

1. DFTB2/CPE energy

1.1 CPE energy

The CPE energy is given by:[1]

$$E_{\text{cpe}}[\mathbf{q}, \mathbf{c}] = \mathbf{c}^T \cdot \mathbf{M} \cdot \mathbf{q} + \frac{1}{2} \mathbf{c}^T \cdot \mathbf{N} \cdot \mathbf{c}, \quad (1.1)$$

where the first order CPE-CPE Coulomb interaction matrix elements are given by:

$$N_{ij} = \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}) \phi_j^{\text{cpe}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (1.2)$$

and the second order CPE-DFTB2 Coulomb interaction matrix elements are given by:

$$M_{ij} = f(R_{ij}) \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}) \phi_j^{\text{dftb2}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (1.3)$$

The CPE basis functions depend on the Mulliken charge, while the DFTB basis functions only have a charge dependence in DFTB3.

The set of coefficients of the CPE response density basis that variationally minimizes the total CPE energy in Eqn. 1.1 is given (analytically) by:

$$\mathbf{c} = -\mathbf{N}^{-1} \cdot \mathbf{M} \cdot \mathbf{q} \quad (1.4)$$

1.2 DFTB2 energy

The DFTB2 energy is given by:[2]

$$E_{\text{dftb2}} = \sum_i^{\text{occ}} n_i \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} H_{\mu\nu}^0 + \frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab} + \frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}} \quad (1.5)$$

The DFTB2 Hamiltonian matrix elements are given by:[2]

$$H_{\mu\nu}^{(\text{dftb2})} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_c (\gamma_{ac} + \gamma_{bc}) \Delta q_c \quad (1.6)$$

1.3 Combined DFTB2/CPE energy

The CPE Hamiltonian shift is given by:[3]

$$\Delta H_{\mu\nu}^{(\text{cpe})} = -\frac{1}{2} S_{\mu\nu} \left(\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} + \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_b} \right) \quad \mu \in a, \nu \in b \quad (1.7)$$

See Appendix A for details.

The full DFTB2/CPE energy is given by:

$$\begin{aligned}
E_{\text{dftb2/cpe}} &= \sum_i^{\text{occ}} n_i \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} \left(H_{\mu\nu}^{(\text{dftb2})} + \Delta H_{\mu\nu}^{(\text{cpe})} \right) + \frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}} + E_{\text{cpe}}[\mathbf{q}, \mathbf{c}] \\
&= \underbrace{\sum_i^{\text{occ}} n_i \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} H_{\mu\nu}^0}_{E_{\text{H0}}} + \underbrace{\frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab}}_{E_{\gamma}} + \underbrace{\frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}}}_{E_{\text{rep}}} \\
&\quad - \underbrace{\frac{1}{2} \sum_i^{\text{occ}} n_i \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu\nu} \left(\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} + \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_b} \right)}_{E_{\text{shift}}} \\
&\quad + \underbrace{E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}_{E_{\text{cpe}}}
\end{aligned} \tag{1.8}$$

$$= E_{\text{H0}} + E_{\gamma} + E_{\text{rep}} + E_{\text{shift}} + E_{\text{cpe}} \tag{1.9}$$

2. DFTB2/CPE energy gradient

The energy gradient is the derivative of the energy with respect to the nuclear coordinates under the variational constraint:

$$-F_{kx} = \frac{\partial}{\partial R_{kx}} \left[E_{\text{dftb2/cpe}} - \sum_i^{\text{occ}} n_i \varepsilon_i \left(\sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu\nu} - 1 \right) \right] \tag{2.1}$$

Using the notation of Eq. 1.9, we can rewrite this as:

$$-F_{kx} = \frac{\partial}{\partial R_{kx}} \left[E_{\text{H0}} + E_{\gamma} + E_{\text{rep}} + E_{\text{shift}} + E_{\text{cpe}} - \sum_i^{\text{occ}} n_i \varepsilon_i \left(\sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu\nu} - 1 \right) \right] \tag{2.2}$$

