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

Part I

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

Part II

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4. Extensions
5. Performance and Applications

Resources

1. http://www.dftb.org
2. **DFTB** Porezag, D., T. Frauenheim, T. Köhler, G. Seifert, and R. Kaschner, *Construction of tight-binding-like potentials on the basis of density-functional theory: application to carbon.* Phys. Rev. B, 1995. **51**: p. 12947-12957.
3. **DFTB** Seifert, G., D. Porezag, and T. Frauenheim, *Calculations of molecules, clusters, and solids with a simplified LCAO-DFT-LDA scheme.* Int. J. Quantum Chem., 1996. **58**: p. 185-192.
4. **SCC-DFTB** Elstner, M., D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, T. Frauenheim, S. Suhai, and G. Seifert, *Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties.* Phys. Rev. B, 1998. **58**: p. 7260-7268.
5. **SCC-DFTB-D** Elstner, M., P. Hobza, T. Frauenheim, S. Suhai, and E. Kaxiras, *Hydrogen bonding and stacking interactions of nucleic acid base pairs: A density-functional-theory based treatment.* J. Chem. Phys,, 2001. **114**: p. 5149-5155.
6. **SDFTB** Kohler, C., G. Seifert, U. Gerstmann, M. Elstner, H. Overhof, and T. Frauenheim, *Approximate density-functional calculations of spin densities in large molecular systems and complex solids.* Phys. Chem. Chem. Phys., 2001. **3**: p. 5109-5114.
7. **DFTB3** Gaus, M.; Cui, C.; Elstner, M. *DFTB3: Extension of the Self-Consistent-Charge Density-Functional Tight-Binding Method (SCC-DFTB).* J. Chem. Theory Comput., 2011. **7**: p. 931-948.

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) (Qiang 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)

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:**

$$E_{\mathrm{TB}} = \boxed{\sum_i^N \epsilon_i} + \boxed{\frac{1}{2}\sum_{j\neq k}^M v^{j,k}(|R_j - R_k|)}$$

- This separation of one-electron energies and interatomic distance-dependent potential $v^{j,k}$ **constitutes the TB method**

Tight-Binding

- ε_ι are eigenvalues of a Schrodinger-like equation

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

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

$$|\underline{H} - \epsilon\underline{S}| = 0$$

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

- $\underline{H}$ and $\underline{S}$ are constructed using nearest-neighbor relationships; typically *only nearest-neighbor interactions* are considered: **Similarity to extended Hückel method**

Extended Huckel (EHT) Method

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

  $\mathbf{H}\,\mathbf{C}_i = \varepsilon_i\,\mathbf{S}\,\mathbf{C}_i$

- **H** – Hamiltonian matrix constructed using nearest neighbor relationships
- $\mathbf{C}_i$ – column vector of the i-th molecular orbital coefficients
- ε_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 $\mathbf{S}$:
  - Orthogonal TB $\mathbf{H}\Psi = E\Psi$
  - Non-orthogonal TB $\mathbf{H}\Psi = E\mathbf{S}\Psi$
- 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

$$\mathbf{f}_I = -\langle\psi \mid \frac{\partial H}{\partial \mathbf{R}_I} \mid \psi\rangle$$

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

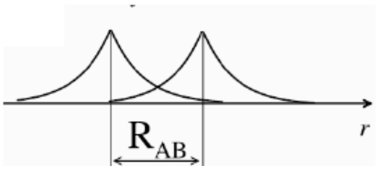
Slater-Koster (SK) Approximation (I)

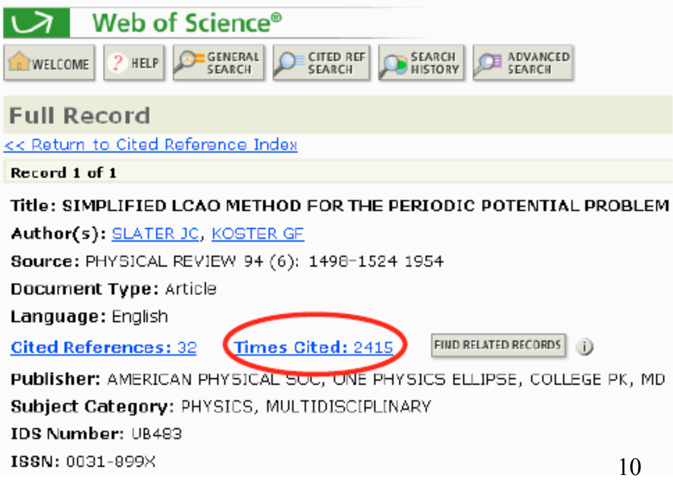
- The key moment is how we calculate one-electron integrals

$$h_{pq} = \langle p \mid h \mid q\rangle = \int d^3r\chi_p^*(\mathbf{r})\left[-\frac{1}{2}\nabla^2 - \sum_{\mathbf{n}}\frac{Z_{\mathbf{n}}}{|\mathbf{R}_{\mathbf{n}} - \mathbf{r}|}\right]\chi_{\mathbf{q}}(\mathbf{r})$$

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

- Instead of introducing basis functions, e.g., Slater-like for the radial part and s,p,d for the angular part, then doing the integrals, we introduce an analytical function which depends on R_{AB} only times another function which depends on the overlap of the angular functions localized at the atoms





Full Record

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Record 1 of 1

Title: SIMPLIFIED LCAO METHOD FOR THE PERIODIC POTENTIAL PROBLEM

Author(s): SLATER JC, KOSTER GF

Source: PHYSICAL REVIEW 94 (6): 1498-1524 1954

Document Type: Article

Language: English

Cited References: 32 **Times Cited:** 2415

Publisher: AMERICAN PHYSICAL SOC, ONE PHYSICS ELLIPSE, COLLEGE PK, MD

Subject Category: PHYSICS, MULTIDISCIPLINARY

IDS Number: UB483

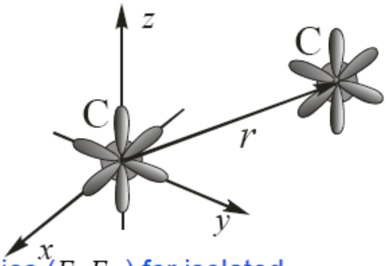
ISSN: 0031-899X

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)

	s	p_x	p_y	p_z
Atom 1:	$\mid s_1\rangle,$	$\mid x_1\rangle,$	$\mid y_1\rangle,$	$\mid z_1\rangle$
Atom 2:	$\mid s_2\rangle,$	$\mid x_2\rangle,$	$\mid y_2\rangle,$	$\mid z_2\rangle$



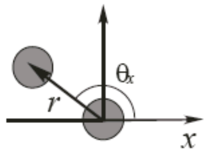
$$h_{pq} = \langle p \mid h \mid q \rangle = \int d^3r\, \chi_p^*(\mathbf{r}) \left[-\frac{1}{2}\nabla^2 - \sum_{\mathbf{n}} \frac{Z_{\mathbf{n}}}{|\mathbf{R_n} - \mathbf{r}|} \right] \chi_{\mathbf{q}}(\mathbf{r})$$

- 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

$$h_{qq} = E_s \quad = \quad \langle q \mid H \mid q \rangle \qquad q \text{ is the s orbital}$$

$$h_{qq} = E_p \quad = \quad \langle q \mid H \mid q \rangle \qquad q \text{ is any of the p orbitals}$$

- Off-diagonal elements:



s-s: Assume that for s-s atomic orbitals, $h_{p_s q_s} = s(r)E_{s,s} = s(r)V_{ss}$

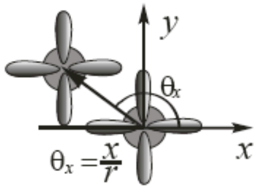
$s(r)$ is an analytical function which depends on r only

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,

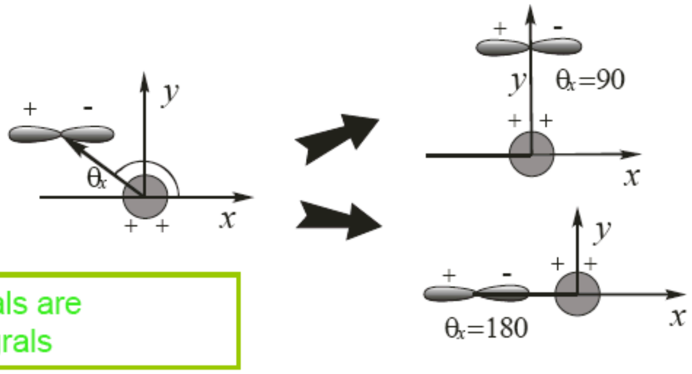
$$h_{q_s q_{p_x}} = s(r)E_{s,x} = s(r)V_{sp\sigma}l$$

$s(r)$ is the same analytical function

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

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

l reflects the anisotropy o f 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_x-p_x atomic orbitals, the matrix element is

$$h_{p_x p_x} = s(r)E_{x,x} = s(r)[l^2 V_{pp\sigma} + (1-l^2)V_{pp\pi}]$$

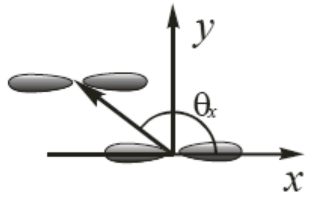
Analogously, p_x-p_y matrix element is

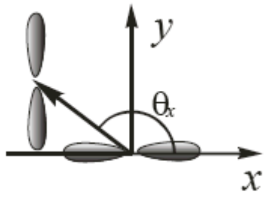
$$h_{p_x p_y} = s(r)E_{x,y} = s(r)[lmV_{pp\sigma} - lmV_{pp\pi}]$$

p_z-p_z matrix element is

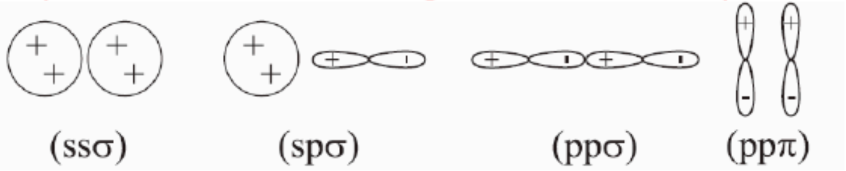
$$h_{p_z p_z} = s(r)E_{z,z} = s(r)[n^2 V_{pp\sigma} + (1-n^2)V_{pp\pi}]$$

$$l = x/r,\ m = y/r,\ n = z/r$$





- Four non-equivalent fundamental ontegrals between s and p atomic orbitals

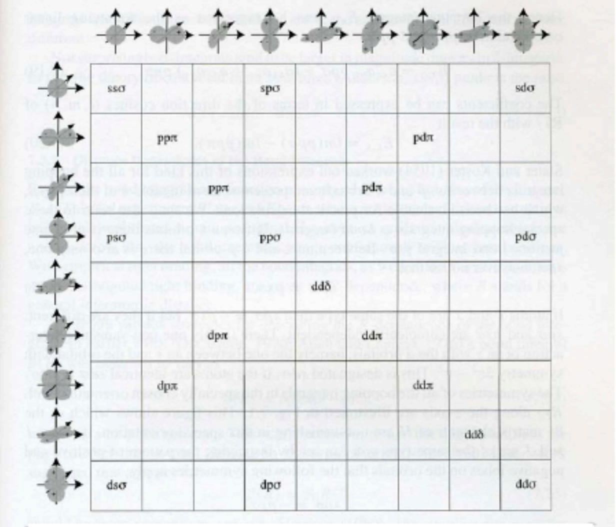


- p-d: We can derive similar formulas for d orbitals as well

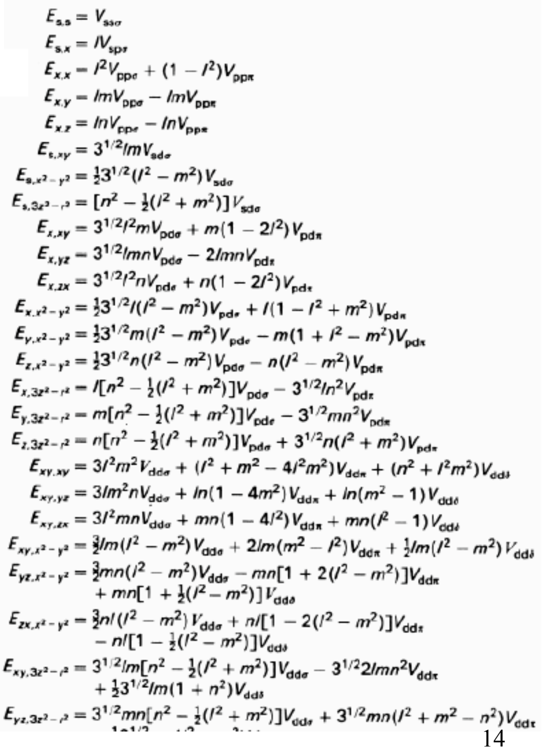
Source: http://beam.acclab.helsinki.fi/~akrashen/esctmp.html

SK Tables

So, all together, the integral look as follow:



