Supporting Information Part 1

DFTB3: Extension of the self-consistent-charge density-functional tight-binding method (SCC-DFTB)

Michael Gaus,[†] Qiang Cui,[‡] and Marcus Elstner[*,†]

Institute of Physical Chemistry, Karlsruhe Institute of Technology, Kaiserstr. 12, 76131 Karlsruhe, Germany, and Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin, Madison, 1101 University Avenue, Madison, Wisconsin 53706

E-mail: marcus.elstner@kit.edu

γ-Function and Derivative $\frac{\partial \gamma_{ab}}{\partial U_a}$

The γ-function is described in detail in refs 1,2 and when introducing the abbreviations $\alpha = \frac{16}{5}U_a$, $\beta = \frac{16}{5}U_b$, $r = |R_b - R_a|$ it can be written as (for the γ^{h}-function see below)

$$\gamma_{ab} = \begin{cases} \frac{1}{r} - S^{\mathrm{f}} & r \neq 0, \alpha \neq \beta \\ \frac{1}{r} - S^{\mathrm{g}} & r \neq 0, \alpha = \beta \\ \frac{5}{16}\alpha & r = 0 \end{cases} \tag{1}$$

(2)

[†]Karlsruhe Institute of Technology
[‡]University of Wisconsin, Madison

$$S^{\mathrm{f}} = \mathrm{e}^{-\alpha r} f(\alpha,\beta,r) + \mathrm{e}^{-\beta r} f(\beta,\alpha,r) \tag{3}$$

$$S^{\mathrm{g}} = \mathrm{e}^{-\alpha r} g(\alpha,r) \tag{4}$$

$$f(\alpha,\beta,r) = \frac{\alpha\beta^4}{2(\alpha^2-\beta^2)^2} - \frac{\beta^6-3\alpha^2\beta^4}{(\alpha^2-\beta^2)^3 r} \tag{5}$$

$$g(\alpha,r) = \frac{1}{48r}\left(48+33\alpha r+9\alpha^2 r^2+\alpha^3 r^3\right) \tag{6}$$

Thus, we find for the derivative (for the derivative of the γ^{h}-function see below):

$$\frac{\partial\gamma_{ab}}{\partial U_a} = \frac{16}{5}\frac{\partial\gamma_{ab}}{\partial\alpha} = \frac{16}{5}\begin{cases} -\frac{\partial S^{\mathrm{f}}}{\partial\alpha} & r\neq 0, \alpha\neq\beta \\ -\frac{\partial S^{\mathrm{g}}}{\partial\alpha} & r\neq 0, \alpha=\beta \\ \frac{5}{16} & r=0 \end{cases} \tag{7}$$

$$\frac{\partial S^{\mathrm{f}}}{\partial\alpha} = \mathrm{e}^{-\alpha r}\frac{\partial}{\partial\alpha}f(\alpha,\beta,r) - r\mathrm{e}^{-\alpha r}f(\alpha,\beta,r) + \mathrm{e}^{-\beta r}\frac{\partial}{\partial\alpha}f(\beta,\alpha,r) \tag{8}$$

$$\frac{\partial S^{\mathrm{g}}}{\partial\alpha} = \mathrm{e}^{-\alpha r}\frac{\partial}{\partial\alpha}g(\alpha,r) - r\mathrm{e}^{-\alpha r}g(\alpha,r) \tag{9}$$

$$\frac{\partial}{\partial\alpha}f(\alpha,\beta,r) = -\frac{\beta^6+3\alpha^2\beta^4}{2(\alpha^2-\beta^2)^3} - \frac{12\alpha^3\beta^4}{(\alpha^2-\beta^2)^4 r} \tag{10}$$

$$\frac{\partial}{\partial\alpha}f(\beta,\alpha,r) = \frac{2\beta^3\alpha^3}{(\beta^2-\alpha^2)^3} + \frac{12\beta^4\alpha^3}{(\beta^2-\alpha^2)^4 r} \tag{11}$$

$$\frac{\partial}{\partial\alpha}g(\alpha,r) = \frac{1}{48}\left(33+18\alpha r+3\alpha^2 r^2\right) \tag{12}$$

Note the symmetry of γ: $\gamma_{ab}=\gamma_{ba}$ and $\frac{\partial\gamma_{ab}}{\partial U_a} = \frac{\partial\gamma_{ba}}{\partial U_a}$.

Kohn-Sham Equations

To determine the MO coefficients $c_{\mu i}$ of the LCAO ansatz

$$\psi_i = \sum_a \sum_{\mu\in a} c_{\mu i}\phi_\mu \tag{13}$$

approximate Kohn-Sham equations are derived by finding the maximum of the total energy with respect to the coefficient $c_{\delta_d i}$, the basis function δ being located at atom d. Therefore, taking into account the constraints

$$\int \psi_i \psi_i \mathrm{d}^3 r = 1 \qquad \forall i \tag{14}$$

the respective derivative is given by

$$\frac{\partial}{\partial c_{\delta_d i}} \left[E^{\mathrm{DFTB3}} - \sum_j n_j \varepsilon_j \left(\sum_{ab} \sum_{\mu \in a} \sum_{\nu \in b} c_{\mu j} c_{\nu j} S_{\mu\nu} - 1 \right) \right] \; = \; 0 \qquad \forall d, \delta \in d, i. \tag{15}$$

