Bremen Center for Computational Materials Science
Bremen Center for Computational Materials Science
http://www.bccms.uni-bremen.de/

Founding Chair - 2006
Computational Materials Science

Thomas Frauenheim

Conrad-Naber Endowed Chair - 2008
Hybrid Materials Interfaces

Vasily Ploshikhin

Airbus Endowed Chair – 2009/2010
Integrative Materials and Process Simulation & Engineering

Tim Wehling

Electronic Structure and Correlated Nanosystems – ECN 2012

Lucio Colombi Ciacchi
Bremen Center for Computational Materials Science
http://www.bccms.uni-bremen.de

Collagen adhesion on silicon surfaces

Integrative Materials and Process Simulation & Engineering
Non-linear FEM-Simulation of welding distortion
Carbon Fiber reinforced polymers

Hybrid Materials Interfaces

Oxidation of Co-alloys

ES & Correlated Nanosystems

Chemical reactive processes

Computational Materials Science

Physics of Graphene and novel layered materials/devices
Atomistic modeling of quantum processes in nanoscale devices

Photovoltaic devices

NW-LED

Hot electron injection
Solution of the many-body Schrödinger equation

$$\hat{H} \Psi(r_1, r_2, \ldots, r_N) = E \Psi(r_1, r_2, \ldots, r_N)$$

$$H_0 = T_e + V_{e-K}(\mathbf{r}, \mathbf{R}) + V_{e-e}(\mathbf{r}) + V_{K-K}(\mathbf{R})$$

$$T_e = \sum_{i=1}^{N_e} \frac{p_i^2}{2m}$$

$$V_{e-e} = \sum_{i<j} v_{e-e}(r_i - r_j)$$

$$v_{e-e}(r - r') = \frac{e^2}{|r - r'|}$$

Very challenging and expensive to solve directly though not impossible (for small systems)

Variational / diffusion Quantum Monte Carlo
Post-Hartree-Fock Quantum Chemistry
Density-Functional-Theory: DFT

For $|\text{GS}>$ use density $n(r)$ instead of $\Psi(r_1,r_2,...,r_N)$

$$E[\rho(r)] = \sum_{i=1}^{N} \int \psi_i(r) \left( -\frac{\nabla^2}{2} \right) \psi_i(r) \, dr + \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 + E_{\text{XC}}[\rho(r)]$$

$$- \sum_{A=1}^{M} \int \frac{Z_A}{|r - R_A|} \rho(r) \, dr$$

$$E_H[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2$$

$$\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$

$$E_{\text{XC}}[\rho(r)] = \int \rho(r)\varepsilon_{\text{XC}}(\rho(r)) \, dr$$

Kohn-Sham equation

$$\left\{ -\frac{\nabla^2}{2} - \left( \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(r_2)}{r_{12}} \, dr_2 + V_{\text{XC}}[r_1] \right\} \psi_i(r_1) = \varepsilon_i \psi_i(r_1)$$

$$V_{\text{XC}}[r] = \left( \frac{\delta E_{\text{XC}}[\rho(r)]}{\delta \rho(r)} \right)$$

Today can be solved self-consistently for several 100 atoms

Includes all many-body effects
Atomistic modeling of quantum processes in nanoscale devices

Photovoltaic devices

NW-LED

Hot electron injection

We need to go beyond 10,000 atom simulations
Atomistic modeling of photo-induced processes and energy conversion in nanoscale devices
Multi-scale hierarchy in materials simulations

- Continuum theory
  - Thermodynamics

- Microstructure
  - Finite elements

- Classical
  - Force fields MM

- Semp.QC & TB

- Ab initio
  - DFT/QC

- QM

Predictivity of chemical processes

Length scale

Time scale
From the LCAO-$X_\alpha$—method to a modern DFTB-scheme
Construction of tight-binding-like potentials on the basis of density-functional theory: Application to carbon

