Conceptual DFT Analysis of the Fragility Spectra of Atoms along the Minimum Energy Reaction Coordinate.

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Supporting Material for Publication

1. Notation

$$\nabla_B \cdot \mathbf{F}_A = \left(\frac{\partial \mathbf{F}_A}{\partial \mathbf{R}_B}\right)_N = \left(\frac{\partial F_{A,x}}{\partial R_{B,x}}\right)_N + \left(\frac{\partial F_{A,y}}{\partial R_{B,y}}\right)_N + \left(\frac{\partial F_{A,z}}{\partial R_{B,z}}\right)_N \equiv \mathrm{k}_{BA} \tag{S.1}$$

$$\nabla_C \cdot \nabla_B \cdot \mathbf{F}_A = \left(\frac{\partial \mathrm{k}_{BA}}{\partial R_{C,x}}\right)_N \vec{\boldsymbol{i}} + \left(\frac{\partial \mathrm{k}_{BA}}{\partial R_{C,y}}\right)_N \vec{\boldsymbol{j}} + \left(\frac{\partial \mathrm{k}_{BA}}{\partial R_{C,z}}\right)_N \vec{\boldsymbol{k}} \equiv \boldsymbol{a}_{CBA} \tag{S.2}$$

2. Electric field in closed and open system

The differential of the external potential in a closed system is given by:

$$d\upsilon(\mathbf{r}) = \sum_A \left(\frac{\partial \upsilon(\mathbf{r})}{\partial \mathbf{R}_A}\right)_N d\mathbf{R}_A + \left(\frac{\partial \upsilon(\mathbf{r})}{\partial N}\right)_{\mathbf{R}} dN \tag{S.3}$$

Since $$\left(\frac{\partial \upsilon(\mathbf{r})}{\partial N}\right)_{\mathbf{Q}} = 0 \tag{S.4}$$

we have $$d\upsilon(\mathbf{r}) = \sum_A \left(\frac{\partial \upsilon(\mathbf{r})}{\partial \mathbf{R}_A}\right)_N d\mathbf{R}_A \tag{S.5}$$

By the same token, in an open system:

$$d\upsilon(\mathbf{r}) = \sum_A \left(\frac{\partial \upsilon(\mathbf{r})}{\partial \mathbf{R}_A}\right)_\mu d\mathbf{R}_A . \tag{S.6}$$

Since $\mathbf{R}_A$ are independent variables, it must obtain that:

$$\left(\frac{\partial \upsilon(\mathbf{r})}{\partial \mathbf{R}_A}\right)_N = \left(\frac{\partial \upsilon(\mathbf{r})}{\partial \mathbf{R}_A}\right)_\mu \equiv -\boldsymbol{\varepsilon}_A(\mathbf{r}) \tag{S.7}$$

3. **Derivatives of the nuclear potential**

The external potential $\upsilon(\mathbf{r})$ at $\mathbf{r}$ and at $\mathbf{R}_B$ is given by the standard formula:

$$\upsilon(\mathbf{r}) = \sum_{A}^{atoms} \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} \quad \text{(a)} \qquad \upsilon(\mathbf{R}_B) = \sum_{A \neq B}^{atoms} \frac{Z_A}{|\mathbf{R}_A - \mathbf{R}_B|} \quad \text{(b)} \qquad \text{(S.8)}$$

The electric field associated with the nucleus A at $\mathbf{r}$:

$$\vec{\boldsymbol{\varepsilon}}_A(\mathbf{r}) = -\frac{\partial \upsilon(\mathbf{r})}{\partial \mathbf{R}_A} = -\nabla_A \upsilon(\mathbf{r}) = -Z_A \nabla_A \left(\frac{1}{|\mathbf{R}_A - \mathbf{r}|} \right) \qquad \text{(S.9)}$$

and

$$\nabla_{B \neq A} \cdot \vec{\boldsymbol{\varepsilon}}_A(\mathbf{r}) = 0 \qquad \text{(S.10)}$$

From the Laplace equation:[1]

$$\nabla_A \cdot \nabla_A \left(\frac{1}{|\mathbf{R}_A - \mathbf{X}|} \right) = -4\pi \delta\left(\mathbf{R}_A - \mathbf{X}\right) \qquad \text{(S.11)}$$

Hence

$$\nabla_A \cdot \vec{\boldsymbol{\varepsilon}}_A(\mathbf{r}) = -\nabla_A \cdot \nabla_A \upsilon(\mathbf{r}) = -Z_A \nabla_A \cdot \nabla_A \left(\frac{1}{|\mathbf{R}_A - \mathbf{r}|} \right) = +4\pi Z_A \delta\left(\mathbf{R}_A - \mathbf{r}\right) \qquad \text{(S.12)}$$

And for the nuclear repulsion force:

$$\mathbf{F}_A^{nn} = -\nabla_A E^{nn} = -\sum_{B \neq A}^{atoms} \nabla_A \left(\frac{1}{|\mathbf{R}_A - \mathbf{R}_B|} \right) Z_A Z_B \qquad \text{(S.13)}$$

$$\nabla_A \cdot \mathbf{F}_A^{nn} = 0 \qquad \text{and} \qquad \nabla_B \cdot \mathbf{F}_A^{nn} = 0 \qquad \text{(S.14)}$$

4. **Derivatives in the nuclear coordinate representation for the open system.**[2,3]

One additional derivative is necessary – the hyperhardness: $E^{(NNN)} = \gamma$ [4,5]

$$\Omega^{(R\mu\mu)} = S^2 \left(\mathbf{G}_A + \gamma S \mathbf{\Phi}_A \right) \qquad \text{(S.15)}$$

$$\Omega^{(RR\mu)} \equiv \lambda_{AB} = S\lambda_{AB} + S^2 \left(\mathbf{\Phi}_A \cdot \mathbf{G}_B + \mathbf{\Phi}_A \cdot \mathbf{G}_B \right) + \gamma S^3 \mathbf{\Phi}_A \cdot \mathbf{\Phi}_B \qquad \text{(S.16)}$$

$$\begin{aligned} \Omega^{(RRR)} \equiv \boldsymbol{a}_{CBA} = \boldsymbol{a}_{CBA} &+ S\left(\lambda_{CB} \mathbf{\Phi}_A + \lambda_{CA} \mathbf{\Phi}_B + \lambda_{BC} \mathbf{\Phi}_A \right) + \\ &+ S^2 \left(\mathbf{\Phi}_C \cdot \mathbf{\Phi}_B \cdot \mathbf{G}_A + \mathbf{\Phi}_A \cdot \mathbf{\Phi}_B \cdot \mathbf{G}_C + \mathbf{\Phi}_C \cdot \mathbf{\Phi}_A \cdot \mathbf{G}_B \right) + \gamma S^3 \mathbf{\Phi}_C \cdot \mathbf{\Phi}_B \cdot \mathbf{\Phi}_A \end{aligned} \qquad \text{(S.17)}$$

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