1. Notation

Summation over atom centers is denoted by summation over indices a, b, c, etc. Summation over AO-basis functions is denoted by summation over indices such as μ, ν, etc. The notation "$\mu \in a$" means that the basis function μ is centered on the atom a.

In the following sections we let q_a be the *Mulliken population* (always a strictly positive quantity), defined as:

$$q_a = \sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu \nu} \tag{1.1}$$

The charge fluctuation is then:

$$\Delta q_a = q_a - q_a^0 \tag{1.2}$$

All the equations are presented for DFTB2, but the presented derived terms are the same for DFTB3, since the extra DFTB3 energy terms are additive.

2. DFTB2/CPE energy

2.1 CPE energy

The CPE energy is given by:[1]

$$E_{\text{cpe}} = \mathbf{c}^T \cdot \mathbf{M} \cdot \mathbf{q} + \frac{1}{2} \mathbf{c}^T \cdot \mathbf{N} \cdot \mathbf{c}, \tag{2.1}$$

where the first order CPE-DFTB2 Coulomb interaction matrix elements are given by:

$$M_{ij} = f(R_{ij}) \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}) \phi_j^{\text{dftb2}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{2.2}$$

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

$$N_{ij} = \iint \frac{\phi_i^{\text{cpe}}(\mathbf{r}) \phi_j^{\text{cpe}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \tag{2.3}$$

The CPE basis functions depend on the Mulliken population, 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. 2.1 is given (analytically) by:

$$\mathbf{c} = -\mathbf{N}^{-1} \cdot \mathbf{M} \cdot \mathbf{q} \tag{2.4}$$

Using the above relation, the CPE energy can be recast into:

$$
\begin{aligned}
E_{\text{cpe}} &= \mathbf{c}^T \cdot \mathbf{M} \cdot \mathbf{q} + \frac{1}{2} \mathbf{c}^T \cdot \mathbf{N} \cdot \mathbf{c} & (2.5) \\
&= -(\mathbf{N}^{-1} \cdot \mathbf{M} \cdot \mathbf{q})^T \cdot \mathbf{M} \cdot \mathbf{q} + \frac{1}{2} + (\mathbf{N}^{-1} \cdot \mathbf{M} \cdot \mathbf{q})^T \cdot \mathbf{N} \cdot (\mathbf{N}^{-1} \cdot \mathbf{M} \cdot \mathbf{q}) & (2.6) \\
&= -(\mathbf{N}^{-1} \cdot \mathbf{M} \cdot \mathbf{q})^T \cdot \mathbf{M} \cdot \mathbf{q} + \frac{1}{2} (\mathbf{N}^{-1} \cdot \mathbf{M} \cdot \mathbf{q})^T \cdot \mathbf{M} \cdot \mathbf{q} & (2.7) \\
&= -\frac{1}{2} (\mathbf{N}^{-1} \cdot \mathbf{M} \cdot \mathbf{q})^T \cdot \mathbf{M} \cdot \mathbf{q} & (2.8)
\end{aligned}
$$

2.2 DFTB2 energy

The DFTB2 energy is given by:[2]

$$E_{\text{dftb2}} = \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H_{\mu\nu}^0 + \frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab} + \frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}} \qquad (2.9)$$

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

$$H_{\mu\nu}^{(\text{dftb2})} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_c (\gamma_{ac} + \gamma_{bc}) \Delta q_c \qquad (2.10)$$

2.3 Combined DFTB2/CPE energy

The full DFTB2/CPE energy is given by:

$$
\begin{aligned}
E_{\text{dftb2/cpe}} &= \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H_{\mu\nu}^{(\text{dftb2})} + \frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}} + E_{\text{cpe}} \\
&= \underbrace{\sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H_{\mu\nu}^0}_{E_{\text{H0}}} + \underbrace{\frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab}}_{E_\gamma} + \underbrace{\frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}}}_{E_{\text{rep}}} + E_{\text{cpe}} \qquad (2.11) \\
&= E_{\text{H0}} + E_\gamma + E_{\text{rep}} + E_{\text{cpe}} \qquad (2.12)
\end{aligned}
$$

The CPE Hamiltonian shift is given by:[3]

$$\Delta H_{\mu\nu}^{(\text{cpe})} = \frac{1}{2} S_{\mu\nu} \left(\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} + \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_b} \right) \qquad \mu \in a, \nu \in b \qquad (2.13)$$

Note that here q_a and q_b are the Mulliken populations. Giese and York (2012) give the derivative in terms of the Mulliken charge and differ by a sign. See Appendix A for details.