D. Porezag,* Th. Frauenheim, and Th. Köhler
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G. Seifert and R. Kaschner
Technische Universität Dresden, Institut für Theoretische Physik, Mommsenstrasse

(Received 2 November 1994)

We present a density-functional-based scheme for determining the necessary nonorthogonal tight-binding (TB) models within the framework of the atomic-orbitals formalism using the local-density approximation (LDA). By center integrals the Hamiltonian and overlap matrix elements are calculated for densities and potentials rather than fitted to experimental data. We can determine the C-C, C-H, and H-H Hamiltonian and overlap matrix elements. The effective potential appearing in most TB models is fitted to self-consistent calculations of the LDA. The calculation of forces is easy and allows an application of the scheme to dynamics simulations. Despite its extreme simplicity, the method is transferable to a variety of systems. The determination of equilibrium geometries, transition modes of carbon clusters, hydrocarbon molecules, and solid-state as well as yield results showing an overall good agreement with more sophisticated methods.
Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties

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19 September 1997; revised manuscript received 19 March 1998

UPB Dr. habil 2003
DFTB-method

Theory of complex materials @ UPB
supported by DFG, DAAD, VW, EC, BMBF, FhG, Humboldt

Collaborative effort

Marcus Elstner
KIT-Karlsruhe

Gotthard Seifert
TU Dresden
Outline of the Talk

1. Brief introduction of the DFTB-method
2. Examples for device modeling
3. Ways to improve ground state accuracy and efficiency
4. TD-DFTB properties in linear response
5. NO-reduction on TiO₂ surfaces
6. Charge transfer exitations using pp-DFTB
7. Non-adiabatic Ehrenfest molecular dynamics
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DFTB relies on Density-Functional-Theory

For $|\text{GS}>$ use density $n(r)$ instead of $\Psi(r_1, r_2, \ldots, r_N)$

$$E[\rho(r)] = \sum_{i=1}^{N} \int \psi_i(r) \left( -\frac{\nabla^2}{2} \right) \psi_i(r) \, dr + \frac{1}{2} \int \int \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2 + E_{\text{XC}}[\rho(r)]$$

$$- \sum_{A=1}^{M} \frac{Z_A}{|r - R_A|} \rho(r) \, dr$$

$$E_H[\rho(r)] = \frac{1}{2} \int \int \frac{\rho(r_1) \rho(r_2)}{|r_1 - r_2|} \, dr_1 \, dr_2$$

$$\rho(r) = \sum_{i=1}^{N} |\psi_i(r)|^2$$

$$E_{\text{XC}}[\rho(r)] = \int \rho(r) \epsilon_{\text{XC}}(\rho(r)) \, dr$$

Kohn-Sham equation

$$\left\{ -\frac{\nabla^2}{2} - \left( \sum_{A=1}^{M} \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(r_2)}{r_{12}} \, dr_2 + V_{\text{XC}}[r_1] \right\} \psi_i(r_1) = \epsilon_i \psi_i(r_1)$$

$$V_{\text{XC}}[r] = \left( \frac{\delta E_{\text{XC}}[\rho(r)]}{\delta \rho(r)} \right)$$

Today can be solved self-consistently for several 100 atoms

Includes all many-body effects
Major approximations in DFTB compared to DFT

- Expansion of KSh-energy in 2\textsuperscript{nd} or more recently 3\textsuperscript{rd} order density fluctuation
- Reference density as atomic superposition
  \[ n(r) = n_0(r) + \delta n(r) \]
  \[ n_0(r) = \sum \alpha n_0^\alpha (r - R_\alpha) \]
- Minimal basis representation of KSh-eigenstates
  \[ \psi_i = \sum_v c_{i v} \phi(r - R_{\alpha(v)}) \]
- Two-center integral approximation, fitting of repulsive interactions
- Self-consistency in atom-centered Mulliken charges in monopole approximation

\[
H_{\mu \nu}^{\text{bs}} = \langle \phi_\nu | \hat{T} + V_{\text{eff}}[n_0^\alpha + n_0^\beta] | \phi_\nu \rangle \\
S_{\mu \nu} = \langle \phi_\mu | \phi_\nu \rangle \\
H_{\mu \mu}^{\text{bs}} = \epsilon_\mu^{\text{free atom}}
\]

\[
E_{\text{rep}}^{\alpha \beta}(R_{\alpha \beta}) = E_{\text{ab initio}}(R_{\alpha \beta}) - [E_{bs} + E_2](R_{\alpha \beta})
\]

