

Introduction to DFTB

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I. Non-selfconsistent solution of the KS equations

DFT can treat up to 100 atoms in routine applications, sometimes even more and about several ps in MD simulations. Very often, one would like to go to larger systems, therefore approximations to DFT are required.

To get started, consider a case, where you know the ground state density ρ_0 already to sufficient accuracy. In this case, one can omit the self consistent solution of the KS equations and get the orbitals immediately through:

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

(ρ_0 stands for a proper chosen input density in the following). This saves a factor of 5 -10 already, however, it is the starting point for further approximations.

Consider a minimal basis set consisting of atomic orbitals, i.e. $\eta_\mu = 2s, 2p_x, 2p_y, 2p_z$ for first row elements (we omit the core states in the following, since they are in a good approximation chemically inactive) and $\eta_\mu = 1s$ for H. With the basis set expansion

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

and the Hamiltonian

$$\hat{H}[\rho_0] = \hat{T} + v_{eff}[\rho_0]$$

we find:

$$\sum_{\mu} c_{\mu}^i \hat{H}[\rho_0] |\eta_{\mu}\rangle = \epsilon_i \sum_{\mu} c_{\mu}^i |\eta_{\mu}\rangle \quad (1)$$

Multiplication with $\langle \eta_{\nu} |$

$$\sum_{\mu} c_{\mu}^i \langle \eta_{\nu} | \hat{H}[\rho_0] | \eta_{\mu} \rangle = \epsilon_i \sum_{\mu} c_{\mu}^i \langle \eta_{\nu} | \eta_{\mu} \rangle \quad (2)$$

or in matrix notation

$$\mathbf{HC} = \mathbf{SC}\epsilon \quad (3)$$

This means, we just have to solve the **eigenvalue equation** once, i.e. we have to diagonalize the **Hamilton matrix** $H_{\mu\nu} = \langle \eta_\nu | \hat{H}[\rho_0] | \eta_\mu \rangle$. Note, that our basis set is **non-orthogonal**, i.e. the **overlap matrix** $S_{\mu\nu} = \langle \eta_\nu | \eta_\mu \rangle$ appears in the eigenvalue equations.

In empirical schemes, the basis functions are taken to be orthogonal, i.e. $S_{\mu\nu} = \delta_{\mu\nu}$.

Background is the so called Löwdin orthogonalization. Introducing orthonormal orbitals means multiplying with $\mathbf{S}^{-1/2}$ and inserting a '1':

$$\mathbf{S}^{-1/2}\mathbf{HS}^{-1/2}\mathbf{S}^{1/2}\mathbf{C} = \mathbf{S}^{-1/2}\mathbf{S}^{1/2}\mathbf{S}^{1/2}\mathbf{C}\epsilon$$

to get the orthonormal equations ($\mathbf{C}' = \mathbf{S}^{1/2}\mathbf{C}$):

$$\mathbf{H}'\mathbf{C}' = \mathbf{C}'\epsilon$$

Introducing orthonormal orbitals means effectively changing the Hamiltonian. And this is convenient, since in empirical schemes the Hamiltonmatrix is completely fitted to empirical data, e.g. for Carbon to the solid state bandstructures of several crystal structures (diamond, graphite, bcc etc.), or, in

Hückel theory, to properties of Hydrocarbons.

Diagonalization leads to the one-particle energies ϵ_i , i.e. to the so called electronic energy:

$$E_{elec} = \sum_i \epsilon_i$$

If we compare this to the total energy in DFT,

$$E[\rho] = \sum_i^{occ} \epsilon_i - \frac{1}{2} \int \frac{\rho_0(r)\rho_0(r')}{|r-r'|} dr dr' + E_{xc}[\rho_0] - \int v_{xc}(r)\rho_0(r) dr + \frac{1}{2} \sum_{\alpha\beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} \quad (4)$$

it is obvious, that a big part of energy is missing, the so called **double-counting** and core-core repulsion terms in DFT. First of all, it is interesting to note, that the double counting terms depend on the input/reference density ρ_0 only. The XC parts are hard to evaluate, however, in GGA we can say that they decay exponentially due to the exponential decay of the density-overlap.

