferred conformation in the gas-phase (Open(3)) is not preferred in the adsorbed state; the most stable adsorption geometry features binding through both the quinoline group and the quinuclidine-vinyl group, $E_{ads} = -40.2$ kcal mol⁻¹ (-1.74 eV). The authors dismiss this adsorption site given its instability under hydrogenation conditions and instead focus on the next best site, which features the Closed(1) conformer which is anchored to the surface exclusively through the quinoline group, and has $E_{ads} = -33.0 \text{ kcal mol}^{-1}$ (-1.43 eV). It is worth noting here that the work of Vargas and Baiker does not make use of vdW corrected-DFT which is expected to increase the adsorption energy and potentially also change the relative energetic ordering of adsorption sites. In spite of this, it is interesting to draw a parallel to this work; the second best CD conformer Closed(1) adsorbs more strongly to the Pt{111} surface than the more stable conformer Open(3) ($E_{ads} = -31.3 \text{ kcal mol}^{-1}$ or -1.36 eV), a similar outcome to what is observed in this chapter. Additionally, the preferred CD adsorption configuration Open(3) features contributions from both quinoline and quinuclidine groups, similarly to the naphthyl and quinolinium contributions of NMQ+/Fe{110}. What is very different between CD and NMQ+ adsorption, however, is that dehydrogenation is not observed in any of the eight minimal energy CD/Pt{111} adsorption geometries. Experiments on the aqueous CD/Pt{111} system however do provide support for dissociative adsorption, in the form of ATR-IR spectroscopy.²³¹ At moderate coverages of CD on the Pt surface, the anchoring quinoline group loses a H (on the carbon atom next to nitrogen) to the surface, and adopts a slightly tilted orientation with respect to the surface (see figure 6.3). This behaviour is still quite different to what is observed for NMQ+/Fe{110}, because the quinoline group serves as the anchor for CD on the surface while also losing one H atom. If NMQ+ behaved similarly on Fe{110}, a configuration with quinolinium anchoring NMQ+ (i.e. B-Q-HH or C-Q-HH) could be expected to also show dehydrogenation, but this is not the case. It is likely this is observed for CD because the quinoline-N atom can bind directly to a surface Pt

atom in addition to the neighbouring dehydrogenated C atom, while the NMQ+-N atom connects three carbon atoms, and therefore can only weakly interact with an underlying Fe atom. In both cases, CD-quinoline and NMQ+-quinolinium groups have the ability to lose hydrogen atoms in order to stabilise adsorption upon a metal surface.

As for the loss of two H atoms as exhibited in C-N-HH, a relevant analogue would be benzyne (C_6H_4) which has been observed on Ir{100}.^{272–274} When benzene is adsorbed on Ir{100} at 465 K, the formation of an ordered c(2 × 4) benzyne overlayer is accompanied by H₂ desorption. LEED I-V analysis finds benzyne adsorbs centered above a short bridge site (for di- σ bonding) with a tilt angle of 47° with respect to the surface. Later DFT calculations reveal the tilt results from improved overlap of π orbitals with surface *d* orbitals.²⁷³ The double-dehydrogenated NMQ+-quinolinium group also sits centered above a bridge site (albeit a long bridge) which allows for di- σ bonding. The C-N-LC site, where only one H atom dissociates from quinolinium, also centers above the long bridge site, which provides evidence for this being the preferred adsorption site. Still, further work is planned for the future to establish the preferred upright partially dehydrogenated quinolinium adsorption site independent of the rest of the NMQ+ molecule. As for the tilt, the C-N-HH-quinolinium also displays a tilt, on the order of 16°. Again, it would be necessary to study the dehydrogenatedquinolinium separately to better understand whether the tilt angle provides improved overlap of π orbitals with the iron d orbitals; this is planned for the future, see chapter 7.

