DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

DFTB method: bridging DFT-TB gap

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Molding & Fabrication of Nano-structure
July 2019

Outline

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DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

❶ Materials Simulation

❷ DFTB

❸ SCC DFTB

❹ In practice

❺ Summary

Materials Simulation

The governing Eq. is already known:

$$H\Psi = E\Psi$$

Ψ determines everything that can be known about the system.

The high dimensionality problem:

$$\Psi = \Psi(\mathbf{x}_1, ...\mathbf{x}_N; \mathbf{R}_1, ...\mathbf{R}_{N_{atom}}) \quad , \quad \mathbf{x}_i = \mathbf{r}_i \sigma_i$$

Paul Dirac (1929):

> "The underlying physical laws necessary for the
> mathematical theory of a large part of physics and
> the whole of chemistry are thus completely known,
> and **the difficulty is only that the exact
> application of these laws leads to equations
> much too complicated to be soluble**.

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bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

Materials Simulation

... It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation. [from: wikiquote]

Born-Oppenheimer approx.: separate elec. from ionic part:

- *still high dimensional* $\Psi_{el.}(\mathbf{x}_1, ... \mathbf{x}_N)$

If each spatial axis is discretized to p parts, we need p^{3N} grid points for spin=0 case.
$N = 10, p = 10 \rightarrow 8 \times 10^{21}$GB of memory!
$\Rightarrow$ further simplifications are required!

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

Materials Simulation

- **Wavefunction based** methods:
  QMC
  HF, Post-HF, ... $\Psi \to \prod \psi_i$
  only a few atoms
  The most accurate method available

- **Density based** methods (e.g. KS-DFT)

  Basic quantity is $\rho(\mathbf{r})$, a function of $\mathbf{r} = (x, y, z)$
  Suffer from unknown shape of the XC functional
  can treat 100-1000 atoms
 *$\sim$ps of MD*

- **?**
- **Non-QM methods**

  Model force fields with many tunable parameters
  1,000,000 atoms!
  $\sim$ns-μs MD

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method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

Materials Simulation

The gap between QM and classical methods is bridged by
semi empirical methods:

- *few* parameters to fit
- essentially quantum mechanical
- AM1, PM6, ... , SE-TB, **DFTB**
- $\Rightarrow$ Like DFT, DFTB suffers from the XC problem
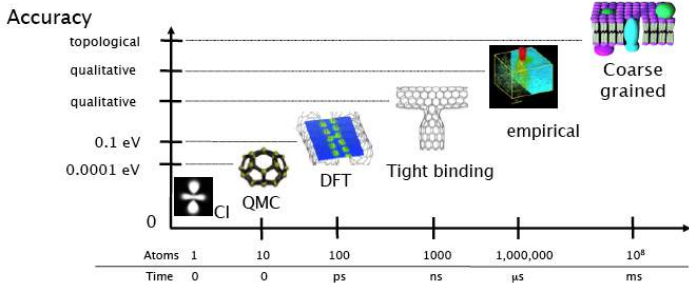
Image from Gábor Csányi's homepage

Outline

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

1 Materials Simulation

2 DFTB

3 SCC DFTB

4 In practice

5 Summary

What is DFTB = Density Functional based Tight Binding?

- Is it an approximate variant of DFT?
  Keeping first terms in Taylor series of DFT energy wrt ρ

- or, some special kind of tight binding?
  Fitted parameters to DFT calculations

Both may be true!! The latter fits better to the name

- It **IS** a quantum mechanical method:

  (Approximate) Schrödinger Eq is solved.
  Wavefunction & charge density are calculated.
  Electronic structures, magnetism, ...
  Produces almost any output that a DFT code does!

- It **IS NOT** strictly *ab initio*, however:

  Needs tabulated parameters.

DFT

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

"Ψ determines everything that can be known about the system" $\Rightarrow$ "ρ_0 determines everything that ..."

KS-DFT: One N-electron Eq. $\Rightarrow$ N one-electron Eqs.

(Coupled) Kohn Sham Eqs.: $\hat{H}\Psi_i = \epsilon_i\Psi_i$ where

$$\hat{H} = -\frac{1}{2}\nabla_r^2 + V^{\text{eff}}[\rho(\mathbf{r})]$$

$$V^{\text{eff}}[\rho(\mathbf{r})] = \int \frac{\rho(\mathbf{r})d\mathbf{r}}{r} + v_{xc}[\rho(\mathbf{r})] - \sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}$$

H depends on the solution Ψ (nonlinear eqs.)

