SCC-DFTB: What Is the Proper Degree of Self-Consistency?[†]

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The approximate SCC-DFTB method (Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, Th.; Suhai, S.; Seifert, G. *Phys. Rev. B* **1998**, *58*, 7260) is derived from DFT by a second-order expansion of the total energy expression. In this article, basic approximations and assumptions underlying the DFTB method are discussed in detail, and further extensions to include third-order terms are proposed. Further, the SCC-DFTB and semiempirical NDDO formalisms are compared to elucidate similarities and differences.

Introduction

The non-self-consistent DFTB method, as introduced in refs 1 and 2, is an approximation to density functional theory (DFT) in a LCAO formulation.

G. Seifert[3] (this volume) reviews the underlying assumptions and approximations of the DFTB method in great detail; therefore, the following is only a brief introduction, necessary to understand the concepts behind the self-consistent charge (SCC) extension.

Consider a case where the ground-state density ρ_0 is known already to sufficient accuracy. In this case,[5] the self-consistent solution of the Kohn−Sham (KS) equations can be omitted. The KS orbitals are calculated by solving

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}[\rho_0]\right]\phi_i = \epsilon_i\phi_i \tag{1}$$

with the effective KS potential

$$v_{\text{eff}}[\rho_0] = \sum_\alpha \frac{Z_\alpha}{R_\alpha - r} + \int \frac{\rho_0(r)}{r}\,\mathrm{d}r + v_{\text{xc}}[\rho_0(r)] \tag{2}$$

Introduction of a LCAO basis set

$$\phi_i = \sum_\mu c_\mu^i \eta_\mu \tag{3}$$

and the Hamiltonian

$$\hat{H}(\rho_0) = \hat{T} + v_{\text{eff}}[\rho_0] \tag{4}$$

leads to the generalized eigenvalue problem

$$\sum_\mu c_\mu^i <\eta_\nu|\hat{H}[\rho_0]|\eta_\mu> = \epsilon_i \sum_\mu c_\mu^i <\eta_\nu|\eta_\mu> \tag{5}$$

which is usually solved using matrix diagonalization methods. Note that the DFTB method makes use of the overlap matrix

$$S_{\mu\nu} = <\eta_\mu|\eta_\nu>$$

which is calculated from the atomic orbitals. Nonorthogonal methods (i.e., those including the overlap matrix) are thought to be more robust and transferable compared to orthogonal methods, where the atomic orbitals are assumed to be orthogonal.

The DFTB Hamilton matrix elements calculated for the minimal LCAO basis set η_ν

$$H_{\mu\nu}^0 = <\eta_\mu|\hat{H}[\rho_0]|\eta_\nu>$$

are subject to several approximations, in particular a two-center approximation is applied, as discussed in the article of G. Seifert (in this volume).[3] $H_{\mu\nu}^0$ (the index 0 indicates the reference density ρ_0) and $S_{\mu\nu}$ are calculated once using an atomic DFT program and are tabulated. Therefore, that main computational cost of DFTB is the solution of the generalized eigenvalue problem, that is, the diagonalization of the Hamilton matrix.

The sum of the Kohn−Sham eigenvalues

$$E_{\text{el}} = \sum_i \epsilon_i \tag{6}$$

is only one part of the DFTB total energy; the second part represents the DFT double-counting contributions and core−core repulsion terms. These contributions are approximated as repulsive and pairwise potentials (between atoms α and β)

$$E_{\text{rep}} = \frac{1}{2}\sum_{\alpha\beta} U(R_{\alpha\beta}) \tag{7}$$

The total energy therefore reads

$$E_{\text{DFTB}} = \sum_i^{\text{occ}} \epsilon_i + \sum_{\alpha\beta} U(R_{\alpha\beta}) =$$
$$\sum_i^{\text{occ}}\sum_{\mu\nu} c_\mu^i c_\nu^i H_{\mu\nu}^0 + \frac{1}{2}\sum_{\alpha\beta} U(R_{\alpha\beta}) \tag{8}$$

This scheme is computationally very efficient, about 3 orders of magnitude faster than DFT calculations with medium-sized basis sets. Its accuracy is satisfactory for many applications;

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especially molecular geometries are comparable to those of DFT, but vibrational properties being slightly worse. Of course, the accuracy depends critically on the quality of the Hamilton matrix elements. Here, we focus on a different point, the limitations due to the non-self-consistent treatment of the KS equations. This approximation is expected to work satisfactorily when the ground-state density is close to the reference density ρ_0, a point discussed in detail by Foulkes and Haydock.[6] In DFTB, we choose ρ_0 as a superposition of the atomic densities of the neutral atoms in the system. Combination of atoms into a molecule leads primarily to a charge equilibration, that is, a charge flow between the atoms due to the different atomic electronegativities. This charge flow will stop when the electronegativities are equilibrated.[4] A second effect is that the atomic-like densities will change their shape. This is taken into account by the solution of the KS equations, that is, the diagonalization of the Hamilton matrix leads to a charge density in the non-self-consistent formalism, which represents the molecular charge density and is no more a superposition of spherical atomic charge densities.

Therefore, we expect the method to work when the system contains atoms with comparable electronegativities; typical examples are hydrocarbons.[1] Many other homo- and hetero-nuclear molecular systems have been approached successfully with DFTB, containing, for example, silicon, nitrogen, and other elements. Dramatic failures have been found when oxygen is present.[8] However, there is no clear limit for the use of the non-self-consistent method. Large electronegativity differences between the atoms of the system are an indicator, but the method does not necessarily fail here. Ionic systems like NaCl with large charge transfer between the atoms have been treated successfully with non-self-consistent methods (e.g., ref 7). Systems with intermediate charge transfer, where the electronegativity difference favors a significant charge transfer but the equilibration of electronegativities leads to a partial back-transfer, seem to be most problematic. This is often the case for biological and organic systems containing oxygen; therefore, a self-consistent scheme is usually required.

