Introduction to the Density-Functional Tight-Binding (DFTB) Method

Part I

*Density-Functional Tight-Binding (DFTB) as fast approximate DFT method*

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Density-Functional Tight-Binding

Part I

1. Tight-Binding
2. Density-Functional Tight-Binding (DFTB)

Part II

3. Bond Breaking in DFTB
4. Extensions
5. Performance and Applications
Density-Functional Tight-Binding

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Resources

1. Tight-Binding

**Implementations**

- **DFTB+**
  Standalone fast and efficient DFTB implementation with several useful extensions of the original DFTB method. It is developed at the Bremen Center for Computational Materials Science (Prof. Frauenheim, Balint Aradi). Based on previous DYLAX code. Free for non-commercial use.

- **DFTB+/Accelrys**
  DFTB+ as part of Accelrys' Materials Studio package, providing a user friendly graphical interface and the possibility to combine DFTB with other higher or lower level methods.

- **deMon**
  DFTB integrated in the ab initio DFT code deMon (Thomas Heine)

- **GAUSSIAN G09**
  DFTB in the Gaussian code (Keiji Morokuma)

- **AMBER**
  Amber is a package of molecular simulation programs distributed by UCSF, developed mainly for biomolecular simulations. The current version of Amber includes QM/MM. (Marcus Elstner et al.)

- **CHARMm**
  CHARMm (Chemistry at HARvard Macromolecular Mechanics) (Qian Cui.)

- **ADF**
  DFTB integrated in the Amsterdam Density Functional (ADF) program suite. (Thomas Heine)

- **GAMESS-US**
  DFTB1/2/3 and FMO2-DFTB1/2/3 (Yoshio Nishimoto, Dmitri Fedorov, Stephan Irle)

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**Tight-Binding**

- Tight binding (TB) approaches work on the principle of treating electronic wavefunction of a system as a superposition of atom-like wavefunction (known to chemists as LCAO approach)

- Valence electrons are tightly bound to the cores (not allowed to delocalize beyond the confines of a minimal LCAO basis)

- Semi-empirical tight-binding (SETB): Hamiltonian Matrix elements are approximated by analytical functions (no need to compute integrals)

- **TB energy for** $N$ electrons, $M$ atoms system:

$$E_{TB} = \sum_{i}^{N} c_i^2 - \frac{1}{2} \sum_{j \neq k}^{M} v_{j,k}(|R_j - R_k|)$$

- This separation of one-electron energies and interatomic distance-dependent potential $v_{j,k}$ constitutes the TB method
Tight-Binding

• $\varepsilon_i$ are eigenvalues of a Schrödinger-like equation

$$\varepsilon_i \Psi_i(\vec{r}) = \left[-\frac{1}{2}\Delta + V(\vec{r})\right] \Psi_i(\vec{r})$$

• solved variationally using atom-like (minimum, single-zeta) AO basis set, leading to a secular equation:

$$|H - \varepsilon S| = 0$$

where $H$ and $S$ are Hamiltonian and overlap matrices in the basis of the AO functions. In orthogonal TB, $S = 1$ (overlap between atoms is neglected)

• $H$ and $S$ are constructed using nearest-neighbor relationships; typically only nearest-neighbor interactions are considered: Similarity to extended Hückel method

Extended Hückel (EHT) Method

• Based on approximation by M. Wolfsberg and L. J. Helmholz (1952)

$$H C_i = \varepsilon_i S C_i$$

• $H$ – Hamiltonian matrix constructed using nearest neighbor relationships

• $C_i$ – column vector of the i-th molecular orbital coefficients

• $\varepsilon_i$ – orbital energy

• $S$ – overlap matrix

• $H_{\mu\mu}$ - choose as a constant – valence shell ionization potentials

• $H_{\mu\nu} = K S_{\mu\nu} (H_{\mu\mu} + H_{\nu\nu})/2$

• $K$ – Wolfsberg Helmholz constant, typically 1.75
Categories of TB approaches

TB models can conditionally be divided:

- Depending on how we treat the overlap matrix $S$:
  - Orthogonal TB
    $$H\Psi = E\Psi$$
  - Non-orthogonal TB
    $$H\Psi = ES\Psi$$

- Depending on how we derive the parameters:
  - Ab initio TB (derive from DFT)
  - Empirical (fit to experiments, or ab initio results)

- Depending on how we treat the charge self-consistency problem:
  - Non-self-consistent
  - Self-consistent

Important: in all modifications we can use the Hellmann-Feynman theorem

$$f_j = -\langle \psi | \frac{\partial H}{\partial R_j} | \psi \rangle$$

Source: http://beam.acclab.helsinki.fi/~akrashen/esctmp.html

Slater-Koster (SK) Approximation (I)

- The key moment is how we calculate one-electron integrals
  $$h_{pq} = \langle p | h | q \rangle = \int d^3r \chi_p^*(r) \left[ -\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|R_n - r|} \right] \chi_q(r)$$

Note that the matrix element depends on the positions of ALL atoms.