$\Rightarrow$ iteration until convergence **SCF**

Main error sources:

- Systematic problem: unknown XC
- Incompleteness of basis set
- Pseudopotentials

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

Tight Binding?

Basic assumptions:

- Valence electrons **tightly bound** to the cores (localized)

- LCAO (minimal set): $\Psi_i = \sum_\mu c_{i\mu} \chi_\mu$
  χ_μ are valance Atomic Orbitals: $\chi_\mu =$ 1s (for H and He)
  2s, $2p_x$, $2p_y$, $2p_z$ (for 2nd row), ...

- Hamiltonian matrix is obtained from pairwise values $\Rightarrow$ no
  costly integration is performed
  In case of DFTB: tabulated Slater-Koster data

Depending on the approximations, several variants exist:

- SCC or non-SCC?

  Are atomic charges self-consistent?

- Empirical or *ab initio* based?

  Are parameters fitted to experimental data or obtained from ab initio calculations?

DFTB = DFT-based TB:

⇒ *gets parameters from DFT calculations*

⇒ *DFTB (traditional DFTB) is non-SCC*

⇒ *DFTB2 & DFTB3 are SCC (but not SCF!)*

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DFT-TB gap

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Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

DFTB from DFT

"*Consider a case where the ground-state density ρ_0 is known already to sufficient accuracy. In this case, the self-consistent solution of the Kohn-Sham (KS) equations can be omitted.*" [M. Elstner, JPCA 111]

no SCF = no iteration

$$\hat{H}\Psi_i = \epsilon_i \Psi_i$$

is reduced to

$$\hat{H}^0 \Psi_i = \epsilon_i \Psi_i$$

The diagonalization has to be solved only once
$\Rightarrow$ *a factor of ~ 10 is gained*

where $\hat{H}^0 = \hat{H}^0[\rho_0] = -\frac{1}{2}\nabla_r^2 + V^{\text{eff}}[\rho_0(\mathbf{r})]$ and

$$V^{\text{eff}}[\rho_0(\mathbf{r})] = \int \frac{\rho_0(\mathbf{r})d\mathbf{r}}{r} + v_{xc}[\rho_0(\mathbf{r})] - \sum_\alpha \frac{Z_\alpha}{|\mathbf{r} - \mathbf{R}_\alpha|}$$

- Density & potential: superposition of atomic densities and potentials

$$\rho_0(\mathbf{r}) = \sum_{\alpha} \rho_{\alpha,0}(\mathbf{r})$$

$$V_{\text{eff}}[\rho_0(\mathbf{r})] = \sum_{\alpha} V_{\text{eff}}[\rho_{\alpha,0}(\mathbf{r})]$$

- KS orbitals: LC of non-interacting AOs

$$\psi_i = \sum_{\mu} c_{\mu,i}\chi_{\mu}$$

- Hamiltonian $H^0 = H^0[\rho_0]$ is constructed (no integration!) from tabulated data calculated by DFT for pairs.
  χ_{μ}'s are too diffuse $\Rightarrow$ compression with a harmonic potential: $H^0 = -\frac{1}{2}\nabla^2 + V_{\text{eff}}[\rho_0] + \left(\frac{r}{r_0}\right)^2$

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

Band energy

TB version of KS eq.: $\hat{H}^0\Psi_i = \epsilon_i\Psi_i$
and LCAO: $\Psi_i = \sum_\mu c_{\mu,i}\chi_\mu$

$$\sum_\mu c_{\mu,i}\hat{H}^0|\chi_\mu\rangle = \epsilon_i\sum_\mu c_{\mu,i}|\chi_\mu\rangle$$

$$\sum_\mu c_{\mu,i}\langle\chi_\nu|\hat{H}^0|\chi_\mu\rangle = \epsilon_i\sum_\mu c_{\mu,i}\langle\chi_\nu|\chi_\mu\rangle$$

