Supplementary Information

Extended polarization in 2nd order SCC-DFTB from chemical potential equilization

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Content:

1. Implementation and Parametrization of charge dependent and independent CPE formalisms into DFTB2.
2. Performance of the CPE implementations.

Implementation and parametrization of the CPE formalism into DFTB2

The theory of 2nd order SCC-DFTB (DFTB2) is described in detail elswhere in the literature and will not be reviewed here. For related articles please refer to the list of references in the paper. The CPE formalism and implementation is described in detail in the related paper for 3rd order SCC-DFTB (DFTB3) and differ only in a few aspects for the DFTB2/CPE approach. Therefore, we will just focus on these differences here.

In contrast to DFTB3 (see Eq. (19) in the paper), the monopol Slater functions in the 2nd order code, describing charge density fluctuations, do not take derivatives of the Hubbard parameter into consideration and are written as

$$\varphi^{dftb2}(\mathbf{r}) = \frac{\tau_i^3}{8\pi} e^{-\tau_i|\mathbf{r}-\mathbf{R}_i|} \quad \text{with } \tau_i = \frac{16}{5} U_i \; . \tag{1}$$

Therefore, $\varphi^{dftb2}(\mathbf{r})$ becomes independent of the DFTB2 Mulliken charges. For DFTB2, two different types of the CPE methodology were implemented in this work. In the charge independent framework, which will be further abbreviated with CPE-indep, the exponent ζ of the CPE basis functions φ_i^{cpe} (compare to Eq. (18) in the paper) is defined as

$$\zeta = Z \cdot U_i \; , \tag{2}$$

where Z is a single fit parameter, valid for all atom types i. With this definition of ζ, the CPE basis functions also become independent of the atomic charges. As a consequence, the Coulomb integral expressions M and N (see Eq. (15) and Eq. (16) in the paper) do not change during DFTB2 SCF cycles and must therefore be calculated only once pre-SCF and stored.

In the second scheme, the ζ exponent is identical to the one used for DFTB3 (see Eq. (18) in the paper), where the CPE basis function exponent depends exponentially on the partial atomic charges. For this charge dependent implementation, which will be further abbreviated with CPE-qdep, the Coulomb integral expressions M and N depend explizitly on the DFTB2 Mulliken charges q_i, so they must be repeatedly calculated for each new SCC-DFTB SCF cycle.

Due to the fact M and N are independent of charge in the CPE-indep scheme, also the atom potentials p_i (see Eq. (25) in the paper) differ from the DFTB3/CPE framework and are written as

$$p_i = \frac{\partial E_{cpe}[\mathbf{q},\mathbf{c}]}{\partial q_i} = \mathbf{c} \cdot \mathbf{M} \, . \tag{3}$$

In the CPE-qdep framework, however, p_i is again identical to the one in the DFTB3/CPE approach. For both DFTB2/CPE methods (CPE-indep and CPE-qdep), the Hamilton matrix correction $\Delta H_{\mu\nu}$ remains unchanged compared to the one used for DFTB3/CPE (see Eq. (26) in the paper).