If we assume an atomic density decomposition, $\rho = \sum_{\alpha} \rho_{\alpha}$, the coulomb contributions

$$\frac{1}{2} \sum_{\alpha\beta} \left[\frac{Z_{\alpha}Z_{\beta}}{R_{\alpha\beta}} - \int \frac{\rho_{\alpha}(r)\rho_{\beta}(r')}{|r-r'|} dr dr' \right]$$

show an exponential decay as well!

Therefore, first ETB models had the form:

$$E_{tot} = \sum_i \epsilon_i + \frac{1}{2} \sum_{\alpha\beta} U_{\alpha\beta}$$

with the two-body terms $U_{\alpha\beta}$ being exponentials fitted to reproduce e.g. geometries, vibrational frequencies and reaction energies of suitable systems.

II. Density Functional based Tight Binding: DFTB

The derivation of parameters via fitting is a quite complicated process. If one could derive the parameters from DFT calculations one would gain much more flexibility and a simplified parametrization scheme.

In a first step, one needs a basis set. In TB theory, basis functions are atomic orbitals, and these can be calculated from the atomic KS equations:

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}[\rho_{atom}] \right] \eta_{\mu} = \epsilon_{\mu}\eta_{\mu}$$

For a basis, we are free to choose whatever we want. Atomic orbitals have the disadvantage, that they are very diffuse, in solids, molecules or clusters the size of the orbitals is 'compressed' due to the interaction with the neighbors. A measure for the distance between neighbors is given by the so called 'covalent radius' r_0 and is determined for all atoms empirically.

Therefore, it is wise to use orbitals, which incorporate this information somehow. One way to enforce this, is to add an additional (harmonic) potential to

the atomic Kohn-Sham equations, which leads to compressed atomic orbitals, or optimized atomic orbitals (O-LCAO).

$$\left[-\frac{1}{2}\nabla^2 + v_{eff}[\rho_{atom}] + \left(\frac{r}{r_0}\right)^2 \right] \eta_\mu = \epsilon_\mu \eta_\mu \quad (5)$$

As a result of the atomic calculations, we get the orbitals η_μ , the electron density at atom α , $\rho_\alpha = \sum |\eta_\mu|^2$ and the overlap matrix $S_{\mu\nu} = \langle \eta_\nu | \eta_\mu \rangle$. To solve the eigenvalue problem eq. 2 or eq. 3, we only need the Hamiltonian matrix. This leads to further approximations, since although we have the complete input density $\rho_0 = \sum \rho_\alpha$ the Hamiltonian evaluation would be very complicated:

$$H_{\mu\nu} = \langle \eta_\nu | \hat{H}[\rho_0] | \eta_\mu \rangle = \langle \eta_\nu | \hat{H}[\sum \rho_\alpha] | \eta_\mu \rangle$$

We therefore usually make the so called 2-center approximation for $\mu \neq \nu$:

$$H_{\mu\nu} = \langle \eta_\nu | \hat{H}[\rho_0] | \eta_\mu \rangle = \langle \eta_\nu | \hat{H}[\rho_\alpha + \rho_\beta] | \eta_\mu \rangle \quad (6)$$

where orbital ν is located on atom α and orbital μ is located on atom β . The diagonal Hamiltonian elements $H_{\mu\mu} = \epsilon_\mu$ are taken from eq. 5.

$H_{\mu\nu}$ and $S_{\mu\nu}$ are tabulated for various distances between atom pairs up to 10 Å, where they vanish (also due to compression!). For any molecular geometry, these matrix elements are read in based on the distance between to atoms and then oriented in space using the Slater-Koster sin/cos combination rules. Then the generalized eigenvalue problem eq. 3 is solved and the first part of the energy can be calculated. It should be emphasized that this is a non-orthogonal TB scheme, which is more **transferable** due to the appearance of the overlap matrix.