The effective Kohn—Sham potentials in the non-self-consistent case contain only the neutral reference density ρ_0, which does not account for charge transfer between atoms. To account for that, a simple (functional) expansion of the potential with the ground-state density ρ around the reference density ρ_0 leads to

$$v_{\text{eff}}[\rho] = v_{\text{eff}}[\rho_0] + \int \frac{\delta v_{\text{eff}}[\rho]}{\delta \rho} \delta \rho \mathrm{d}\vec{r} \quad (9)$$

The advantage of this perturbative approach is that it corrects the zero-order Hamilton matrix elements $H_{\mu\nu}[\rho_0]$, which depend on the reference density as above, by terms depending on the charge density fluctuation with respect to the reference density. Therefore, a self-consistent procedure based on such an expansion can use the formalism of the non-self-consistent method and has to take corrections into account only for the case of nonnegligible charge flow between the atoms.

Self-Consistent Charge (SCC) Extension of DFTB

Instead of expanding the potentials in the KS equations, it is more convenient to start from the DFT total energy by a second-order expansion[8] with respect to the charge density fluctuations $\delta \rho$ around a given reference density ρ_0

$$(\rho_0' = \rho_0(\vec{r}'), \smallint' = \smallint \mathrm{d}\vec{r}')$$

$$E = \sum_{i}^{\text{occ}} \langle \phi_i | \hat{H}^0 | \phi_i \rangle +$$

$$\frac{1}{2} \int \int' \left(\frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta\rho\delta\rho'} \bigg|_{n_0} \right) \Delta\rho\Delta\rho'$$

$$-\frac{1}{2} \int \int' \frac{\rho_0'\rho_0}{|\vec{r} - \vec{r}'|} + E_{\text{xc}}[\rho_0] - \int V_{\text{xc}}[\rho_0]\eta_0 + E_{\text{cc}} \quad (10)$$

After introducing the LCAO basis $\Psi_i = \sum c_\mu^i \eta_\mu$, the first term becomes

$$\langle \phi_i | \hat{H}^0 | \phi_i \rangle = \sum_{\mu\nu} c_\mu^i c_\nu^i H_{\mu\nu}^0$$

and can be evaluated as discussed above. The last four terms depend only on the reference density ρ_0 and represent (together with the core—core repulsion) the repulsive energy contribution E_{rep}, as discussed in the contribution of G. Seifert.[3]

The second-order term in the charge density fluctuations $\Delta\rho$ (the second term in eq 10) is approximated by writing $\Delta\rho$ as a superposition of atomic contributions

$$\Delta\rho = \sum_{\alpha} \Delta\rho_{\alpha}$$

To further simplify E^{2nd}, we apply a monopole approximation

$$\Delta\rho_{\alpha} \approx \Delta q_{\alpha} F_{00}^{\alpha} Y_{00} \quad (11)$$

F_{00}^{α} denotes the normalized radial dependence of the density fluctuation on atom α, which is constrained (approximated) to be spherical (Y_{00}), that is, the angular deformation of the charge density change in second order is neglected. Therefore, we only treat the charge-transfer effects but neglect the change in the shape of the charge density (with respect to the reference density) in the second-order expression. Note that this is partly taken care of in the first-order terms (see Introduction). The diagonalization of the Hamilton matrix describes this density shape change of the neutral atomic input densities, however, only in a non-self-consistent way. The second-order part becomes

$$E^{\text{2nd}} \approx$$

$$\frac{1}{2} \sum_{\alpha\beta} \Delta q_{\alpha} \Delta q_{\beta} \int \int' \left(\frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{\text{xc}}}{\delta\rho\delta\rho'} \bigg|_{n_0} \right) F_{00}^{\alpha} F_{00}^{\beta} Y_{00}^2 \quad (12)$$

This formula looks complicated but has a quite simple curve shape. For large distances, $R_{\alpha\beta} = |\vec{r} - \vec{r}'| \rightarrow \infty$, the XC terms vanish (in DFT-GGA), and the integral describes the coulomb interaction of two spherical normalized charge densities, which reduces basically to $1/R_{\alpha\beta}$, that is, we get

$$E^{\text{2nd}} \approx \frac{1}{2} \sum_{\alpha\beta} \frac{\Delta q_{\alpha} \Delta q_{\beta}}{R_{\alpha\beta}}$$

For a vanishing interatomic distance, $R_{\alpha\beta} = |\vec{r} - \vec{r}'| \rightarrow 0$, the integral describes the e—e interaction on atom α. We can approximate the integral as

$$E^{\text{2nd}} \approx \frac{1}{2} \frac{\partial^2 E_{\alpha}}{\partial^2 q_{\alpha}} \Delta q_{\alpha}^2 = \frac{1}{2} U_{\alpha} \Delta q_{\alpha}^2$$

U_{α} is known as the Hubbard parameter or the chemical hardness. It describes, how much the energy of a system changes upon the addition or removal of electrons. For SCC-DFTB, it is

calculated using Janak's theorem by taking the first derivative of the energy of the highest occupied molecular orbital with respect to occupation number.