Separating the terms that appear in the standard DFTB2 gradient, and the DFTB2/CPE gradient, we arrive at the CPE gradient correction:

$$\begin{aligned}
-F_{kx} &= \frac{\partial}{\partial R_{kx}} \left[E_{\text{H0}} + E_{\gamma} + E_{\text{rep}} + E_{\text{shift}} + E_{\text{cpe}} - \sum_i^{\text{occ}} n_i \varepsilon_i \left(\sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu\nu} - 1 \right) \right] \\
&= \underbrace{\frac{\partial}{\partial R_{kx}} \left[E_{\text{H0}} + E_{\gamma} + E_{\text{rep}} - \sum_i^{\text{occ}} n_i \varepsilon_i \left(\sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu\nu} - 1 \right) \right]}_{\text{Same as the DFTB2 gradient}} + \frac{\partial}{\partial R_{kx}} [E_{\text{shift}} + E_{\text{cpe}}] \\
&= -F_{kx}^{(\text{dftb2})} + \frac{\partial E_{\text{shift}}}{\partial R_{kx}} + \frac{\partial E_{\text{cpe}}}{\partial R_{kx}} \\
&= -F_{kx}^{(\text{dftb2})} - F_{kx}^{(\text{shift})} - F_{kx}^{(\text{cpe})}
\end{aligned} \tag{2.3}$$

$$= -F_{kx}^{(\text{dftb2})} - F_{kx}^{(\text{shift})} - F_{kx}^{(\text{cpe})} \tag{2.4}$$

The last two terms are new and are presented in the next sections.

2.1 CPE gradient: $-F_{kx}^{(\text{cpe})} = \frac{\partial E_{\text{cpe}}}{\partial R_{kx}}$

The CPE energy depends explicitly on the coordinates via the Coulomb integrals, and implicitly on the coordinates via the CPE coefficients and the Mulliken charges:

$$\begin{aligned}
-F_{kx}^{(\text{cpe})} &= \frac{dE_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{dR_{kx}} \\
&= \sum_i \frac{\partial E_{\text{cpe}}(\mathbf{q}, c_i(R_{kx}))}{\partial c_i} \frac{dc_i(R_{kx})}{dR_{kx}} + \sum_a \frac{\partial E_{\text{cpe}}(q_a(R_{kx}), \mathbf{c})}{\partial q_a} \frac{dq_a(R_{kx})}{dR_{kx}} + \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial R_{kx}} \quad (2.5)
\end{aligned}$$

The first derivative term is zero, since the CPE energy is variationally optimized with respect to the \mathbf{c} coefficients.

2.1.1 Dependence on q_a

The second term can be divided into two factors. The first factor can be calculated as described in the previous section (it is the same term as found in the Hamiltonian-shift.) E.g. in the CPE charge-independent case:

$$\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} = [\mathbf{c}^T \cdot \mathbf{M}]_a \quad (2.6)$$

And in the CPE charge-dependent case:

$$\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} = \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{M}}{\partial q_a} \right) \cdot \mathbf{q} + [\mathbf{c}^T \cdot \mathbf{M}]_a + \frac{1}{2} \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{N}}{\partial q_a} \right) \cdot \mathbf{c}. \quad (2.7)$$

The second factor can be calculated for $a \neq k$ by:[4]

$$\frac{\partial q_{a \neq k}}{\partial R_{kx}} = \sum_i^{\text{occ}} n_i \sum_{\mu \in a} \sum_{\nu \in k} C_{\mu i} C_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \quad (2.8)$$

or for $a = k$:

$$\frac{\partial q_k}{\partial R_{kx}} = \sum_i^{\text{occ}} n_i \sum_{\mu \in k} \sum_{\nu \notin k} C_{\mu i} C_{\nu i} \frac{\partial S_{\mu\nu}}{\partial R_{kx}} \quad (2.9)$$

This term must be calculated in the DFTB2 gradient code (missing up to now).