Source: http://beam.acclab.helsinki.fi/~akrashen/esctmp.html
SK Approximation (II)

Let’s consider two atoms with s and p atomic orbitals (e.g. Carbon)

Atom 1: \( | s_1 \rangle, \ | x_1 \rangle, \ | y_1 \rangle, \ | z_1 \rangle \)

Atom 2: \( | s_2 \rangle, \ | x_2 \rangle, \ | y_2 \rangle, \ | z_2 \rangle \)

\[
h_{pq} = \langle p | H | q \rangle = \int d^3r \chi_p^*(r) \left[ -\frac{1}{2} \nabla^2 - \sum_n \frac{Z_n}{|\mathbf{R}_n - \mathbf{r}|} \right] \chi_q(r)
\]

Diagonal elements: Assume we know s and p energies \( (E_s, E_p) \) for isolated single atom; we further assume that these “on-site” energies are the same when the bonds are formed

\[
h_{qq} = E_q = \langle q | H | q \rangle \quad q \text{ is the s orbital}
\]

\[
h_{qq} = E_p = \langle q | H | q \rangle \quad q \text{ is any of the p orbitals}
\]

Off-diagonal elements:

s-s: Assume that for s-s atomic orbitals, \( h_{psps} = s(r)E_{s,s} = s(r)V_{ss} \)

\( s(r) \) is an analytical function which depends on \( r \) only

\( V_{ss} \) is a parameter chosen to fit the results for a reference system

Source: http://beam.acclab.helsinki.fi/~akrashen/esctmp.html

SK Approximation (III)

Off-diagonal elements:

s-p: Assume that for s-p atomic orbitals,

\[
h_{spsp} = s(r)E_{s,p} = s(r)V_{sp}
\]

\( s(r) \) is the same analytical function

\( l = \cos(\theta_s) = x/r \) is the directional cosine of the vector between the atoms

\( V_{sp} \) is another parameter chosen to fit the results for a reference system

\( l \) reflects the anisotropy of the orbitals; note that p functions have a positive and negative part

Two-center one electron integrals are sometimes called hopping integrals

Source: http://beam.acclab.helsinki.fi/~akrashen/esctmp.html
SK Approximation (IV)

- Off-diagonal elements:
  - $p$-$p$: For $p_z P_y$ atomic orbitals, the matrix element is
  \[ h_{p_z p_y} = s(r) E_{p_z p_y} = s(r) [l^2 V_{ppp} + (1 - l^2) V_{ppp}] \]
  Analogously, $p_z P_x$ matrix element is
  \[ h_{p_z p_x} = s(r) E_{p_z p_x} = s(r) [m V_{pnp} - mn V_{ppn}] \]
  $p_z P_z$ matrix element is
  \[ h_{p_z p_z} = s(r) E_{p_z p_z} = s(r) [n^2 V_{ppp} + (1 - n^2) V_{ppp}] \]
  \[ l = x/r, \ m = y/r, \ n = z/r \]

- Four non-equivalent fundamental integrals between $s$ and $p$ atomic orbitals

- $p$-$d$: We can derive similar formulas for $d$ orbitals as well

Source: http://beam.acclab.helsinki.fi/~akrashen/esctmp.html

SK Tables

So, all together, the integral look as follow:

Source: http://beam.acclab.helsinki.fi/~akrashen/esctmp.html
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Taken from Oliveira, Seifert, Heine, Duarte, J. Braz. Chem. Soc. 20, 1193-1205 (2009)

...open access
Density Functional Theory (DFT)

Walter Kohn/John A. Pople

at convergence:

\[ E[\rho] = \sum_{i=1}^{M} n_i \langle \psi_i \mid -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3r' |\psi_i \rangle \]

\[ + E_{xc}[\rho] - \frac{1}{2} \int \rho(\vec{r}) \rho(\vec{r}') |\vec{r} - \vec{r}'| d^3r d^3r' + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{1}{\alpha \beta} \int Z_{\alpha} Z_{\beta} \frac{R_{\alpha} - R_{\beta}}{|R_{\alpha} - R_{\beta}|} \]

\[ = \sum_{i=1}^{M} n_i \epsilon_i + E_{\text{rep}} \]