Denoting $H^0_{\mu,\nu} = \langle\chi_\nu|\hat{H}^0|\chi_\mu\rangle$ and $S_{\mu,\nu} = \langle\chi_\nu|\chi_\mu\rangle$, we have

$$H^0\mathbf{c}_i = \epsilon_i S\mathbf{c}_i$$

Diagonalizing $\rightarrow$ Sum of eigenvalues: $E^{\text{band}} = \sum_i \epsilon_i$
All other contributions are lammed as $E^{\text{rep}} = E^{\text{rep}}(\{R_{\alpha\beta}\})$

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

$E^{\text{rep}}(\{R_{\alpha,\beta}\})$

$$E^{\text{DFT}}[\rho_0] = \sum_i \epsilon_i + \sum_{\alpha > \beta} \frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \frac{1}{2} \int \frac{\rho_0(\mathbf{r})\rho_0(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$

$$+ E_{xc}[\rho_0] + \int v_{xc}[\rho_0]\rho_0 d\mathbf{r}$$

Terms 4 & 5 (XC) are too complicated to be estimated, but decay fast $\Rightarrow$ **vanish** outside the atoms

If $\rho_0 = \sum \rho_{\alpha,0}$, terms 2 & 3 become $\sum_{\alpha > \beta} U_{\alpha,\beta}$ where
$U_{\alpha,\beta} = -\frac{Z_\alpha Z_\beta}{R_{\alpha\beta}} + \int \frac{\rho_{\alpha,0}(\mathbf{r})\rho_{\beta,0}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$

non-SCC DFTB energy

$$E = \sum_i \epsilon_i + \sum_{\alpha > \beta} U_{\alpha\beta}$$

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

The practical way to get $U_{\alpha,\beta}$:
spline interpolating based on DFT results for each pair at different distances:

$$U_{\alpha,\beta}^{\mathsf{DFT}}(R_{\alpha\beta}) = E_{\alpha-\beta\ \mathsf{pair}}^{\mathsf{DFT}}(R_{\alpha\beta}) - \sum_i \epsilon_i(R_{\alpha\beta})$$

At finite electronic temperature, Fermi-Dirac distribution gives **fractional occupancies**: $f_i = 1/[e^{(\epsilon_i - \mu)/kT} + 1]$

non-SCC DFTB Mermin energy

$$F = \sum_{i=1} f_i \epsilon_i + \sum_{\alpha > \beta} U_{\alpha,\beta}^{\mathsf{DFT}}(R_{\alpha\beta}) - TS$$

Entropy: $S = -2k \sum f_i \log f_i + (1 - f_i) \log(1 - f_i)$
Mermin free energy: $E - TS$

Outline

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

1 Materials Simulation

2 DFTB

3 SCC DFTB

4 In practice

5 Summary

SCC DFTB

- DFT: finds ρ which minimizes the energy $E[\rho]$
- DFTB: starting from ρ_0, finds $\delta\rho$ to minimize $E[\rho_0 + \delta\rho]$

If $\delta\rho$ is small: same atomic species (no charge transferred) or ionic systems (completely transferred), non-SCC DFTB is OK. Otherwise, SCC DFTB i.e. DFTB2/3 has to be employed.

$$E[\rho_0 + \delta\rho] =$$
$$\underbrace{\underbrace{E^0[\rho_0] + E^1[\rho_0, \delta\rho]}_{\text{DBTB1=non-SCC DFTB}} + E^2[\rho_0, (\delta\rho)^2]}_{\text{DFTB2}} + E^3[\rho_0, (\delta\rho)^3] + \ldots$$
$$\underbrace{}_{\text{DFTB3}}$$

$$E^0 = \sum_{\alpha > \beta} U_{\alpha,\beta} , \ E^1 = \sum_i f_i \epsilon_i$$

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

Basic assumptions:

- Atomic charge fluctuations are superimposed:

$$\delta\rho(\mathbf{r}) = \sum_\alpha \delta\rho_\alpha(\mathbf{r})$$

- Atomic charge fluctuations are represented by monopoles only, and decay exponentially, s.g. as:

$$\delta\rho_\alpha(\mathbf{r}) \simeq \delta q_\alpha \frac{\tau_\alpha}{8\pi} e^{-\tau_\alpha|\mathbf{r}-\mathbf{R}_\alpha|}$$

Two important limits:

- Large distances: point-like charges

$$E^2 = \frac{1}{2}\sum_{\alpha,\beta}\frac{\delta q_\alpha \delta q_\beta}{R_{\alpha\beta}}$$

- Vanishingly short distances ($R_{\alpha\beta} \to 0$): $E^2 = \frac{1}{2}\delta q_\alpha^2 \frac{\partial^2 E_\alpha}{\partial q_\alpha^2}$ from DFT.