Independent two center hopping integrals between atoms on the z-axis (from M. Finnis, “Interatomic forces in Condensed Matter)



$$E_{s,s} = V_{ss\sigma}$$
$$E_{s,x} = lV_{sp\sigma}$$
$$E_{x,x} = l^2V_{pp\sigma} + (1-l^2)V_{pp\pi}$$
$$E_{x,y} = lmV_{pp\sigma} - lmV_{pp\pi}$$
$$E_{x,z} = lnV_{pp\sigma} - lnV_{pp\pi}$$
$$E_{s,xy} = 3^{1/2}lmV_{sd\sigma}$$
$$E_{s,x^2-y^2} = \tfrac{1}{2}3^{1/2}(l^2-m^2)V_{sd\sigma}$$
$$E_{s,3z^2-r^2} = [n^2 - \tfrac{1}{2}(l^2+m^2)]V_{sd\sigma}$$
$$E_{x,xy} = 3^{1/2}l^2mV_{pd\sigma} + m(1-2l^2)V_{pd\pi}$$
$$E_{x,yz} = 3^{1/2}lmnV_{pd\sigma} - 2lmnV_{pd\pi}$$
$$E_{x,zx} = 3^{1/2}l^2nV_{pd\sigma} + n(1-2l^2)V_{pd\pi}$$
$$E_{x,x^2-y^2} = \tfrac{1}{2}3^{1/2}l(l^2-m^2)V_{pd\sigma} + l(1-l^2+m^2)V_{pd\pi}$$
$$E_{y,x^2-y^2} = \tfrac{1}{2}3^{1/2}m(l^2-m^2)V_{pd\sigma} - m(1+l^2-m^2)V_{pd\pi}$$
$$E_{z,x^2-y^2} = \tfrac{1}{2}3^{1/2}n(l^2-m^2)V_{pd\sigma} - n(l^2-m^2)V_{pd\pi}$$
$$E_{x,3z^2-r^2} = l[n^2 - \tfrac{1}{2}(l^2+m^2)]V_{pd\sigma} - 3^{1/2}ln^2V_{pd\pi}$$
$$E_{y,3z^2-r^2} = m[n^2 - \tfrac{1}{2}(l^2+m^2)]V_{pd\sigma} - 3^{1/2}mn^2V_{pd\pi}$$
$$E_{z,3z^2-r^2} = n[n^2 - \tfrac{1}{2}(l^2+m^2)]V_{pd\sigma} + 3^{1/2}n(l^2+m^2)V_{pd\pi}$$
$$E_{xy,xy} = 3l^2m^2V_{dd\sigma} + (l^2+m^2-4l^2m^2)V_{dd\pi} + (n^2+l^2m^2)V_{dd\delta}$$
$$E_{xy,yz} = 3lm^2nV_{dd\sigma} + ln(1-4m^2)V_{dd\pi} + ln(m^2-1)V_{dd\delta}$$
$$E_{xy,zx} = 3l^2mnV_{dd\sigma} + mn(1-4l^2)V_{dd\pi} + mn(l^2-1)V_{dd\delta}$$
$$E_{xy,x^2-y^2} = \tfrac{3}{2}lm(l^2-m^2)V_{dd\sigma} + 2lm(m^2-l^2)V_{dd\pi} + \tfrac{1}{2}lm(l^2-m^2)V_{dd\delta}$$
$$E_{yz,x^2-y^2} = \tfrac{3}{2}mn(l^2-m^2)V_{dd\sigma} - mn[1+2(l^2-m^2)]V_{dd\pi} + mn[1+\tfrac{1}{2}(l^2-m^2)]V_{dd\delta}$$
$$E_{zx,x^2-y^2} = \tfrac{3}{2}nl(l^2-m^2)V_{dd\sigma} + nl[1-2(l^2-m^2)]V_{dd\pi} - nl[1-\tfrac{1}{2}(l^2-m^2)]V_{dd\delta}$$
$$E_{xy,3z^2-r^2} = 3^{1/2}lm[n^2-\tfrac{1}{2}(l^2+m^2)]V_{dd\sigma} - 3^{1/2}2lmn^2V_{dd\pi} + \tfrac{1}{2}3^{1/2}lm(1+n^2)V_{dd\delta}$$
$$E_{yz,3z^2-r^2} = 3^{1/2}mn[n^2-\tfrac{1}{2}(l^2+m^2)]V_{dd\sigma} + 3^{1/2}mn(l^2+m^2-n^2)V_{dd\pi}$$

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

Density-Functional Tight-Binding

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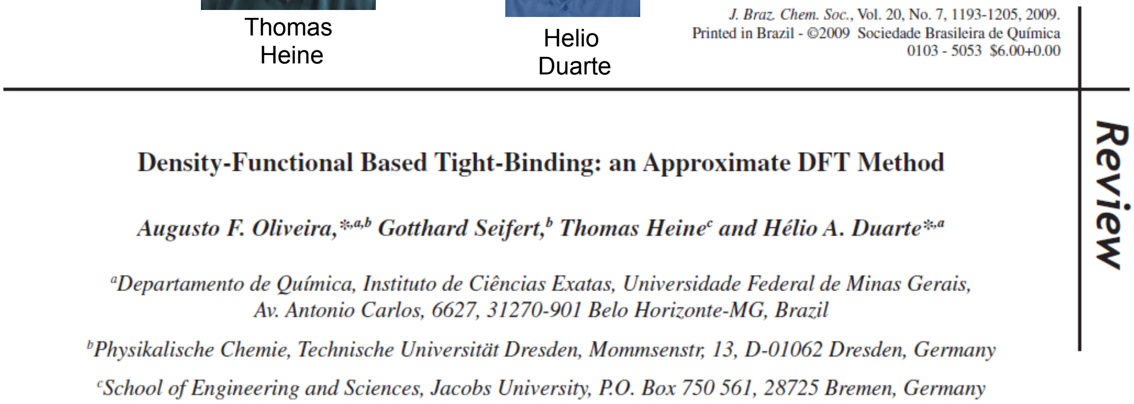
4. Extensions
5. Performance and Applications

Taken from Oliviera, Seifert, Heine, Duarte, *J. Braz. Chem. Soc. 20*, 1193-1205 (2009)

Thomas
Heine

Helio
Duarte



J. Braz. Chem. Soc., Vol. 20, No. 7, 1193-1205, 2009.
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Review

Density-Functional Based Tight-Binding: an Approximate DFT Method

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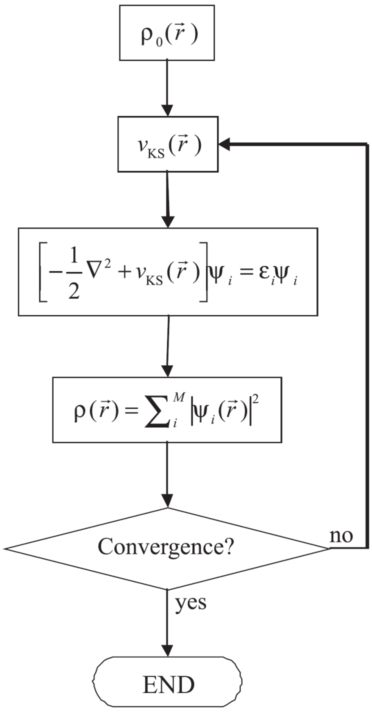
...open access

Density Functional Theory (DFT)

Walter Kohn/John A. Pople 1998


$\rho_0(\vec r)$

$v_{KS}(\vec r)$

$\left[-\frac{1}{2}\nabla^2 + v_{KS}(\vec r)\right]\psi_i = \varepsilon_i\psi_i$

$\rho(\vec r) = \sum_i^M |\psi_i(\vec r)|^2$

at convergence:

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

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

$$= \sum_{i=1}^{M} n_i \varepsilon_i + E_{rep}$$

Various criteria for convergence possible:

- Electron density
- Potential
- Orbitals
- Energy
- Combinations of above quantities

Foulkes + Haydock Ansatz

Phys. Rev. B, *39*, 12520 (1989)

$$\rho(\vec r) = \rho_0(\vec r) + \delta\rho(\vec r)$$

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

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

$$+\frac{1}{2}\iint \frac{\delta\rho'(\rho_0 + \delta\rho)}{|\vec r - \vec r\,'|} d\vec r d\vec r\,' + E_{xc}[\rho_0 + \delta\rho] + E_{nn}$$

Self-consistent-charge density-functional tight-binding (SCC-DFTB)

M. Elstner *et al.*, *Phys. Rev. B* **58** 7260 (1998)

Approximate density functional theory (DFT) method!

Second order-expansion of DFT energy in terms of reference density ρ_0 and charge fluctuation ρ_1 ($\rho \cong \rho_0 + \rho_1$) yields:

$$E[\rho] = \underbrace{\sum_{i}^{\substack{\text{valence}\\\text{orbitals}}} n_i \langle \phi_i | \hat{H}[\rho_0] | \phi_i \rangle}_{1} + \underbrace{\sum_{i}^{\substack{\text{core}\\\text{orbitals}}} n_i \langle \phi_i | \hat{H}[\rho_0] | \phi_i \rangle}_{2} + \underbrace{E_{\text{xc}}[\rho_0]}_{3} - \underbrace{\frac{1}{2}\int_{\mathbf{R}^3} \rho_0 V_H[\rho_0]}_{4} -$$

$$- \underbrace{\int_{\mathbf{R}^3} \rho_0 V_{\text{xc}}[\rho_0]}_{5} + \underbrace{E_{\text{nucl}}}_{6} + \underbrace{\frac{1}{2}\int_{\mathbf{R}^3} \rho_1 V_H[\rho_1]}_{7} + \underbrace{\frac{1}{2}\iint_{\mathbf{R}^3} \frac{\delta^2 E_{\text{xc}}}{\delta \rho_1^2}\bigg|_{\rho_0} \rho_1^2}_{8} + o(3)$$

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

$$E^{\text{DFTB}} = \underbrace{\sum_{i}^{\substack{\text{valence}\\\text{orbitals}}} n_i \varepsilon_i}_{\text{term 1}} + \underbrace{\frac{1}{2}\sum_{A \neq B}^{\text{atoms}} E_{\text{rep}}^{AB}}_{\text{terms 2–6}}$$

$$E^{\text{SCC–DFTB}} = \underbrace{\sum_{i}^{\substack{\text{valence}\\\text{orbitals}}} n_i \varepsilon_i}_{\text{term 1}} + \underbrace{\frac{1}{2}\sum_{A,B}^{\text{atoms}} \gamma_{AB} \Delta q_A \Delta q_B}_{\text{terms 7–8}} + \underbrace{\frac{1}{2}\sum_{A \neq B}^{\text{atoms}} E_{\text{rep}}^{AB}}_{\text{terms 2–6}}$$

- where
  - n_i and ε_i — occupation and orbital energy ot the i^{th} Kohn-Sham eigenstate
  - E_{rep} — distance-dependent diatomic repulsive potentials
  - Δq_A — induced charge on atom A
  - γ_{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 ρ_0 is constructed from atomic densities

$$\rho_0 = \sum_{A}^{\text{atoms}} \rho_0^A$$

- Kohn-Sham eigenstates ϕ_i are expanded in Slater basis of valence pseudoatomic orbitals χ_i

$$\phi_i = \sum_{\mu}^{\text{AO}} c_{\mu i}\chi_\mu$$

- The DFTB energy is obtained by solving a generalized DFTB eigenvalue problem with **H**^{0} computed by atomic and diatomic DFT

$$\mathbf{H}^0\mathbf{C} = \mathbf{SC}\varepsilon \qquad \text{with} \quad S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$$

$$H^0_{\mu\nu} = \langle \chi_\mu | \hat{H}\left[\rho_0^M, \rho_0^N\right] | \chi_\nu \rangle$$

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_{rep}.

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

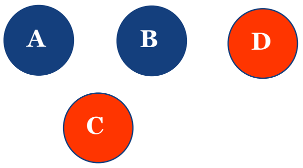
From Elstner et al., PRB 1998

$$V_{eff}\left[\rho_0\right] \approx V_{eff}\left[\rho_A + \rho_B\right] \qquad \text{(Density superposition)}$$

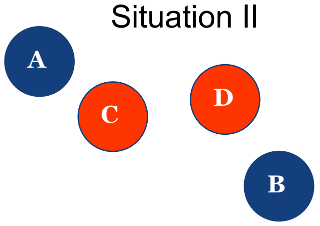
$$V_{eff}\left[\rho_0\right] \approx V_{eff}\left[\rho_A\right] + V_{eff}\left[\rho_B\right] \qquad \text{(Potential superposition)}$$

Both approximations are justified by the screening argument: Far away, neutral atoms have no Coulomb contribution.