The second part,

$$E_{rep}[\rho_0] = \frac{1}{2} \sum_{\alpha\beta} U_{\alpha\beta}$$

is calculated pointwise as follows: To get the repulsive potential e.g. for Carbon one could take the Carbon dimer C_2 , stretch its bond and for each distance calculate the total energy with DFT and the electronic TB part $\sum_i \epsilon_i$. $U_{CC}(R_{C-C})$ is the given point-wise for every R_{C-C} by:

$$U_{CC}(R_{C-C}) = E_{tot}^{DFT}(R_{C-C}) - \sum_i \epsilon_i$$

The resulting DFTB method works very well for homo-nuclear systems, where charge transfer between the atoms in the system does not occur or is very small. As soon as charge is flowing between atoms because of an electronegativity difference, the resulting density is no more well approximated by the superposition of the atomic densities $\rho_0 = \sum \rho_\alpha$. However, the formalism works very well, when charge flow is small, therefore an extension will try to start from the non-selfconsistent scheme.

The problem is, that the effective Kohn-Sham potentials contain only the neutral reference density ρ_0 , which does not account for charge transfer between atoms. Lets try a Taylor series expansion (functional expansion) of the potential with the ground state density ρ around the reference density ρ_0 :

$$v_{eff}[\rho] = v_{eff}[\rho_0] + \int \frac{\delta v_{eff}[\rho]}{\delta \rho} \delta \rho dr$$

This is a very interesting procedure, since now the potential inserted into the KS equations will lead to the same matrix elements of $H_{\mu\nu}[\rho_0]$ depending on the reference density as above, and corrections terms, which have to deal with the functional derivative.

III. Selfconsistent solution of the KS equations

Since we need the total energy and not only the KS equations, it is better to start the functional expansion with the DFT total energy. The SCC-DFTB method is derived from density functional theory (DFT) by a second order expansion of the DFT total energy functional with respect to the charge density fluctuations $\delta\rho$ around a given reference density ρ_0 ($\rho'_0 = \rho_0(\vec{r}')$, $\int' = \int d\vec{r}'$):

$$\begin{aligned}
 E &= \sum_i^{occ} \langle \Psi_i | \hat{H}^0 | \Psi_i \rangle + \frac{1}{2} \iint' \left(\frac{1}{|\vec{r} - \vec{r}'|} + \left. \frac{\delta^2 E_{xc}}{\delta\rho \delta\rho'} \right|_{n_0} \right) \Delta\rho \Delta\rho'. \\
 &- \frac{1}{2} \iint' \frac{\rho'_0 \rho_0}{|\vec{r} - \vec{r}'|} + E_{xc}[\rho_0] - \int V_{xc}[\rho_0] n_0 + E_{cc}
 \end{aligned} \tag{7}$$

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

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

and can be evaluated as discussed above. The last four terms depend only on the reference density ρ_0 and represent the repulsive energy contribution E_{rep} discussed above. Therefore, we only have to deal with the second order terms.

The second order term in the charge density fluctuations $\Delta\rho$ (second term in Eq.7) is approximated by writing $\Delta\rho$ as a superposition of atomic contributions

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

which decay quickly with increasing distance from the corresponding center. To further simplify E^{2nd} , we apply a monopole approximation

$$\Delta\rho_{\alpha} \approx \Delta q_{\alpha} F_{00}^{\alpha} Y_{00}, \quad (8)$$

Basically, $\Delta\rho_{\alpha}$ is assumed to look like an 1s orbital. F_{00}^{α} denotes the normalized radial dependence of the density fluctuation on atom α , which is constrained (approximated) to be spherical (Y_{00}); i.e., the angular deformation of the charge density change in second order is neglected.