Between these two limits (inside one atom): E^2 is too complicated to be estimated because of XC effects.
$\Rightarrow$ interpolating:

$$E^2 = \frac{1}{2} \sum_{\alpha,\beta} \delta q_\alpha \delta q_\beta \gamma_{\alpha\beta}$$

$$\gamma_{\alpha,\beta} = 1 / \sqrt{R_{\alpha\beta}^2 + \frac{1}{4}(\frac{1}{U_\alpha} + \frac{1}{U_\beta})^2}$$

$E^2(R_{\alpha\alpha}) = \frac{1}{2}\delta q_\alpha^2 U_\alpha$ where $U_\alpha = \frac{\partial^2 E_\alpha}{\partial q_\alpha^2}$ is the Hubbard parameter of atom α (chemical hardness), and describes how much is the energy cost for adding/removing electrons from atom α.
(the atomic radius is inversely proportional to the chemical hardness: $\tau_\alpha = \frac{16}{5}\gamma_{\alpha\alpha}$)

Energy change upon atomic charge density fluctuation, which is absent in non-SCC DFTB, is now modeled by γ in DFTB2.

$E^2[\rho_0, (\delta\rho)^2]$

$$E^2 = \frac{1}{2} \sum_{\alpha,\beta} \delta q_\alpha \delta q_\beta \gamma_{\alpha\beta}$$

In DFTB3, the derivative $\Gamma_{\alpha\beta}$ of U_α comes into play, too. It would hopefully compensates for minor effects haven't capterd bt DFTB2 due to very small size of the basis set, and simplifying density fluctuation as point charges.

$E^3[\rho_0, (\delta\rho)^3]$

$$E^3 = \frac{1}{3} \sum_{\alpha\beta} \delta q_\alpha^2 \delta q_\beta \Gamma_{\alpha\beta}$$

Minimization $\frac{\partial}{\partial c_{i\mu}}\big(E - \epsilon_i(\langle\Psi|\Psi\rangle - 1)\big) = 0$

$$E = E^0 + E^1 + E^2 + E^3 = \sum_{\alpha > \beta} U_{\alpha\beta}$$

$$+ \sum_{i,\mu,\nu} c_{i,\mu} c_{i,\nu} H_{\mu\nu}^0 + \frac{1}{2} \sum_{\alpha\beta} \delta q_\alpha \delta q_\beta \gamma_{\alpha\beta} + \frac{1}{3} \sum_{\alpha\beta} \delta q_\alpha^2 \delta q_\beta \Gamma_{\alpha\beta}$$

$$H\mathbf{c}_i = \epsilon_i S\mathbf{c}_i$$

Despite its shape, not a generalized eigenvalue equation

Mulliken charges q_α depend on $\mathbf{c}_i \Rightarrow \delta q_\alpha = q_\alpha - Z_\alpha$ depend on $\mathbf{c}_i \Rightarrow$ Hamiltonian $H^{\mathsf{DFTB2/3}}$ depends on solution $\mathbf{c}_i$.

DFTB method: bridging DFT-TB gap

Ali Sadeghi

Materials Simulation

DFTB

SCC DFTB

In practice

Summary

Since matrices H and S depends on the solution $\mathbf{c_i}$, one cannot solve the equation $H\mathbf{c}_i = \epsilon_i S\mathbf{c}_i$ in single step. One has to do it **iteratively**:

1. Start from some initial guess $\mathbf{c}_i$
2. Evaluate Mulliken charges, and construct H and S
3. Solve the Eq. as a generalized eigenvalue problem for $\mathbf{c}_{i,\text{new}}$
4. If $\xi = ||\mathbf{c}_i^{\text{new}} - \mathbf{c}_i^{\text{old}}||$ is not tiny, go to step 2.
5. Using this correct $\mathbf{c}_i$ determine/report any other quantity: energy, energy bands, forces/stress, Mulliken charges, wavefunction, electron density, etc.