Within the corrosion space, there are a number of DFT works which bear common ground with the NMQ+/Fe{110}. The closest work comes in the form of a DFTB study of heteroatomic cyclic molecule adsorption on Fe{110} conducted by Guo *et al.*⁷⁷ Three aromatic-ketone-based adsorbates are studied which have a scaffold reminiscent of the NMQ+ structure, but without replacement of any aromatic ring atoms with heteroatoms. The presence of heteroatoms arises from N(CH₃)₂ and OH substituent groups on benzyl rings or carbonyl groups inserted near the equivalent of the NMQ+ methyl group. All three inhibitors adsorb in completely flat-lying geometries. The strongest adsorption energy is provided by the N(CH₃)₂-substituted inhibitor ($E_{ads} = -1.94$ eV). It should be noted here that DFTB, like DFT, lacks a description of vdW interactions, so the E_{ads} reported by Guo *et al.*⁷⁷ is

likely to increase when such interactions are accounted for. The nitrogen atom lies above an atop site for the preferred N(CH₃)₂-substituted inhibitor adsorption site. Clearly, there are some similarities between these two adsorption modes, but a major difference between the N(CH₃)₂-substituted inhibitor and NMQ+ is the completely flat-lying geometry observed for the former. Additionally, dehydrogenation is not observed for any of the adsorbates studied by Guo et al.⁷⁷ Another key difference between the inhibitors in the study of Guo et al.⁷⁷ and this thesis is the inhibitor's benzyl (Guo et al. 77) or naphthyl-based (this work) scaffold. As is shown in the work of Schmitt and Bedbur²²⁸, major differences in the inhibited corrosion rate are found for benzyl or naphthyl-based compounds, where compounds containing two fused aromatic rings perform significantly better. Based on these considerations, a reasonable hypothesis would be that the benzyl scaffold prevents dissociative adsorption which appears to be important in strong corrosion inhibition. Further support for the importance of dehydrogenation within corrosion inhibition has been identified in recent years. A recent study by Gattinoni et al.⁷⁰ uses DFT to ascertain the mode of corrosion inhibitory and lubrication action of surfactants (hexanoic acid, hexanamide and glycerol monohexanate) upon iron oxide surfaces. Dehydrogenation is found to be thermodynamically favourable for all surfactants under different circumstances (dependant on coverage, presence of defect sites, temperature and pressure). The loss of hydrogen forms surface hydroxyl groups upon the metal oxide surface's oxygen sites. The study also reveals that dehydrogenation is thermodynamically preferred under most conditions for glycerol monohexanate upon the oxide surface, and the inhibitor shows lesser thermodynamic drive towards forming high coverage films. Calculations show glycerides outperform carboxylic acids as lubricants, which combined with these results demonstrate that a low-coverage lubricant film performs better than a more densely packed surface film.⁷⁰ Parallels between lubrication and corrosion inhibition can be drawn, and the finding suggests that film density/thickness is not the sole determining factor for corrosion inhibitory action. Finally, dehydrogenation has also recently been studied for azole corrosion inhibitors upon copper oxide surfaces, and distinguishes different azole species' inhibitory action by how well the new, dissociated molecular geometry can form N-Cu bonds.⁴³ In conclusion, dehydrogenation could be a key element to the

function of superior corrosion inhibiting adsorbates.

6.4.3 Conclusions

This chapter presents results of computational studies of NMQ+, the naphthylmethylquinolinium cation, which is a known acid corrosion inhibitor of steel. To provide a better understanding of its behaviour in the gas phase, a semi-empirical level conformational scan is performed. After DFT-level geometry optimisation of the preferred conformers, three unique conformers (referred to as B, C and D-type) are identified. B is more stable than C by 0.10 eV, and features perpendicular arrangement of the naphthyl and quinolinium groups. Calculations reveal that under aqueous conditions, although B is still preferred, C increases in relative stability, so that C is only 0.03 eV away from B. The D-type conformer is of significantly lower stability than B (0.17 eV).

The adsorption behaviour of NMQ+ on the Fe{110} is studied using DFT. Six adsorption geometries, based on conformers B and C in addition to anchoring via the naphthyl or quinolinium groups, are studied. One site (C-N-HH), which features the C conformer and surface-anchoring through the naphthyl group, is strongly favoured above all others, on the order of 1.12 eV. The marked preference is a result of double dehydrogenation of the quinolinium linker; two C atoms in the vicinity of the nitrogen atom lose their H atoms, enabling direct C-Fe bonds to form with the quinolinium group. The dehydrogenation and related tilt of quinolinium with respect to the surface shares certain similarities with DFT findings for CD/Pt{111} as well as benzyne/Ir{100}. The next best site (C-N-LC) also demonstrates double dehydrogenation, although upon different carbon atoms. The affected carbon atoms for C-N-LC are the quinolinium-C nearest to the nitrogen atom as well as one of the methyl-C atoms. None of the other adsorption sites tested feature dehydrogenation of any kind, and as a result have significantly weaker adsorption strength on Fe{110}. The geometry optimised adsorption configurations demonstrate NMQ+ has a significant degree of flexibility at the surface.