Situation I



Situation II



SCC-DFTB matrix elements

LCAO ansatz of wave function

$$\Psi_i = \sum_\nu c_\nu^i \underset{\text{pseudoatomic orbital}}{\underline{\underline{\phi_\nu(\mathbf{r}-\mathbf{R}_\alpha)}}} \xrightarrow[\text{principle}]{\text{variational}}$$

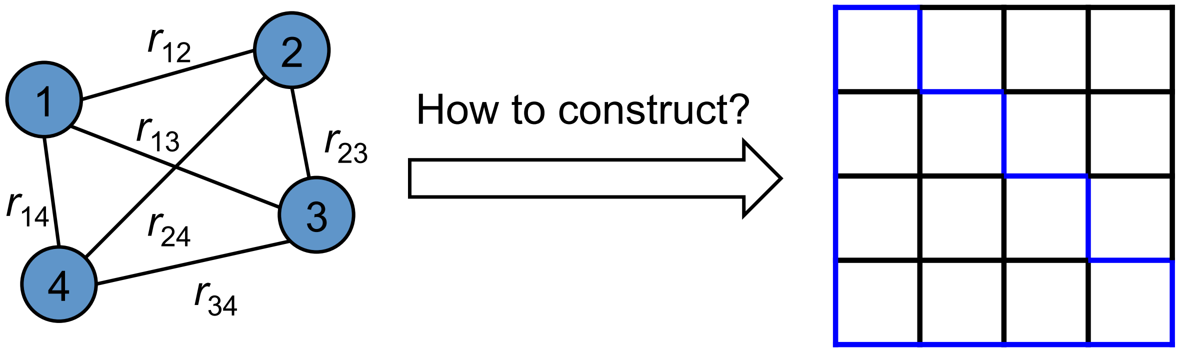
secular equations

$$\sum_\nu c_\nu^i \left(\underset{\uparrow\ \text{Hamiltonian}}{H_{\mu\nu}} - \varepsilon_i \underset{\nwarrow\ \text{Overlap}}{S_{\mu\nu}}\right) = 0$$

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



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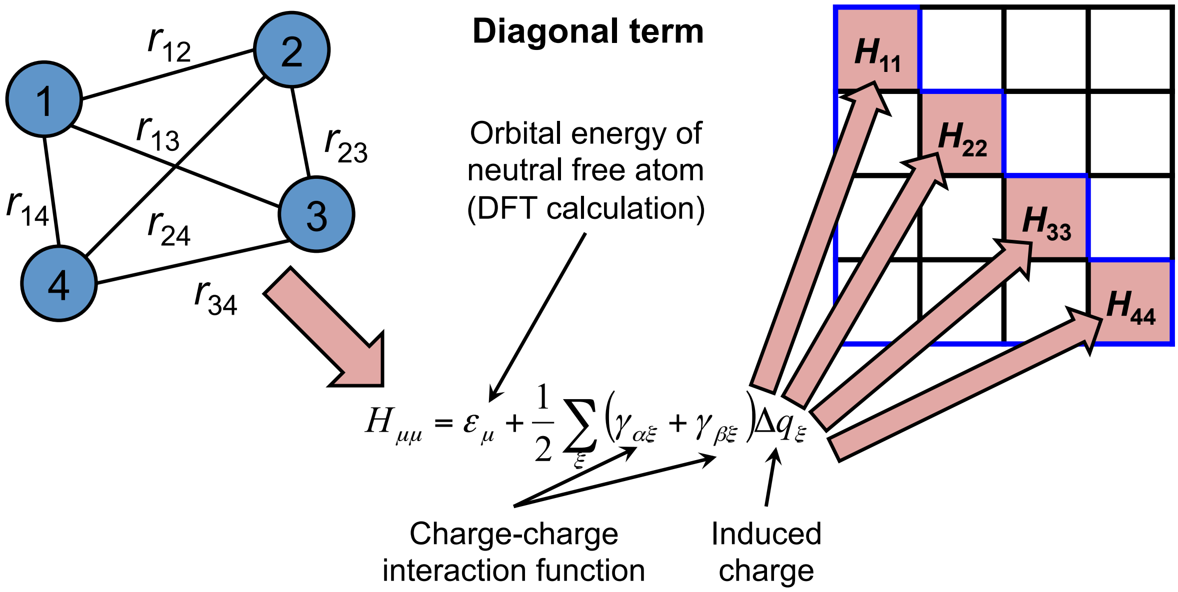


Diagonal term

Orbital energy of neutral free atom (DFT calculation)

$$H_{\mu\mu} = \varepsilon_\mu + \frac{1}{2}\sum_\xi \left(\gamma_{\alpha\xi} + \gamma_{\beta\xi}\right)\Delta q_\xi$$

Charge-charge interaction function

Induced charge

SCC-DFTB matrix elements

LCAO ansatz of wave function

$$\Psi_i = \sum_\nu c_\nu^i \underset{\text{pseudoatomic orbital}}{\underline{\underline{\phi_\nu(\mathbf{r}-\mathbf{R}_\alpha)}}}$$

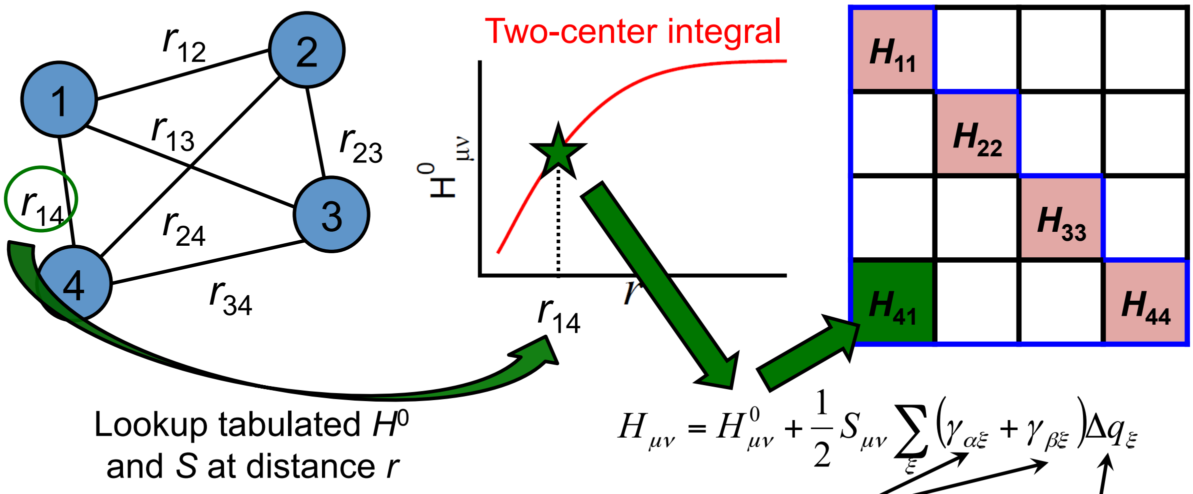
$\xrightarrow[\text{principle}]{\text{variational}}$

secular equations

$$\sum_\nu c_\nu^i \left(\underset{\uparrow}{H_{\mu\nu}} - \varepsilon_i \underset{\nwarrow}{S_{\mu\nu}}\right) = 0$$

Hamiltonian Overlap

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



Lookup tabulated H^0
and S at distance r

$$H_{\mu\nu} = H^0_{\mu\nu} + \frac{1}{2} S_{\mu\nu} \sum_\xi \left(\gamma_{\alpha\xi} + \gamma_{\beta\xi}\right) \Delta q_\xi$$

Charge-charge interaction function

Induced charge

SCC-DFTB matrix elements

LCAO ansatz of wave function

$$\Psi_i = \sum_\nu c_\nu^i \underset{\text{pseudoatomic orbital}}{\underline{\underline{\phi_\nu(\mathbf{r}-\mathbf{R}_\alpha)}}}$$

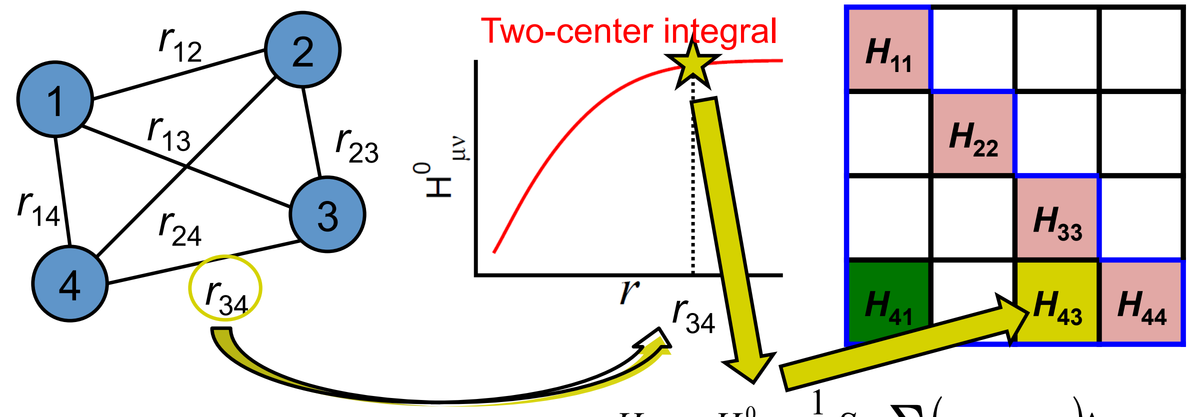
$\xrightarrow[\text{principle}]{\text{variational}}$

secular equations

$$\sum_\nu c_\nu^i \left(\underset{\uparrow}{H_{\mu\nu}} - \varepsilon_i \underset{\nwarrow}{S_{\mu\nu}}\right) = 0$$

Hamiltonian Overlap

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



Lookup tabulated H^0
and S at distance r

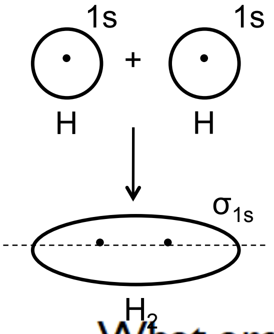
$$H_{\mu\nu} = H^0_{\mu\nu} + \frac{1}{2} S_{\mu\nu} \sum_\xi \left(\gamma_{\alpha\xi} + \gamma_{\beta\xi}\right) \Delta q_\xi$$

Charge-charge interaction function

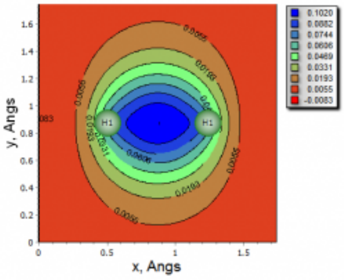
Induced charge

- Repeat until building **off-diagonal term**

DFTB parameters



H_2 difference density $\Delta\rho = \rho - \Sigma_a \rho_a$

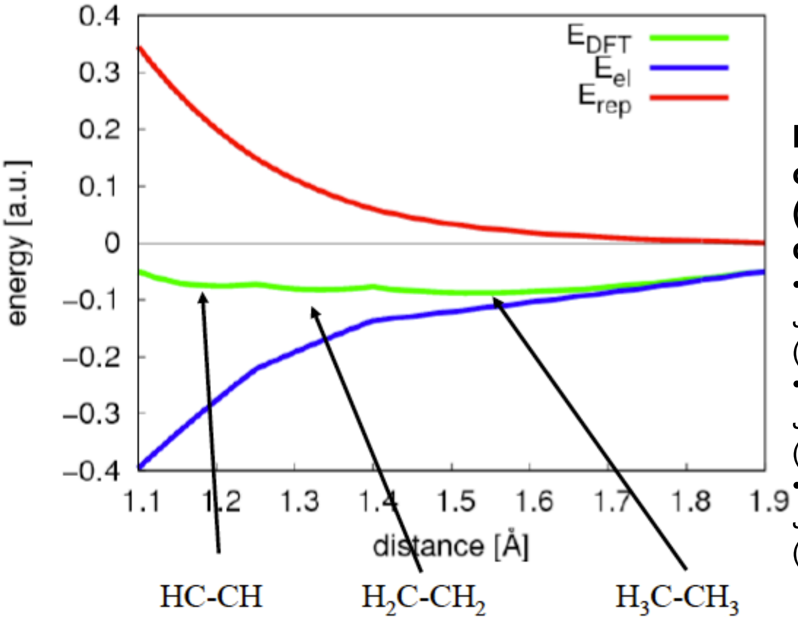


What are the 'free' parameters?

- 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

DFTB repulsive potential E_{rep}

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



Development of (semi-)automatic fitting:

- Knaup, J. *et al.*, *JPCA*, **111**, 5637, (2007)
- Gaus, M. *et al.*, *JPCA*, **113**, 11866, (2009)
- Bodrog Z. *et al.*, *JCTC*, **7**, 2654, (2011)

Which molecular systems to include?