SCC = self consistent charge

Once ξ is very small, **self consistency is achieved**, i.e. Mulliken charges q_α used to construct H are consistent with those obatained by solving $H\mathbf{c}_i = \epsilon_i S\mathbf{c}_i$

$$E = E^0 + E^1 + E^2 + E^3$$

$$= \underbrace{\sum_{\alpha > \beta} U_{\alpha\beta} + \sum_i f_i \epsilon_i + \frac{1}{2} \sum_{\alpha\beta} \delta q_\alpha \delta q_\beta \gamma_{\alpha\beta} + \frac{1}{3} \sum_{\alpha\beta} \delta q_\alpha^2 \delta q_\beta \Gamma_{\alpha\beta}}$$

DFTB

DFTB2

DFTB3

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

$$E^{\mathrm{SCC-DFTB}} = \sum_i^{\substack{\text{valence} \\ \text{orbitals}}} n_i \varepsilon_i + \frac{1}{2} \sum_{A \neq B}^{\text{atoms}} \gamma_{AB} \Delta q_A \Delta q_B + \frac{1}{2} \sum_{A \neq B}^{\text{atoms}} E_{\mathrm{rep}}^{AB}$$

Outline

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary
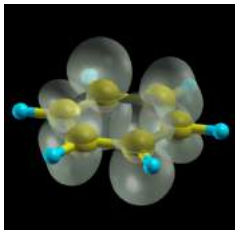
1 Materials Simulation

2 DFTB

3 SCC DFTB

4 In practice

5 Summary

Several implementations are available (some are free fro academic usage)

- DFTB+ dftb-plus.org
  A very helpful and active forum
- Fireball nanosurf.fzu.cz/wiki/doku.php?id=fireball
- ADF
- Gaussian
- Atomistix Toolkit
- . . .

Extensions:

- Dispersion correction (empirical)

$$E_{\text{tot}} = E_{\text{DFTB}} - \sum_{\alpha\beta} \frac{f_{\alpha\beta} C_6(\alpha, \beta)}{R_{\alpha\beta}^6}$$

- Transport
- Time dependent DFTB
- . . .

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

Both accuracy and limitations of the method is *mainly due to the SK parameters data set*!

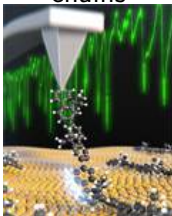+ Several reports on very accurate (compared to DFT) for biomolecules, and carbon-based structures

- The main practical limitation:
very limited number of published parameters for atomic pairs

www.dftb.org/parameters/download/

They have been thoroughly tested for a broad range of systems. However, if you intend to use them for systems very different from those included in the tests, please evaluate the sets first.
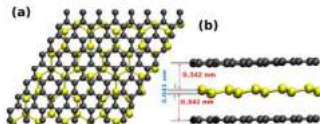
Name	Requires	Elements	Short description
3ob		C-H-N-O-P-S	DFTB3 files for bio and organic molecules
matsci		Al-O-H | Al-Si-O-H | Cu-Si-Al-Na-O-H | Ti-P-O-N-C-H | O-N-C-B-H | Al-O-C-H | Si-P-N-O-C-H	Collection of some sets used for various problems in materials science. (For some of the interactions no published tests available!)
mio		H - C - N - O - S - P	SCC files for bio or organic molecules
pbc		Si - F - O - N - C - H | Fe	SCC files for solids and surfaces

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

A few applications

Mechanical stiffness of fluorene chains

Silicene sandwiched by graphene layers

Accuracy of DFTB for biomolecules

APL 103, 261904

PNAS 111, 3968
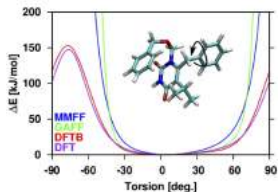
unpublished

Outline

DFTB
method:
bridging
DFT-TB gap

Ali Sadeghi

Materials
Simulation

DFTB

SCC DFTB

In practice

Summary

❶ Materials Simulation

❷ DFTB

❸ SCC DFTB

❹ In practice

❺ Summary

Summary

- DFTB bridges the gap between DFT and empirical methods
- SCC-DFTB is a quantum mechanical, but not fully first principles, method
- SCC-DFTB combines the accuracy of DFT and efficiency of TB: $\sim 100 - 1000 \times$ faster than DFT
- Only a limited atomic-pairs have been parametrized
- Very accurate for bio-systems, carbon based systems. Moderate accuracy for many others

Thanks for your attention!