In the preferred adsorption geometry, C-N-HH, the dehydrogenated adsorbate acquires a slight positive charge upon adsorption (+0.19e) and significant minority spin polarisation

(-0.74 μ_{β}). The distribution of spin density on the quinolinium group, which is distant from the surface, is unusually well defined, particularly in considering that there is minimal change in the charge density on the same atoms. The PDOS for C-N-HH also supports unusual spin behaviour, as certain orbitals show greater population of minority spin states than majority spin states. The workfunction of the Fe{110} slab is reduced through adsorption of NMQ+ ($\Delta \phi = 1.63 \text{ eV}$) and is justified given that it lies between the values found for naphthalene ($\Delta \phi = -1.51 \text{ eV}$) and quinolinium ($\Delta \phi = -1.82 \text{ eV}$).

The findings disprove all hypothesis models put forward to explain the preferred interaction mode of NMQ+ with the Fe{110} surface. This is because an alternative mechanism, which features dissociative adsorption, had not been considered. This result is supported by several other DFT studies of corrosion inhibitor adsorption, which have identified dehydrogenation to play an important role in stabilisation of the adsorbates.
Chapter 7

Conclusions

7.1 Summary

This thesis describes the interaction of several aromatic molecules with iron surfaces. The goal of this is twofold; first, to better understand the mode of action of an ACI used in oil and gas drilling and second, to develop a fundamental theory for aromatic adsorption on iron. A side-goal of this project aims to study the impact of a vdW DFT correction scheme (TS) upon adsorption, as these corrections have been shown to have particularly important effects for aromatic adsorption on metal surfaces.

First, the adsorption of the smallest aromatic subunit, benzene, is studied using DFT on three different bcc iron facets; the flat Fe{110}, the kinked Fe{100} and the stepped Fe{211} surfaces. Using DFT without vdW corrections, adsorption geometries which feature benzene centred upon a hollow-like site are preferred. Upon inclusion of the TS vdW correction, the preferred adsorption site changes only for the Fe{110}, where benzene prefers to center above a short bridge site. All adsorption geometries feature some level of C-H bonds tilting above the plane of the benzene molecule towards the vacuum; this behaviour is observed for benzene adsorption on many other metal surfaces i.e. the cushion effect. Some charge and spin transfer to benzene from the metal surface is observed; across all surfaces, benzene presents overall minority spin but can carry a slight positive (Fe{110}, Fe{211}) or negative (Fe{100}) charge. In all cases, the iron surface workfunction is reduced by the adsorption

process. The results in this thesis compare well to those derived from other DFT works for benzene adsorption on Fe{110} and Fe{100}. Aside from some changes in relative energetic ordering of sites, the inclusion of the TS vdW correction greatly increases binding strengths and has a negligible effect on adsorption geometries. The preferred adsorption geometry for Fe{211} in particular is unusual, as it features strong deformation of the benzene molecule within a surface trough, resulting in a resemblance of the adsorbed benzene molecule to the cyclohexane boat conformation.

Second, the adsorption behaviour of two polyaromatic hydrocarbons, naphthalene and quinolinium, is studied on the bcc Fe{110} surface using DFT. These two molecules are chosen because they represent logical candidates for study after benzene as well as being key moieties within a number of industrially relevant corrosion inhibitor molecules. For naphthalene/Fe{110}, an interesting change in relative energetic ordering using PBE-TS compared to PBE appears for the top adsorption site. Without use of the TS correction, the HH site, which features benzyl rings centered about hollow sites, is favoured, which agrees with the findings for benzene adsorption on Fe{110}. Once the TS correction is used, however, a highly symmetrical, long bridge-centred site is instead the preferred adsorption geometry. As for quinolinium/Fe{110}, the best three adsorption sites are consistent whether or not PBE-TS is employed. This is because the three preferred sites feature localisation of the nitrogen atom in an atop site on the Fe{110} surface, which is consistent with findings from the literature for NHx adsorption on the Fe{211} surface. Overall, quinolinium has a higher adsorption energy on the Fe{110} surface than naphthalene. Compared to naphthalene, the N functionality in quinolinium is estimated to contribute just over 1 eV (including the vdW correction) to the adsorption energy.