SCC-DFTB method (I)

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

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

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

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

$$H_{\mu\nu} = \langle \chi_\mu | \hat{H}[\rho_0^M, \rho_0^N] | \chi_\nu \rangle + \frac{1}{2} S_{\mu\nu} \sum_{K}^{\text{atoms}} (\gamma_{MK} + \gamma_{NK}) \Delta q_K$$

SCC-DFTB method (II)

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

$$E^2[\rho, \rho_0] = \frac{1}{2} \iint' \left(\frac{1}{|\vec{r} - \vec{r}'|} + \left. \frac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho'} \right|_{n_0} \right) \Delta\rho\,\Delta\rho'$$

Represent by atomic contributions:

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

Monopole approximation

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

$$E^2[\rho, \rho_0] \approx \frac{1}{2} \sum_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \iint' \left(\frac{1}{|\vec{r} - \vec{r}'|} + \left. \frac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho'} \right|_{n_0} \right) F_{00}^\alpha F_{00}^\beta Y_{00}^2$$

Basic assumptions:

- Only transfer of net charge between atoms
- Size and shape of atom (in molecule) unchanged

SCC-DFTB method (III)

$$E^2[\rho,\rho_0] \approx \frac{1}{2}\sum_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \iint' \left(\frac{1}{|\vec{r}-\vec{r}'|} + \left.\frac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho'}\right|_{n_0} \right) F_{00}^{\alpha} F_{00}^{\beta} Y_{00}^2$$

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. $\alpha = \beta$

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

New (Hubbard) parameter U_α: computed from DFT (PBE)

SCC-DFTB method (IV)

Derive analytical function which interpolates between these two cases

$$E^2[\rho,\rho_0] \approx \frac{1}{2}\sum_{\alpha\beta} \Delta q_\alpha \Delta q_\beta \iint' \left(\frac{1}{|\vec{r}-\vec{r}'|} + \left.\frac{\delta^2 E_{xc}}{\delta\rho\,\delta\rho'}\right|_{n_0} \right) F_{00}^{\alpha} F_{00}^{\beta} Y_{00}^2$$

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

Klopmann-Ohno: $\gamma_{\alpha\beta} = \dfrac{1}{\sqrt{R^2 + \frac{1}{4}\left(U_\alpha^{-1} + U_\beta^{-1}\right)^2}}$

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

Elstner et al. (1998): Phys. Rev. B **58**, 7260 (1998)

Gradient for the DFTB methods

The DFTB force formula

$$F_a = -\sum_{i}^{\text{MO}} n_i \sum_{\mu\nu}^{\text{AO}} c_{\mu i} c_{\nu i} \left[\frac{\partial H^0_{\mu\nu}}{\partial a} - \varepsilon_i \frac{\partial S_{\mu\nu}}{\partial a} \right] - \frac{\partial E_{\text{rep}}}{\partial a}$$

The SCC-DFTB force formula

$$F_a = -\sum_{i}^{\text{MO}} n_i \sum_{\mu\nu}^{\text{AO}} c_{\mu i} c_{\nu i} \left[\frac{\partial H^0_{\mu\nu}}{\partial a} - \left(\varepsilon_i - \frac{1}{2} \sum_{K}^{\text{atoms}} (\gamma_{MK} + \gamma_{NK}) \Delta q_K \right) \frac{\partial S_{\mu\nu}}{\partial a} \right] -$$

$$- \Delta q_A \sum_{K}^{\text{atoms}} \frac{\partial \gamma_{AK}}{\partial a} \Delta q_K - \frac{\partial E_{\text{rep}}}{\partial a}$$

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 $(\rho_0, 0)$ yields

$$E\left[\rho,\rho^{S}\right] = \underbrace{\sum_{i}^{\substack{\text{valence}\\\text{orbitals}}} n_i \langle \phi_i | \hat{H}[\rho_0] | \phi_i \rangle}_{1} + \underbrace{\sum_{i}^{\substack{\text{core}\\\text{orbitals}}} n_i \langle \phi_i | \hat{H}[\rho_0] | \phi_i \rangle}_{2} + \underbrace{E_{\text{xc}}[\rho_0]}_{3} - \underbrace{\frac{1}{2} \int_{\mathbf{R}^3} \rho_0 V_H[\rho_0]}_{4} -$$

$$-\underbrace{\int_{\mathbf{R}^3} \rho_0 V_{\text{xc}}[\rho_0]}_{5} + \underbrace{E_{\text{nucl}}}_{6} + \underbrace{\frac{1}{2} \int_{\mathbf{R}^3} \rho_1 V_H[\rho_1]}_{7} + \underbrace{\frac{1}{2} \iint_{\mathbf{R}^3} \left. \frac{\delta^2 E_{\text{xc}}}{\delta \rho_1^2} \right|_{(\rho_0,0)} \rho_1^2}_{8} + \underbrace{\frac{1}{2} \iint_{\mathbf{R}^3} \left. \frac{\delta^2 E_{\text{xc}}}{\left(\delta \rho^{S}\right)^2} \right|_{(\rho_0,0)} \left(\rho^{S}\right)^2}_{9} + o(3)$$

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

Spin-polarized DFTB (SDFTB)

$$E^{\mathrm{SDFTB}} = \underbrace{\sum_{i}^{\substack{\text{valence}\\ \text{orbitals}}} n_i^{\uparrow}\varepsilon_i^{\uparrow} + \sum_{i}^{\substack{\text{valence}\\ \text{orbitals}}} n_i^{\downarrow}\varepsilon_i^{\downarrow}}_{\text{term 1}} + \underbrace{\frac{1}{2}\sum_{A\neq B}^{\text{atoms}} \gamma_{AB}\Delta q_A \Delta q_B}_{\text{terms 7-8}} + \underbrace{\frac{1}{2}\sum_{A\neq B}^{\text{atoms}} E_{\text{rep}}^{AB}}_{\text{terms 2-6}} + \underbrace{\frac{1}{2}\sum_{A}^{\text{atoms}}\sum_{l\in A}\sum_{l'\in A} p_{A\,l}\,p_{A\,l'}\,W_{A\,ll'}}_{\text{term 9}}$$

where $p_{A\,l}$ — spin population of shell l on atom A

$W_{A\,ll'}$ — spin-population interaction functional $$W_{All'} = \frac{1}{2}\left(\frac{\partial\epsilon_{Al}^{\uparrow}}{\partial n_{l'}^{\uparrow}} - \frac{\epsilon_{Al}^{\uparrow}}{\partial n_{l'}^{\downarrow}}\right)_{\rho=0} = W_{Al'l}$$

- Spin populations $p_{A\,l}$ and induced charges Δq_A are obtained from Mulliken population analysis

$$\Delta q_A = \sum_{i}^{\text{MO}}\sum_{\mu\in A}\sum_{\nu}^{\text{AO}}\left(n_i^{\uparrow}c_{\mu i}^{\uparrow}c_{\nu i}^{\uparrow} + n_i^{\downarrow}c_{\mu i}^{\downarrow}c_{\nu i}^{\downarrow}\right)S_{\mu\nu} - q_A^0$$

$$p_{A\,l} = \sum_{i}^{\text{MO}}\sum_{\mu\in A,l}\sum_{\nu}^{\text{AO}}\left(n_i^{\uparrow}c_{\mu i}^{\uparrow}c_{\nu i}^{\uparrow} - n_i^{\downarrow}c_{\mu i}^{\downarrow}c_{\nu i}^{\downarrow}\right)S_{\mu\nu}$$

Spin-polarized DFTB (SDFTB)

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

$$\mathbf{H}^{\uparrow}\mathbf{C}^{\uparrow} = \mathbf{S}\mathbf{C}^{\uparrow}\varepsilon^{\uparrow}$$

$$\mathbf{H}^{\downarrow}\mathbf{C}^{\downarrow} = \mathbf{S}\mathbf{C}^{\downarrow}\varepsilon^{\downarrow}$$

where

$$S_{\mu\nu} = \left\langle \chi_\mu \middle| \chi_\nu \right\rangle$$

$$H_{\mu\nu}^{\uparrow} = \left\langle \chi_\mu \middle| \hat{H}\left[\rho_0^M, \rho_0^N\right] \middle| \chi_\mu \right\rangle + \frac{1}{2}S_{\mu\nu}\sum_{K}^{\text{atoms}}\left(\gamma_{MK} + \gamma_{NK}\right)\Delta q_K + \delta_{MN}\frac{1}{2}S_{\mu\nu}\sum_{l''\in M}\left(W_{All'} + W_{All''}\right)p_{M\,l''}$$

$$H_{\mu\nu}^{\downarrow} = \left\langle \chi_\mu \middle| \hat{H}\left[\rho_0^M, \rho_0^N\right] \middle| \chi_\mu \right\rangle + \frac{1}{2}S_{\mu\nu}\sum_{K}^{\text{atoms}}\left(\gamma_{MK} + \gamma_{NK}\right)\Delta q_K - \delta_{MN}\frac{1}{2}S_{\mu\nu}\sum_{l''\in M}\left(W_{All'} + W_{All''}\right)p_{M\,l''}$$

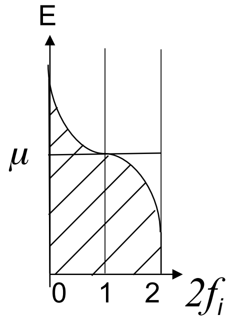
M,N,K: indexing specific atoms

SCC-DFTB w/fractional orbital occupation numbers

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

TB-eigenvalue equation $\sum_{\nu} c_{\nu i}\left(H_{\mu\nu} - \varepsilon_i S_{\mu\nu}\right) = 0$

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



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

M. Weinert, J. W. Davenport, *Phys. Rev. B* **45**, 13709 (1992)

$$f_i = \frac{1}{\exp\left[\left(\varepsilon_i - \mu\right)/k_B T_e\right] + 1}$$

T_e: electronic temperature

S_e: electronic entropy

$0 \le f_i \le 1$

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

$$S_e = -2k_B \sum_i^{\infty} f_i \ln f_i + \left(1 - f_i\right)\ln\left(1 - f_i\right)$$

Atomic force

$$\vec{F}_\alpha = -2\sum_i f_i \sum_{\mu\nu} c_{\mu i} c_{\nu i}\left[\frac{\partial H^0_{\mu\nu}}{\partial \vec{R}_\alpha} - \left(\varepsilon_i - \frac{H^1_{\mu\nu}}{S_{\mu\nu}}\right)\frac{\partial S_{\mu\nu}}{\partial \vec{R}_\alpha}\right] - \Delta q_\alpha \sum_{\xi}^{N} \frac{\partial \gamma_{\alpha\xi}}{\partial \vec{R}_\alpha}\Delta q_\xi - \frac{\partial E_{rep}}{\partial \vec{R}_\alpha}$$

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

M. Weinert, J. W. Davenport, *Phys. Rev. B* **45**, 13709 (1992)

$$F_\alpha^{elect} \equiv \vec{F}_{HF} + \vec{F}_{pulay} + \vec{F}_{charge}$$

$$= \sum_i^{\infty} \frac{\partial}{\partial x}\left(\varepsilon_i f_i\right) = \sum_i^{\infty} f_i \frac{\partial \varepsilon_i}{\partial x} + \sum_i^{\infty} \varepsilon_i \frac{\partial f_i}{\partial x}$$

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

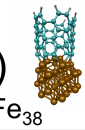
$$= \sum_i^{\infty} \frac{\partial}{\partial x}\left(\varepsilon_i f_i\right) + \frac{\partial\left(-T_e S\right)}{\partial x}$$

$$= \sum_i^{\infty} f_i \frac{\partial \varepsilon_i}{\partial x} + \boxed{\sum_i^{\infty} \varepsilon_i \frac{\partial f_i}{\partial x} - \sum_i^{\infty} \varepsilon_i \frac{\partial f_i}{\partial x}}$$

Correction term arising from Fermi distribution function cancels out

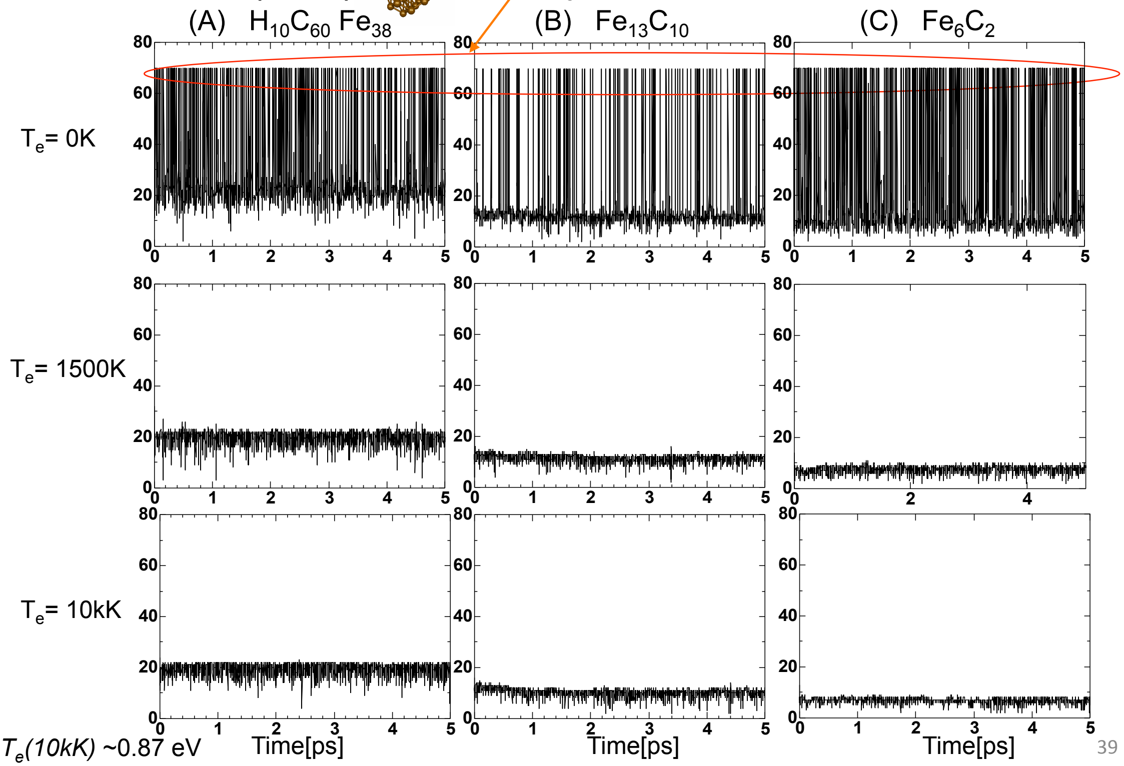
$$= \sum_i^{\infty} f_i \frac{\partial \varepsilon_i}{\partial x}$$