The total energy expression

$$\begin{aligned} E^{\mathrm{DFTB3}} &= E^{\mathrm{H0}} + E^{\gamma} + E^{\Gamma} + E^{\mathrm{rep}} \\ &= \sum_{iab} \sum_{\mu \in a} \sum_{\nu \in b} n_i c_{\mu i} c_{\nu i} H^0_{\mu\nu} + \frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab} + \frac{1}{3} \sum_{ab} \Delta q_a^2 \Delta q_b \Gamma_{ab} + E^{\mathrm{rep}} \end{aligned} \tag{16}$$

as derived in the manuscript can now be inserted, and the Mulliken charge analysis for estimating the charge fluctuations $\Delta q_a = q_a - q_a^0$ can be employed

$$q_a \; = \; \sum_j n_j \sum_{\mu \in a} \sum_b \sum_{\nu \in b} c_{\mu j} c_{\nu j} S_{\mu\nu} \tag{17}$$

where $S_{\mu\nu} = \langle \phi_\mu | \phi_\nu \rangle$ are the overlap matrix elements. Taking advantage of the symmetry of $H^0_{\mu\nu} = H^0_{\nu\mu}$ and $S_{\mu\nu} = S_{\nu\mu}$ eq 15 can be formed to

$$2 \sum_b \sum_{\nu \in b} n_i c_{\nu i} H^0_{\delta_d \nu} + \frac{\partial E^{\gamma}}{\partial c_{\delta_d i}} + \frac{\partial E^{\Gamma}}{\partial c_{\delta_d i}} - 2 n_i \varepsilon_i \sum_b \sum_{\nu \in b} c_{\nu i} S_{\delta_d \nu} \; = \; 0 \tag{18}$$

$$\frac{\partial E^{\gamma}}{\partial c_{\delta_d i}} \; = \; \frac{\partial}{\partial c_{\delta_d i}} \frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab} \; = \; \frac{1}{2} \sum_{ab} \frac{\partial q_a}{\partial c_{\delta_d i}} \Delta q_b \left(\gamma_{ab} + \gamma_{ba} \right) \tag{19}$$

$$\frac{\partial E^{\Gamma}}{\partial c_{\delta_d i}} \; = \; \frac{\partial}{\partial c_{\delta_d i}} \frac{1}{3} \sum_{ab} \Delta q_a^2 \Delta q_b \Gamma_{ab} \; = \; \frac{1}{3} \sum_{ab} \frac{\partial q_a}{\partial c_{\delta_d i}} \Delta q_b \left(2 \Delta q_a \Gamma_{ab} + \Delta q_b \Gamma_{ba} \right) \tag{20}$$

The derivative of the Mulliken charge with respect to $c_{\delta_d i}$ can be written as

$$\frac{\partial q_a}{\partial c_{\delta_d i}} = \delta_{ad} \sum_c \sum_{\nu \in c} n_i c_{\nu i} S_{\delta_d \nu} + \sum_{\mu \in a} n_i c_{\mu i} S_{\delta_d \mu}. \tag{21}$$

Thus, eqs 19 and 20 expand to

$$\frac{\partial E^{\gamma}}{\partial c_{\delta_d i}} = \frac{1}{2} \sum_{bc} \Delta q_b (\gamma_{db} + \gamma_{bd} + \gamma_{cb} + \gamma_{bc}) \sum_{\nu \in c} n_i c_{\nu i} S_{\delta_d \nu} \tag{22}$$

$$\frac{\partial E^{\Gamma}}{\partial c_{\delta_d i}} = \frac{1}{3} \sum_{bc} \Delta q_b \left(2\Delta q_d \Gamma_{db} + \Delta q_b \Gamma_{bd} + 2\Delta q_c \Gamma_{cb} + \Delta q_b \Gamma_{bc}\right) \sum_{\nu \in c} n_i c_{\nu i} S_{\delta_d \nu}. \tag{23}$$

Dividing eq 18 by $(2n_i)$, combining with eqs 22 and 23, and renaming indices gives

$$\sum_b \sum_{\nu \in b} c_{\nu i} \left(H_{\mu\nu} - \varepsilon_i S_{\mu\nu}\right) = 0, \qquad \forall a, \mu \in a, i \tag{24}$$

$$\begin{aligned} H_{\mu\nu} &= H^0_{\mu\nu} + S_{\mu\nu} \sum_c \Delta q_c \left(\frac{1}{4} (\gamma_{ac} + \gamma_{ca} + \gamma_{bc} + \gamma_{cb}) + \right. \\ &\left. + \frac{1}{3} (\Delta q_a \Gamma_{ac} + \Delta q_b \Gamma_{bc}) + \frac{\Delta q_c}{6} (\Gamma_{ca} + \Gamma_{cb}) \right) \\ &\forall a, b, \mu \in a, \nu \in b. \end{aligned} \tag{25}$$