- H and S matrix versus distance for each At-type, At-type pair (s/p/d – 10 SK-tables)
- Automized tools will be made available – NEW SK-data format

2-3 order of magnitude faster than DFT
Welcome to DFTB!

This site contains some information about the Density Functional Theory (DFT) method and its applications. If you want to know more about this fast and efficient quantum mechanical method, you can read a short description about DFTB and eventually some references.

The DFTB method has several implementations. For a (non-exhaustive) list of implementations, please see the implementations subpage.

If you are looking for parameters (Slater-Koster files), you can download them at DFTB/Slater-Koster and DFTB/Gaussian (soon).

Three Slater-Koster sets available

There are three Slater-Koster parameter sets (mio-0-1, pbc-0-1, hyb-0-1) available for download. They are provided by the groups of Prof. Frauenheim (BCCMS, Uni Bremen) and Prof. Elstner (Theoretical Chemistry, TU Braunschweig). With the help of these sets, the DFTB method can be applied to a broad range of systems, including organic and inorganic molecules, solid semiconductors and semiconductor surfaces, and hybrid organic/inorganic systems.

DFTB+ on www.dftb-plus.info

The dftb.org site is being redesigned now. It should become a general site for distributing Slater-Koster parameterisation files for the method. Information about DFTB+ can be found on www.dftb-plus.info from now on.

DFTB at the ACS Fall Meeting in San Francisco (presentations)

The DFTB symposium at the ACS Fall Meeting in San Francisco was a real success. Abstracts and some of the presentations are available on our website now.

DFTB+ since 2007 distributed as open source code

about 3000 downloads
TB+ (Implemented/progress)

MM
M. Elstner, Q. Cui, M. Karplus

NEGree-N-DFT
Charge trans.
A. DiCarlo, A. Poirier

Linear scaling
W. Yang

CPMD
T. Heine

GW/BSE-DFTB
T. Niehaus

LDA+U/SO
non-collin. magnetism
B. Hourahine

inter.

DFTB+
We think its now time to go even further! The aim is to extend the active community and to make DFTB+ useful for an even broader scientific community in future years. Therefore, we have changed the license of the software to the open source license LGPL, enabling you to

* obtain and use DFTB+ without any registration process, independent of whether your research is commercial or not,

* interface and distribute DFTB+ as part of your academic or commercial software package,

* easily contribute to DFTB+ by using our publicly hosted repository.

For more details see [http://www.dftbplus.org](http://www.dftbplus.org)
Worldwide network DFTB developers
DFTB Developer Meeting, October 2015
Next generation approximate DFTB method
International CECAM-Workshop on approximate quantum methods in the ab initio world

Objective: The primary goal of the proposed CECAM workshop is to facilitate communication and collaboration between users and developers of multi-scale quantum methods, with emphasis on approximate DFT and semi-empirical (SE) methods, linear-scaling quantum mechanical and hybrid quantum mechanical/molecular mechanics approaches. The meeting is intended to provide a unique forum to bring together world leaders of different communities in method development to discuss recent advances in current methodologies, to assess their similarities, and to identify critical challenges in the field as well as future directions for research and development of the next generation of computational tools. On the more technical side, this will include the discussion of the state of the art in efficient parameterization techniques, reference databases, and multi-objective optimization. Simultaneously, the workshop will involve people from the DFT and ab initio communities, who are interested in SE/DFTB methods as a supplement to their first principles codes, for example to use the more approximate quantum techniques for screening large numbers of structures in high-dimensional configuration space and for exploring extended trajectories under real environmental conditions (e.g. deMon2k, ATK, ADF, SIESTA).