SCC iterations(time)



Maximum iteration number is 70

T_e=0 K always yields SCC convergence problem



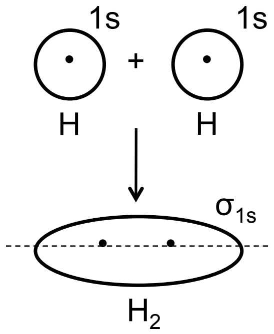
k_bT_e(10kK) ~0.87 eV

~half-width of *3d* band in Fe_{38}

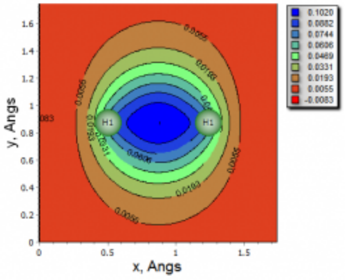
Electronic Parameters

New Confining Potentials

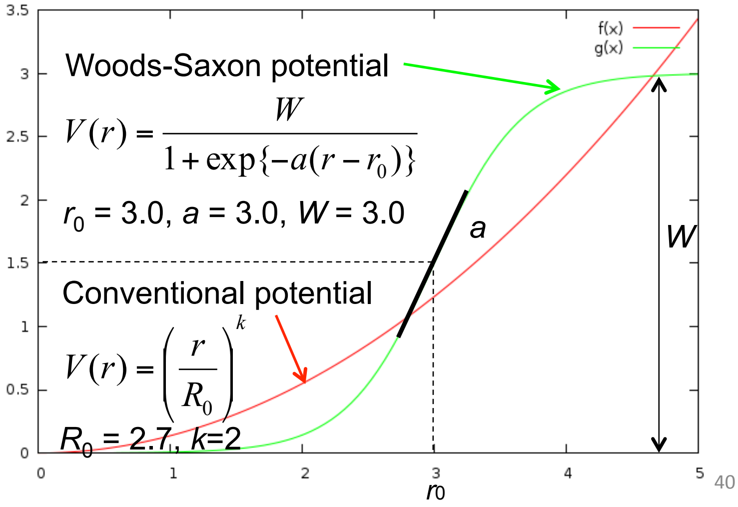
- ➢Typically, electron density contracts under covalent bond formation.
- ➢In standard *ab initio* methods, this problem can be remedied by including more basis functions.
- ➢DFTB uses minimal valence basis set: the confining potential is adopted to mimic contraction



H_2 difference density



$\Delta\rho = \rho - \Sigma_a \rho_a$



Woods-Saxon potential

$$V(r) = \frac{W}{1+\exp\{-a(r-r_0)\}}$$

r_0 = 3.0, *a* = 3.0, *W* = 3.0

Conventional potential

$$V(r) = \left(\frac{r}{R_0}\right)^k$$

R_0 = 2.7, *k*=2

Henryk Witek

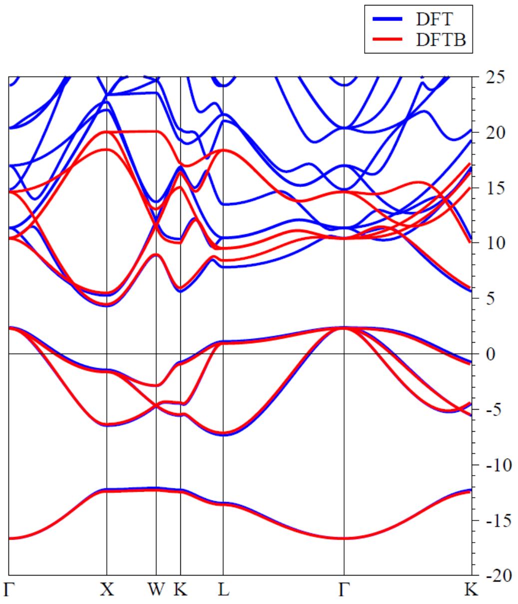
1). DFT band structure calculations

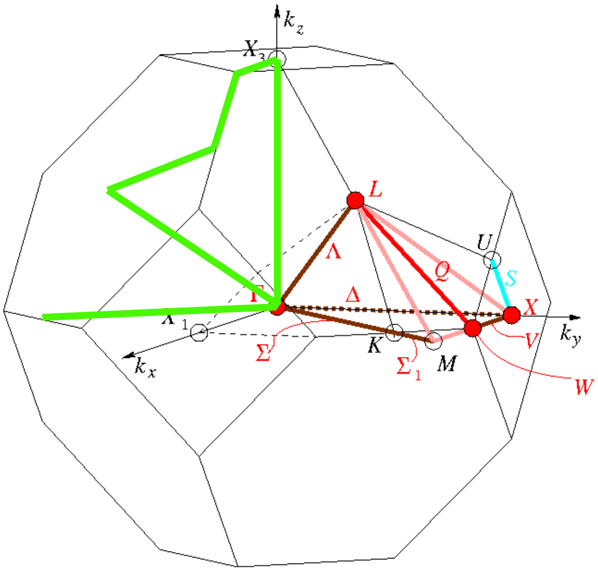
- •VASP 4.6
- •One atom per unit cell
- •PAW (projector augmented wave) method
- •32 x 32 x 32 Monkhorst-Pack *k*-point sampling
- •cutoff = 400 eV
- •Fermi level is shifted to 0 eV

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 : [1*s*] for 1st row
  [2*s*, 2*p*] for 2nd row
  [n*s*, n*p*, m*d*] for 3rd – 6th row
  (n ≥ 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 ~+5 eV with respect to Fermi level)

Band structure for Se (FCC)





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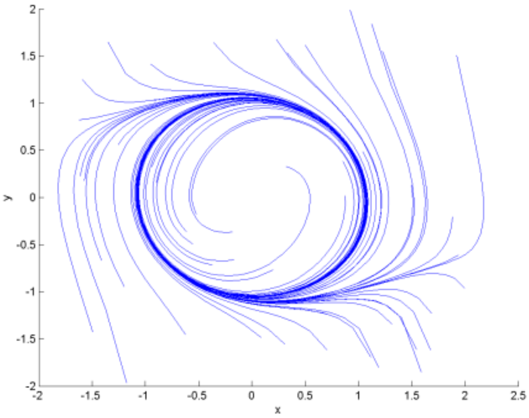
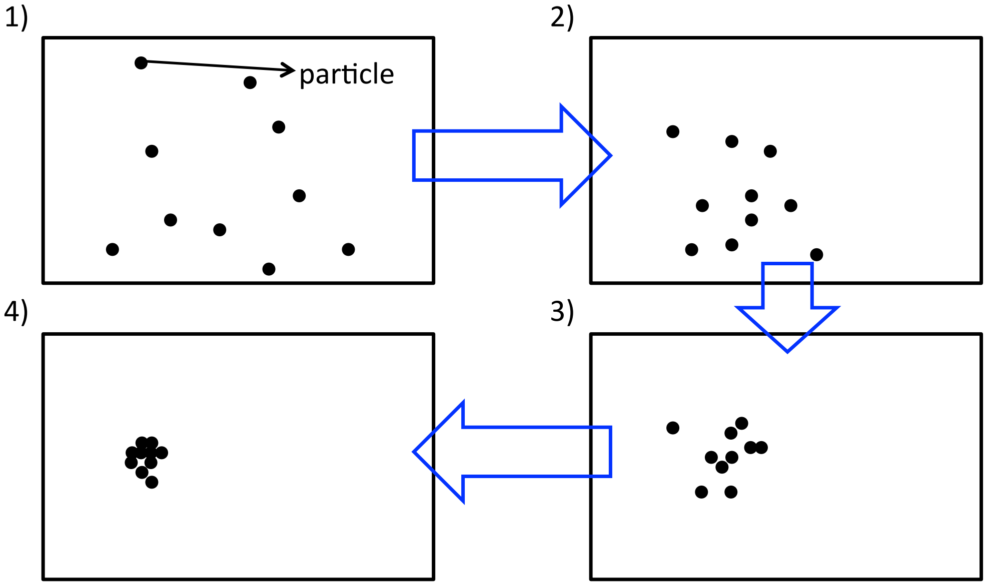
Brillouin zone

Electronic Parameters

Particle swarm optimization (PSO)

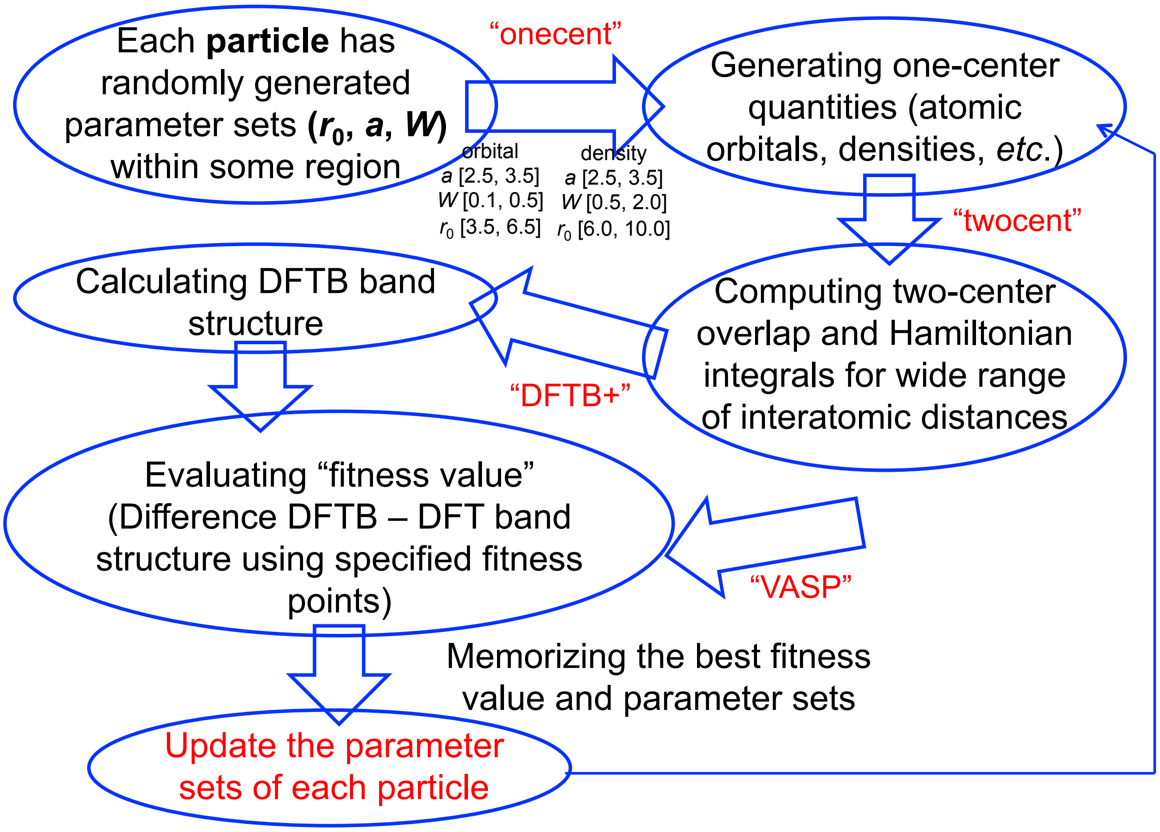


Particle Swarm Optimization



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.