Taking advantage of the symmetry $\gamma_{ab} = \gamma_{ba}$ (note, that $\Gamma_{ab} \neq \Gamma_{ba}$ is not symmetric!), and renaming the indices results in

$$\sum_b \sum_{\nu \in b} c_{\nu i} \left(H_{\mu\nu} - \varepsilon_i S_{\mu\nu}\right) = 0, \qquad \forall a, \mu \in a, i \tag{26}$$

$$H_{\mu\nu} = H^0_{\mu\nu} + S_{\mu\nu} \sum_c \Delta q_c \left(\frac{1}{2} (\gamma_{ac} + \gamma_{bc}) + \frac{1}{3} (\Delta q_a \Gamma_{ac} + \Delta q_b \Gamma_{bc}) + \frac{\Delta q_c}{6} (\Gamma_{ca} + \Gamma_{cb}) \right) \tag{27}$$

$$\forall a, b, \mu \in a, \nu \in b$$

Total Energy

The total energy (eq 16) as derived in the manuscript can also be express the energy in terms of ε_i using eqs 13, 14, 24, 25, the symmetry $S_{\mu\nu} = S_{\nu\mu}$, and the definition of q_a (eq 17):

$$\begin{aligned}
\sum_i n_i\varepsilon_i &= \sum_{iab}\sum_{\mu\in a}\sum_{\nu\in b} n_i c_{\mu i} c_{\nu i} H_{\mu\nu} \\
&= \sum_{iab}\sum_{\mu\in a}\sum_{\nu\in b} n_i c_{\mu i} c_{\nu i} H^0_{\mu\nu} + \sum_{iab}\sum_{\mu\in a}\sum_{\nu\in b} n_i c_{\mu i} c_{\nu i} \\
&\quad S_{\mu\nu}\sum_c \Delta q_c\left(\frac{1}{4}(\gamma_{ac}+\gamma_{ca}+\gamma_{bc}+\gamma_{cb}) + \frac{1}{3}(\Delta q_a\Gamma_{ac}+\Delta q_b\Gamma_{bc}) + \frac{\Delta q_c}{6}(\Gamma_{ca}+\Gamma_{cb})\right) \\
&= \sum_{iab}\sum_{\mu\in a}\sum_{\nu\in b} n_i c_{\mu i} c_{\nu i} H^0_{\mu\nu} + \sum_{ac} q_a\Delta q_c\left(\frac{1}{2}(\gamma_{ac}+\gamma_{ca}) + \frac{2}{3}\Delta q_a\Gamma_{ac} + \frac{1}{3}\Delta q_c\Gamma_{ca}\right)
\end{aligned} \tag{28}$$

Thus, inserting eq 28 into eq 16 and using $\Delta q_a = q_a - q_a^0$, the total energy can be written as

$$\begin{aligned}
E^{\text{DFTB3}} &= \sum_i n_i\varepsilon_i - \sum_{ac} q_a\Delta q_c\left(\frac{1}{2}(\gamma_{ac}+\gamma_{ca}) + \frac{2}{3}\Delta q_a\Gamma_{ac} + \frac{1}{3}\Delta q_c\Gamma_{ca}\right) + \frac{1}{2}\sum_{ab}\Delta q_a\Delta q_b\gamma_{ab} \\
&\quad + \frac{1}{3}\sum_{ab}\Delta q_a^2\Delta q_b\Gamma_{ab} + E^{\text{rep}} \\
&= \sum_i n_i\varepsilon_i - \frac{1}{2}\sum_{ab}\Delta q_b(q_a\gamma_{ba}+q_a^0\gamma_{ab}) - \frac{1}{3}\sum_{ab}\Delta q_a\Delta q_b\Gamma_{ab}(q_a+q_a^0) - \frac{1}{3}\sum_{ab} q_a\Delta q_b^2\Gamma_{ba} + E^{\text{rep}}
\end{aligned} \tag{29}$$

Considering the symmetry $\gamma_{ab} = \gamma_{ba}$ the total energy can be simplified to

$$E^{\text{DFTB3}} = \sum_i n_i\varepsilon_i - \frac{1}{2}\sum_{ab}(q_a+q_a^0)\Delta q_b\gamma_{ab} - \frac{1}{3}\sum_{ab}(q_a+q_a^0)\Delta q_a\Delta q_b\Gamma_{ab} - \frac{1}{3}\sum_{ab} q_a\Delta q_b^2\Gamma_{ba} + E^{\text{rep}}. \tag{30}$$

Forces

An analytical force equation is derived for a Cartesian coordinate system using the derivative of the total energy with respect to the atomic coordinates R_{kx}, while subjecting to the constraints eq 14. With k, the respective atom index, and an index $x \in \{1,2,3\}$ for the Cartesian coordinate we can write using eq 13:

$$F_{kx} = -\frac{\partial}{\partial R_{kx}}\left[E^{\text{DFTB3}} - \sum_i n_i \varepsilon_i \left(\sum_{ab}\sum_{\mu\in a}\sum_{\nu\in b} c_{\mu i} c_{\nu i} S_{\mu\nu} - 1\right)\right] \qquad \forall k,x \tag{31}$$