Various criteria for convergence possible:
- Electron density
- Potential
- Orbitals
- Energy
- Combinations of above quantities

Foulkes + Haydock Ansatz


\[ \rho(\vec{r}) = \rho_0(\vec{r}) + \delta \rho(\vec{r}) \]

\[ E[\rho_0 + \delta \rho] = \sum_{i=1}^{M} n_i \left\langle \psi_i \left| -\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r}) + \int \frac{\rho_0'(\vec{r})}{|\vec{r} - \vec{r}'|} d\vec{r}' + v_{xc}[\rho_0] \right| \psi_i \right\rangle \]

\[ - \frac{1}{2} \int \int \frac{\rho_0'(\rho_0 + \delta \rho)}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' - \int v_{xc}[\rho_0](\rho_0 + \delta \rho) d\vec{r} \]

\[ + \frac{1}{2} \int \int \frac{\delta \rho'(\rho_0 + \delta \rho)}{|\vec{r} - \vec{r}'|} d\vec{r} d\vec{r}' + E_{xc}[\rho_0 + \delta \rho] + E_{nn} \]
Self-consistent-charge density-functional tight-binding (SCC-DFTB)


Approximate density functional theory (DFT) method!

Second order-expansion of DFT energy in terms of reference density \( \rho_0 \) and charge fluctuation \( \rho_1 (\rho = \rho_0 + \rho_1) \) yields:

\[
E[\rho] = \sum_i^n n_i \langle \phi_i | \hat{H} [\rho_0] | \phi_i \rangle + \sum_i^n n_i \langle \phi_i | \hat{H} [\rho_1] | \phi_i \rangle + E_{xc}[\rho_0] - \frac{1}{2} \int \rho_0 V_H [\rho_0] - \frac{1}{2} \int \rho_0 V_{xc} [\rho_0] + \frac{1}{2} \int \rho_1 V_H [\rho_1] + \frac{1}{2} \int \rho_1 V_{xc} [\rho_1] - \frac{1}{2} \int \rho_2 V_{rep} - \frac{1}{2} \int \rho_2 V_{rep} - \frac{1}{2} \int \rho_2 V_{rep} + \frac{1}{2} \int \rho_2 V_{rep} + \frac{1}{2} \int \rho_2 V_{rep} + o(3)
\]

Density-functional tight-binding (DFTB) method is derived from terms 1-6

Self-consistent-charge density-functional tight-binding (SCC-DFTB) method is derived from terms 1-8

DFTB and SCC-DFTB methods

\[
E^{DFTB} = \sum_i^n n_i \varepsilon_i + \frac{1}{2} \sum_{A \neq B} E^{AB}_{rep}
\]

\[
E^{SCC-DFTB} = \sum_i^n n_i \varepsilon_i + \frac{1}{2} \sum_{A,B} \gamma_{AB} \Delta q_A \Delta q_B + \frac{1}{2} \sum_{A \neq B} E^{AB}_{rep}
\]

\[\text{where}\]

- \( n_i \) and \( \varepsilon_i \) — occupation and orbital energy of the \( i \)th Kohn-Sham eigenstate
- \( E_{rep} \) — distance-dependent diatomic repulsive potentials
- \( \Delta q_A \) — induced charge on atom \( A \)
- \( \gamma_{AB} \) — distance-dependent charge-charge interaction functional; obtained from chemical hardness (IP – EA)
DFTB method

- Repulsive diatomic potentials replace usual nuclear repulsion energy
- Reference density $\rho_0$ is constructed from atomic densities
  $$\rho_0 = \sum_A^{\text{atoms}} P_A^i$$
- Kohn-Sham eigenstates $\phi_i$ are expanded in Slater basis of valence pseudoatomic orbitals $\chi_i$
  $$\phi_i = \sum_{\mu}^{\Lambda_0} c_{\mu} \chi_\mu$$
- The DFTB energy is obtained by solving a generalized DFTB eigenvalue problem with $H^0$ computed by atomic and diatomic DFT
  $$H^0C = SC\varepsilon$$  \text{with}  $$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$$
  $$H^0_{\mu\nu} = \langle \chi_\mu | \hat{H} \left[ P_0^N, P_0^N \right] \chi_\nu \rangle$$