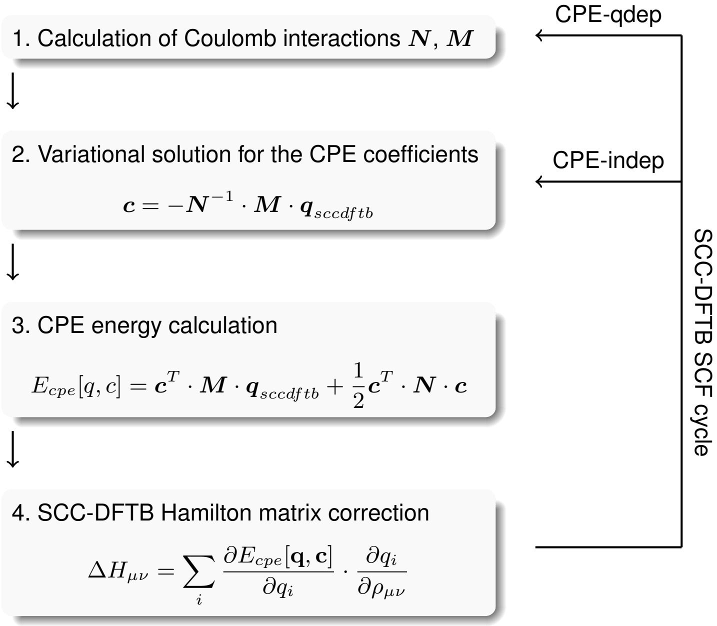

Figure 1: Schematic representation of the workflow in the charge dependent (CPE-indep) and independent (CPE-qdep) implementation of CPE into DFTB2.

Parametrization and performance of CPE for SCC-DFTB

For the parametrization of DFTB2, the same procedure was used as already described in the paper for DFTB3, however, with a reduced number of test molecules. Because phosphorus containing molecules can not be properly described in 2nd order, they were left out. This results in a set of overall 137 organic molecules which were either neutral (90) or monoanionic (27) or monocationic (20) respectively.

For the CPE-indep implementation, a set of overall 11 parameters were fitted against a subset of 90 neutral model compounds. For each atom type, a pair of distance paramerters $R_{i,l}$, $R_{i,u}$ for the switching function f (see Eq. (20) paper) and a single parameter Z for the CPE slater exponent 2 were used, valid for all atom types.

For the CPE-qdep approach, the entire set of 137 molecules including neutral and monoionic species were used for parameter evaluation, resulting in an overall number of 20 fit parameters to be determined.

Results

The optimized set of empirical parameters for both CPE implementations into DFTB2 are listed in Table 1 and Table 2.

Table 1: Optimized set of empirical fit parameters for the DFTB2/CPE-indep approach.

	$R_{i,l}$ (a.u.)	$R_{i,u}$ (a.u.)
H	0.74798218	1.50716590
C	2.49984840	2.95014640
O	2.19967670	2.30151040
N	6.98927950	7.20096220
S	8.22980390	124.963630
Z (a.u.): 6.92305060		

In Figure 2 to Figure 4, the results of polarizability calculations from the parametrized DFTB2/CPE-indep and DFTB2/CPE-qdep approaches are presented. Since these results are qualitatively in

Table 2: Optimized set of empirical fit parameters for the CPE-qdep approach.

	Z (a.u.)	B (a.u.)	$R_{i,l}$ (a.u.)	$R_{i,u}$ (a.u.)
H	2.77571090	1.56273240	1.16301160	1.70453510
C	2.66363440	1.00624210	1.87714180	2.40000000
O	5.02062920	1.51149370	2.08006730	2.55623820
N	3.15554870	0.88924465	6.00978630	6.20430960
S	2.91192320	1.13571690	16.1882790	145.718470

agreement with those from the DFTB3/CPE method and the degree of deviation from the DFT reference is very similar, we abstain from a detailed discussion of the DFTB2/CPE results at this point and refer the reader to the related paper.