2.1.2 (Explicit) dependence on R_{kx}

The derivative with respect to R_{kx} is written via the matrix derivatives.

$$\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial R_{kx}} = \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{M}}{\partial R_{kx}} \right) \cdot \mathbf{q} + \frac{1}{2} \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{N}}{\partial R_{kx}} \right) \cdot \mathbf{c}. \quad (2.10)$$

The elements of the derivative matrices are the integral derivatives, shown in the appendix.

2.2 Shift gradient: $-F_{kx}^{(\text{shift})} = \frac{\partial E_{\text{shift}}}{\partial R_{kx}}$

$$\begin{aligned}
\frac{\partial E_{\text{shift}}}{\partial R_{kx}} &= -\frac{1}{2} \frac{\partial}{\partial R_{kx}} \left[\sum_i^{\text{occ}} n_i \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu\nu} \left(\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} + \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_b} \right) \right] \\
&= -\frac{1}{2} \sum_i^{\text{occ}} n_i \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} \left[\frac{\partial S_{\mu\nu}}{\partial R_{kx}} \left(\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} + \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_b} \right) \right. \\
&\quad \left. + S_{\mu\nu} \left(\frac{\partial^2 E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial R_{kx} \partial q_a} + \frac{\partial^2 E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial R_{kx} \partial q_b} \right) \right] \quad (2.11)
\end{aligned}$$

The derivative of the overlap matrix is performed numerically, while the derivative of the CPE-energy is given by (in the charge-independent case):

$$\frac{\partial^2 E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial R_{kx} \partial q_a} = \frac{\partial}{\partial R_{kx}} [\mathbf{c}^T \cdot \mathbf{M}]_a = \left[\mathbf{c}^T \cdot \frac{\partial \mathbf{M}}{\partial R_{kx}} \right]_a \quad (2.12)$$

and similarly in the charge-dependent case:

$$\begin{aligned} \frac{\partial^2 E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial R_{kx} \partial q_a} &= \frac{\partial}{\partial R_{kx}} \left[\mathbf{c}^T \cdot \left(\frac{\partial \mathbf{M}}{\partial q_a} \right) \cdot \mathbf{q} + [\mathbf{c}^T \cdot \mathbf{M}]_a + \frac{1}{2} \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{N}}{\partial q_a} \right) \cdot \mathbf{c} \right] \\ &= \mathbf{c}^T \cdot \left(\frac{\partial^2 \mathbf{M}}{\partial R_{kx} \partial q_a} \right) \cdot \mathbf{q} + \left[\mathbf{c}^T \cdot \frac{\partial \mathbf{M}}{\partial R_{kx}} \right]_a + \frac{1}{2} \mathbf{c}^T \cdot \left(\frac{\partial^2 \mathbf{N}}{\partial R_{kx} \partial q_a} \right) \cdot \mathbf{c} \end{aligned} \quad (2.13)$$

The matrix derivatives $\frac{\partial^2 \mathbf{M}}{\partial R_{kx} \partial q_a}$ and $\frac{\partial^2 \mathbf{N}}{\partial R_{kx} \partial q_a}$ are new and not implemented.

References

- [1] Steve Kaminski, Timothy J. Giese, Michael Gaus, Darrin M. York, and Marcus Elstner. Extended Polarization in Third-Order SCC-DFTB from Chemical-Potential Equalization. *The Journal of Physical Chemistry A*, 116(36):9131–9141, 2012.
- [2] M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, Th. Frauenheim, S. Suhai, and G. Seifert. Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties. *Phys. Rev. B*, 58:7260–7268, Sep 1998.
- [3] Timothy J. Giese and Darrin M. York. Density-functional expansion methods: grand challenges. *Theoretical Chemistry Accounts*, 131(3), 2012.
- [4] Michael Gaus, Qiang Cui, and Marcus Elstner. DFTB3: Extension of the Self-Consistent-Charge Density-Functional Tight-Binding Method (SCC-DFTB). *Journal of Chemical Theory and Computation*, 7(4):931–948, 2011.