Approximations in the DFTB Hamiltonian

Traditional DFTB concept: Hamiltonian matrix elements are approximated to two-center terms. The same types of approximations are done to $E_{\text{rep}}$.

$$H^0_{\mu\nu} = \begin{cases} 
\epsilon_{\mu} & \text{if } \mu = \nu \\
\langle \phi_\mu^\alpha | \hat{T} + V_0^\alpha + V_0^\beta | \phi_\nu^\beta \rangle & \text{if } \alpha \neq \beta \\
0 & \text{otherwise.}
\end{cases}$$

From Elstner et al., PRB 1998

- $V_{\text{eff}} \left[ \rho_0 \right] \approx V_{\text{eff}} \left[ \rho_A + \rho_B \right]$ \hspace{1cm} (Density superposition)
- $V_{\text{eff}} \left[ \rho_0 \right] \approx V_{\text{eff}} \left[ \rho_A \right] + V_{\text{eff}} \left[ \rho_B \right]$ \hspace{1cm} (Potential superposition)

Both approximations are justified by the screening argument: Far away, neutral atoms have no Coulomb contribution.
SCC-DFTB matrix elements

LCAO ansatz of wave function

\[ \Psi_i = \sum_v c_v \phi_v (r - R_i) \]

pseudoatomic orbital

\[ \text{variational principle} \]

secular equations

\[ \sum_v c_v^* (H_{\mu\nu} - \varepsilon_n S_{\mu\nu}) = 0 \]

Hamiltonian Overlap

pre-computed parameter

- Reference Hamiltonian \( H^0 \)
- Overlap integral \( S_{\mu\nu} \)

✓ two-center approximation
✓ nearest neighbor off-diagonal elements only (choice of cutoff values)

Atom 1 – 4 are the same atom & have only s shell

How to construct?

Diagonal term

Orbital energy of neutral free atom (DFT calculation)

\[ H_{\mu\mu} = \varepsilon_\mu + \frac{1}{2} \sum_{\gamma} (g_{\alpha\gamma} + g_{\beta\gamma}) \Delta q_{\gamma} \]

Charge-charge interaction function

Induced charge
SCC-DFTB matrix elements

LCAO ansatz of wave function
\[ \Psi_i = \sum_v c_v \phi_v (r - R_{ai}) \]
pseudoatomic orbital

Variational principle

Secular equations
\[ \sum_v c_v (H_{\mu\nu} - \epsilon \delta_{\mu\nu}) = 0 \]
Hamiltonian  Overlap

Atom 1 – 4 are the same atom & have only s shell

Two-center integral
\[ H_{\mu\nu} = H_{\mu\nu}^0 + \frac{1}{2} S_{\mu\nu} \sum (\gamma_{\mu\xi} + \gamma_{\nu\xi}) \Delta q_{\xi} \]
Charge-charge interaction function
Induced charge

Lookup tabulated \( H^0 \) and \( S \) at distance \( r \)

➢ Repeat until building off-diagonal term

Charge-charge interaction function
Induced charge
DFTB parameters

What are the ‘free’ parameters?

- confinement for wave-function: \( r_0^X \)
- confinement for density: \( r_D^X \)
- repulsive potential \( U_{\alpha\beta} \):
  - 6th order polynomial (spline)
  - 20-40 DFT data points

\[
\Delta \rho = \rho - \sum_a \rho_a
\]

DFTB repulsive potential \( E_{\text{rep}} \)

\[
E[\rho] = \sum_{i}^{\text{occ}} \epsilon_i^H + \sum_{\alpha\beta} U_{\alpha\beta} \quad \rightarrow \quad U_{\alpha\beta} = E^{\text{DFT}}[\rho](R_{\alpha\beta}) - \sum_i^{\text{occ}} \epsilon_i^H(R_{\alpha\beta})
\]

Which molecular systems to include?