Particle Swarm Optimization



Each **particle** has randomly generated parameter sets **(r_0, a, W)** within some region

"onecent"

orbital
a [2.5, 3.5]
W [0.1, 0.5]
r_0 [3.5, 6.5]

density
a [2.5, 3.5]
W [0.5, 2.0]
r_0 [6.0, 10.0]

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

"twocent"

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

"DFTB+"

Calculating DFTB band structure

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

"VASP"

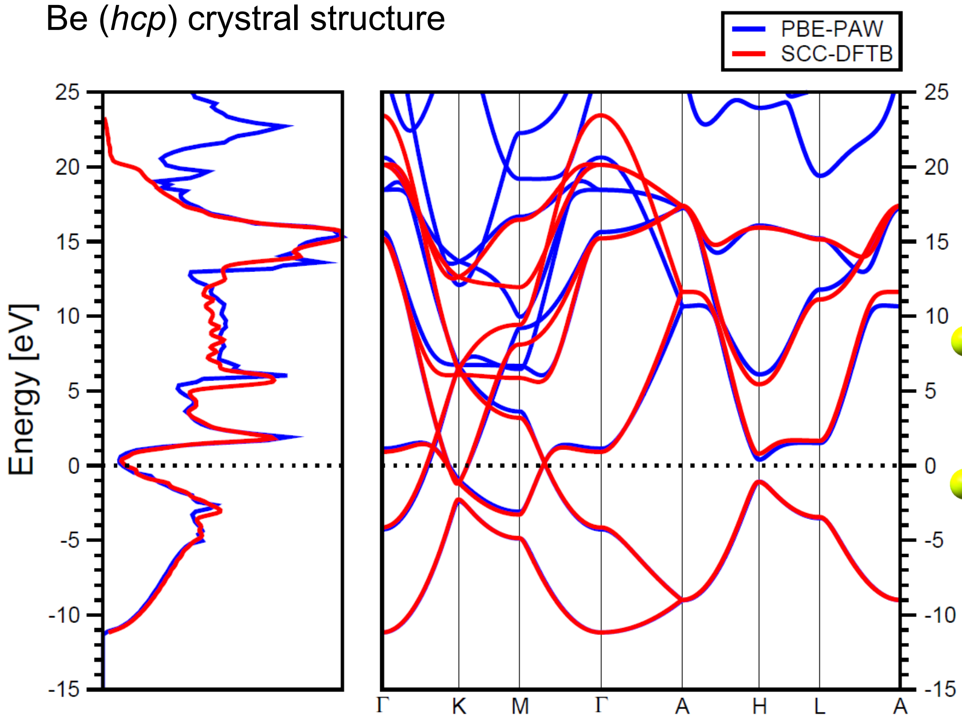
Memorizing the best fitness value and parameter sets

Update the parameter sets of each particle

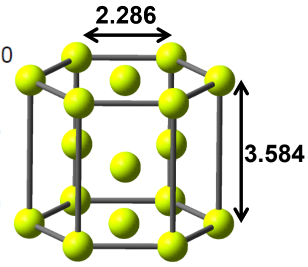
Electronic Parameters

Example: Be, HCP crystal structure

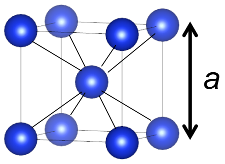
Total density of states (left) and band structure (right) of Be (*hcp*) crystral structure



- •Experimental lattice constants
- •Fermi energy is shifted to 0 eV

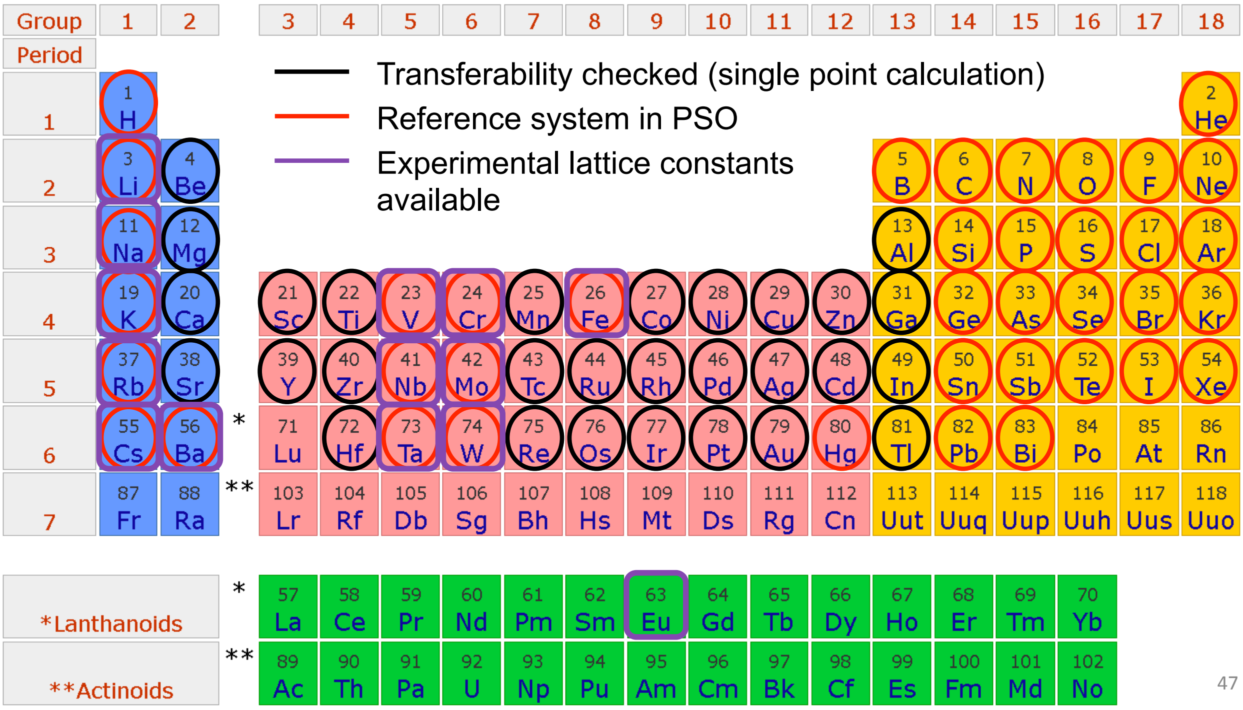


Band structure fitting for BCC crystal structures



- space group No. 229
- 1 lattice constant (*a*)

➢No POTCAR file for $Z \geq 84$ in VASP



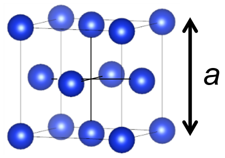
— Transferability checked (single point calculation)

— Reference system in PSO

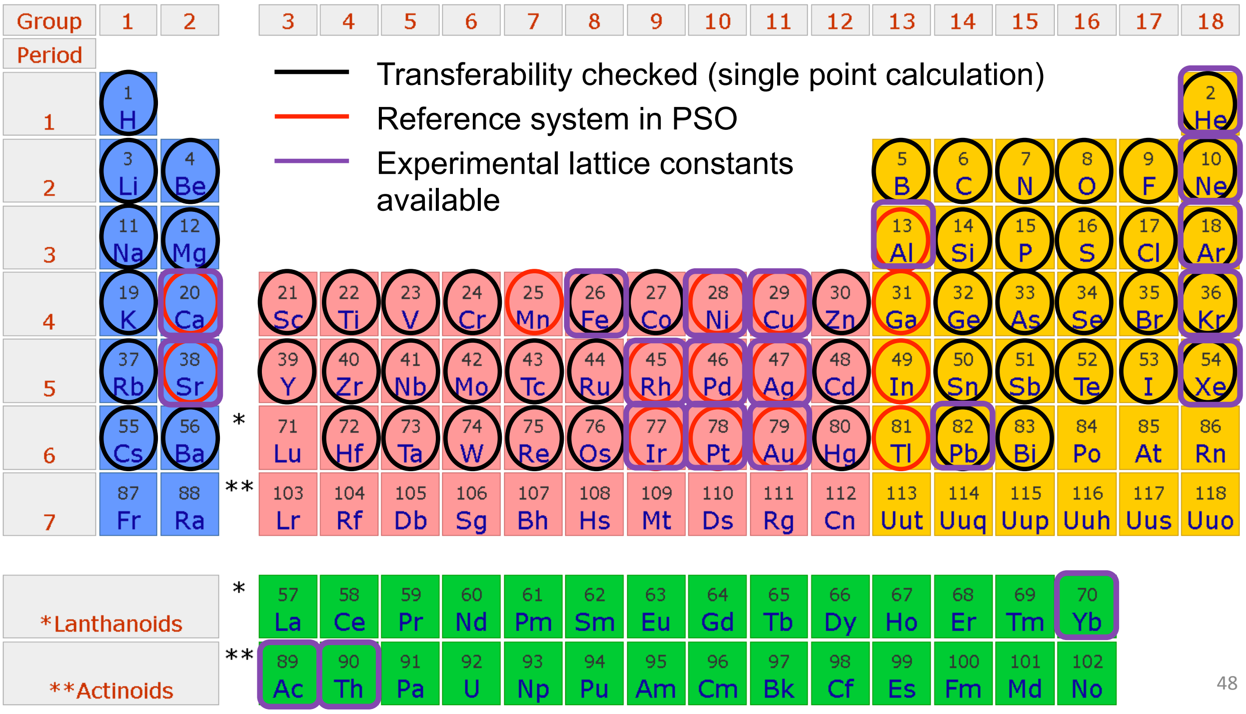
— Experimental lattice constants available

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids		*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids		**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Band structure fitting for FCC crystal structures



- space group No. 225
- 1 lattice constant (*a*)



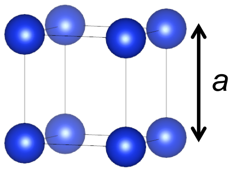
— Transferability checked (single point calculation)

— Reference system in PSO

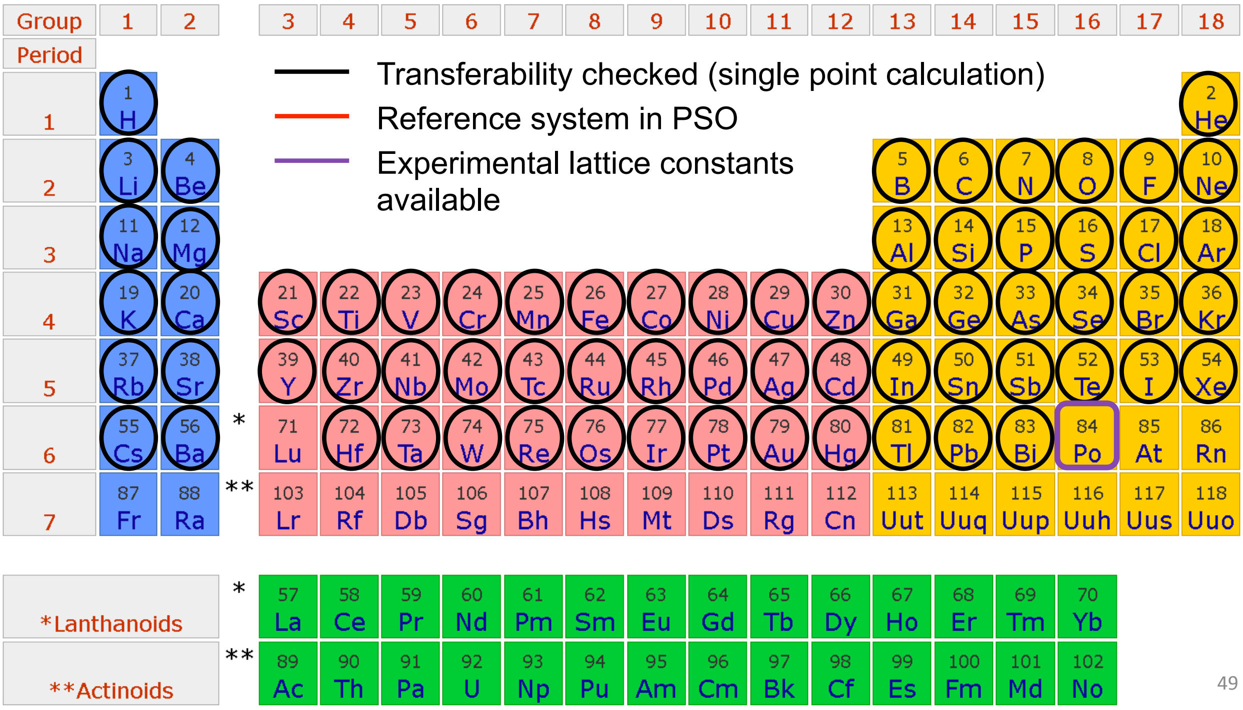
— Experimental lattice constants available

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	** 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids		*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids		**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Band structure fitting for SCL crystal structures



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



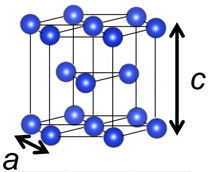
Transferability checked (single point calculation)

Reference system in PSO

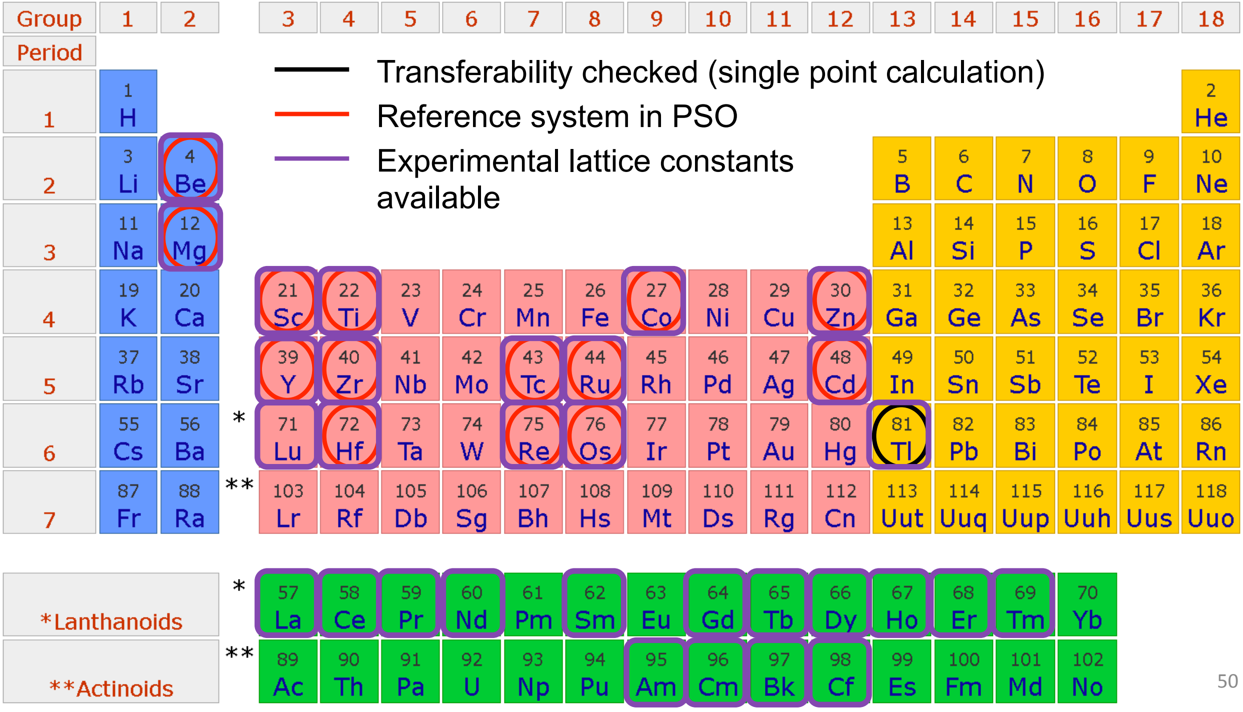
Experimental lattice constants available