$$E^{2nd} \approx \frac{1}{2} \sum_{\alpha\beta} \Delta q_{\alpha} \Delta q_{\beta} \iint' \left(\frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{xc}}{\delta\rho \delta\rho'} \Big|_{n_0} \right) F_{00}^{\alpha} F_{00}^{\beta} Y_{00}^2 dr dr' \quad (9)$$

This formular 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, and the integral describes the coulomb-interaction of two spherical normalized charge densities, which reduces basically to $1/R_{\alpha\beta}$, i.e. we get:

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

- For 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:

$$E^{2nd} \approx 0.5 \frac{\partial^2 E_{\alpha}}{\partial^2 q_{\alpha}} = U_{\alpha}$$

U_{α} is known as the Hubbard parameter or the chemical hardness. It describes, how much the energy of a system changes upon adding or removing electrons.

Now we need a formula to interpolate between these two cases. A very similar situation appears in semi-empirical quantum chemical methods like MNDO,

AM1 or PM3, where γ has a simple form, as given, for example, by the Klopman-Ohno approximation,

$$\gamma_{\alpha\beta} = \frac{1}{\sqrt{R_{\alpha\beta}^2 + 0.25(1/U_{\alpha} + 1/U_{\beta})^2}}. \quad (10)$$

To derive analytically an expression, we approximate the charge density fluctuations with spherical charge densities. Slater like distributions

$$F_{00}^{\alpha} = \frac{\tau_{\alpha}}{8\pi} \exp(-\tau_{\alpha}|r - R_{\alpha}|) \quad (11)$$

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 zero interatomic distances, i.e. $\alpha = \beta$, one finds that:

$$\tau_{\alpha} = \frac{16}{5} \gamma_{\alpha\alpha} \quad (12)$$

Eq. 12 implies, that the extension of the charge distribution is inversely proportional to the chemical hardness of the respective atom; i.e. the size of an

atom is inversely related to its chemical hardness.

After integration, E^{2nd} becomes a simple two-body expression depending on atomic-like charges

$$E^{2nd} = \frac{1}{2} \sum_{\alpha\beta} \Delta q_{\alpha} \Delta q_{\beta} \gamma_{\alpha\beta} \quad (13)$$

The diagonal terms $\gamma_{\alpha\alpha}$ model the dependence of the total energy on charge density fluctuations (decomposed into atomic contributions) in second order. The monopole approximation restricts the change of the electron density considered and no spatial deformations are included; only the change of energy with respect to change of charge on the atom α is considered. 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,

$$\gamma_{\alpha\alpha} = 2\eta_{\alpha} = U_{\alpha} = \frac{\partial^2 E_{\alpha}}{\partial^2 q_{\alpha}}, \quad (14)$$

E_{α} is the energy of the isolated atom α . U_{α} is known as the Hubbard parameter and is twice the chemical hardness of atom α , which can be estimated from the difference of the ionization potential and the electron affinity of atom α . 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.

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

$$E^{SCC} = \sum_{i\mu\nu} c_{\mu}^i c_{\nu}^i H_{\mu\nu}^0 + \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta} \Delta q_{\alpha} \Delta q_{\beta} + \frac{1}{2} \sum_{\alpha\beta} U[\rho_0^{\alpha}, \rho_0^{\beta}] \quad (15)$$

The variational principle leads to approximate Kohn-Sham equations, which have to be solved iteratively for the wavefunction expansion coefficients c_{μ}^i , since the Hamilton matrix elements depend on the c_{μ}^i due to the Mulliken charges. The two-body contributions $U[R_{\alpha\beta}]$ are determined by comparison of the energy according to Eq. 15 with that from full DFT calculations with respect to the interatomic distance $R_{\alpha\beta}$ of the atoms α and β . The resulting energy curve $U[R_{\alpha\beta}]$ is then analytically represented by splines.