Development of (semi-)automatic fitting:
- Bodrog Z. et al., JCTC, 7, 2654, (2011)
SCC-DFTB method (I)

- Additional induced-charges term allows for a proper description of charge-transfer phenomena
- Induced charge $\Delta q_A$ on atom $A$ is determined from Mulliken population analysis

$$\Delta q_A = \sum_{i} n_i \sum_{\mu \in A} \sum_{\nu} c_{\mu \nu} c_{\nu} S_{\mu \nu} - q_A^0$$

- Kohn-Sham eigenenergies are obtained from a generalized, self-consistent SCC-DFTB eigenvalue problem

$$HC = S \varepsilon \quad \text{with} \quad S_{\mu \nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle \quad \text{and}$$

$$H_{\mu \nu} = \langle \chi_{\mu} | \hat{H} [\rho^0, \rho^0] | \chi_{\nu} \rangle + \frac{1}{2} S_{\mu \nu} \sum_{K} (\gamma_{MK} + \gamma_{NK}) \Delta q_K$$

SCC-DFTB method (II)

Only second-order terms (terms 7-8 on slide 16):

$$E^2[\rho, \rho_0] = \frac{1}{2} \int \int' \left( \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho \delta \rho'} \bigg|_{\rho_0} \right) \Delta \rho \Delta \rho'$$

Represent by atomic contributions:

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

Monopole approximation

$$\Delta \rho_{\alpha} \approx \Delta q_\alpha F_{00}^\alpha \gamma_{00}$$

$$E^2[\rho, \rho_0] \approx \frac{1}{2} \sum_{\alpha \beta} \Delta q_\alpha \Delta q_\beta \int \int' \left( \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho \delta \rho'} \bigg|_{\rho_0} \right) F_{00}^\alpha F_{00}^\beta \gamma_{00}^2$$

Basic assumptions:
- Only transfer of net charge between atoms
- Size and shape of atom (in molecule) unchanged
SCC-DFTB method (III)

\[ E^2[\rho, \rho_0] \approx \frac{1}{2} \sum_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \int \int' \left( \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho \delta \rho'} \right) F^{\alpha}_{00} F^{\beta}_{00} \gamma^2_{00} \]

Consider two limiting cases:

A) Large distance: \(|\vec{r} - \vec{r}'| \approx R_{\alpha\beta} \to \infty\)

\[ E^2[\rho, \rho_0] \to \frac{1}{2} \sum_{\alpha\beta} \frac{\Delta q_\alpha \Delta q_\beta}{R_{\alpha\beta}} \]

B) 'On-site' e-e repulsion: \(R_{\alpha\beta} \to 0\), i.e. \(\alpha = \beta\)

\[ E^2[\rho, \rho_0] \to \frac{1}{2} \sum_{\alpha} \frac{\delta^2 E_{xc}}{\delta q_\alpha^2} \Delta q_\alpha^2 = \frac{1}{2} \sum_{\alpha} U_\alpha \Delta q_\alpha^2 \]

New (Hubbard) parameter \(U_\alpha\): computed from DFT (PBE)

SCC-DFTB method (IV)

Derive analytical function which interpolates between these two cases

\[ E^2[\rho, \rho_0] \approx \frac{1}{2} \sum_{\alpha, \beta} \Delta q_\alpha \Delta q_\beta \int \int' \left( \frac{1}{|\vec{r} - \vec{r}'|} + \frac{\delta^2 E_{xc}}{\delta \rho \delta \rho'} \right) F^{\alpha}_{00} F^{\beta}_{00} \gamma^2_{00} \]

\[ E^2[\rho, \rho_0] \approx \frac{1}{2} \sum_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \gamma_{\alpha\beta} \]

Klopmann-Ohno: \(\gamma_{\alpha\beta} = \frac{1}{\sqrt{R^2 + \frac{1}{4}(u_a^2 + u_b^2)}}\)

Several possible formulations for \(\gamma_{\alpha\beta}\): Mataga-Nishimoto < Klopmann-Ohno < DFTB

Gradient for the DFTB methods

The DFTB force formula

$$ F_a = - \sum_i n_i \sum_{\mu \nu} c_{\mu \nu} \left[ \frac{\partial H_{\mu \nu}^0}{\partial a} - \epsilon_i \frac{\partial S_{\mu \nu}}{\partial a} - \frac{\partial E_{\text{rep}}}{\partial a} \right] $$

The SCC-DFTB force formula

$$ F_a = - \sum_i n_i \sum_{\mu \nu} c_{\mu \nu} \left[ \frac{\partial H_{\mu \nu}^0}{\partial a} \left( \epsilon_i - \frac{1}{2} \sum_K (\gamma_{MK} + \gamma_{NK}) \Delta q_K \right) \frac{\partial S_{\mu \nu}}{\partial a} \right] - \Delta q_A \sum_K \frac{\partial \gamma_{AK}}{\partial a} \Delta q_K - \frac{\partial E_{\text{rep}}}{\partial a} $$

computational effort: energy calculation 90%
gradient calculation 10%

Spin-polarized DFTB (SDFTB)

