Charge transfer and chemisorption of fullerene molecules on metal surfaces: Application to dynamics of nanocars

(Supporting Information)

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S1 Derivation of forces for the charge-transfer model

Here we will derive the expressions for the forces, acting on atoms, which are due to the position dependence of the charges. Since our charge model is based on many-body potential the derivation of the forces may be quite elaborate. Therefore we will present corresponding expression for calculations of the forces.

If the expression of the potential energy $E = E(\{\vec{r}\})$ is known, the force acting on atom i is given by:

$$f_i = -\frac{\partial E}{\partial r_{ij}} \hat{r}_{ij}, \qquad \text{(S1)}$$

where $\hat{r}_{ij} = \frac{\vec{r}_{ij}}{|\vec{r}_{ij}|}$ is a unit-norm direction vector, connecting the atoms with indices i and j.

We are interested in the potential energy terms of Coulombic form, which depend on charges on different atoms q_i and q_j:

$$E = \frac{1}{2} \sum_{\substack{i,j \\ i \in real \\ j \in image}} C \frac{q_i q_j}{|\vec{r}_{ij}|}. \qquad \text{(S2)}$$

The charges are position-dependent and are given by expression:

$$q_i = \beta \rho_i - \gamma \sum_{\substack{j \neq i \\ j \in C}} \rho_j S_2(r_{ij}), \qquad \text{(S3, a)}$$

$$\rho_i = \frac{1}{Z} \sum_{k \in Au} e^{-\alpha r_{ik}} S_1(r_{ik}), \qquad \text{(S3, b)}$$

$$Z = \sum_{i \in C} \sum_{k \in Au} e^{-\alpha r_{ik}} S_1(r_{ik}). \qquad \text{(S3, c)}$$

Consider interaction in each pair $i - j$ $C \frac{q_i q_j}{|\vec{r}_{ij}|}$ separately. In such case there are 3 types of forces:

Type 1)

$$f_i = -\frac{\partial E_{ij}}{\partial \vec{r}_i} = -\frac{\partial}{\partial \vec{r}_i} C \frac{q_i q_j}{r_{ij}} = \frac{E_{ij}}{r_{ij}} \hat{r}_{ij} - C \frac{\left(\frac{\partial q_i}{\partial \vec{r}_i} q_j + q_i \frac{\partial q_j}{\partial \vec{r}_i} \right)}{r_{ij}}. \qquad \text{(S4)}$$

Type 2)

$$f_j = -\frac{\partial E_{ij}}{\partial \vec{r}_j} = -\frac{\partial}{\partial \vec{r}_j} C \frac{q_i q_j}{r_{ij}} = -\frac{E_{ij}}{r_{ij}} \hat{r}_{ij} - C \frac{\left(\frac{\partial q_i}{\partial \vec{r}_j} q_j + q_i \frac{\partial q_j}{\partial \vec{r}_j} \right)}{r_{ij}}. \qquad \text{(S5)}$$

Type 3)

$$f_k = -\frac{\partial E_{ij}}{\partial \vec{r}_k} = -\frac{\partial}{\partial \vec{r}_k} C \frac{q_i q_j}{r_{ij}} = -C \frac{\left(\frac{\partial q_i}{\partial \vec{r}_k} q_j + q_i \frac{\partial q_j}{\partial \vec{r}_k} \right)}{r_{ij}} . \tag{S6}$$

$k \neq i, j$

Now we need to calculate quantities $\frac{\partial q_i}{\partial \vec{r}_k}$. They are of 2 types:

<u>Type 1)</u>

$$\frac{dq_i}{d\vec{r}_i} = \beta \frac{d\rho_i}{d\vec{r}_i} - \gamma \sum_{\substack{j \neq i \\ j \in C}} \left(\frac{d\rho_j}{d\vec{r}_i} S_2(r_{ij}) + \rho_j \frac{dS_2(r_{ij})}{dr_{ij}} \hat{r}_{ij} \right). \tag{S7}$$