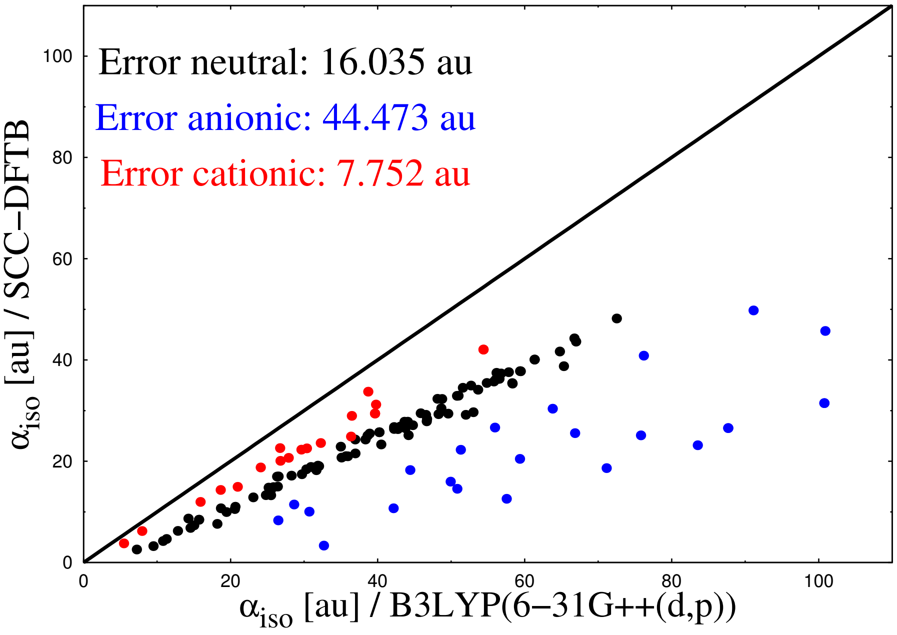

Figure 2: Comparison of calculated isotropic molecular polarizabilities from DFTB2 (scatter plot) and DFT/B3LYP (diagonal line) levels of theory. The color code denotes polarizabilities for either neutral (black), monocationic (red) or monoinaionic (blue) model compounds.

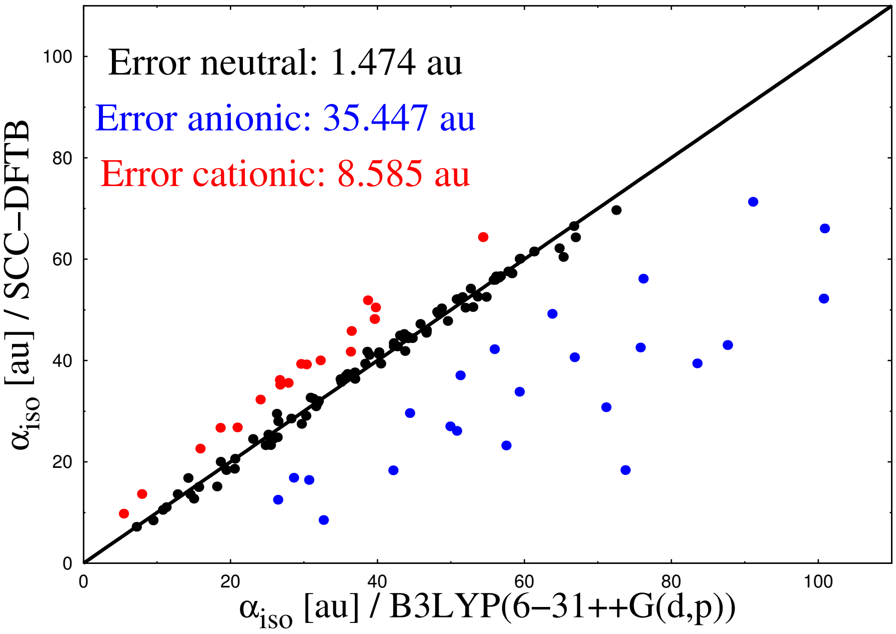

Figure 3: Comparison of calculated isotropic molecular polarizabilities from DFTB2/CPE-indep (scatter plot) and DFT/B3LYP (diagonal line) levels of theory. The color code denotes polarizabilities for either neutral (black), monocationic (red) or monoinaionic (blue) model compounds.