Appendices

A Hamiltonian shift

A1 Mulliken charges

The Mulliken charge is given by:

$$q_a = \sum_i^{\text{occ}} n_i \sum_{\mu \in a} \sum_{\nu} C_{\mu i} C_{\nu i} S_{\mu \nu} \quad (\text{A1})$$

The charge fluctuation is then:

$$\Delta q_a = q_a - q_a^0 \quad (\text{A2})$$

A2 Density matrix elements

The density matrix is defined in terms of the coefficient matrix:

$$\rho_{\mu \nu} = \sum_i^{\text{occ}} n_i C_{\mu i} C_{\nu i} \quad (\text{A3})$$

A3 Hamiltonian shift

The Hamiltonian shift is calculated using the chain rule:

$$\Delta H_{\mu \nu}^{(\text{cpe})} = \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial \rho_{\mu \nu}} \quad (\text{A4})$$

$$= \sum_i \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial c_i} \frac{\partial c_i}{\partial \rho_{\mu \nu}} + \sum_a \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} \frac{\partial q_a}{\partial \rho_{\mu \nu}} \quad (\text{A5})$$

$$= -\frac{1}{2} S_{\mu \nu} \left(\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} + \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_b} \right) \quad \mu \in a, \nu \in b \quad (\text{A6})$$

The CPE energy has no parametric dependence on the density, but depends implicitly via the charges and coefficients. The first term is zero due to the CPE energy being variationally minimized with respect to the coefficients. The first part of the second term is in the CPE charge-independent case:

$$\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} = [\mathbf{c}^T \cdot \mathbf{M}]_a \quad (\text{A7})$$

In the CPE charge-dependent case:

$$\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} = \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{M}}{\partial q_a} \right) \cdot \mathbf{q} + [\mathbf{c}^T \cdot \mathbf{M}]_a + \frac{1}{2} \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{N}}{\partial q_a} \right) \cdot \mathbf{c}. \quad (\text{A8})$$

See Giese and York (2012) for details.[3]

B Derivative matrix elements

B1 First order matrix (geometry)

The matrix elements are:

$$\frac{\partial N_{ij}}{\partial R_{kx}} = \frac{\partial}{\partial R_{kx}} \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}) \phi_j^{\text{cpe}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (\text{B1})$$

This is already implemented.

B2 First order matrix (charge)

The matrix elements are:

$$\frac{\partial N_{ij}}{\partial q_k} = \frac{\partial}{\partial q_k} \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}) \phi_j^{\text{cpe}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (\text{B2})$$

This is already implemented.

B3 Second order matrix (geometry)

The matrix elements are:

$$\frac{\partial M_{ij}}{\partial R_{kx}} = f(R_{ij}) \frac{\partial}{\partial R_{kx}} \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}) \phi_j^{\text{dftb}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + \frac{\partial f(R_{ij})}{\partial R_{kx}} \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}) \phi_j^{\text{dftb}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (\text{B3})$$

This is already implemented.

B4 Second order matrix (charge)

The matrix elements are (for DFTB2):

$$\frac{\partial M_{ij}}{\partial q_k} = f(R_{ij}) \frac{\partial}{\partial q_k} \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}, q_i) \phi_j^{\text{dftb2}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (\text{B4})$$

This is already implemented, where as for DFTB3, the DFTB basis function is also dependent on the charge, and the integral derivative is thus different:

$$\frac{\partial M_{ij}}{\partial q_k} = f(R_{ij}) \frac{\partial}{\partial q_k} \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}, q_i) \phi_j^{\text{dftb3}}(\mathbf{r}', q_j)}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \quad (\text{B5})$$

Looks like this derivative is wrongly (or not at all) implemented.