The energy depends explicitely on the atomic coordinates via $S_{\mu\nu}$, $H^0_{\mu\nu}$, and γ_{ab} and implicitly via the coefficients $c_{\mu i}$:

$$E^{\text{DFTB3}} = E^{\text{DFTB3}}\left(c_{\mu i}(R_{kx}), R_{kx}\right) \tag{32}$$

$$\frac{\mathrm{d}E^{\text{DFTB3}}}{\mathrm{d}R_{kx}} = \sum_{\mu i} \frac{\mathrm{d}E^{\text{DFTB3}}\left(c_{\mu i}(R_{kx}), R_{kx}\right)}{\mathrm{d}c_{\mu i}} \frac{\mathrm{d}c_{\mu i}}{\mathrm{d}R_{kx}} + \frac{\partial E^{\text{DFTB3}}}{\partial R_{kx}} \tag{33}$$

Because of the variational principle (see eq 15) the implicit dependence via the coefficients $c_{\mu i}$, i.e., the first term of eq 32 is equal to zero. The second term, i.e., the explicit dependence of the energy with respect to the coordinates $\frac{\partial E^{\text{DFTB3}}}{\partial R_{kx}}$ needs to be carried out and is shown in the following. Inserting

$$E^{\text{DFTB3}} = E^{\text{H0}} + E^{\gamma} + E^{\Gamma} + E^{\text{rep}} \tag{34}$$

into eq 31 gives

$$\begin{aligned} F_{kx} &= -\frac{\partial}{\partial R_{kx}}\left[E^{\text{H0}} + E^{\gamma} + E^{\Gamma} + E^{\text{rep}} - \sum_i n_i \varepsilon_i \left(\sum_{ab}\sum_{\mu\in a}\sum_{\nu\in b} c_{\mu i} c_{\nu i} S_{\mu\nu} - 1\right)\right] \\ &= F^{\text{H0}}_{kx} + F^{\gamma}_{kx} + F^{\Gamma}_{kx} + F^{\text{rep}}_{kx} + F^{\text{norm}}_{kx} \qquad \forall k,x, \end{aligned} \tag{35}$$

where

$$F_{kx}^{\mathrm{H0}} = -\frac{\partial}{\partial R_{kx}} \sum_{iab} \sum_{\mu \in a} \sum_{\nu \in b} n_i c_{\mu i} c_{\nu i} H^0_{\mu\nu} = -\sum_{iab} \sum_{\mu \in a} \sum_{\nu \in b} n_i c_{\mu i} c_{\nu i} \frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} \tag{36}$$

$$\begin{aligned} F_{kx}^{\gamma} &= -\frac{\partial}{\partial R_{kx}} \frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab} \\ &= -\frac{1}{2} \sum_{ab} \gamma_{ab} \left(\frac{\partial \Delta q_a}{\partial R_{kx}} \Delta q_b + \Delta q_a \frac{\partial \Delta q_b}{\partial R_{kx}} \right) - \frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \frac{\partial \gamma_{ab}}{\partial R_{kx}} \\ &= \quad F^{\gamma 1} \quad + \quad F^{\gamma 2} \end{aligned} \tag{37}$$

$$\begin{aligned} F_{kx}^{\Gamma} &= -\frac{\partial}{\partial R_{kx}} \frac{1}{3} \sum_{ab} \Delta q_a^2 \Delta q_b \Gamma_{ab} \\ &= -\frac{1}{3} \sum_{ab} \Delta q_a \Gamma_{ab} \left(2 \frac{\partial \Delta q_a}{\partial R_{kx}} \Delta q_b + \Delta q_a \frac{\partial \Delta q_b}{\partial R_{kx}} \right) - \frac{1}{3} \sum_{ab} \Delta q_a^2 \Delta q_b \frac{\partial \Gamma_{ab}}{\partial R_{kx}} \\ &= -\frac{1}{3} \sum_{ab} \frac{\partial q_a}{\partial R_{kx}} \Delta q_b \left(2 \Delta q_a \Gamma_{ab} + \Delta q_b \Gamma_{ba} \right) - \frac{1}{3} \sum_{ab} \Delta q_a^2 \Delta q_b \frac{\partial \Gamma_{ab}}{\partial R_{kx}} \\ &= \quad F^{\Gamma 1} \quad + \quad F^{\Gamma 2} \end{aligned} \tag{38}$$

$$F_{kx}^{\mathrm{rep}} = -\frac{\partial E^{\mathrm{rep}}}{\partial R_{kx}} = -\sum_{ab} \frac{\partial V_{ab}^{\mathrm{rep}}}{\partial R_{kx}} \tag{39}$$

$$F_{kx}^{\mathrm{norm}} = \frac{\partial}{\partial R_{kx}} \sum_i n_i \varepsilon_i \left(\sum_{ab} \sum_{\mu \in a} \sum_{\nu \in b} c_{\mu i} c_{\nu i} S_{\mu\nu} - 1 \right) = \sum_{iab} \sum_{\mu \in a} \sum_{\nu \in b} n_i \varepsilon_i c_{\mu i} c_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}}. \tag{40}$$