The intermediate region of chemical bonding (1−3 Å), however, is not covered in these limits. It is therefore crucial to find a good way to interpolate between the limits since an explicit calculation of the integrals would be too costly. A very similar situation appears in semiempirical quantum chemical methods like MNDO, AM1, or PM3, where the interpolating function $\gamma_{\alpha\beta}$ has a simple form, as given, for example, by the Klopman−Ohno approximation

$$\gamma_{\alpha\beta} = \frac{1}{\sqrt{R_{\alpha\beta}^2 + 0.25(1/U_\alpha + 1/U_\beta)^2}} \qquad (13)$$

In a first version, this form was implemented into DFTB; however, the Ewald sum using this form exhibited convergence problems. Therefore, an analytic expression has been derived by approximating the charge density fluctuations with spherical charge densities.[8] Slater-like distributions

$$F_{00}^\alpha = \frac{\tau_\alpha}{8\pi}\exp(-\tau_\alpha|r - R_\alpha|) \qquad (14)$$

located at R_α allow for an analytical evaluation of the Hartree contribution of two spherical charge distributions. This leads to a function of $\gamma_{\alpha\beta}$, which depends on the parameters τ_α and τ_β, determining the extension of the charge densities of the atoms α and β. This function has a $1/R_{\alpha\beta}$ dependence for large $R_{\alpha\beta}$ and approaches a finite value for $R_{\alpha\beta} \rightarrow 0$. For $\alpha = \beta$, one finds that[8]

$$\tau_\alpha = \frac{16}{5}\gamma_{\alpha\alpha} \qquad (15)$$

Equation 15 implies that the extension of the charge distribution is inversely proportional to the chemical hardness of the respective atom, that is, the size of an atom is inversely related to its chemical hardness. By neglecting the effect of the chemical environment on atom α, the diagonal part of γ can be approximated by the chemical hardness η of the atom

$$\gamma_{\alpha\alpha} = 2\eta_\alpha = U_\alpha = \frac{\partial^2 E_\alpha}{\partial^2 q_\alpha} \qquad (16)$$

Using the interpolation formula $\gamma_{\alpha\beta}$, E^{2nd} becomes a simple two-body expression, depending on atomic-like charges (from a Mulliken population analysis)

$$E^{2nd} \approx \frac{1}{2}\sum_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \gamma_{\alpha\beta} \qquad (17)$$

With these definitions and approximations, the SCC-DFTB energy finally reads

$$E^{SCC} = \sum_{i\mu\nu} c_\mu^i c_\nu^i H_{\mu\nu}^0 + \frac{1}{2}\sum_{\alpha\beta} \gamma_{\alpha\beta}\Delta q_\alpha \Delta q_\beta + \frac{1}{2}\sum_{\alpha\beta} U[\rho_0^\alpha, \rho_0^\beta] \qquad (18)$$

The variational principle leads to a generalized eigenvalue problem like that in eq 5, which has to be solved iteratively for the wave function expansion coefficients c_μ^i since the Hamilton matrix elements depend on the c_μ^i due to the Mulliken charges $(\mu\epsilon\alpha, \nu\epsilon\beta)$

$$H_{\mu\nu}^{\alpha\beta} = H_{\mu\nu}^{0\alpha\beta} + \frac{1}{2}S_{\mu\nu}^{\alpha\beta}\sum_\delta \Delta q_\delta(\gamma_{\alpha\delta} + \gamma_{\beta\delta}) \qquad (19)$$

The two-body contributions $U[R_{\alpha\beta}]$ are determined by comparison of the energy according to eq 18 with that from full DFT calculations with respect to the interatomic distance $R_{\alpha\beta}$ of the atoms α and β (see refs 3 and 9). The resulting energy curve $U[R_{\alpha\beta}]$ is then analytically represented by splines. The determination of repulsive potentials for organic molecules has been reviewed briefly recently.[9]

Let's recall the basic assumptions in the SCC approximations. (1) The starting (input) density is generated from a superposition of spherical atomic densities (neutral atoms). The density change from this reference density is described by the first-order terms, by diagonalization of $H_{\mu\nu}^{0\alpha\beta}$ in a non-self-consistent way. At the second order, due to the monopole approximation, only the net charge flow between the atoms is treated self-consistently. Higher multipole terms in the interaction of the difference density $\Delta\rho$ are neglected at second order but included in first order partially by $\sum_{i\mu\nu} c_\mu^i c_\nu^i H_{\mu\nu}^0$.

(2) The monopole interaction in second order is approximated by the interaction of point charges, where the effects of charge overlap, exchange, and correlation are taken into account effectively by the function $\gamma_{\alpha\beta}$. This function is derived from the interaction of two spherical charge densities. It interpolates between the two limiting cases, the $1/R$ dependence of the interaction for large interatomic distances and the on-site electron−electron repulsion, which is (for the neutral atom) given by the chemical hardness (Hubbard) parameter U_α. The limiting case for $R = 0$, $\gamma_{\alpha\alpha} = U_\alpha^{Hartree}$, however, is derived only for the Hartree part of the electron−electron interaction. Practically, U_α contains also the exchange correlation (XC) part, U_α^{XC}. Therefore, by using $U_\alpha = U_\alpha^{Hartree} + U_\alpha^{XC}$ in $\gamma_{\alpha\beta}$ for $R \neq 0$, we extrapolate the XC contributions into the binding region.