<u>Type 2)</u>

$$\frac{dq_i}{d\vec{r}_k} = \beta \frac{d\rho_i}{d\vec{r}_k} - \gamma \sum_{\substack{j \neq i \\ j \in C}} \left(\frac{d\rho_j}{d\vec{r}_k} S_2(r_{ij}) - \rho_j \frac{dS_2(r_{ij})}{dr_{ij}} \hat{r}_{ij} \delta_{kj} \right) =$$

$$= \beta \frac{d\rho_i}{d\vec{r}_k} + \gamma \left(\rho_j \frac{dS_2(r_{ik})}{dr_{ik}} \hat{r}_{ik} - \frac{d\rho_k}{d\vec{r}_k} S_2(r_{ij}) \right) - \gamma \sum_{\substack{j \neq i \\ j \neq k \\ j \in C}} \frac{d\rho_j}{d\vec{r}_k} S_2(r_{ij}). \tag{S8}$$

$k \neq i$

Now we need to calculate the quantity $\frac{d\rho_i}{d\vec{r}_a}$. Using the definitions:

$$\rho_i = \frac{1}{Z} \sum_{k \in Au} \varphi(r_{ik}), \tag{S9, a}$$

$$Z = \sum_{i \in C} \sum_{k \in Au} \varphi(r_{ik}), \tag{S9, b}$$

$$\varphi(r_{ik}) = e^{-\alpha r_{ik}} S_1(r_{ik}), \tag{S9, c}$$

we obtain:

$$\frac{d\rho_i}{d\vec{r}_a} = \frac{\left(\sum_{k \in Au} \varphi'(r_{ik}) \right) Z - Z' \left(\sum_{k \in Au} \varphi(r_{ik}) \right)}{Z^2} = \frac{1}{Z} \left(\sum_{k \in Au} \frac{d}{d\vec{r}_a} \varphi(r_{ik}) \right) - \frac{1}{Z} \rho_i \left(\sum_{i \in C} \sum_{k \in Au} \frac{d}{d\vec{r}_a} \varphi(r_{ik}) \right). \tag{S10}$$

Using

$$\frac{d}{d\vec{r}_a}\varphi(r_{ik}) = \varphi'(r_{ik})(\delta_{ia} - \delta_{ik})\hat{r}_{ik}$$
$$\varphi'(r_{ik}) = -\alpha e^{-\alpha r_{ik}} S_1(r_{ik}) + e^{-\alpha r_{ik}} S'_1(r_{ik}) = -\alpha\varphi(r_{ik}) + e^{-\alpha r_{ik}} S'_1(r_{ik}), \tag{S11}$$

we obtain:

$$\begin{aligned}\frac{d\rho_i}{d\vec{r}_a} &= \frac{1}{Z}\left(\sum_{k\in Au}\frac{d}{d\vec{r}_a}\varphi(r_{ik})\right) - \frac{1}{Z}\rho_i\left(\sum_{i\in C}\sum_{k\in Au}\frac{d}{d\vec{r}_a}\varphi(r_{ik})\right) = \\ &= \frac{1}{Z}\left(\sum_{k\in Au}\varphi'(r_{ik})(\delta_{ia} - \delta_{ik})\hat{r}_{ik} - \rho_i\left(\sum_{i\in C}\sum_{k\in Au}\varphi'(r_{ik})(\delta_{ia} - \delta_{ik})\hat{r}_{ik}\right)\right).\end{aligned} \tag{S12}$$

The index k is never the same as any of indices i, because they enumerate different sets of atoms, thus only first delta-symbol will survive in firsts sum. It may also be taken in front of the sum, since it does not depend on index k. Similar situation takes place in the second summation term. So we obtain:

$$\frac{d\rho_i}{d\vec{r}_a} = \frac{1}{Z}\left(\delta_{ia}\sum_{k\in Au}\varphi'(r_{ik})\hat{r}_{ik} - \rho_i\left(\sum_{i\in C}\delta_{ia}\sum_{k\in Au}\varphi'(r_{ik})\hat{r}_{ik}\right)\right) = \frac{1}{Z}\left(\delta_{ia}\sum_{k\in Au}\varphi'(r_{ik})\hat{r}_{ik} - \rho_i\left(\sum_{k\in Au}\varphi'(r_{ak})\hat{r}_{ak}\right)\right). \tag{S13}$$

If we denote

$\rho'(r_i) = \frac{1}{Z}\sum_{k\in Au}\varphi'(r_{ik})\hat{r}_{ik}$ then the final expression for $\frac{d\rho_i}{d\vec{r}_a}$ will be:

$$\frac{d\rho_i}{d\vec{r}_a} = \delta_{ia}\rho'(r_i) - \rho_i\rho'(r_a). \tag{S14}$$

S2 Complete list of names in longer references

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