Because $H^0_{\mu\nu} = H^0_{\nu\mu}$, $\frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} = \frac{\partial H^0_{\nu\mu}}{\partial R_{kx}}$, and $H^0_{\mu\nu}$ with $\mu \in a$ and $\nu \in b$ is only dependent on the coordinates R_a and R_b,[1] and for $a = b$ it is not dependent on any coordinate[1] F_{kx}^{H0} can be simplified to

$$\begin{aligned} F_{kx}^{\mathrm{H0}} &= -\sum_{ab} \sum_{\mu \in a} \sum_{\nu \in b} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} \\ &= -\sum_{b \neq k} \sum_{\mu \in k} \sum_{\nu \in b} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} - \sum_{a \neq k} \sum_{\mu \in a} \sum_{\nu \in k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} \\ &\quad - \sum_{\mu \in k} \sum_{\nu \in k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} - \sum_{a \neq k} \sum_{b \neq k} \sum_{\mu \in a} \sum_{\nu \in k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} \\ &= -2 \sum_{a \neq k} \sum_{\mu \in a} \sum_{\nu \in k} \sum_i n_i c_{\mu i} c_{\nu i} \frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} \end{aligned} \tag{41}$$

The same applies for F_{kx}^{norm} which can be simplified to

$$F_{kx}^{\text{norm}} = \sum_{iab}\sum_{\mu\in a}\sum_{\nu\in b} n_i\varepsilon_i c_{\mu i}c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} = 2\sum_{a\neq k}\sum_{\mu\in a}\sum_{\nu\in k} n_i\varepsilon_i c_{\mu i}c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} \tag{42}$$

The derivative of the atomic charge with respect to an atomic coordinate is given by

$$\frac{\partial q_{a\neq k}}{\partial R_{kx}} = \sum_{\mu\in a}\sum_{\nu\in k}\sum_{i} n_i c_{\mu i}c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} \tag{43}$$

$$\begin{aligned}\frac{\partial q_k}{\partial R_{kx}} &= \sum_{\mu\in k}\sum_{b\neq k}\sum_{\nu\in b}\sum_{i} n_i c_{\mu i}c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} + \sum_{\mu\in k}\sum_{\nu\in k}\sum_{i} n_i c_{\mu i}c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} \\ &= \sum_{\mu\in k}\sum_{b\neq k}\sum_{\nu\in b}\sum_{i} n_i c_{\mu i}c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}},\end{aligned} \tag{44}$$

where the last recasting in latter equation is due to the fact that the overlap of two basis functions centered at one atom does not change with a change in the coordinate of that atom. Further the basis functions centered on one atom are orthogonal to each other. Taking advantage of the symmetry

$S_{\mu\nu} = S_{\nu\mu}$ and $\frac{\partial S_{\mu\nu}}{\partial R_{kx}} = \frac{\partial S_{\nu\mu}}{\partial R_{kx}}$ we can rewrite $F^{\gamma 1}$ and $F^{\Gamma 1}$ (see eqs 37 and 38).

$$\begin{aligned}
F^{\gamma 1}_{kx} &= -\frac{1}{2}\sum_{a\neq k}\frac{\partial q_a}{\partial R_{kx}}\sum_b \Delta q_b(\gamma_{ab}+\gamma_{ba}) - \frac{1}{2}\frac{\partial q_k}{\partial R_{kx}}\sum_b \Delta q_b(\gamma_{kb}+\gamma_{bk}) \\
&= -\frac{1}{2}\sum_{a\neq k}\sum_b \Delta q_b(\gamma_{ab}+\gamma_{ba})\sum_{\mu\in a}\sum_{\nu\in k}\sum_i n_i c_{\mu i} c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} \\
&\quad -\frac{1}{2}\sum_b \Delta q_b(\gamma_{kb}+\gamma_{bk})\sum_{\mu\in k}\sum_{c\neq k}\sum_{\nu\in c}\sum_i n_i c_{\mu i} c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} \\
&= -\frac{1}{2}\sum_{a\neq k}\sum_b \Delta q_b(\gamma_{ab}+\gamma_{ba}+\gamma_{kb}+\gamma_{bk})\sum_{\mu\in a}\sum_{\nu\in k}\sum_i n_i c_{\mu i} c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} \qquad (45) \\
F^{\Gamma 1}_{kx} &= -\frac{1}{3}\sum_{a\neq k}\frac{\partial q_a}{\partial R_{kx}}\sum_b \Delta q_b\left(2\Delta q_a \Gamma_{ab} + \Delta q_b \Gamma_{ba}\right) - \frac{1}{3}\frac{\partial q_k}{\partial R_{kx}}\sum_b \Delta q_b\left(2\Delta q_k \Gamma_{kb} + \Delta q_b \Gamma_{bk}\right) \\
&= -\frac{1}{3}\sum_{a\neq k}\sum_{\mu\in a}\sum_{\nu\in k}\sum_i n_i c_{\mu i} c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}}\sum_b \Delta q_b\left(2\Delta q_a \Gamma_{ab} + \Delta q_b \Gamma_{ba}\right) \\
&\quad -\frac{1}{3}\sum_{\mu\in k}\sum_{b\neq k}\sum_{\nu\in b}\sum_i n_i c_{\mu i} c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}}\sum_c \Delta q_c\left(2\Delta q_k \Gamma_{kc} + \Delta q_c \Gamma_{ck}\right) \\
&= -\frac{1}{3}\sum_{a\neq k}\sum_b \Delta q_b\left(2\Delta q_a \Gamma_{ab} + \Delta q_b \Gamma_{ba} + 2\Delta q_k \Gamma_{kb} + \Delta q_b \Gamma_{bk}\right)\sum_{\mu\in a}\sum_{\nu\in k}\sum_i n_i c_{\mu i} c_{\nu i}\frac{\partial S_{\mu\nu}}{\partial R_{kx}} \qquad (46)
\end{aligned}$$