(3) The shape of $\gamma_{\alpha\beta}$ is, to some degree, arbitrary; one could use the Klopman−Ohno form, as discussed above, or the Mataga−Nishimoto form

$$\gamma_{\alpha\beta} = \frac{1}{R_{\alpha\beta} + 0.5(1/U_\alpha + 1/U_\beta)} \qquad (20)$$

Both forms are used in the common semiempirical methods. They differ in the intermediate region between 1 and 3 Å, with DFTB-γ being more repulsive than Klopman−Ohno being more repulsive than Mataga−Nishimoto. This has influence, for example, on excited states or on hydrogen-bonding energies. The Klopman−Ohno scaling in DFTB leads to weaker H-bonding energies by roughly 1 kcal/mol. However, none of the functions is a priori the best.

(4) The form of $\gamma_{\alpha\beta}$ has the inverse relationship between U_α and the size of the atomic charge distribution, τ_α, built in. While, for $R = 0$, $\gamma_{\alpha\alpha}$ is a parameter defining the on-site electron−electron interaction, for $R \neq 0$, it has a very different function (interpretation); it is the inverse size of the atom. Therefore, the chemical hardness values are used in DFTB to estimate the atomic sizes. The coulomb interaction will be smaller for larger atoms and larger for smaller; this can be seen easily from the Klopman−Ohno and Mataga−Nishimoto forms. The same holds for the DFTB γ.

(5) Due to the second-order approximation, the chemical hardness parameter is a constant for every atom type. In

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particular, it does not change with the charge state of the atom. The on-site interaction U is the same for the neutral and charged atom, and the form of γ is also independent of the charge state.

Comparison to Semiempirical Methods

The DFTB formalism is often compared to other semiempirical methods. These methods are discussed in terms of Fock matrix elements, which can be compared to the DFTB Hamilton matrix elements in eq 19.

To make the similarities and differences more obvious, we derive them in an alternative way using the expansion of the KS potentials in eqs 9 and 2

$$H_{\mu\nu}^{\alpha\beta} = <\mu|T + v_{\text{eff}}[\rho]|\nu>$$

$$= <\mu|T + v_{\text{eff}}[\rho_0]|\nu> + <\mu|\int \frac{\delta v_{\text{eff}}[\rho]}{\delta\rho}\delta\rho dr|\nu>$$

$$\approx H_{\mu\nu}^{0\alpha\beta} = <\mu|\int\frac{\delta\rho(r)}{r}dr|\nu> + <\mu|\delta v_{\text{xc}}[\rho]|\nu> \quad (21)$$

Using the density matrix $P_{\delta\sigma}$, we write the density as

$$\rho = \sum_{\delta\sigma} P_{\delta\sigma}\eta_\delta^*\eta_\sigma \quad (22)$$

Similarily, we can represent the density ρ_0 using $P_{\delta\sigma}^0$, and defining $\delta P_{\delta\sigma} = P_{\delta\sigma} - P_{\delta\sigma}^0$, we can write

$$\delta\rho = \sum_{\delta\sigma}\delta P_{\delta\sigma}\eta_\delta^*\eta_\sigma \quad (23)$$

This leads to the SCC-DFTB matrix elements

$$H_{\mu\nu}^{\alpha\beta} = H_{\mu\nu}^{0\alpha\beta} + \sum_{\delta\sigma}\delta P_{\delta\sigma} <\mu\nu|\delta\sigma> + <\mu|\delta v_{\text{xc}}[\rho]|\nu> \quad (24)$$

For NDDO methods, the Fock matrix elements are

$$F_{\mu\nu}^{\alpha\beta} = h_{\mu\nu}^{\alpha\beta} + g_{\mu\nu}^{\alpha\beta} \quad (25)$$

with the one-electron integrals

$$h_{\mu\nu}^{\alpha\beta} = <\mu|T|\nu> - <\mu|\sum_\gamma \frac{Z_\gamma}{r_{i\gamma}}|\nu> \quad (26)$$

and the two-electron integrals

$$g_{\mu\nu}^{\alpha\beta} = \sum_{\sigma\delta} P_{\sigma\delta}\left(<\mu\nu|\sigma\delta> - \frac{1}{2}<\mu\sigma|\nu\delta>\right) \quad (27)$$

In the following, a comparison is presented.

First of all, the main difference is that DFTB makes use of the overlap matrix, while most popular semiempirical methods are orthogonal methods (except, e.g., the OMx methods developed by W. Thiel and co-workers; see ref 10).

Despite this, DFTB and NDDO matrix elements look quite similar; one could identify $h_{\mu\nu}^{\alpha\beta}$ with $H_{\mu\nu}^{0\alpha\beta}$ and the explicit two-electron integrals in DFTB with $g_{\mu\nu}$. On that basis, DFTB looks very much like CNDO since both methods apply a monopole approximation to the two-electron Coulomb interactions $<\mu\nu|\sigma\delta>$, using a function $\gamma_{\alpha\beta}$ to describe the deviation from the Coulomb law for short distances. Both methods implicitly include XC effects in that function, DFTB by calculating the chemical hardness values and CNDO by fitting them to

experimental data. The reduction of the Coulomb interactions due to the use of the γ function is seen as an effective way to include dynamical correlation in NDDO methods.[12]

NDDO methods, however, do not contain correlation effects explicitly; their functional form is determined by the Hartree−Fock method, and correlation is covered due to the parametrization process, while DFTB includes correlation effects explicitly due to its descent from DFT in the one-electron Hamiltonian (matrix elements $H_{\mu\nu}^0$) by construction.