Finally, the adsorption of a known acid corrosion inhibitor, NMQ+, is studied on the bcc Fe{110} surface again using DFT calculations. A search of the conformational space of NMQ+ reveals three different stable conformers. Compared to the preferred conformer (B-type), another (C-type) has lower stability (+0.10 eV) and the third (D-type) has even lower stability (+0.17 eV). For the NMQ+/Fe{110} study, six unique starting configurations are tested, and are based on the combination of the B and C conformers as well as results

for naphthalene and quinolinium adsorption on Fe{110}. Of the six sites tested, one is strongly preferred, on the order of 1.12 eV stronger adsorption energy than the next best site. This is achieved thanks to double dehydrogenation of the quinolinium moiety, allowing it to interact directly with the metal surface while the naphthyl group serves as the anchor upon Fe{110}. Spontaneous dehydrogenation at the metal surface may be a key feature in justifying the exceptional corrosion resistance offered by NMQ+, as dissociative adsorption has been highlighted in other recent DFT studies of corrosion inhibitors. Parallels can also be drawn to the structurally similar cinchonidine/Pt{111} system used in enantionselective catalysis, as cinchonidine presents dehydrogenation of its quinoline group on the Pt{111} surface. These results demonstrate that all hypotheses regarding the adsorption mode of NMQ+ on metal surfaces are incomplete, as the possibility of dissociative adsorption had never before been considered.

In summary, this thesis has improved the understanding of the seldom studied interaction of aromatic molecules with iron surfaces. It has additionally provided novel mechanistic insights which contribute towards the understanding of the function of ACI. These results form part of a collection of studies at different time and length scales which are necessary for a complete understanding of ACI inhibitory action. Such studies contribute towards the rational design of novel effective ACI in oil and gas processing. Rational design of ACI has the potential for important positive consequences in oilfields, including reduced operational costs, safer working conditions and mitigation of environmental risks.

7.2 Future Work

In a realistic acid corrosion oil well scenario, there are many factors which can have a significant impact upon the adsorption behaviour of the inhibitor. Many of the future work directions arising from this work stem from the simplifications made in order to study the molecule-surface interactions independently of other interactions present in the ACI environment.

The first major additional consideration would be the impact of solvation upon adsorption.

Aqueous solvation is undeniably important in the context of the mode of action of ACI, and needs to be incorporated into the calculations presented throughout this thesis to provide a full understanding of inhibitory action. Solvation is known to impact adsorption energetics upon metal surfaces as well as metal and steel surface structure, as other works have shown.^{275,276} In addition to conformational analysis of NMQ+ immersed in aqueous solution, a study of the interaction of explicit water molecules with NMQ+ would also be required. Given the positive charge on NMQ+, it is likely an implicit solvation scheme is insufficient to describe the real interaction and possible reactivity of the inhibitor in bulk water. Some combination of implicit and explicit solvation schemes may therefore be helpful in this context. As for the $NMQ+/Fe{110}$ system, it is possible to probe the preferred adsorption geometry in the presence of an implicit solvation scheme (something akin to the work of Mathew and Hennig^{277,278} developed for VASP). Again, dependant on the results of NMQ+ interaction with water, it may be necessary to first study NMQ+/Fe{110} in the vicinity of explicit water molecules, perhaps coupled with the use of implicit solvation. A current technical limitation is the lack of support for periodic implicit solvation in CASTEP (we have received communication that this is under active development, to be based on an open source three dimensional multigrid solver for the Poisson Boltzmann equation²⁷⁹). Given these limitations and depending on results for interaction of NMQ+ with water, it may be sensible to approach the aqueous $NMQ+/Fe{110}$ situation differently, for example through use of QM/MM-based molecular dynamics simulations, which would also allow for the study of potentially important dynamic effects. This type of approach has been implemented in the CP2K code.²⁸⁰ An entirely different approach would be to study the system at the molecular mechanics level using a reactive force field such as ReaxFF,²⁸¹ which offers the advantage of low computational expense while allowing for bonds to break and form. Indeed, several studies on the surface chemistry of small molecules adsorbed on iron surfaces have been carried out within the ReaxFF environment.^{282,283} A potentially important contribution to this type of project would be the derivation of appropriate Fe-N parameters which we have been told are currently lacking from the ReaxFF force field.