Taking advantage of the derivatives $\frac{\partial \gamma_{kk}}{R_{kx}} = 0$ and $\frac{\partial \Gamma_{kk}}{R_{kx}} = 0$ we can also expand $F^{\gamma 2}_{kx}$ (eq 37) and $F^{\Gamma 2}_{kx}$ (eq 38) to

$$\begin{aligned}
F^{\gamma 2}_{kx} &= -\frac{1}{2}\sum_a \Delta q_a \Delta q_k \frac{\partial \gamma_{ak}}{\partial R_{kx}} - \frac{1}{2}\sum_b \Delta q_k \Delta q_b \frac{\partial \gamma_{kb}}{\partial R_{kx}} \\
&= -\frac{1}{2}\Delta q_k \sum_{a\neq k}\Delta q_a\left(\frac{\partial \gamma_{ak}}{\partial R_{kx}} + \frac{\partial \gamma_{ka}}{\partial R_{kx}}\right) \qquad (47) \\
F^{\Gamma 2}_{kx} &= -\frac{1}{3}\left(\sum_{a\neq k}\Delta q_a^2 \Delta q_k \frac{\partial \Gamma_{ak}}{\partial R_{kx}} + \sum_{b\neq k}\Delta q_k^2 \Delta q_b \frac{\partial \Gamma_{kb}}{\partial R_{kx}}\right) \\
&= -\frac{1}{3}\Delta q_k \sum_{a\neq k}\Delta q_a\left(\Delta q_a \frac{\partial \Gamma_{ak}}{\partial R_{kx}} + \Delta q_k \frac{\partial \Gamma_{ka}}{\partial R_{kx}}\right) \qquad (48)
\end{aligned}$$

Thus, the final expression for the force can be shortly written by instering eqs 37, 38, 41, 42, and

45 - 48 into eq 35, using $\gamma_{ab} = \gamma_{ba}$ and reordering terms as

$$\begin{aligned} F_{kx} = & -\sum_{a\neq k}\sum_{\mu\in a}\sum_{\nu\in k}\sum_{i} n_i c_{\mu i} c_{\nu i}\Bigg(2\frac{\partial H^0_{\mu\nu}}{\partial R_{kx}} - 2\varepsilon_i \frac{\partial S_{\mu\nu}}{\partial R_{kx}} + \frac{\partial S_{\mu\nu}}{\partial R_{kx}}\cdot \\ & \left(\sum_c \Delta q_c \left(\gamma_{ac} + \gamma_{kc} + \frac{1}{3}(2\Delta q_a \Gamma_{ac} + \Delta q_c \Gamma_{ca} + 2\Delta q_k \Gamma_{kc} + \Delta q_c \Gamma_{ck})\right)\right)\Bigg) \\ & -\Delta q_k \sum_{a\neq k} \Delta q_a \frac{\partial \gamma_{ak}}{\partial R_{kx}} - \frac{1}{3}\Delta q_k \sum_{a\neq k}\Delta q_a \left(\Delta q_a \frac{\partial \Gamma_{ak}}{\partial R_{kx}} + \Delta q_k \frac{\partial \Gamma_{ka}}{\partial R_{kx}}\right) - \frac{\partial E^{\text{rep}}}{\partial R_{kx}} \qquad \forall k, x. \end{aligned} \tag{49}$$

The derivatives $\frac{\partial H^0_{\mu\nu}}{\partial R_{kx}}$ and $\frac{\partial S_{\mu\nu}}{\partial R_{kx}}$ are determined by taking the numerical derivative of the tabulated integrals $H^0_{\mu\nu}$ and $S_{\mu\nu}$. The force contribution $\frac{\partial E^{\text{rep}}}{\partial R_{kx}}$ is also calculated analytically. Details about the representation of E^{rep} can be found in ref 3.

In the remainder of this subsection the analytical expressions for $\frac{\partial \gamma_{kb}}{\partial R_{kx}}$ and $\frac{\partial \Gamma_{kb}}{\partial R_{kx}}$ are derived. With eq 1, the definition of Γ (as discussed in the manuscript)

$$\begin{aligned} \Gamma_{ab} &= \left.\frac{\partial \gamma_{ab}}{\partial q_a}\right|_{q_a^0} = \left.\frac{\partial \gamma_{ab}}{\partial U_a}\frac{\partial U_a}{\partial q_a}\right|_{q_a^0} \qquad \text{with } a \neq b, \\ \Gamma_{ba} &= \left.\frac{\partial \gamma_{ab}}{\partial q_b}\right|_{q_b^0} = \left.\frac{\partial \gamma_{ab}}{\partial U_b}\frac{\partial U_b}{\partial q_b}\right|_{q_b^0} \qquad \text{with } a \neq b, \\ \Gamma_{aa} &= \left.\frac{\partial \gamma_{aa}}{\partial q_a}\right|_{q_a^0} = \left.\frac{1}{2}\frac{\partial \gamma_{aa}}{\partial U_a}\frac{\partial U_a}{\partial q_a}\right|_{q_a^0}, \end{aligned} \tag{50}$$