However, these similarities are only at the first sight since $h_{\mu\nu}$ and $H_{\mu\nu}^0$ are fundamentally different. While the first one is a true one-electron term, the DFTB core Hamiltonian contains the full two-electron part, however, evaluated at the reference density. For systems without significant charge transfer, the DFTB description is complete with this term, while the NDDO methods have to include the $g_{\mu\nu}$ terms as well. For systems with vanishing charge transfer, DFTB is essentially a non-self-consistent method, while the NDDO methods always evaluate the electron−electron interaction self-consistently.

Therefore, the starting point to include the two-electron integrals is fundamentally different; DFTB adds them as a perturbation to treat the charge density fluctuations, while in the NDDO methods, these terms cover the complete e−e interaction. Clearly, MNDO treats these integrals much more accurately by modeling higher multipole moments of the interacting charge distributions, while DFTB stops at the monopole term like CNDO. However, DFTB multiplies the simplified Coulomb interaction only with $\delta P_{\delta\sigma}$ since the e−e interaction for the neutral reference system is already covered in $H_{\mu\nu}^0$.

Summarizing, although formally similar, DFTB should not be compared directly with CNDO- or NDDO-type methods since the foundations are very different. Similar looking terms have a completely different meaning and formal origin!

A similar comment applies when comparing DFTB to (extended) Hückel Theory (EHT). Both methods look formally similar at the first sight, but there is, of course, a large difference in the determination of the matrix elements. EHT (as well as CNDO) can be derived from DFTB through further simplifications/approximations. The most striking (formal) similarity of SCC-DFTB is to the Fenske Hall scheme,[11] which has matrix elements nearly identical to those of DFTB eq 19.

In DFTB, the parametrization effort is clearly N^2 across the periodic table since parameters for atom pairs have to be calculated. However, the calculation of the matrix elements is not very time-consuming. The more involved part is the determination of the two-body potentials for the repulsive energy. This approximates the last line in eq 10; neglecting the XC contributions for a moment, we have

$$-\frac{1}{2}\int\int'\frac{\rho_0'\rho_0}{|\vec{r} - \vec{r}'|} + E_{\text{cc}} \quad (28)$$

The two contributions cancel each other for long distances. The first term therefore can be approximated by the function $\gamma_{\alpha\beta}$, leading to

$$-\frac{1}{2}\sum_{\alpha\beta}Z_\alpha Z_\beta\gamma_{\alpha\beta} + \frac{1}{2}\sum_{\alpha\beta}Z_\alpha Z_\beta/R_{\alpha\beta} \quad (29)$$

These terms can, of course, be cast into a form that they contain only atomic parameters, similar to the situation in the NDDO methods. However, the good performance of DFTB for geometries and vibrational frequencies is partly due to a very careful

treatment of E_{rep}. Further, the parametrization effort may only be reduced at the cost of accuracy. Consider the situation with four different atom types A, B, C, and D. We determine the atomic parameters by fitting atoms A and B for molecular properties and do the same, independently, for C and D. Then, all atomic parameters would be determined, and systems with bonds between B and C could be treated. However, it can be expected that the accuracy for the B–C interactions would be much better when having those compounds in the fitting set. At the end, the interaction of all relevant atom pairs has to be considered in the parametrization process, irrespective of whether the method contains only atomic parameters or also parameters for atom pairs, as DFTB does.

Performance of SCC-DFTB for Organic and Biological Molecules

A summary of the performance of DFTB for organic and biological molecules can be found in ref 9; therefore, we will give only a brief update for completeness.

In ref 13, the deviation of DFTB with respect to G2 for 28 reactions of O-, N-, C-, and H-containing molecules was found to be 4.3 kcal/mol. A more comprehensive study of Jorgensen and co-workers[15] calculated the heats of formation of a large set of organic molecules. The mean average error of 5.8 kcal/mol of DFTB is lower than that of AM1 (6.8 kcal/mol) but higher than that of PM3 (4.4 kcal/mol) and PDDG-PM3 (3.2 kcal/mol).

The current DFTB method shows a slight overbinding, as pointed out by the work of Thiel and co-workers.[10] This leads, of course, to increasing errors in heats of formation for increasing molecule sizes.

The strength of DFTB is the good description of molecular structures.[9,13,14,15] Also relative energies, for example, of polypeptides, are reproduced quite well, on average.[17] In this case, the overbinding is not problematic since similar structures are compared and only energy differences for different conformations are calculated.

Vibrational frequencies have been significantly improved by using a special parametrization of the repulsive potential.[16] This work has employed a more sophisticated parametrization scheme using experimental data rather than DFT calculations on selected reference molecules. Current work explores different strategies for a more extensive use of experimental data since the much simpler former parametrization approaches did not fully exploit the methodological flexibility and capability of DFTB. In this way, an improvement in energies and frequencies seems to be possible.

Since DFTB is an approximation to DFT, it inherits also the well-known shortcomings of current DFT-GGA functionals.[9] This concerns the DFT-GGA problem of over-polarizability in extended conjugated systems,[18] the problem of excited charge-transfer states, and the problem of van der Waals interactions. The latter problem is tackled in DFTB in an ad hoc way by adding empirical dispersion correction to the total energy.[19]

The Role of the Gamma Function

Any semiempirical method using a Coulomb scaling function like the Klopman–Ohno (KO) (eq 13) or Matagan–Nishimoto (MN) (eq 20) forms or the DFTB form as proposed in ref 8 assumes the inverse relationship of atomic size and chemical hardness. In the MN and KO forms, the chemical hardness determines the limiting value for small interatomic distances, that is, introducing the damping of the Coulomb law due to overlap. In the DFTB formulation, we get a quantitative estimate