On the subject of solvation, experimental results show certain ionic species, particularly

inorganic ions and especially iodide, have an important amplifying effect on the corrosion protection by ACI molecules.^{284–288} Any future work aiming to study the activity of ACI molecules in a complete way would require study of the interplay of ion-ACI, ion-surface, and ACI-surface interactions alongside solvation. Given the acidic environment and use of intensifier alongside ACI, the high priority ions for study would be H_3O^+ , Cl^- , I^- and I_3^- .

Corrosion is inherently an electrochemical process, so accurate simulations require the presence of a realistic and complete electrochemical environment. This builds upon use of solvent, which can act as electrolyte, as well as the possibility of varying potential bias in the metal slab. Treating the surface DFT calculation in this way can result in important changes in the preferred adsorption geometry, as shown for example in the work of Steinmann and Sautet⁷³ on pyridine/Au{111} system. Their work finds that the preferred adsorption geometry of pyridine can be flat or "standing up" depending on the potential applied to the gold surface. This is still a relatively new research area, so the underlying theory and methods are under active development; a recent review provides a good summary of the available methods as well as developments to come.²⁸⁹

There are a number of other research directions which could improve the understanding of the corrosion resistance provided by NMQ+. This includes varying the nature of the surface slab used in our calculations to more closely match the surface structure present under realistic oil well conditions i.e. low-carbon steel, austenitic (fcc) steel and iron, iron sulphides, oxides and carbides, chromate overlayers, etc. Additionally, studying the adsorption behaviour of other inhibitor molecules could be quite useful, particularly inhibitors with similar structure to NMQCl which show significantly lower experimental corrosion resistance as shown in the work of Schmitt and Bedbur.²²⁸ On that note, the study of isolated doubly dehydrogenated NMQ+ is worthwhile given the strong preference for its existence at the Fe{110} surface. Finally, calculations performed at higher inhibitor coverages would also be beneficial, as the adsorption mode may differ significantly at increase surface packing.

There are additionally future work directions which apply more generally to aromatic adsorption on iron. Studying the effect of application of more sophisticated van der Waals correction schemes would form the basis of an important future work. The DFT+vdW^{surf}

method²⁹⁰ has recently been validated against experimental data for a number of aromatic adsorbates on metal substrates, showing excellent agreement.⁷⁵ Testing the DFT+vdW^{surf} methodology for the systems presented in this thesis would provide a greater level of confidence regarding the effect of van der Waals corrections on DFT calculations. It would also be useful to extend the studies of naphthalene, quinolinium and NMQ+ to other surface facets, in particular reactive facets such as the Fe{211} or defective surfaces which are said to be key to corrosion protection.³⁹ There are also plans to more deeply investigate the PDOS shown throughout this thesis. Namely, this involves studying the appearance of adsorbate-surface mixed orbitals at highly occupied states, which can more clearly indicate the surface and molecular orbitals involved in stabilising the preferred adsorption site. One project which has currently been initiated is experimental validation of our results for the preferred adsorption geometry of NMQ+ on the iron surface. This will be achieved by studying the tilt angle of NMQ+ at the aqueous metal interface through ATR-IR experiments carried out by Professor Stuart Clarke's group.

Appendix A

Fe Slab Convergence Testing

The sections below list the convergence of various parameters as a function of the number of slab layers and the vacuum spacing for $Fe\{110\}$, $Fe\{100\}$ and $Fe\{211\}$ which are used throughout the thesis in the study of aromatic adsorption.

A.1 Fe{110}

A.1.1 Slab layer number

Table A.1 lists the effect of increasing slab layer number for Fe{110} upon workfunction, surface energy and upper layer spin value. The models studied for bcc Fe{110} slabs include 4 (2 movable layer), 6 (3 movable layer), 8 (4 movable layer), 10 (5 movable layer) and 12 (6 movable layers) layer slabs. In all cases, the vacuum was fixed at 10 Å and a $9 \times 9 \times 1$ Monkhorst-Pack mesh was used for all calculations.