The occupied orbital energies is given in the terms of the (optimized) coefficients and the matrix elements mentioned previously:

$$
\begin{aligned}
\sum_i^{\text{occ}} n_i \varepsilon_i &= \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H_{\mu\nu} \\
&= \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} \left(H_{\mu\nu}^{(\text{dftb2})} + \Delta H_{\mu\nu}^{(\text{cpe})} \right) \\
&= \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H_{\mu\nu}^0 + \frac{1}{2} \sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu\nu} \sum_c (\gamma_{ac} + \gamma_{bc}) \Delta q_c \\
&\quad + \frac{1}{2} \sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu\nu} \left(\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_a} + \frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial q_b} \right) \qquad (2.14)
\end{aligned}
$$

Using the relation above, the energy can be calculated in terms of the orbital energies (as implemented in CHARMM), by isolating E_{H0} in Eqn. 2.14 and inserting into Eqn. 2.12.

$$
\begin{aligned}
E_{\text{dftb2/cpe}} \;=\; & \sum_i^{\text{occ}} n_i \varepsilon_i - \frac{1}{2}\sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu \nu} \sum_c \left(\gamma_{ac} + \gamma_{bc}\right)\Delta q_c \\
& \underbrace{- \frac{1}{2}\sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu \nu} \left(\frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_a} + \frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_b}\right)}_{E_{\text{shift}}} \\
& + \frac{1}{2}\sum_{ab} \Delta q_a \Delta q_b \gamma_{ab} + \frac{1}{2}\sum_{ab} V_{ab}^{\text{rep}} + E_{\text{cpe}} \qquad (2.15)
\end{aligned}
$$

The E_{shift} must be subtracted from the electronic energy to compensate for double counting when adding E_{cpe} to the electronic energy in terms of the occupied orbital energies.

The following relation is useful:

$$
\begin{aligned}
E_{\text{shift}} \;=\; & -\frac{1}{2}\sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu \nu} \left(\frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_a} + \frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_b}\right) \\
\;=\; & -\frac{1}{2}\sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu \nu} \frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_a} \\
& -\frac{1}{2}\sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu \nu} \frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_b} \\
\;=\; & -\sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu \nu} \frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_a} \\
\;=\; & -\sum_a \frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_a} q_a \qquad (2.16)
\end{aligned}
$$

Using the above relation, the DFTB2/CPE energy can be simplified to:

$$
E_{\text{dftb2/cpe}} = \sum_i^{\text{occ}} n_i \varepsilon_i - \frac{1}{2}\sum_{ab}\left(q_a + q_a^0\right)\Delta q_b \gamma_{ab} - \sum_a \frac{\partial E_{\text{cpe}}\left[\mathbf{q},\mathbf{c}\right]}{\partial q_a} q_a + E_{\text{cpe}} \qquad (2.17)
$$

3. DFTB2/CPE energy gradient

The energy gradient is the derivative of the energy with respect to the nuclear coordinates under the following constraint:[4]

$$-F_{kx} = \frac{\partial}{\partial R_{kx}} \left[E_{\text{dftb2/cpe}} - \sum_i^{\text{occ}} n_i \varepsilon_i \left(\sum_\mu \sum_\nu C_{\mu i} C_{\nu i} S_{\mu \nu} - 1 \right) \right] \tag{3.1}$$