TABLE 1: The Covalent Radii r_{cov} (Å) Estimated by Politzer et al.[23] (First Three Lines), Calculated Atomic Radii from Gosh and Biswas,[22] Calculated Hubbard Parameters Used in DFTB (U_H), and Experimental (U_H^{exp}) Hubbard Parameters (in H)

	H	C	N	O	F	Si	P	S	Cl
r_{cov}									
with H		0.70	0.65	0.62	0.59	1.00	0.96	0.91	0.59
with first row	0.37	0.74	0.72	0.70	0.69	0.96	0.97	0.98	0.97
with second row	0.46	0.82	0.77	0.74	0.69	1.09	1.08	1.03	1.00
Gosh/Biswas	0.53	0.65	0.54	0.46	0.41	1.15	0.99	0.87	0.78
U_H	0.42	0.36	0.43	0.50	0.59	0.25	0.29	0.33	0.37
U_H^{exp}	0.47	0.37	0.53	0.45	0.52	0.25	0.36	0.30	0.34

from eq 15. Therefore, the chemical hardness parameter has two functions in a semiempirical theory; the diagonal terms $\gamma_{\alpha\alpha}$ describe the electron–electron interaction of the atom, given by U_α, and for the two-center terms $\gamma_{\alpha\beta}$, the chemical hardness parameter is an estimate of the atomic size.

Pearson[20] suggested estimating the atomic chemical hardness value from a simple model, treating atoms as conducting spheres with radius R, yielding

$$2\eta = U = \frac{1}{R} \qquad (30)$$

Comparison with the MN and KO formulas suggests that these formulas use this relationship implicitly. Hati and Datta[21] used this relation to calculate chemical hardness values from experimental atomic polarizabilities, showing quite surprising correlation with experimental results.

Gosh and Biswas[22] calculated atomic radii corresponding to the principal maximum in the radial distribution function for 103 elements of the periodic table. Using eq 30, the computed chemical hardness values show, qualitatively, very nicely trends throughout the periodic table. Focusing on the first three rows, however, it turns out that the chemical hardness is overestimated by roughly a factor of 2 for most of the main group elements, while agreeing nicely for the metals.

In a recent work of Politzer and co-workers,[23] various sets of covalent radii have been examined, and an overall reasonable agreement between the different concepts has been found. Table 1 shows the covalent radii calculated by Politzer et al. in comparison with the atomic radii of Gosh as Biswas. Interesting is the finding that atomic radii predict the hydrogen atom to be larger than covalent radii, a finding discussed already by Politzer and coworkers.[23] Clearly, the atomic radii of hydrogen and, for example, nitrogen (Gosh and Biswas) are quite similar, which is also reflected in the similar chemical hardness values. The covalent radii, reflecting the size of hydrogen in chemical environments, is much smaller. Using the chemical hardness to estimate the size of hydrogen in molecules largely overestimates it.

Therefore, the determination of the size of an atom based on chemical hardness values will give at least reasonable ratios for main group elements but will overestimate the size (covalent radius) of hydrogen when compared to the other elements.

Since $\gamma_{\alpha\beta}$ approaches the value $\gamma_{\alpha\alpha} = U_\alpha$ at short distances, the poor relation between its size and the chemical hardness for H means that modifications have to be made for $\gamma_{\alpha\beta}$ for all X–H (X being heavy atoms) pairs. In principle, this could be done by modifying the value of U_H for hydrogen according to its atomic size, which would, however, make the on-site interaction on H, γ_{H-H}, inconsistent with its chemical hardness.

We propose to modify $\gamma_{\alpha\beta}$ in the intermediate region only, leaving the limiting cases at short and long interatomic distances

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unchanged. Specifically, $\gamma_{\alpha\beta}$ has the following form in the standard implementation of SCC-DFTB[8]

$$\gamma_{\alpha\beta} = \frac{1}{R_{\alpha\beta}} - S \qquad (31)$$

with S being a short-range function that leads to the desired limit for small interatomic distance. Since the hydrogen atom size according to $r_c = 5/(16U_H)$ is too large, the density overlap is overestimated; that is, the electronic interaction starts to deviate from $1/R_{\alpha\beta}$ too early. To correct for this, an additional damping term is added for the X−H pairs

$$\gamma_{\alpha H} = \frac{1}{R_{\alpha H}} - S \times \exp\left[-\left(\frac{U_\alpha + U_H}{2}\right)^\zeta R_{\alpha H}^2\right] \qquad (32)$$

This leads to a faster decay of $\gamma_{\alpha H}$, thereby taking into account the smaller size of the H atom according to its smaller covalent radius. This modification contains a single parameter, the exponent ζ, which can be fitted to appropriate reference systems.

The change of $\gamma_{\alpha H}$ leads to a stronger electrostatic interaction, that is, the bonds involving hydrogen are more polarized than those with the original γ function. In particular, it leads to consistently improved hydrogen binding interactions. With the original γ function, the binding energy of weakly hydrogen-bonded complexes is underestimated by about 1−2 kcal/mol per bond. The modified $\gamma_{\alpha H}$ increases the hydrogen-bonding strengths on average, leading to a rms error of less than 1 kcal/mol when compared to high-level ab initio calculations.[24] For example, standard SCC-DFTB yields a binding energy of 3.3 kcal/mol for the water dimer. Choosing $\zeta = 3.6$ in eq 32 increases this binding energy to 4.6 kcal/mol, which is close to the expected value of 5.0 kcal/mol.[25]

Higher-Order Terms in DFTB

The Hubbard parameters are assumed to be constant; in particular, they are independent of the atomic charge state. However, for positively charged atoms, U should become larger than in the neutral atom; larger U implies a smaller atomic size, relevant for the two-center part of γ and a stronger on-site interaction. For negatively charged atoms, a smaller U will lead to a larger atomic size and a reduced on-site interaction. Since U is the second derivative of the total energy, the change of U with charge on an atom is given by the third and higher-energy derivatives with respect to the charge (density).

