

Supplementary Material: [Testing the quas centroid molecular dynamics method on gas-phase ammonia]

Transformation of forces:

Let $(r_1, r_2, r_3, \theta_1, \theta_2, \theta_3)$ denote the bond lengths and bond angles respectively in ammonia, as shown in the figure below:

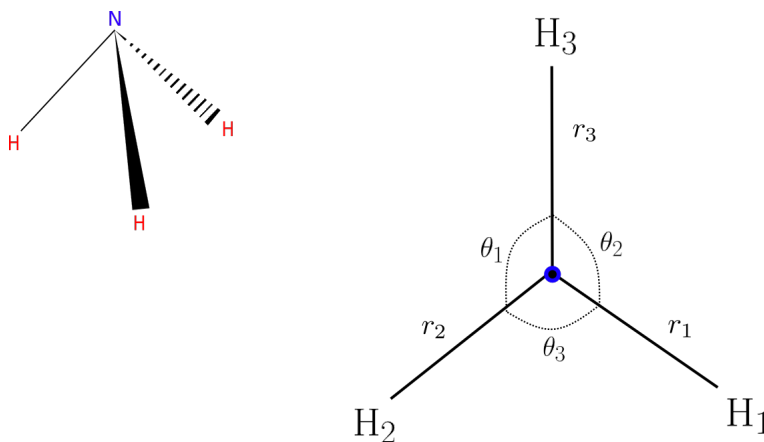


Figure 1: Bond angles and bond lengths in ammonia

We assume that the potential energy $U(\mathbf{Q})$ of an ammonia molecule can be completely described in terms of these curvilinear coordinates. (Note here that \mathbf{Q} denotes a general point in space in Cartesian coordinates, not necessarily the quas centroid or bead position). Then, for a given configuration of atoms in a molecule denoted as \mathbf{Q}_{H_1} , \mathbf{Q}_{H_2} , \mathbf{Q}_{H_3} and \mathbf{Q}_N , the cartesian forces on the atoms are given by:

$$\mathbf{f}_\alpha = -\frac{\partial U(\mathbf{Q})}{\partial \mathbf{Q}_\alpha} = -\left(\sum_{i=1}^3 \frac{\partial U(\mathbf{Q})}{\partial r_i} \nabla_{\mathbf{Q}_\alpha}(r_i) + \sum_{i=1}^3 \frac{\partial U(\mathbf{Q})}{\partial \theta_i} \nabla_{\mathbf{Q}_\alpha}(\theta_i) \right) \quad (1)$$

$$\implies f_\alpha = \sum_{i=1}^3 f_{r_i} \nabla_{\mathbf{Q}_\alpha}(r_i) + \sum_{i=1}^3 f_{\theta_i} \nabla_{\mathbf{Q}_\alpha}(\theta_i) \quad (2)$$

where $\alpha = (H_1, H_2, H_3, N)$.

We derive the cartesian force on one of the hydrogen atoms, say H_1 . The forces on the other two can be obtained by exploiting the C_{3v} symmetry of ammonia. The force on the nitrogen atom can be obtained as:

$$\mathbf{f}_N = -(\mathbf{f}_{H_1} + \mathbf{f}_{H_2} + \mathbf{f}_{H_3}) \quad (3)$$

as the total force on the molecule adds up to zero.

We begin by considering the transformation from cartesian to curvilinear coordinates as follows:

$$r_i = \|\mathbf{Q}_{NH_i}\| = \|\mathbf{Q}_{H_i} - \mathbf{Q}_N\| \quad (4)$$

$$\theta_i = \cos^{-1} \left(\frac{\mathbf{Q}_{NH_j} \cdot \mathbf{Q}_{NH_k}}{r_j r_k} \right) \quad (5)$$

From the above expressions, it is clear that $\nabla_{\mathbf{Q}_{H_1}}(r_2)$, $\nabla_{\mathbf{Q}_{H_1}}(r_3)$ and $\nabla_{\mathbf{Q}_{H_1}}(\theta_1)$ vanish thereby yielding:

$$\frac{\partial U(\mathbf{Q})}{\partial \mathbf{Q}_{H_1}} = \frac{\partial U}{\partial r_1} \nabla_{\mathbf{Q}_{H_1}}(r_1) + \frac{\partial U}{\partial \theta_2} \nabla_{\mathbf{Q}_{H_1}}(\theta_2) + \frac{\partial U}{\partial \theta_3} \nabla_{\mathbf{Q}_{H_1}}(\theta_3) \quad (6)$$

It is easy to check that:

$$\nabla_{\mathbf{Q}_{H_1}}(r_1) = \boldsymbol{\xi}_1 \quad (7)$$

$$\nabla_{\mathbf{Q}_{H_1}}(\theta_2) = \boldsymbol{\Phi}_{213} \quad \text{and} \quad \nabla_{\mathbf{Q}_{H_1}}(\theta_3) = \boldsymbol{\Phi}_{312} \quad (8)$$

where

$$\boldsymbol{\xi}_i := \frac{\mathbf{Q}_{H_i}}{r_i} \quad (9)$$

$$\boldsymbol{\Phi}_{ijk} := \frac{1}{r_j \sin \theta_i} \left(\frac{\mathbf{Q}_{NH_j}}{r_j} \cos \theta_i - \frac{\mathbf{Q}_{NH_k}}{r_k} \right) \quad (10)$$