❖ for systems with different ↑ and ↓ spin densities, we have
  ➢ total density \( \rho = \rho^\uparrow + \rho^\downarrow \)
  ➢ magnetization density \( \rho^S = \rho^\uparrow - \rho^\downarrow \)

❖ 2nd-order expansion of DFT energy at \( (\rho_0^\uparrow,0) \) yields

$$ E[\rho,\rho^S] = \sum_i n_i \langle \phi_i | \hat{H}[\rho_0^\uparrow] | \phi_i \rangle + \sum_i n_i \langle \phi_i | \hat{H}[\rho_0^\downarrow] | \phi_i \rangle + E_{xc}[\rho_0^\uparrow] - \frac{1}{2} \int E_{\text{xc}}[\rho_0^\downarrow] - $$

$$ - \int \rho_0 V_{\text{xc}}[\rho_0] + E_{\text{max}} + \frac{1}{2} \int \rho_0 V_{\text{H}}[\rho_0] + \frac{1}{2} \int_0^1 \frac{\delta^2 E_{\text{xc}}}{\delta \rho^2_{\rho_0}} |_{\rho_0^\uparrow,0} \rho_0^2 + \frac{1}{2} \int_0^1 \frac{\delta^2 E_{\text{xc}}}{\delta \rho^2 S} |_{\rho_0^\uparrow,0} \left( \rho^S \right)^2 + o(3) $$

The Spin-Polarized SCC-DFTB (SDFTB) method is derived from terms 1-9
Spin-polarized DFTB (SDFTB)

\[ E_{\text{SDFTB}} = \sum_i n_i^\uparrow \varepsilon_i^\uparrow + \sum_i n_i^\downarrow \varepsilon_i^\downarrow + \frac{1}{2} \sum_{A \neq B} \gamma_{AB} \Delta q_A \Delta q_B + \frac{1}{2} \sum_{A \neq B} E_{\text{rep}} + \frac{1}{2} \sum_{A, l \in A \atop l' \in A} \sum_{l \neq l'} p_{Al} p_{Al'} W_{All'} \]

where \( p_{Al} \) — spin population of shell \( l \) on atom \( A \)

\[ W_{All'} \] — spin-population interaction functional

\[ W_{Al} = \frac{1}{2} \left( \frac{\partial \varepsilon_{Al}}{\partial \eta_{Al}} - \frac{1}{\eta_{Al}} \right) = W_{Al} \]

Spin populations \( p_{Al} \) and induced charges \( \Delta q_A \) are obtained from Mulliken population analysis

\[ \Delta q_A = \sum_i \sum_{\mu} \sum_{\nu} \left( n_i^\uparrow c_{\mu i}^\dagger c_{\nu i}^\dagger + n_i^\downarrow c_{\mu i}^\dagger c_{\nu i}^\dagger \right) S_{\mu \nu} - q^0_A \]

\[ p_{Al} = \sum_i \sum_{\mu} \sum_{\nu} \left( n_i^\uparrow c_{\mu i}^\dagger c_{\nu i}^\dagger - n_i^\downarrow c_{\mu i}^\dagger c_{\nu i}^\dagger \right) S_{\mu \nu} \]

Spin-polarized DFTB (SDFTB)

Spin-polarized DFTB (SDFTB)

Kohn-Sham energies are obtained by solving generalized, self-consistent SDFTB eigenvalue problems

\[ H^\uparrow C^\uparrow = SC^\uparrow \varepsilon^\uparrow \]

\[ H^\downarrow C^\downarrow = SC^\downarrow \varepsilon^\downarrow \]

where

\[ S_{\mu \nu} = \langle \chi_\mu | \chi_\nu \rangle \]

\[ H_{\mu \nu} = \langle \chi_\mu | \hat{H}\left[ \rho_0^\mu, \rho_0^\nu \right] | \chi_\nu \rangle + \frac{1}{2} S_{\mu \nu} \sum_{k} \left( \gamma_{MK} + \gamma_{NK} \right) \Delta q_k + \delta_{MN} \frac{1}{2} S_{\mu \nu} \sum_{l \in M} (W_{Al} + W_{Al'}) p_{Ml'} \]

\[ H_{\mu \nu} = \langle \chi_\mu | \hat{H}\left[ \rho_0^\mu, \rho_0^\nu \right] | \chi_\nu \rangle + \frac{1}{2} S_{\mu \nu} \sum_{k} \left( \gamma_{MK} + \gamma_{NK} \right) \Delta q_k - \delta_{MN} \frac{1}{2} S_{\mu \nu} \sum_{l \in M} (W_{Al} + W_{Al'}) p_{Ml'} \]

\[ M,N,K: \text{indexing specific atoms} \]
SCC-DFTB w/fractional orbital occupation numbers