The change of the (neutral atomic) chemical hardness parameters due to environmental factors can be estimated by their derivatives with respect to the atomic charge. These chemical hardness derivatives were determined by Fuentealba and Parr[26] from fitting to experimental data. Later on, Liu and Parr[27] proposed a formula for the orbital electronegativity and hardness values, which depend on orbital occupation numbers and the atomic number Z. These formulas result from orbital electronegativity and hardness data for various charge states of the atoms. For example, the 2p orbital hardness of the atoms O, N, and F depends on the orbital occupation number n_{2s}, n_{2p}, n_{3s}, and Z as follows (in eV)[27]

$$\eta_{2p,2p} = -4.609 - 2.002n_{2s} - 2.027n_{2p} - 1.030n_{3s} + 2.889Z \qquad (33)$$

In DFTB, no 3s orbitals are present, and if we assume a constant occupation of the 2s orbital with $n_{2s} = 2$, we find, with the atomic net charge q

$$\eta_{2p,2p} = -0.505 + 0.862Z + 2.027q \qquad (34)$$

These formulas lead to chemical hardness values close to the experimental ones. They assume a linear dependence of the chemical hardness on the atomic number and on the orbital occupation. The hardness derivative for these three first-row elements is $\partial\eta/\partial q = 2.027$ eV.

For DFTB, we can evaluate these values by taking the numerical derivative of the Hubbard parameters, that is, by taking the third derivatives of the energy of an atom with respect to the occupation number of the highest occupied molecular orbital (HOMO) using the numerical derivatives as suggested by Mineva.[28] The results are shown in Table 2. These values show consistent trends, and it is encouraging that the Hubbard derivatives are consistent with the findings of Liu and Parr. Further, all elements evaluated so far have negative chemical hardness derivatives, opposite to the finding of Fuentealba and Parr.[26] Maybe the convergence problems of the Taylor series expansion of the DFT total energy with respect to the number of electrons is a problem of the higher ionization potentials used[26,29] and less problematic for higher-energy derivatives calculated for neutral atoms as a reference point. However, it indicates that the use of higher derivatives may be problematic when treating highly charged systems.

Now, these charge-dependent chemical hardness parameters could be directly substituted into the second-order SCC term, making the γ function charge-dependent. However, it would be more consistent with the perturbational character of SCC-DFTB to derive these corrections in a higher-order expansion; the charge dependence of the Hubbard parameter can be accounted for in a third-order expansion,[30,31] that is, expanding the total DFT energy up to third order in the density fluctuations $(\int dr' = \int')$

$$E[\rho] = E[\rho_0] + \int \left[\frac{\delta E[\rho]}{\delta\rho}\right]_{\rho_0} \Delta\rho +$$

$$\frac{1}{2} \int \int' \left[\frac{\delta^2 E[\rho]}{\delta\rho\delta\rho'}\right]_{\rho_0} \Delta\rho\Delta\rho'$$

$$+ \frac{1}{6} \int \int' \int'' \left[\frac{\delta^3 E[\rho]}{\delta\rho\delta\rho'\delta\rho''}\right]_{\rho_0} \Delta\rho\Delta\rho'\Delta\rho'' \qquad (35)$$

$$E^3 \approx \frac{1}{6} \int \int' \int'' \left[\frac{\delta^3 E[\rho]}{\delta\rho\delta\rho'\delta\rho''}\right]_{\rho_0} \Delta\rho\Delta\rho'\Delta\rho'' =$$

$$\frac{1}{6} \int \int' \int'' \Delta\rho\Delta\rho'\Delta\rho'' \frac{\delta}{\delta\rho''}\left[\frac{\delta^2 E[\rho]}{\delta\rho\delta\rho'}\right]_{\rho_0} \qquad (36)$$

The functional derivative with respect to ρ'' is approximated by a derivative with respect to charge (neglecting also three-center contributions)

$$E^3 \approx \frac{1}{6} \sum_{\alpha\beta\gamma} \Delta q_\alpha\Delta q_\beta\Delta q_\gamma \int'' F_{00}^\gamma Y_{00} \frac{d}{dq_\gamma}\gamma_{\alpha\beta} =$$

$$\frac{1}{6} \sum_{\alpha\beta\gamma} \Delta q_\alpha\Delta q_\beta\Delta q_\gamma \frac{d}{dq_\gamma}\gamma_{\alpha\beta} \qquad (37)$$

$$= \frac{1}{6} \sum_\alpha \Delta q_\alpha^3 \frac{\partial\gamma_{\alpha\alpha}}{\partial q_\alpha} + \frac{1}{6} \sum_{\alpha\neq\beta} \Delta q_\alpha\Delta q_\beta\left[\Delta q_\alpha \frac{\partial\gamma_{\alpha\beta}}{\partial q_\alpha} + \Delta q_\beta \frac{\partial\gamma_{\alpha\beta}}{\partial q_\beta}\right] \qquad (38)$$

TABLE 2: Derivatives of the Hubbard Parameter $U = 2\eta$ (H) with Respect to the Occupation Number of the Highest Occupied Molecular Orbital