The results of table A.1 show the expected enhanced spin in the top layer (relative to bulk Fe) which remains unchanged when increasing the number of layers past 6.¹⁶² As for workfunction, it converges to within 0.01 eV at 6 layers. The excellent convergence of surface energy, work function and spin using 6 layers gives confidence in making use of 6 slab layers for the 110 surface.

Surface layer no.	Spin in top layer (μ_B)	ϕ (eV)	$\gamma (J/m^2)$
4	2.74	4.934	2.76
6	2.68	4.866	2.74
8	2.68	4.876	2.75
10	2.68	4.862	2.74
12	2.68	4.866	2.74

Table A.1. Spin in top layer, workfunction (ϕ) and surface energy (γ) values according to the number of slab layers of bcc Fe{110} used

Table A.2. Workfunction (ϕ) and surface energy (γ) values as a function of vacuum spacing for a 6-layer bcc Fe{110} slab

Vacuum Spacing (Å)	φ (eV)	$\gamma (J/m^2)$
8	4.856	2.742
10	4.864	2.742
12	4.866	2.742
14	4.869	2.741
16	4.868	2.740
18	4.869	2.740
20	4.870	2.739

A.1.2 Vacuum spacing

The results of the effect of increasing vacuum spacing on the workfunction and surface energy for the 6-layer Fe{110} slab are shown in table A.2. All other parameters are the same as those used for the slab layer tests in section A.1.1.

Workfunction values vary by ≤ 0.006 eV for spacings of 10 Å or higher. Changes in surface energy are negligible across all spacings. The use of a 10 Å vacuum spacing is therefore justified for the bare Fe{110} slab.

# Surface layers	Spin in top layer (μ_B)	ϕ (eV)	$\gamma~(J/m^2)$
6	3.28	3.976	2.81
8	3.28	3.924	2.81
10	3.28	3.923	2.81
12	3.28	3.915	2.80

Table A.3. Spin in top layer, workfunction (ϕ) and surface energy (γ) values according to the number of slab layers of bcc Fe{100} used

A.2 Fe{100}

A.2.1 Slab layer number

In this section, the convergence of work function, surface energy and magnetic behaviour with increasing number of slab layers is tested for the bcc Fe{100}. The slabs studied include 6 (3 movable layer), 8 (4 movable layer), 10 (5 movable layer) and 12 (6 movable layers) layers. The results for all slab models are compared in table A.3. In all cases, the vacuum is fixed at approximately 10 Å (specifically, 6 layers-worth of bcc Fe{100} were used for the vacuum) and a $9 \times 9 \times 1$ Monkhorst-Pack mesh is used for all calculations.

The workfunction converges to within 0.01 eV at 8 layers. Spin in the top layer shows the expected enhanced magnetism compared to bulk Fe (2.22 μ_B), but does not appear to be affected at all by the number of layers included for study.¹⁶² As the {100} is a more "open" surface, i.e. the underlying layers are more accessible, it is unsurprising that a higher number of layers is required for a well converged description of the surface. This behaviour is also expected for the stepped {211} surface.

A.2.2 Vacuum spacing

The effect of vacuum spacing on the convergence of work function and surface energy is quantified in table A.4 for the Fe{100}. The results are shown for an 8-layer bcc Fe{100} slab and all other parameters are the same as those used for the Fe{100} slab layer tests in section A.2.1.

Table A.4. Workfunction (ϕ) and surface energy (γ) values as a function of vacuum spacing for an 8-layer bcc Fe{100} slab

Vacuum Spacing (Å)	ϕ (eV)	$\gamma (J/m^2)$
8	3.939	2.806
10	3.924	2.806
12	3.920	2.806
14	3.925	2.806
16	3.918	2.807
18	3.920	2.806
20	3.929	2.807

Workfunction values vary by ≤ 0.01 eV for spacings of 10 Å or higher. Changes in surface energy are of ≤ 0.03 eV across all spacings. The use of a 10 Å vacuum spacing is therefore justified.