Date: November 6-13, 2016
Multi-Scale Quantum Mechanical Analysis of Condensed Phase Systems: Methods and Applications
NEGF quantum transport under open boundary conditions

$H^0_{\mu \nu}$

Multigrid Poisson solver

$\Delta q_i \uparrow$

Density matrix $\rho$

$H^1_{\mu \nu}$

Self-consistent solutions

$G^R e^\Sigma^R$

Greens function

Evaluation of $G^< \sum^<$
Single molecule quantum transport

\[ I = \frac{2e}{h} \int_{\mu_R}^{\mu_L} Tr[\Sigma^< G^> - \Sigma^> G^<] dE \]

Atomistic modeling of quantum processes in nanoscale devices

Photovoltaic devices

NW-LED

Hot electron injection

Electron – photon interaction
Electron-Photon Interactions

SiNW-SC PN-junction, linearly polarized light applied:

\[ H = \frac{1}{2m} (p + e\mathbf{A})^2 + V(\mathbf{r}) \equiv H_e + \frac{e}{m} \mathbf{A} \cdot \mathbf{p} + \frac{e^2}{2m} \mathbf{A}^2 \]

Hamiltonian in Coulomb Gauge:

In dipole approximation - vector potential in second quantization:

\[ \mathbf{\tilde{A}} = \tilde{a} \left( \frac{\hbar \sqrt{\mu \varepsilon}}{2N \omega \varepsilon c} F_r \right)^{1/2} \left( b e^{-i\omega t} + b^+ e^{i\omega t} \right) \]

interaction Hamiltonian in atomic basis

\[ H_{ep} = \sum_{\mu\nu} \frac{e}{m} \langle \mu | \mathbf{A} \cdot \mathbf{p} | \nu \rangle d_{\mu}^* d_{\nu} = \sum_{\mu\nu} M_{\mu\nu} (b e^{-i\omega t} + b^* e^{i\omega t}) d_{\mu}^* d_{\nu} \]

very similar to electron-phonon interaction
Electron-Photon Interactions

\[ \sum_{\text{e-photon}} \equiv \sum_{\text{e-photon}} \]

\[ \sum_{\varphi} (\tau, \tau') = iM \left[ D(\tau, \tau')G(\tau, \tau') \right] M \]

Photon Green's Function:

\[ D^\geq (t, t') = \left[ Ne^{-i\omega (t-t')} + (N+1)e^{+i\omega (t-t')} \right] \]

\[ D^\searrow (t, t') = \left[ Ne^{-i\omega (t-t')} + (N+1)e^{+i\omega (t-t')} \right] \]

Fourier transform:

\[ \sum_{\varphi \rightarrow eq} (E) = M \left[ NG^{\searrow \rightarrow} (E \mp \hbar \omega) + (N+1)G^{\nearrow \rightarrow} (E \pm \hbar \omega) \right] M \]

Both Green's functions and self-energies to be calculated self-consistently.
Electron-Photon Interactions

Extra terms in self-energy

\[ G^r(E) = \left[ ES - H - \Sigma^r_L(E) - \Sigma^r_R(E) - \Sigma^r_{\varphi}(E) \right]^{-1} \]

Current in NEGF:

\[ I_\alpha = \frac{2e}{\hbar} \int \frac{dE}{2\pi} \text{Tr} \left[ \Sigma^<_\alpha(E) G^>(E) - \Sigma^>_{\alpha}(E) G^<(E) \right] \]