	H	B	C	N	O	F
$\partial U/\partial n$	−0.1857	−0.1008	−0.1492	−0.1535	−0.1575	−0.161

	Na	Mg	Si	P	S	Cl
$\partial U/\partial n$	−0.0447	−0.0497	−0.0718	−0.0702	−0.0695	−0.0691

$\gamma_{\alpha\beta}$ is dependent on the atomic charges only via the Hubbard parameters U_α, that is

$$\frac{\partial\gamma_{\alpha\beta}}{\partial q_\alpha} = \frac{\partial\gamma_{\alpha\beta}}{\partial U_\alpha}\frac{\partial U_\alpha}{\partial q_\alpha} \tag{39}$$

$$\Gamma_{\alpha\beta} = \frac{\gamma_{\alpha\beta}}{\partial U_\alpha}\frac{\partial U_\alpha}{\partial q_\alpha} \quad U'_\alpha = \frac{\partial U_\alpha}{\partial q_\alpha} \tag{40}$$

which leads to

$$E^3 = \frac{1}{6}\sum_\alpha \Delta q_\alpha^3 \frac{\partial\gamma_{\alpha\alpha}}{\partial q_\alpha} + \frac{1}{6}\sum_{\alpha\neq\beta}\Delta q_\alpha\Delta q_\beta[\Delta q_\alpha\Gamma_{\alpha\beta} + \Delta q_\beta\Gamma_{\beta\alpha}]$$

$$= \frac{1}{6}\sum_\alpha \Delta q_\alpha^3 \frac{\partial\gamma_{\alpha\alpha}}{\partial q_\alpha} + \frac{1}{6}\sum_{\alpha\neq\beta}\Delta q_\alpha^2\Delta q_\beta\Gamma_{\alpha\beta} \tag{41}$$

The diagonal terms are

$$E^3 = \frac{1}{6}\sum_\alpha \Delta q_\alpha^3 \frac{\gamma_{\alpha\alpha}}{\partial U_\alpha}\frac{\partial U_\alpha}{\partial q_\alpha} = \frac{1}{6}\sum_\alpha \Delta q_\alpha^3 U'_\alpha \tag{42}$$

and if we define

$$\Gamma'_{\alpha\alpha} = \frac{1}{2}U'_\alpha \quad \Gamma'_{\alpha\beta} = \Gamma_{\alpha\beta} \tag{43}$$

we can finally write

$$E^3 = \frac{1}{3}\sum_{\alpha\beta}\Delta q_\alpha^2\Delta q_\beta\Gamma'_{\alpha\beta} \tag{44}$$

and

$$E^2 + E^3 = \frac{1}{2}\sum_{\alpha\beta}\Delta q_\alpha\Delta q_\beta\left(\gamma_{\alpha\beta} + \frac{2}{3}\Delta q_\alpha\Gamma'_{\alpha\beta}\right) \tag{45}$$

Since we calculate the Hubbard parameter derivatives from DFT as the third derivative of the total energy, we implicitly include the spacial variation of the atomic size with total charge, however, again only in the monopole approximation.

We have implemented the diagonal contribution of the third-order term recently.[32] The diagonal terms change the electron−electron interaction on the atom with charge state. This is, for example, important for the total energies of ions. In biological systems, (de-)protonation energies are important quantities, which have to be described quite accurately for proton transfer to be processed. The third-order contribution improves the predicted proton affinity substantially. For example, with the estimated U_α^d, based on atomic calculations mentioned above, the error in the calculated proton affinity of water is reduced from 26.5 to −5.4 kcal/mol.

Deprotonation energies of acids (R−COOH) at the second-order DFTB are still about 10 kcal/mol in error, reducing to a few kcal/mol at the third order.

The diagonal third-order terms, however, do not include the effects of chemical hardness changes in the two-center contributions. As discussed above, the larger spacial extension of the electronic densities of anions should lead to a reduced Coulomb interaction via the reduced Hubbard parameter in the γ function. For example, in the second-order and third-order diagonal formalisms, the interaction of anions with water is overestimated by several kilocalories per mole (e.g., hydroxide−water).[32] This may be corrected consistently by including the third-order nondiagonal terms, as preliminary calculations indicate.

Conclusion

We have reviewed the assumptions and approximations constituting the SCC formalism, as implemented in SCC-DFTB. SCC-DFTB treats charge density fluctuations with respect to the input density perturbatively. As we have shown, this approximation becomes critical when atoms carry significant partial charges. This can be corrected by including higher-order terms in the functional expansion. A second critical approximation concerns the effective electron−electron interaction at the second order. It uses a simple law throughout the periodic table, which is quite reasonable for many atom types but may not be appropriate in every case, as shown, for example, for hydrogen. Therefore, the interaction may have to be changed in some cases. The modifications of the $\gamma_{\alpha\beta}$ and the third-order corrections come without additional cost. However, they are not required in many cases. The second-order method is sufficient for many application in biology and organic chemistry. It is slower by a factor of 3−5 on average than the non-SCC method due to the self-consistent solution of the eigenvalue problem (3−5 diagonalization iterations). Therefore, for many applications, the non-SCC method will be favorable. Small differences in electronegativities of the atoms present in the system are an indicator for the applicability of non-SCC. However, large differences are not always an indicator for its failure.

Concerning reaction energies and heats of formation, a more efficient parametrization scheme may lead to improved results (especially by removing the overbinding), that is, the flexibility of DFTB to treat different chemical environments may not be exploited completely with the current parametrization approach. Current efforts for a DFTB reparametrization are along these lines.

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