eq 7, and

$$\begin{aligned} r_{kb} &= |R_b - R_k| & r_{ak} &= |R_k - R_a| \\ r_{kb} &= \sqrt{\textstyle\sum_{x=1}^{3}(R_{bx} - R_{kx})^2} & r_{ak} &= \sqrt{\textstyle\sum_{x=1}^{3}(R_{kx} - R_{ax})^2} \\ \frac{\partial r_{kb}}{\partial R_{kx}} &= \frac{-(R_{bx} - R_{kx})}{r_{kb}} & \frac{\partial r_{ak}}{\partial R_{kx}} &= \frac{(R_{kx} - R_{ax})}{r_{ak}} \end{aligned} \tag{51}$$

$\forall a,b,k,x$, we can write

$$\frac{\partial \gamma_{kb}}{\partial R_{kx}} = \frac{\partial \gamma_{kb}}{\partial r_{kb}}\frac{\partial r_{kb}}{\partial R_{kx}} \qquad \frac{\partial \gamma_{ak}}{\partial R_{kx}} = \frac{\partial \gamma_{ak}}{\partial r_{ak}}\frac{\partial r_{ak}}{\partial R_{kx}} \tag{52}$$

$$\frac{\partial \Gamma_{kb}}{\partial R_{kx}} = \frac{\partial \Gamma_{kb}}{\partial r_{kb}}\frac{\partial r_{kb}}{\partial R_{kx}} \qquad \frac{\partial \Gamma_{ak}}{\partial R_{kx}} = \frac{\partial \Gamma_{ak}}{\partial r_{ak}}\frac{\partial r_{ak}}{\partial R_{kx}}, \tag{53}$$

and for easier writing we use $\alpha = \frac{16}{5}U_a$, $\beta = \frac{16}{5}U_b$, $r = r_{ab}$, and yield (for the derivative of the γ^{h}-function see below)

$$\frac{\partial \gamma_{ab}}{\partial r_{ab}} = \frac{\partial \gamma_{ab}}{\partial r} = \begin{cases} -\frac{1}{r^2} - \frac{\partial S^{\mathrm{f}}}{\partial r} & r \neq 0, \alpha \neq \beta \\ -\frac{1}{r^2} - \frac{\partial S^{\mathrm{g}}}{\partial r} & r \neq 0, \alpha = \beta \\ 0 & r = 0 \end{cases} \tag{54}$$

$$\frac{\partial S^{\mathrm{f}}}{\partial r} = \mathrm{e}^{-\alpha r}\frac{\partial f(\alpha,\beta,r)}{\partial r} - \alpha \mathrm{e}^{-\alpha r} f(\alpha,\beta,r) + \mathrm{e}^{-\beta r}\frac{\partial f(\beta,\alpha,r)}{\partial r} - \beta \mathrm{e}^{-\beta r} f(\beta,\alpha,r) \tag{55}$$

$$\frac{\partial S^{\mathrm{g}}}{\partial r} = \mathrm{e}^{-\alpha r}\frac{\partial g(\alpha,r)}{\partial r} - \alpha \mathrm{e}^{-\alpha r} g(\alpha,r) \tag{56}$$

$$\frac{\partial f(\alpha,\beta,r)}{\partial r} = \frac{\beta^6 - 3\alpha^2\beta^4}{(\alpha^2-\beta^2)^3 r^2} \tag{57}$$

$$\frac{\partial g(\alpha,r)}{\partial r} = -\frac{1}{r^2} + \frac{3\alpha^2}{16} + \frac{\alpha^3}{24}\cdot r. \tag{58}$$

Functions $f(\alpha,\beta,r)$ and $g(\alpha,r)$ are defined in eqs 5 and 6, respectively. Similarly,

$$\begin{aligned} \frac{\partial \Gamma_{ab}}{\partial r_{ab}} &= \frac{\partial \Gamma_{ab}}{\partial r} = \frac{\partial}{\partial r}\left(\frac{\partial \gamma_{ab}}{\partial U_a}\frac{\partial U_a}{\partial q_a}\right) = \frac{\partial^2 \gamma_{ab}}{\partial U_a \partial r}\frac{\partial U_a}{\partial q_a} + \frac{\partial \gamma_{ab}}{\partial U_a}\frac{\partial^2 U_a}{\partial q_a \partial r} = \\ &= \frac{\partial^2 \gamma_{ab}}{\partial U_a \partial r}\frac{\partial U_a}{\partial q_a} \end{aligned} \tag{59}$$

The latter term on right hand side of the first line is equal to zero, because the Hubbard-derivative is not dependent on any atomic coordinate. Thus, we need eqs 7, 54, and (for the derivative of the

