1 Dipole angle restraints

We are going to restraint the dipole orientation of any molecule, to do this we will apply an harmonic restraint to θ among the chosen axis and the molecule's dipole, so the harmonic restraint is given by

$$V(\vec{r}, q) = \frac{1}{2}k(\theta_r - \theta_{\text{ref}})^2 \tag{1}$$

and the force F

$$\begin{aligned} \vec{F}(\vec{r}, q) &= -\vec{\nabla}V(\vec{r}, q) \\ &= -k(\theta_r - \theta_{\text{ref}})\left(\frac{\partial\theta_r}{\partial x}\hat{x} + \frac{\partial\theta_r}{\partial y}\hat{y} + \frac{\partial\theta_r}{\partial z}\hat{z}\right) \end{aligned} \tag{2}$$

Now, we replace θ_r as a function of dipole vector,

$$\theta_r = \arccos\left(\frac{\vec{\mu}(\vec{r}, q)_{com} \cdot \vec{r}}{|\vec{\mu}(\vec{r}, q)_{com}||\vec{r}|}\right) = \arccos\left(\hat{\mu}_{com} \cdot \hat{r}\right) \tag{3}$$

with $\cos\theta = \hat{\mu}_{com} \cdot \hat{r}$ and where

$$\hat{r} = \frac{(x, y, z)}{\sqrt{x^2 + y^2 + z^2}}$$

and dipole vector for a polar molecule is defined by

$$\vec{\mu}(\vec{r}, q)_{\text{com}} = \sum_{i=1}^{n} q_i(\vec{r}_i - \vec{r}_{\text{com}}) \tag{4}$$

where q_i is the charge of atom i, r_i position of atom i and $\vec{r}_{\text{com}}$ center of mass defined by

$$\vec{r}_{\text{com}} = \frac{1}{M}\sum_{i=1}^{n} m_i\vec{r}_i = (x_{\text{com}}, y_{\text{com}}, z_{\text{com}}) \tag{5}$$

where M is total mass, m_i mass of atom i and n number of atoms of the molecule. Now we derive equation (3)

$$\frac{\partial\theta_r}{\partial x} = \frac{\partial \arccos\left(\frac{\vec{\mu}(\vec{r},q)_{com}\cdot\hat{r}}{|\vec{\mu}(\vec{r},q)_{com}|}\right)}{\partial x} \tag{6}$$

$$= \frac{\partial\theta}{\partial\cos\theta}\frac{\partial\cos\theta}{\partial x} \tag{7}$$

$$= \frac{-1}{\sqrt{1 - \cos^2\theta}}\frac{\partial\cos\theta}{\partial x} \tag{8}$$

so, from the second term of equation (8) we have

$$\frac{\partial \cos\theta_r}{\partial x} = \frac{1}{|\vec{\mu}_{\text{com}}|}\frac{\partial}{\partial x}\vec{\mu}_{\text{com}} \cdot \hat{r} + (\vec{\mu}_{\text{com}} \cdot \hat{r})\frac{\partial}{\partial x}\frac{1}{|\vec{\mu}_{\text{com}}|} \tag{9}$$

where

$$\frac{\partial}{\partial x}\vec{\mu}_{\text{com}} \cdot \hat{r} = \frac{x}{|\vec{r}|}\left(q_j - \frac{m_j}{M}\sum_i q_i\right) \tag{10}$$

and

$$\frac{\partial}{\partial x}\frac{1}{|\vec{\mu}_{\text{com}}|} = -\frac{\mu_{xcom}}{|\vec{\mu}_{com}|^3}\left(q_j - \frac{m_j}{M}\sum_{i=1}^{n} q_i\right) \tag{11}$$

Now we replace (11) and (10) in (9) and obtain

$$\begin{aligned}\frac{\partial \cos\theta_r}{\partial x} &= \frac{1}{|\vec{\mu}_{com}|}\frac{x}{|\vec{r}|}\left(q_j - \frac{m_j}{M}\sum_i q_i\right) - (\vec{\mu}_{\text{com}} \cdot \hat{r})\frac{\mu_{xcom}}{|\vec{\mu}_{com}|^3}\left(q_j - \frac{m_j}{M}\sum_{i=1}^{n} q_i\right) &(12)\\ &= \frac{1}{|\vec{\mu}_{com}|}\left(q_j - \frac{m_j}{M}\sum_{i=1}^{n} q_i\right)\left(\frac{x}{|\vec{r}|} - (\hat{\mu}_{\text{com}} \cdot \hat{r})\frac{\mu_{xcom}}{|\vec{\mu}_{com}|}\right) &(13)\end{aligned}$$

analogous for y and z. Finally the force given by (2) results

$$\begin{aligned}\vec{F}_j(\vec{r}, q) &= -k(\theta_r - \theta_{\text{ref}})\left(\frac{\partial \arccos(\hat{\mu}_{\text{com}} \cdot \hat{r})}{\partial x}\hat{x} + \frac{\partial \arccos(\hat{\mu}_{\text{com}} \cdot \hat{r})}{\partial y}\hat{y} + \frac{\partial \arccos(\hat{\mu}_{\text{com}} \cdot \hat{r})}{\partial z}\hat{z}\right)\\ &= k(\theta_r - \theta_{\text{ref}})\frac{1}{\sqrt{1-\cos^2\theta}|\vec{\mu}_{com}|}\left(q_j - \frac{m_j}{M}\sum_{i=1}^{n} q_i\right)\left[\frac{\vec{r}}{|\vec{r}|} - (\hat{\mu}_{\text{com}} \cdot \hat{r})\frac{\vec{\mu}_{com}}{|\vec{\mu}_{com}|}\right] &(14)\\ &= k(\theta_r - \theta_{\text{ref}})\frac{1}{\sqrt{1-(\hat{\mu}_{\text{com}} \cdot \hat{r})^2}|\vec{\mu}_{com}|}\left(q_j - \frac{m_j}{M}\sum_{i=1}^{n} q_i\right)[\hat{r} - (\hat{\mu}_{\text{com}} \cdot \hat{r})\hat{\mu}_{com}]\end{aligned}$$

for each j atom.
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