Thus, we have:

$$\mathbf{f}_{H_1} = f_{r_1} \boldsymbol{\xi}_1 + f_{\theta_2} \boldsymbol{\Phi}_{213} + f_{\theta_3} \boldsymbol{\Phi}_{312} \quad (11)$$

The forces on H_2 and H_3 can be obtained by cyclically permuting the indices in eq. (11), yielding:

$$\mathbf{f}_{H_1} = f_{r_1} \boldsymbol{\xi}_1 + f_{\theta_2} \boldsymbol{\Phi}_{213} + f_{\theta_3} \boldsymbol{\Phi}_{312} \quad (12a)$$

$$\mathbf{f}_{H_2} = f_{r_2} \boldsymbol{\xi}_2 + f_{\theta_3} \boldsymbol{\Phi}_{321} + f_{\theta_1} \boldsymbol{\Phi}_{123} \quad (12b)$$

$$\mathbf{f}_{H_3} = f_{r_3} \boldsymbol{\xi}_3 + f_{\theta_1} \boldsymbol{\Phi}_{132} + f_{\theta_2} \boldsymbol{\Phi}_{231} \quad (12c)$$

Now, in order to obtain the curvilinear forces, given the cartesian forces on the atoms, we start from eq. (12) and take a dot product with the auxiliary variables $\boldsymbol{\xi}_i$ and $\boldsymbol{\Phi}_{ijk}$. It can be easily seen that:

$$f_{r_i} = \mathbf{f}_{H_i} \cdot \boldsymbol{\xi}_i \quad (13)$$

The derivation of the forces along the bond angles is slightly more involved. Considering one of the hydrogen atoms, say H_1 as before, we get:

$$\mathbf{f}_{H_1} \cdot \boldsymbol{\Phi}_{213} = \frac{1}{r_1^2} f_{\theta_2} + \frac{\zeta_{123}}{r_1^2} f_{\theta_3} \quad (14a)$$

$$\mathbf{f}_{H_1} \cdot \boldsymbol{\Phi}_{312} = \frac{\zeta_{123}}{r_1^2} f_{\theta_2} + \frac{1}{r_1^2} f_{\theta_3} \quad (14b)$$

where

$$\zeta_{ijk} = \frac{\cos \theta_i - \cos \theta_j \cos \theta_k}{\sin \theta_j \sin \theta_k} \quad (15)$$

Solving the linear equations (14) yields:

$$f_{\theta_2} = \frac{r_1^2}{\zeta_{123}^2 - 1} (\zeta_{123} \Phi_{312} - \Phi_{213}) \cdot \mathbf{f}_{H_1} \quad (16)$$

$$f_{\theta_3} = \frac{r_1^2}{\zeta_{123}^2 - 1} (\zeta_{132} \Phi_{213} - \Phi_{312}) \cdot \mathbf{f}_{H_1} \quad (17)$$

The force along θ_1 can be obtained by cyclically permuting the indices in one of eqs. (16) and (17). The final equations for the curvilinear forces are as follows:

$$f_{\theta_1} = \frac{r_2^2}{\zeta_{213}^2 - 1} \chi_{213} \cdot \mathbf{f}_{H_2} \quad (18a)$$

$$f_{\theta_2} = \frac{r_3^2}{\zeta_{321}^2 - 1} \chi_{321} \cdot \mathbf{f}_{H_3} \quad (18b)$$

$$f_{\theta_3} = \frac{r_1^2}{\zeta_{132}^2 - 1} \chi_{132} \cdot \mathbf{f}_{H_1} \quad (18c)$$

where

$$\chi_{ijk} = \zeta_{ijk} \Phi_{kij} - \Phi_{jik} \quad (19)$$

Note that several equivalent expressions can be derived for the curvilinear forces.

Derivation of cartesian forces on the quasicentroids:

The curvilinear centroids for ammonia (or any tetra-atomic system with a single heavy atom attached to three lighter atoms) can be defined as the mean of the bond lengths and bond angles of the ring polymer beads, as mentioned in eq. 3 and 4 of the main text. For an N -bead ring polymer, these are:

$$R_i = \frac{1}{N} \sum_{k=1}^N r_i^{(k)} \quad \Theta_i = \frac{1}{N} \sum_{k=1}^N \theta_i^{(k)} \quad (20)$$

where $r_i^{(k)}$ and $\theta_i^{(k)}$ are the i -th bond length and bond angle respectively of the k -th bead.

It follows that the force on the quasicentroid in curvilinear coordinates $(R_1, R_2, R_3, \Theta_1, \Theta_2, \Theta_3)$ is given by:

$$f_{R_i} = -\frac{\partial U_N(\mathbf{q})}{\partial R_i} = -\frac{1}{N} \sum_{k=1}^N \frac{\partial U_N(\mathbf{q})}{\partial r_i^{(k)}} \quad f_{\Theta_i} = -\frac{\partial U_N(\mathbf{q})}{\partial \Theta_i} = -\frac{1}{N} \sum_{k=1}^N \frac{\partial U_N(\mathbf{q})}{\partial \theta_i^{(k)}} \quad (21)$$

where $U_N(\mathbf{q}) = \sum_{i=1}^N U(\mathbf{q}_i)$ as defined in eq. 3 and 4 in the main text.

From the potential energy surface, we get the cartesian forces on the beads, which can be transformed to curvilinear coordinates using eq. (13) and (18). This gives the force on the quasicentroids in curvilinear coordinates, from which cartesian quasicentroid forces can be obtained using (12) and (3).