Fractional occupation numbers $f_i$ of Kohn-Sham eigenstates replace integer $n_i$

TB-eigenvalue equation

$$\sum_{\nu} c_{\nu i} \left( H_{\mu\nu} - \epsilon_i S_{\mu\nu} \right) = 0$$

$$E_{tot} = 2 \sum f_i \epsilon_i + E_{rep} + \frac{1}{2} \sum_{\alpha\beta} \gamma_{\alpha\beta} \Delta q_{\alpha} \Delta q_{\beta}$$

Finite temperature approach (Mermin free energy $E_{Mermin}$)

$$f_i = \frac{1}{1 + \exp ((\epsilon_i - \mu)/k_BT_i)}$$

$T_i$: electronic temperature

$S$: electronic entropy

$0 \leq f_i \leq 1$

$$E_{Mermin} = E_{tot} - T_e S_e$$

Atomic force

$$\vec{F}_\alpha = -2 \sum f_i \sum_{\mu\nu} c_{\mu\nu} \left[ \frac{\partial H_{\mu\nu}^0}{\partial \vec{R}_\alpha} \left( \epsilon_i - \frac{H_{\mu\nu}^0}{S_{\mu\nu}} \right) \frac{\partial S_{\mu\nu}}{\partial \vec{R}_\alpha} \right] - \Delta q_{\alpha} \sum_{\bar{\alpha}} \frac{\partial^2 \epsilon_{\bar{\alpha}}}{\partial \vec{R}_{\bar{\alpha}}} \Delta q_{\bar{\alpha}} - \frac{\partial E_{rep}}{\partial \vec{R}_\alpha}$$

Fermi-Dirac distribution function: Energy derivative for Mermin Free Energy

$$F_{\alpha}^{elect} = \dot{F}_{HF} + \dot{F}_{pulay} + \dot{F}_{charge}$$

$$= \sum \frac{\partial}{\partial x} (\epsilon_i f_i) = \sum f_i \frac{\partial \epsilon_i}{\partial x} + \sum \epsilon_i \frac{\partial f_i}{\partial x}$$

$$F_{\alpha}^{elect-TS} = \dot{F}_{HF} + \dot{F}_{pulay} + \dot{F}_{charge} + \dot{F}_{TS}$$

$$= \sum \frac{\partial}{\partial x} (\epsilon_i f_i) + \frac{\partial (-T_e S)}{\partial x}$$

$$= \sum f_i \frac{\partial \epsilon_i}{\partial x} + \sum \epsilon_i \frac{\partial f_i}{\partial x} - \sum \epsilon_i \frac{\partial f_i}{\partial x}$$

Correction term arising from Fermi distribution function cancels out
Electronic Parameters

New Confining Potentials

- Typically, electron density contracts under covalent bond formation.
- In standard ab initio methods, this problem can be remedied by including more basis functions.
- DFTB uses minimal valence basis set: the confining potential is adopted to mimic contraction.

![DFTB Parameterization](image)

\[ \Delta \rho = \rho - \sum_a \rho_a \]

Woods-Saxon potential
\[ V(r) = \frac{W}{1 + \exp\{-a(r - r_0)\}} \]

Conventional potential
\[ V(r) = \left( \frac{r}{r_0} \right)^k \]

Henryk Witek
1). DFT band structure calculations

- VASP 4.6
- One atom per unit cell
- PAW (projector augmented wave) method
- 32 x 32 x 32 Monkhorst-Pack k-point sampling
- cutoff = 400 eV
- Fermi level is shifted to 0 eV

2). DFTB band structure fitting

- Optimization of parameter sets for Woods-Saxon confining potential (orbital and density) and unoccupied orbital energies
- Fixed orbital energies for electron occupied orbitals
- Valence orbitals: [1s] for 1st row
  [2s, 2p] for 2nd row
  [ns, np, md] for 3rd – 6th row
  \( n \geq 3, \ m = n-1 \) for group 1-12, \( m = n \) for group 13-18
- Fitting points: valence bands + conduction bands (depending on the system, at least including up to \( \sim +5 \text{ eV} \) with respect to Fermi level)
Particle swarm optimization (PSO)

1) Particles (=candidate of a solution) are randomly placed initially in a target space.
2) – 3) Position and velocity of particles are updated based on the exchange of information between particles and particles try to find the best solution.
4) Particles converges to the place which gives the best solution after a number of iterations.
Each particle has randomly generated parameter sets \((r_0, a, W)\) within some region.