A.3 Fe{211}

A.3.1 Slab layer number

The slab models studied for bcc Fe{211} include 6 (3 movable layer), 8 (4 movable layer), 10 (5 movable layer), 12 (6 movable layer) and 14 (7 movable layer) layer slabs. In all cases, the vacuum was fixed at approximately 10 Å and a $9 \times 9 \times 1$ Monkhorst-Pack mesh was used for all calculations (the mesh at which convergence was observed for the bcc unit cell).

Table A.5 shows the workfunction values converge to within 0.01 eV at 8 slab layers, although it shows a slight decrease of 0.02 eV between 10 and 12 layers. The values for spin in the top layer oscillate relatively negligibly between all surface layer numbers. As for surface energy, it shows slight oscillation over the number of slab layers studied, on the order of 0.01 eV. A study by Błoński and Kiejna showed the Fe{211} surface energy and workfunction to converge at a very high number of layers to $2.50 J/m^2$ and 4.12 eV respectively.¹⁴⁰ This is in fair agreement with the 8-layer workfunction (4.193 eV) and

Surface layer no.	Spin in top layer (μ_B)	ϕ (eV)	$\gamma (J/m^2)$
6	3.14	4.131	2.93
8	3.18	4.193	2.95
10	3.16	4.189	2.93
12	3.14	4.164	2.92

Table A.5. Spin in top layer, workfunction (ϕ) and surface energy (γ) values according to the number of slab layers of bcc Fe{211} used

Table A.6. Workfunction (ϕ) and surface energy (γ) values as a function of vacuum spacing for an 8-layer bcc Fe{211} slab

Vacuum Spacing (Å)	φ (eV)	$\gamma~(J/m^2)$
8	4.178	2.954
10	4.193	2.952
12	4.203	2.946
14	4.209	2.951
16	4.168	2.953
18	4.172	2.953
20	4.176	2.943

surface energy $(2.95 J/m^2)$ which we calculated.

A.3.2 Vacuum spacing

The effect of varying vacuum spacing upon the workfunction and surface energy of the 8-layer bcc Fe{211} slab are shown in table A.6. All other parameters are the same as those used for the Fe{211} slab layer tests described in section A.3.1.

Workfunction values vary by ≤ 0.01 eV from 10-14 Å. However, for spacings greater than 14 Å, workfunction values decrease slightly more, by 0.04 eV. These changes are not reflected in the surface energies however, which across all vacuum spacings vary by ≤ 0.01 eV. With that in mind, we believe that the use of a 10 Å vacuum spacing is justified.

Appendix B

Benzene/Fe: Comparisons to Literature

B.1 Benzene/Fe{110}

Table B.1 lists certain simulation parameters used in the study of benzene/Fe $\{110\}$ presented in chapter 4 as well as in the analogous work of Hensley *et al.*⁹⁶ The parameters listed are only those which differ between the two works. All other unlisted parameters (e.g. functional choice) are identical within the two works.

Parameter	Hensley <i>et al</i> . ⁹⁶	This work
E_{cutoff} (eV)	400	340
Cell size	3×3	4 × 4
MP k-point sampling	$3 \times 3 \times 1$	$2 \times 2 \times 1$
Surface layers	4	6
Movable surface layers	2	3
DFT code	VASP	CASTEP
Pseudopotentials	PAW	USPP + NLCC
vdW correction	optB88-vdW	TS

Table B.1. Differing parameters used in the work of Hensley *et al.* and this work in the study of Benzene/Fe{110}

B.2 Benzene/Fe{100}

Table B.2 lists certain simulation parameters used in the study of benzene/Fe{100} presented in chapter 4 as well as in the analogous work of Sun *et al.*¹⁵⁵ The parameters listed are only those which differ between the two works. All other unlisted parameters (e.g. simulation cell dimensions, k-point mesh) are identical within the two works.

Parameter	Sun <i>et al</i> . ¹⁵⁵	This work
E_{cutoff} (eV)	400	340
Surface layers	7	8
Vacuum spacing (Å)	18	10
Movable surface layers	2	4
Constrained bulk layers	5	4
DFT code	VASP	CASTEP
Pseudopotentials	PAW	USPP + NLCC
vdW correction	N/A	TS

Table B.2. Differing parameters used in the work of Sun *et al.*and this work in the study of Benzene/Fe $\{110\}$

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