Using the notation of Eq. 2.12, we can rewrite this as:

$$-F_{kx} = \frac{\partial}{\partial R_{kx}} \left[E_{\text{H0}} + E_\gamma + E_{\text{rep}} + E_{\text{cpe}} - \sum_i^{\text{occ}} n_i \varepsilon_i \left(\sum_\mu \sum_\nu C_{\mu i} C_{\nu i} S_{\mu \nu} - 1 \right) \right] \tag{3.2}$$

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

$$
\begin{aligned}
-F_{kx} &= \frac{\partial}{\partial R_{kx}} \left[E_{\text{H0}} + E_\gamma + E_{\text{rep}} + E_{\text{cpe}} - \sum_i^{\text{occ}} n_i \varepsilon_i \left(\sum_\mu \sum_\nu C_{\mu i} C_{\nu i} S_{\mu \nu} - 1 \right) \right] \\
&= \underbrace{\frac{\partial}{\partial R_{kx}} \left[E_{\text{H0}} + E_\gamma + E_{\text{rep}} - \sum_i^{\text{occ}} n_i \varepsilon_i \left(\sum_\mu \sum_\nu C_{\mu i} C_{\nu i} S_{\mu \nu} - 1 \right) \right]}_{\text{Same as the DFTB2 gradient}} + \frac{\partial}{\partial R_{kx}} E_{\text{cpe}} \\
&= -F_{kx}^{(\text{dftb2})} + \frac{\partial E_{\text{cpe}}}{\partial R_{kx}}
\end{aligned}
\tag{3.3}
$$

The last term is new, and is presented in the next sections.

3.1 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 population:

$$
\begin{aligned}
-F_{kx}^{(\text{cpe})} &= \frac{\partial E_{\text{cpe}} (R_{kx})}{\partial R_{kx}} \\
&= \sum_i \frac{\partial E_{\text{cpe}} (\mathbf{q}, c_i(R_{kx}))}{\partial c_i} \frac{\partial c_i(R_{kx})}{\partial R_{kx}} + \sum_a \frac{\partial E_{\text{cpe}} (q_a(R_{kx}), \mathbf{c})}{\partial q_a} \frac{\partial q_a(R_{kx})}{\partial R_{kx}} + \frac{\partial E_{\text{cpe}} [\mathbf{q}, \mathbf{c}]}{\partial R_{kx}}
\end{aligned}
\tag{3.4}
$$

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

3.1.1 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.) - i.e. the derivatives with respect to the Mulliken populations. In the CPE charge-independent case:

$$\frac{\partial E_{\text{cpe}} [\mathbf{q}, \mathbf{c}]}{\partial q_a} = [\mathbf{c^T} \cdot \mathbf{M}]_a \tag{3.5}$$

And in the CPE charge-dependent case:

$$\frac{\partial E_{\text{cpe}} [\mathbf{q}, \mathbf{c}]}{\partial q_a} = \mathbf{c^T} \cdot \left(\frac{\partial \mathbf{M}}{\partial q_a} \right) \cdot \mathbf{q} + [\mathbf{c^T} \cdot \mathbf{M}]_a + \frac{1}{2} \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{N}}{\partial q_a} \right) \cdot \mathbf{c}. \tag{3.6}$$

4

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

$$\frac{\partial q_{a \neq k}}{\partial R_{kx}} = \sum_i^{\text{occ}} n_i \sum_{\mu \in a} \sum_{\nu \in k} C_{\mu i} C_{\nu i} \frac{\partial S_{\mu \nu}}{\partial R_{kx}} \tag{3.7}$$

or for $a = k$:

$$\frac{\partial q_k}{\partial R_{kx}} = \sum_i^{\text{occ}} n_i \sum_{\mu \in k} \sum_{\nu \notin k} C_{\mu i} C_{\nu i} \frac{\partial S_{\mu \nu}}{\partial R_{kx}} \tag{3.8}$$

This term must be calculated in the DFTB2 gradient code, where the derivative of the overlap matrix is already being calculated.