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Band structure fitting for HCP crystal structures



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



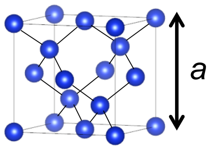
Transferability checked (single point calculation)

Reference system in PSO

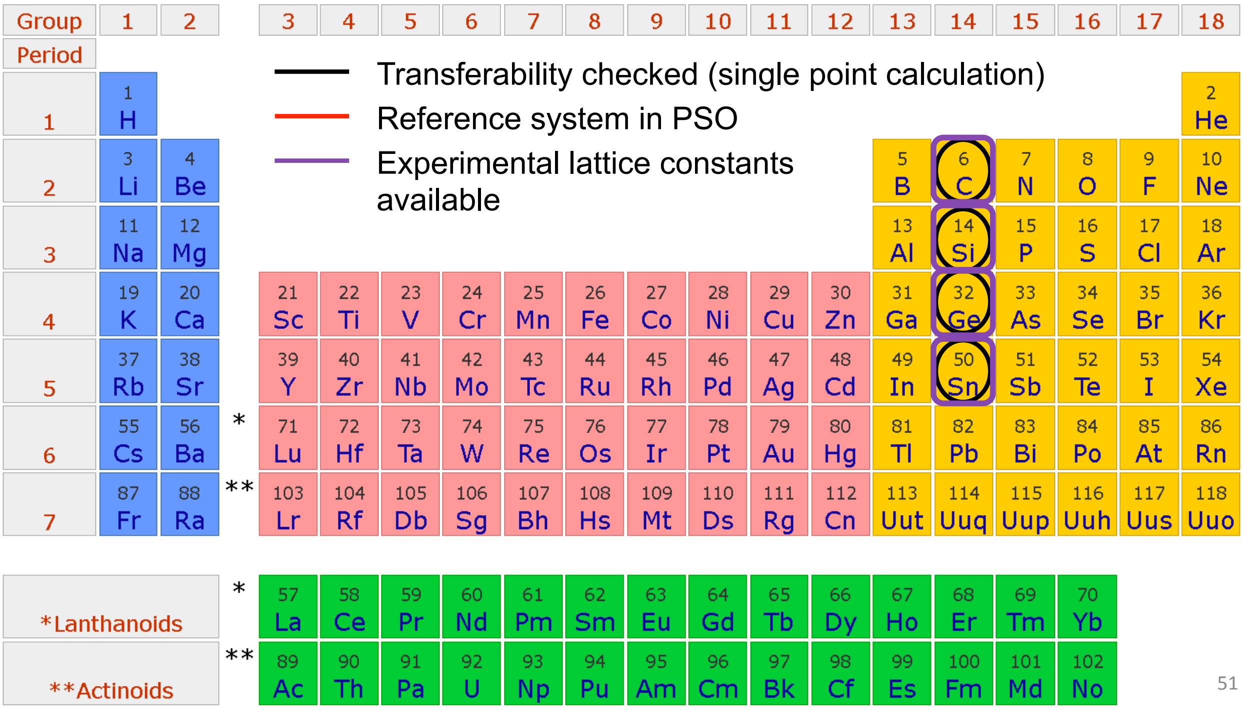
Experimental lattice constants available

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Band structure fitting for Diamond crystal structures



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



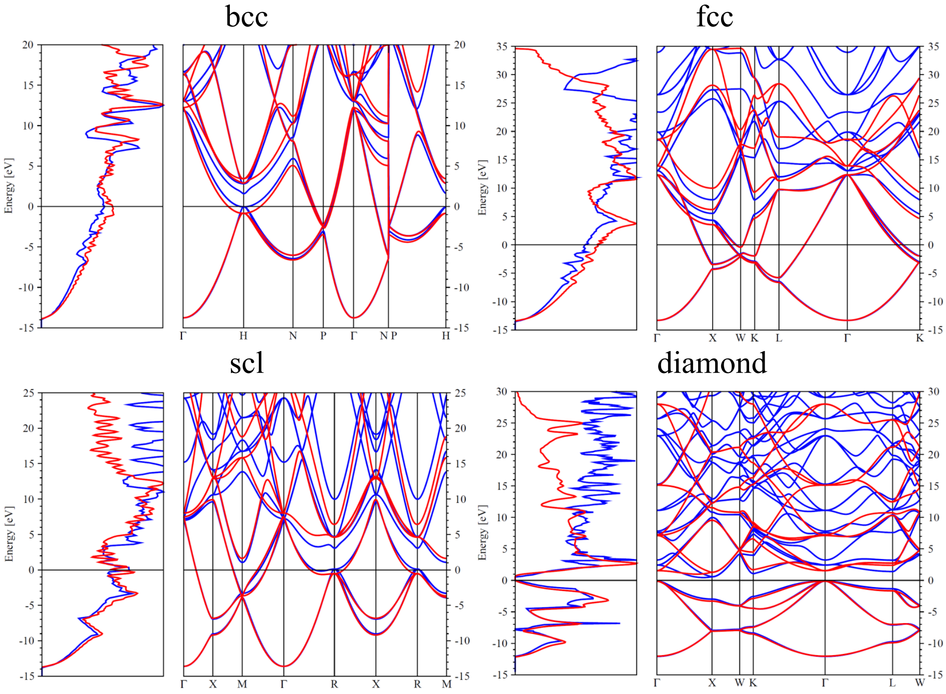
— Transferability checked (single point calculation)
— Reference system in PSO
— Experimental lattice constants available

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Period																			
1	1 H																		2 He
2	3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo
*Lanthanoids			*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
**Actinoids			**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Transferability of optimum parameter sets for different structures

DFTB Parameterization

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



$3s^2 3p^2 3d^0$

Lattice constants:

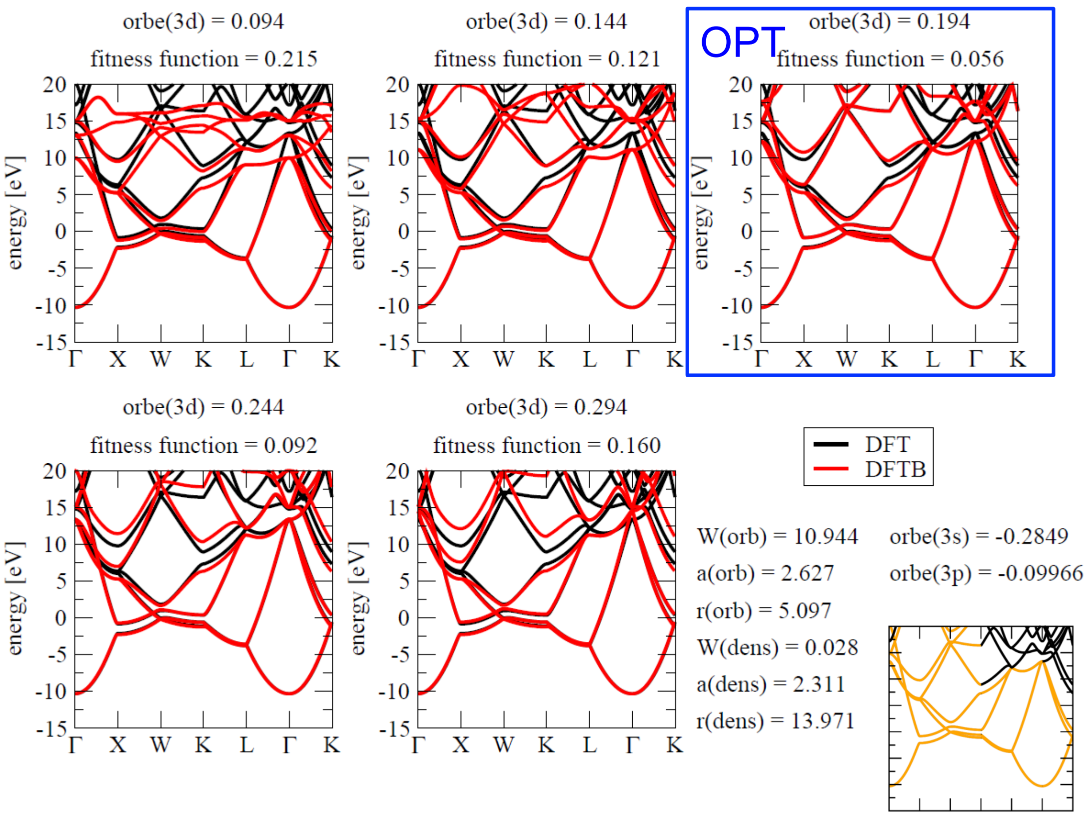
Expt	
· bcc	3.081
fcc	3.868
scl	2.532
diamond	5.431

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
ε_s	-0.39735
ε_p	-0.14998
ε_d	0.21210

➢Artificial crystal structures can be reproduced well

Influence of virtual orbital energy (3d) to Al (*fcc*) band structure



orbe(3d) = 0.094
fitness function = 0.215

orbe(3d) = 0.144
fitness function = 0.121

OPT orbe(3d) = 0.194
fitness function = 0.056

orbe(3d) = 0.244
fitness function = 0.092

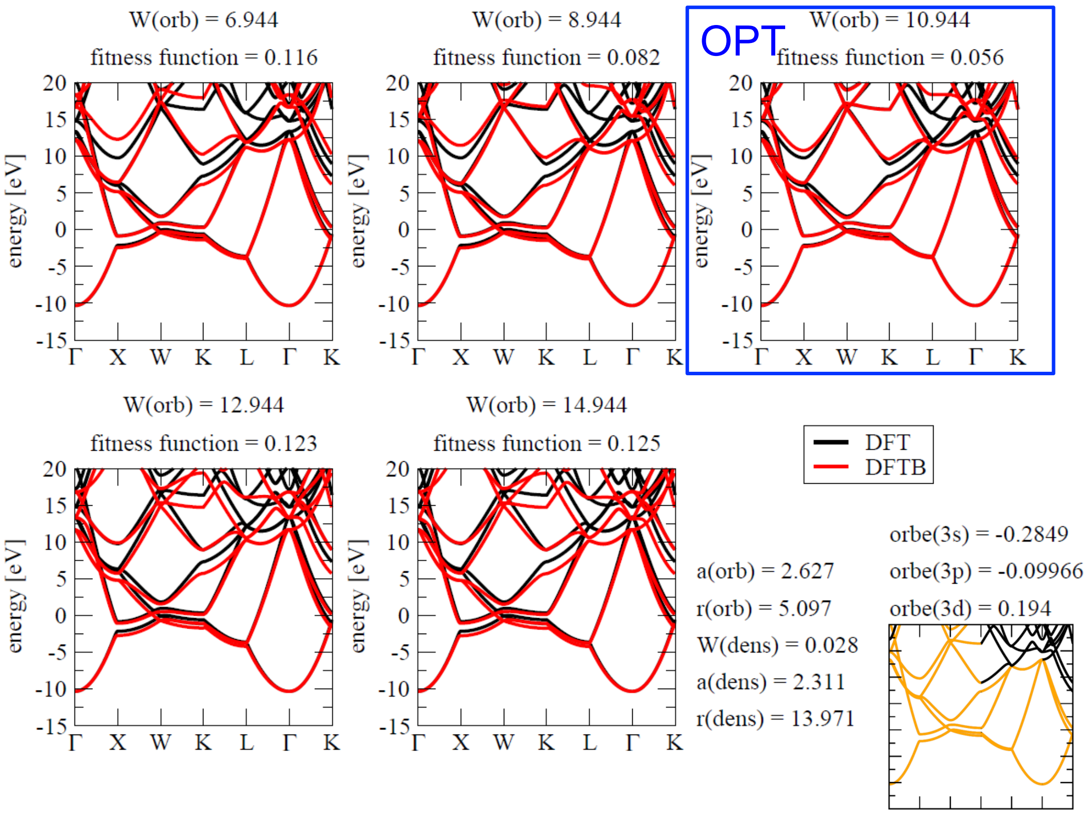
orbe(3d) = 0.294
fitness function = 0.160