γ^{h}-function see below)

$$\frac{\partial^2 \gamma_{ab}}{\partial U_a \partial r} = \begin{cases} -\frac{\partial^2 S^{\mathrm{f}}}{\partial U_a \partial r} & r \neq 0, \alpha \neq \beta \\ -\frac{\partial^2 S^{\mathrm{g}}}{\partial U_a \partial r} & r \neq 0, \alpha = \beta \\ 0 & r = 0 \end{cases} \tag{60}$$

$$\begin{aligned} \frac{\partial^2 S^{\mathrm{f}}}{\partial U_a \partial r} &= \frac{\partial}{\partial r}\left(\frac{16}{5}\frac{\partial S^{\mathrm{f}}}{\partial \alpha}\right) = \\ &= \frac{16}{5}\left[\mathrm{e}^{-\alpha r}\left(f(\alpha,\beta,r)(\alpha r - 1) - \alpha\frac{\partial f(\alpha,\beta,r)}{\partial \alpha} + \frac{\partial^2 f(\alpha,\beta,r)}{\partial \alpha \partial r} - r\frac{\partial f(\alpha,\beta,r)}{\partial r}\right)\right. \\ &\quad \left. + \mathrm{e}^{-\beta r}\left(\frac{\partial^2 f(\beta,\alpha,r)}{\partial \alpha \partial r} - \beta\frac{\partial f(\beta,\alpha,r)}{\partial \alpha}\right)\right] \end{aligned} \tag{61}$$

$$\begin{aligned} \frac{\partial^2 S^{\mathrm{g}}}{\partial U_a \partial r} &= \frac{\partial}{\partial r}\left(\frac{16}{5}\frac{\partial S^{\mathrm{g}}}{\partial \alpha}\right) = \\ &= \frac{16}{5}\mathrm{e}^{-\alpha r}\left((\alpha r - 1)g(\alpha,r) - \alpha\frac{\partial g(\alpha,r)}{\partial \alpha} + \frac{\partial^2 g(\alpha,r)}{\partial \alpha \partial r} - r\frac{\partial g(\alpha,r)}{\partial r}\right) \end{aligned} \tag{62}$$

$$\frac{\partial^2 f(\alpha,\beta,r)}{\partial \alpha \partial r} = \frac{12\alpha^3\beta^4}{(\alpha^2-\beta^2)^4 r^2} \tag{63}$$

$$\frac{\partial^2 f(\beta,\alpha,r)}{\partial \alpha \partial r} = -\frac{12\alpha^3\beta^4}{(\beta^2-\alpha^2)^4 r^2} \tag{64}$$

$$\frac{\partial^2 g(\alpha,r)}{\partial \alpha \partial r} = \frac{3}{8}\alpha + \frac{1}{8}\alpha^2 r. \tag{65}$$

The γ^{h}-Function

The $\gamma^{\mathrm{h}}_{ab} = \gamma^{\mathrm{h}}_{ba}$ function for HX atom pairs (X∈{C, H, N, O, P, S}) takes the form

$$\gamma^{\mathrm{h}}_{ab} = \frac{1}{r} - S \cdot h \tag{66}$$

$$h = \exp\left(-\left(\frac{U_a+U_b}{2}\right)^{\zeta} r^2\right) \tag{67}$$

where $S = S^{\mathrm{f}}$ when $\alpha \neq \beta$ and $S = S^{\mathrm{g}}$ when $\alpha = \beta$. S^{f} and S^{g} as well as α, β, and r are defined in eqs 3 and 4. Eqs 7, 54, and 60 then change to:

$$\frac{\partial \gamma^{\mathrm{h}}_{ab}}{\partial U_a} = -\left(\frac{\partial S}{\partial U_a} h + S \frac{\partial h}{\partial U_a}\right) \tag{68}$$

$$\frac{\partial \gamma^{\mathrm{h}}_{ab}}{\partial r} = -\frac{1}{r^2} - \left(\frac{\partial S}{\partial r} h + S \frac{\partial h}{\partial r}\right) \tag{69}$$

$$\frac{\partial^2 \gamma^{\mathrm{h}}_{ab}}{\partial U_a \partial r} = -\left(\frac{\partial^2 S}{\partial U_a \partial r} h + \frac{\partial S}{\partial U_a}\frac{\partial h}{\partial r} + \frac{\partial S}{\partial r}\frac{\partial h}{\partial U_a} + S \frac{\partial^2 h}{\partial U_a \partial r}\right) \tag{70}$$

with

$$\frac{\partial h}{\partial U_a} = -\frac{\zeta r^2}{2}\left(\frac{U_a+U_b}{2}\right)^{\zeta-1} \cdot h \tag{71}$$

$$\frac{\partial h}{\partial r} = -2r\left(\frac{U_a+U_b}{2}\right)^{\zeta} \cdot h \tag{72}$$

$$\frac{\partial^2 h}{\partial U_a \partial r} = \zeta r \left(\frac{U_a+U_b}{2}\right)^{\zeta-1}\left(r^2\left(\frac{U_a+U_b}{2}\right)^{\zeta} - 1\right) \cdot h. \tag{73}$$

References

(1) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifert, G. *Phys. Rev. B* **1998**, *58*, 7260.

(2) Elsner, J. Ph.D. thesis, Universität-Gesamthochschule Paderborn, 1998.

(3) Gaus, M.; Chou, C. .; Witek, H.; Elstner, M. *J. Phys. Chem. A* **2009**, *113*, 11866.