3.1.2 (Explicit) dependence on R_{kx}

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

$$\frac{\partial E_{\text{cpe}}[\mathbf{q}, \mathbf{c}]}{\partial R_{kx}} = \mathbf{c^T} \cdot \left(\frac{\partial \mathbf{M}}{\partial R_{kx}} \right) \cdot \mathbf{q} + \frac{1}{2} \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{N}}{\partial R_{kx}} \right) \cdot \mathbf{c}. \tag{3.9}$$

4. DFTB2 electric field contribution

The energy in an electric field $\vec{F}$ is given by the interaction of the field with the Mulliken charges (here in terms of the Mulliken populations):

$$E_{\text{EF/dftb2}} = \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H_{\mu\nu}^0 + \frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab} + \frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}} + \underbrace{\sum_a q_a \, \vec{F} \cdot \vec{r}_a}_{\Delta E_{\text{EF/dftb2}}} \qquad (4.1)$$

First we note the following relation:

$$\frac{\partial \Delta E_{\text{EF/dftb2}}}{\partial q_a} = \frac{\partial}{\partial q_a} \sum_{a'} q_{a'} \, \vec{F} \cdot \vec{r}_{a'} = \vec{F} \cdot \vec{r}_a \qquad (4.2)$$

Combining the above with Eq. A4, the corresponding Hamiltonian element to be added to the DFTB2 Hamiltonian element is given by:

$$\begin{aligned}
\Delta H_{\mu\nu}^{(\text{EF/dftb2})} &\equiv \frac{\partial \Delta E_{\text{EF/dftb2}}}{\partial \rho_{\mu\nu}} \\
&= \sum_a \frac{\partial \Delta E_{\text{EF/dftb2}}}{\partial q_a} \frac{\partial q_a}{\partial \rho_{\mu\nu}} \\
&= \frac{1}{2} S_{\mu\nu} \left(\vec{r}_a + \vec{r}_b \right) \cdot \vec{F} \qquad \mu \in a, \nu \in b
\end{aligned} \qquad (4.3)$$

So the matrix elements of the DFTB2 Hamiltonian matrix in the presence of an electric field are:

$$H_{\mu\nu} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum_c \left(\gamma_{ac} + \gamma_{bc} \right) \Delta q_c + \frac{1}{2} S_{\mu\nu} \left(\vec{r}_a + \vec{r}_b \right) \cdot \vec{F} \qquad \mu \in a, \nu \in b \qquad (4.4)$$

The DFTB2 energy in an electric field has the following orbital energies:

$$\begin{aligned}
\sum_i^{\text{occ}} n_i \varepsilon_i &= \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H_{\mu\nu} \\
&= \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} \left(H_{\mu\nu}^{(\text{dftb2})} + \Delta H_{\mu\nu}^{(\text{EF/dftb2})} \right) \\
&= \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H_{\mu\nu}^0 + \frac{1}{2} \sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu\nu} \sum_c \left(\gamma_{ac} + \gamma_{bc} \right) \Delta q_c \\
&\quad + \frac{1}{2} \sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu\nu} \left(\vec{r}_a + \vec{r}_b \right) \cdot \vec{F}
\end{aligned} \qquad (4.5)$$

Isolating H_0 in the above and inserting into Eq. 4.1 the DFTB2 energy in the presence of an external field is written in terms of the orbital energies:

$$\begin{aligned}
E_{\text{EF/dftb2}} &= \sum_i^{\text{occ}} n_i \varepsilon_i - \frac{1}{2} \sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu\nu} \sum_c \left(\gamma_{ac} + \gamma_{bc} \right) \Delta q_c \\
&\quad - \frac{1}{2} \sum_i^{\text{occ}} n_i \sum_a \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu\nu} \left(\vec{r}_a + \vec{r}_b \right) \cdot \vec{F} + \frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}} + \sum_a q_a \, \vec{F} \cdot \vec{r}_a \\
&= \sum_i^{\text{occ}} n_i \varepsilon_i - \frac{1}{2} \sum_{ab} \left(q_a + q_a^0 \right) \Delta q_b \gamma_{ab} + \frac{1}{2} \sum_{ab} V_{ab}^{\text{rep}}
\end{aligned} \qquad (4.6)$$

So no terms have to be added to the energy expressed in terms of the orbital energies.