W(orb) = 10.944
a(orb) = 2.627
r(orb) = 5.097
W(dens) = 0.028
a(dens) = 2.311
r(dens) = 13.971

orbe(3s) = -0.2849
orbe(3p) = -0.09966

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

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



W(orb) = 6.944
fitness function = 0.116

W(orb) = 8.944
fitness function = 0.082

OPT W(orb) = 10.944
fitness function = 0.056

W(orb) = 12.944
fitness function = 0.123

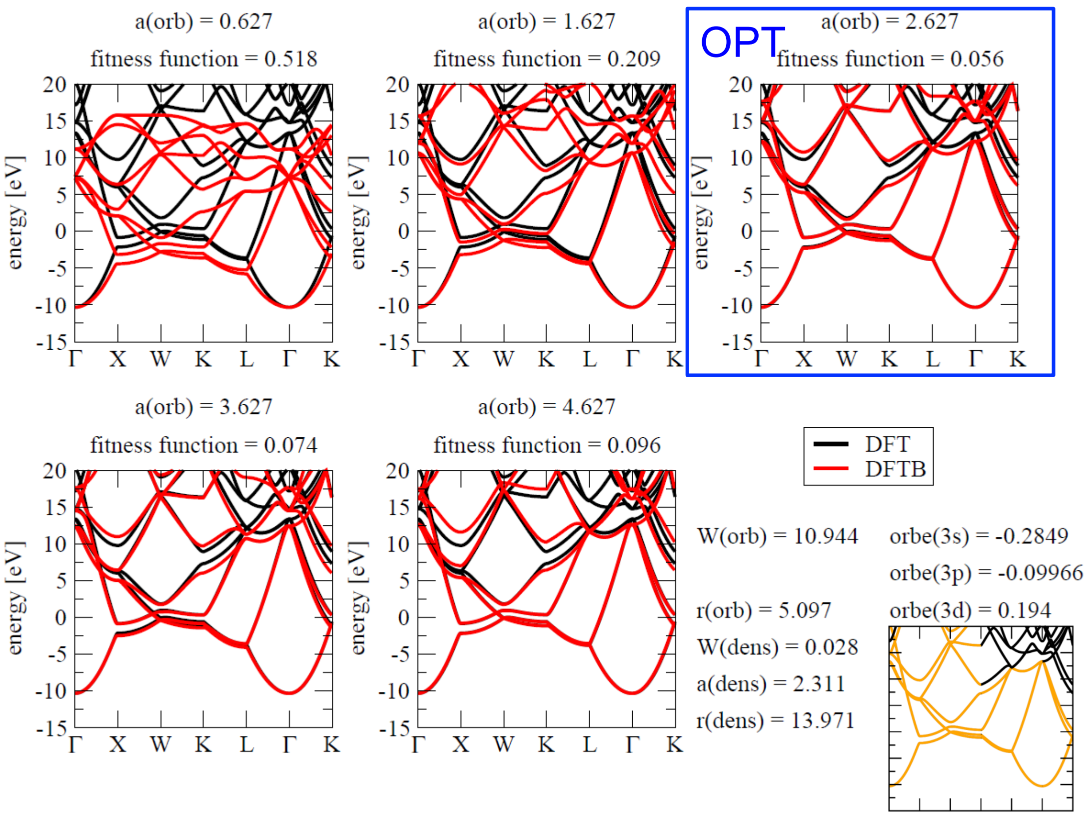
W(orb) = 14.944
fitness function = 0.125

a(orb) = 2.627
r(orb) = 5.097
W(dens) = 0.028
a(dens) = 2.311
r(dens) = 13.971

orbe(3s) = -0.2849
orbe(3p) = -0.09966
orbe(3d) = 0.194

➢The bands of upper part go lower as *W*(orb) becomes larger

Influence of *a*(orb) to Al (*fcc*) band structure

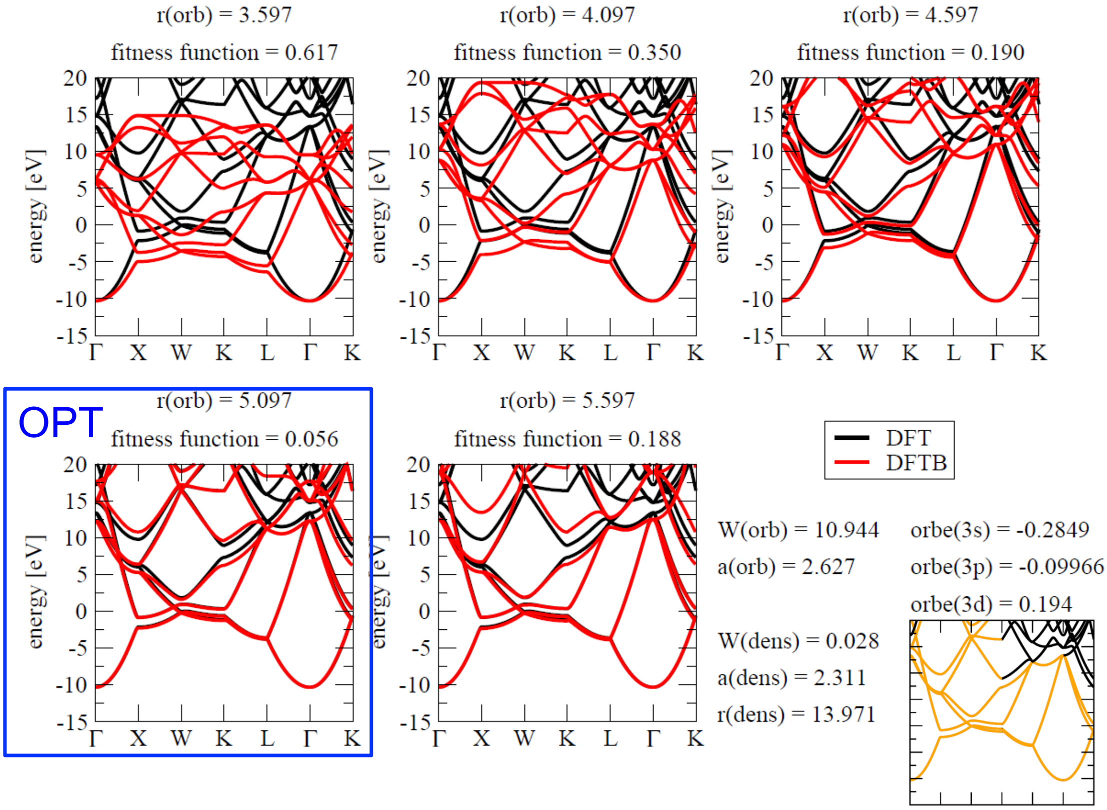


W(orb) = 10.944
r(orb) = 5.097
W(dens) = 0.028
a(dens) = 2.311
r(dens) = 13.971

orbe(3s) = -0.2849
orbe(3p) = -0.09966
orbe(3d) = 0.194

- ➢Too small *a*(orb) gives the worse band structure

Influence of *r*(orb) to Al (*fcc*) band structure

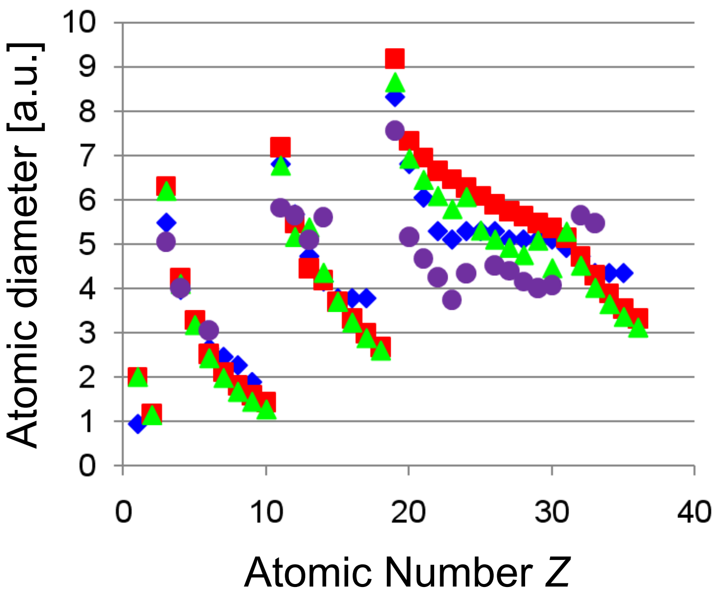


W(orb) = 10.944
a(orb) = 2.627
W(dens) = 0.028
a(dens) = 2.311
r(dens) = 13.971

orbe(3s) = -0.2849
orbe(3p) = -0.09966
orbe(3d) = 0.194

- ➢*r*(orb) strongly influences DFTB band structure

Correlation of *r*(orb) vs. atomic diameter



◆ Empirically measured radii (Slater, J. C., *J. Chem. Phys.*, **41**, 3199-3204, (1964).)

■ Calculated radii with minimal-basis set SCF functions (Clementi, E. *et al.*, *J. Chem. Phys.*, **47**, 1300-1307, (1967).)

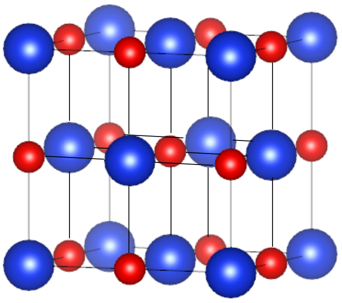
▲ Expected value using relativistic Dirac-Fock calculations (Desclaux, J. P., *Atomic Data and Nuclear Data Tables*, **12**, 311-406, (1973).)

● This work *r*(orb)

➢In particular for main group elements, there seems to be a correlation between *r*(orb) and atomic diameter.

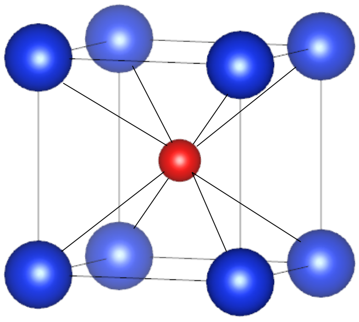
Straightforward application to binary crystal structures

Rocksalt (space group No. 225)



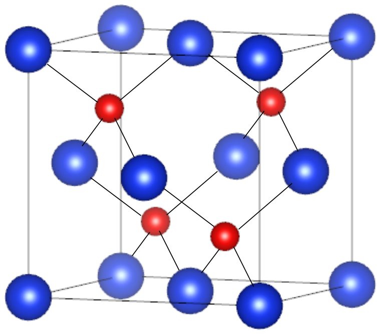
- NaCl
- MgO
- MoC
- AgCl
- …

B2 (space group No. 221)



- CsCl
- FeAl
- …

Zincblende (space group No. 216)



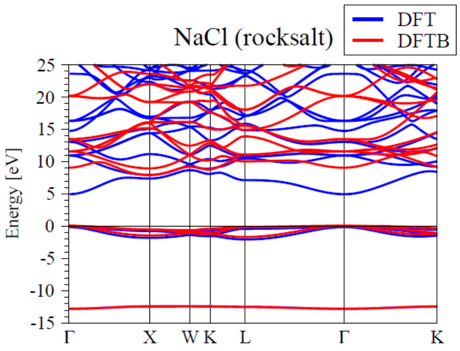
- SiC
- CuCl
- ZnS
- GaAs
- …

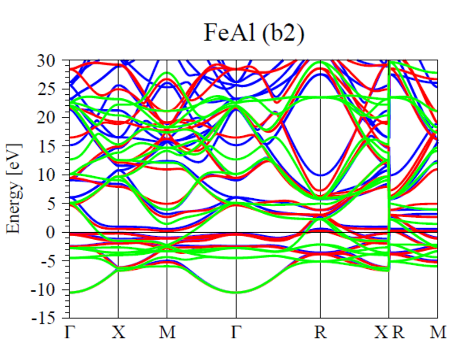
Others

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

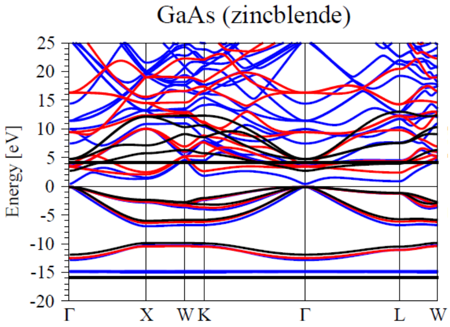
➢ more than 100 pairs tested

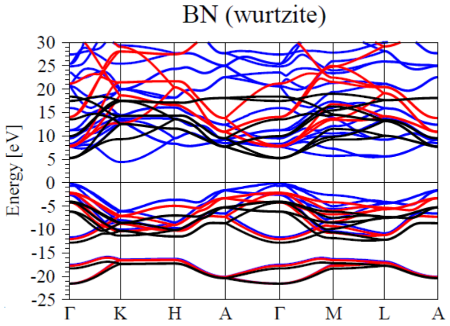
Selected examples for binary crystal structures





•d^7s^1 is used in POTCAR (DFT)





Reference of previous work :

element	name
Ga, As	hyb-0-2
B, N	matsci-0-2

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

Acknowledgements

- Marcus Elstner
- Jan Knaup
- Alexey Krashenninikov
- Yasuhito Ohta
- Thomas Heine
- Keiji Morokuma
- Marcus Lundberg
- Yoshio Nishimoto
- Some others