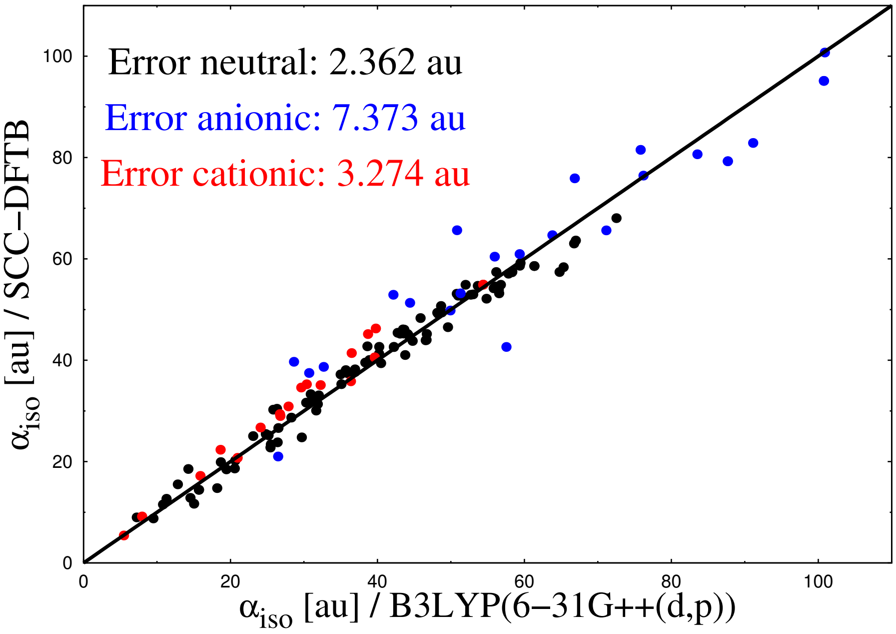

Figure 4: Comparison of calculated isotropic molecular polarizabilities from DFTB2/CPE-qdep (scatter plot) and DFT/B3LYP (diagonal line) levels of theory. The color code denotes polarizabilities for either neutral (black), monocationic (red) or monoinaionic (blue) model compounds.

The computational efficiency for both CPE frameworks (CPE-indep, CPE-qdep) is compared to the speed of the original DFTB2 implementation and illustrated in Figure 5. Here, single point calculations on four model compounds, i.e. carbon dioxide, uracil, anthracene and a retinal cofactor molecule ranging from 3 to 63 atoms were performed. For the largest system in the test, the retinal molecule, almost twice the cpu time is needed within the CPE-qdep framework, compared to CPE-indep and standard DFTB2, while the latter are almost equal in time requirements. For smaller compounds, the differences in time consumption are almost negligible. For larger systems, however, for example biomolecules or polymers, polarizability calculations with the more simple CPE-indep approach can save lots of computational cost, while delivering the same accuracy for polarizabilities for non-ionic molecules.

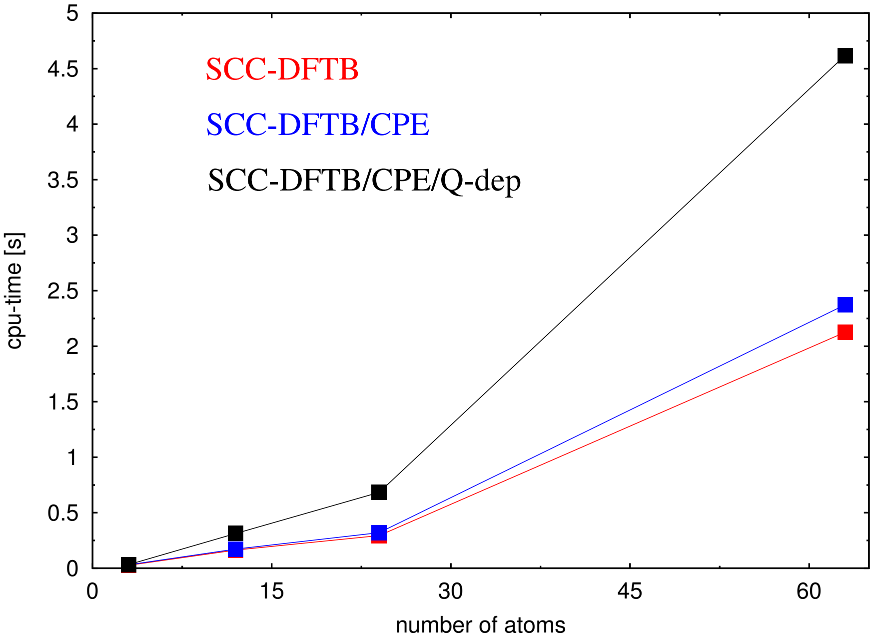

Figure 5: Benchmark calculations to estimate the computational cost of both CPE implementations relative to standard DFTB2.