4.1 DFTB2 dipole moment

The dipole moment of a molecule is given by the DFTB Mulliken populations:

$$\vec{\mu}^{(dftb2)} = \sum_a q_a \ \vec{r}_a \tag{4.7}$$

5. DFTB2/CPE electric field contribution

$$
\begin{aligned}
E_{\text{EF/dftb2/cpe}} \quad = \quad & \sum_i^{\text{occ}} n_i \sum_\mu \sum_\nu C_{\mu i} C_{\nu i} H^0_{\mu\nu} + \frac{1}{2} \sum_{ab} \Delta q_a \Delta q_b \gamma_{ab} + \frac{1}{2} \sum_{ab} V^{\text{rep}}_{ab} + \sum_a q_a \ \vec{F} \cdot \vec{r}_a \\
& + E_{\text{cpe}} + \underbrace{\sum_a \vec{F} \cdot \vec{\mu}^{(\text{cpe})}_a}_{E_{\text{EF/cpe}}}
\end{aligned}
\tag{5.1}
$$

where $\vec{\mu}^{(\text{cpe})}_a$ is the total dipole due to the CPE-basis functions centered on atom a, given by the coefficients to the same functions:

$$\vec{\mu}^{(\text{cpe})}_a = \begin{bmatrix} c_{ax} \\ c_{ay} \\ c_{az} \end{bmatrix} \tag{5.2}$$

where c_{ax} is the coefficient of the dipole function centered on atom a in the x-direction, and so on.

We can use the above definition of the dipole moment to show, that the Hamiltonian contribution due to the CPE-dipoles vanishes (due to the CPE-coefficients being optimized variationally.)

$$
\begin{aligned}
\Delta H^{(\text{EF/cpe})}_{\mu\nu} \quad &\equiv \quad \frac{\partial \Delta E_{\text{EF/cpe}}}{\partial \rho_{\mu\nu}} \\
&= \quad \sum_i \frac{\partial \Delta E_{\text{EF/cpe}}}{\partial c_i} \frac{\partial c_i}{\partial \rho_{\mu\nu}} = 0
\end{aligned}
\tag{5.3}
$$

Since no terms from the CPE basis/electric field interaction enter the Hamiltonian matrix, we can write the DFTB2/CPE energy in the presence of an external field in terms of the orbital energies as:

$$E_{\text{EF/dftb2/cpe}} = \sum_i^{\text{occ}} n_i \varepsilon_i - \frac{1}{2} \sum_{ab} \left(q_a + q^0_a \right) \Delta q_b \gamma_{ab} + \frac{1}{2} \sum_{ab} V^{\text{rep}}_{ab} - \sum_a \frac{\partial E_{\text{cpe}} \left[\mathbf{q}, \mathbf{c} \right]}{\partial q_a} q_a + E_{\text{cpe}} + \sum_a \vec{F} \cdot \vec{\mu}^{(\text{cpe})}_a \tag{5.4}$$

5.1 DFTB2/CPE dipole moment

The total dipole-moment of the molecule in the DFTB2/CPE description is now:

$$\vec{\mu}^{(dftb2/cpe)} = \sum_a q_a \ \vec{r}_a + \sum_a \vec{\mu}^{(\text{cpe})}_a \tag{5.5}$$

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6. DFTB2/CPE polarizability

The elements of the polarizability tensor is calculated as:

$$\alpha_{ij} = \left(\frac{\partial \mu_i}{\partial F_j}\right) \tag{6.1}$$

where i and j are the x, y, z Cartesian components and μ_i is the i-component of the DFTB2 or DFTB2/CPE dipole moment. The partial derivatives are calculated numerically by means of the two-point, forward-backtrack finite differences method.

The isotropic polarizability used in the fitting routine is calculated as:

$$\alpha_{\mathrm{iso}} = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \tag{6.2}$$

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[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.