Generating one-center quantities (atomic orbitals, densities, etc.)

Computing two-center overlap and Hamiltonian integrals for wide range of interatomic distances

Calculating DFTB band structure

Evaluating “fitness value” (Difference DFTB – DFT band structure using specified fitness points)

Memorizing the best fitness value and parameter sets

Update the parameter sets of each particle

**Electronic Parameters**

Example: Be, HCP crystal structure

Total density of states (left) and band structure (right) of Be (hcp) crystal structure

- Experimental lattice constants
- Fermi energy is shifted to 0 eV
Band structure fitting for BCC crystal structures

- Space group No. 229
- 1 lattice constant ($a$)
- Transferability checked (single point calculation)
- Reference system in PSO
- Experimental lattice constants available
- No POTCAR file for $Z \geq 84$ in VASP

Band structure fitting for FCC crystal structures

- Space group No. 225
- 1 lattice constant ($a$)
- Transferability checked (single point calculation)
- Reference system in PSO
- Experimental lattice constants available

* Lanthanoids
** Actinoids
Band structure fitting for SCL crystal structures

- space group No. 221
- 1 lattice constant ($a$)

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- Transferability checked (single point calculation)
- Reference system in PSO
- Experimental lattice constants available

Band structure fitting for HCP crystal structures

- space group No. 194
- 2 lattice constants ($a$, $c$)

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- Transferability checked (single point calculation)
- Reference system in PSO
- Experimental lattice constants available
Band structure fitting for Diamond crystal structures

- space group No. 227
- 1 lattice constant (a)

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</tbody>
</table>

- Transferability checked (single point calculation)
- Reference system in PSO
- Experimental lattice constants available

- Artificial crystal structures can be reproduced well

**Lanthanoids**

**Actinoids**

Transferability of optimum parameter sets for different structures

e.g.: Si, parameters were optimized with bcc only

<table>
<thead>
<tr>
<th>Lattice constants:</th>
<th>DFTB</th>
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<tr>
<td>diamond</td>
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Parameter sets:

- $W$ (orb) 3.33938
- $a$ (orb) 4.52314
- $r$ (orb) 4.22512
- $W$ (dens) 1.68162
- $a$ (dens) 2.55174
- $r$ (dens) 9.96376
- $\varepsilon_s$ -0.39735
- $\varepsilon_p$ -0.14998
- $\varepsilon_d$ 0.21210
Influence of virtual orbital energy (3d) to Al (fcc) band structure

The bands of upper part are shifted up constantly as orbε(3d) becomes larger.

Influence of W(orb) to Al (fcc) band structure

The bands of upper part go lower as W(orb) becomes larger.
Influence of \( a(\text{orb}) \) to Al (fcc) band structure

- Too small \( a(\text{orb}) \) gives the worse band structure

Influence of \( r(\text{orb}) \) to Al (fcc) band structure

- \( r(\text{orb}) \) strongly influences DFTB band structure
In particular for main group elements, there seems to be a correlation between $r(\text{orb})$ and atomic diameter.

**Straightforward application to binary crystal structures**

- **Rocksalt** (space group No. 225)
  - NaCl
  - MgO
  - MoC
  - AgCl
  - ... (more than 100 pairs tested)

- **B2** (space group No. 221)
  - CsCl
  - FeAl
  - ...

- **Zincblende** (space group No. 216)
  - SiC
  - CuCl
  - ZnS
  - GaAs
  - ...

- **Others**
  - Wurtzite (BeO, AlO, ZnO, GaN, …)
  - Hexagonal (BN, WC)
  - Rhombohedral (ABCABC stacking sequence, BN)

  ➢ more than 100 pairs tested
Selected examples for binary crystal structures

- NaCl (rocksalt)  
  ![Graph showing energy levels for NaCl (rocksalt)]

- FeAl (b2)  
  ![Graph showing energy levels for FeAl (b2)]

- GaAs (zincblende)  
  ![Graph showing energy levels for GaAs (zincblende)]

- BN (wurtzite)  
  ![Graph showing energy levels for BN (wurtzite)]

• $d^7s^1$ is used in POTCAR (DFT)

Further improvement can be performed for specific purpose but this preliminary sets will work as good starting points.

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- Marcus Elstner
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