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Appendices

A Hamiltonian shifts

A1 Mulliken population

First we define the density matrix is defined in terms of the coefficient matrix:

$$\rho_{\mu\nu} = \sum_i^{\text{occ}} n_i C_{\mu i} C_{\nu i} \tag{A1}$$

We can then define the Mulliken population by the density matrix:

$$
\begin{aligned}
q_a &= \sum_i^{\text{occ}} n_i \sum_{\mu \in a} \sum_b \sum_{\nu \in b} C_{\mu i} C_{\nu i} S_{\mu\nu} \\
&= \frac{1}{2} \sum_{\mu \in a} \sum_b \sum_{\nu \in b} \left(\rho_{\mu\nu} + \rho_{\nu\mu} \right) S_{\mu\nu}
\end{aligned} \tag{A2}
$$

The charge fluctuation is then:

$$\Delta q_a = q_a - q_a^0 \tag{A3}$$

Using these definitions we derive the following relation:

$$\frac{\partial q_a}{\partial \rho_{\mu\nu}} = \frac{\partial}{\partial \rho_{\mu\nu}} \left[\frac{1}{2} \sum_{\mu \in a} \sum_b \sum_{\nu \in b} \left(\rho_{\mu\nu} + \rho_{\nu\mu} \right) S_{\mu\nu} \right] = \begin{cases} \frac{1}{2} S_{\mu\nu} & \mu \in a \\ \frac{1}{2} S_{\mu\nu} & \nu \in a \\ S_{\mu\nu} & \mu \in a \quad \text{and} \quad \nu \in a \end{cases} \tag{A4}$$

Note that the *Mulliken population* is always a positive number, and the *Mulliken charge* is the negative of the Mulliken population.

A2 CPE Hamiltonian shift

Using the relation from section A1, the CPE Hamiltonian shift is calculated using the chain rule:

$$
\begin{aligned}
\Delta H_{\mu\nu}^{(\text{cpe})} &= \frac{\partial E_{\text{cpe}}\left[\mathbf{q}, \mathbf{c} \right]}{\partial \rho_{\mu\nu}} \tag{A5} \\
&= \sum_i \frac{\partial E_{\text{cpe}}\left[\mathbf{q}, \mathbf{c} \right]}{\partial c_i} \frac{\partial c_i}{\partial \rho_{\mu\nu}} + \sum_a \frac{\partial E_{\text{cpe}}\left[\mathbf{q}, \mathbf{c} \right]}{\partial q_a} \frac{\partial q_a}{\partial \rho_{\mu\nu}} \tag{A6} \\
&= \frac{1}{2} S_{\mu\nu} \left(\frac{\partial E_{\text{cpe}}\left[\mathbf{q}, \mathbf{c} \right]}{\partial q_a} + \frac{\partial E_{\text{cpe}}\left[\mathbf{q}, \mathbf{c} \right]}{\partial q_b} \right) \qquad \mu \in a, \nu \in b \tag{A7}
\end{aligned}
$$

Note that the last derivative is taken with respect to the Mulliken population. In Giese and York (2012) the negative sign is adopted.

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:

$$\frac{\partial E_{\text{cpe}}\left[\mathbf{q}, \mathbf{c} \right]}{\partial q_a} = [\mathbf{c}^{\mathbf{T}} \cdot \mathbf{M}]_a \tag{A8}$$

In the CPE charge-dependent case:

$$\frac{\partial E_{\text{cpe}}\left[\mathbf{q}, \mathbf{c} \right]}{\partial q_a} = \mathbf{c}^{\mathbf{T}} \cdot \left(\frac{\partial \mathbf{M}}{\partial q_a} \right) \cdot \mathbf{q} + [\mathbf{c}^{\mathbf{T}} \cdot \mathbf{M}]_a + \frac{1}{2} \mathbf{c}^T \cdot \left(\frac{\partial \mathbf{N}}{\partial q_a} \right) \cdot \mathbf{c}. \tag{A9}$$

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