Current:

\[ I^{el}_\alpha = \frac{2e}{\hbar} \int \frac{dE}{2\pi} (f_\alpha - f_\beta) \text{Tr} \left[ \Gamma_\alpha(E) G^r(E) \Gamma_\beta(E) G^a(E) \right] \]

\[ I^{inel}_\alpha = \frac{2e}{\hbar} \int \frac{dE}{2\pi} \text{Tr} \left[ \Gamma_\alpha(E) G^r(E) \Gamma_{\text{eff}}(E) G^a(E) \right] \]

Inelastic scatterings

Due to applied bias electrons enter from right

Electron recombines with a hole, while a Photon emitted

Light emission - LED
Inelastic scatterings

Excitation by light Solar Cell

Electrons can absorb a photon leaving the device with higher energy
**2 Si nanowire pn-junctions as photovoltaic device**

SiNWs, [110] direction, 25 nm

NW-A 6656 atoms; NW-B 12672 atoms

<table>
<thead>
<tr>
<th></th>
<th>Cross-section</th>
<th>Length</th>
<th>Doping concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW-A</td>
<td>2nm x 2nm</td>
<td>25nm</td>
<td>8.0x10^{19} cm^{-3}</td>
</tr>
<tr>
<td>NW-B</td>
<td>3nm x 3nm</td>
<td>25nm</td>
<td>3.56x10^{19} cm^{-3}</td>
</tr>
</tbody>
</table>

I-V characteristics, short circuit current, open circuit voltage, power conversion efficiency

Zhang et al. JPC Lett. 5 (2014) 12
Simulation of photovoltaic device

LDOS of the NW-A with forward bias a) 0V b) 0.6V

<table>
<thead>
<tr>
<th></th>
<th>NW-A</th>
<th>NW-B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{SC}$</td>
<td>2.33 mA/cm^2</td>
<td>4.19 mA/cm^2</td>
</tr>
<tr>
<td>$V_{OC}$</td>
<td>0.62 V</td>
<td>0.66 V</td>
</tr>
<tr>
<td>$\alpha^*$</td>
<td>6.5%</td>
<td>12.4%</td>
</tr>
</tbody>
</table>

I-V curves of (a) NW-A and (b) NW-B with and without light illumination.

Photon energy is 2.5 eV

Enhancement by antireflection and light-trapping techniques

Zhang et al. JPC Lett. 5 (2014) 12
COMMUNICATION

Quantum mechanical modeling the emission pattern and polarization of nanoscale light emitting diodes

Rulin Wang, a Yu Zhang, b Fuzhen Bi, a,c Thomas Frauenheim, d GuanHua Chen e and ChiYung Yam*a,e
Outline of the Talk

1. Brief introduction of the DFTB-method
2. Examples for device modeling
3. Ways to improve ground state accuracy and efficiency
4. TD-DFTB properties in linear response
5. NO-reduction on TiO$_2$ surfaces
6. Charge transfer exitations using pp-DFTB
7. Non-adiabatic Ehrenfest molecular dynamics
Improvement of ground and excited state accuracy

SCC-DFTB2 - consistent strong underestimation of Hydrogen bonds
Wrong qualitative description of Singlet-Triplet Excitations in TD-DFTB

Ways to improve ground state accuracy
• 3-rd order DFTB (DFTB3)
• Multipole interactions
• Onsite correction
• Many-body dispersion interactions (Tkatchenko et al. PRL 2012)

All improvements are crucial for studies under environmental conditions, e.g. solvents and in particular for macromolecular systems
Expansion of the total energy up to third order in $\delta n(\mathbf{r})$:

$$E_{\text{tot}} = E_{\text{bs}}[n_0] + E_{\text{rep}}[n_0] + E_2[n_0, \delta n^2] + E_3[n_0, \delta n^3]$$

$$E_3 = \frac{1}{3} \sum_A \sum_B q_A^2 q_B \Gamma_{AB}$$

$$\Gamma_{AB} = \left. \frac{\partial \gamma_{AB}}{\partial U_A} \frac{\partial U_A}{\partial q_A} \right|_{q_A^0} \Gamma_{AA} = \left. \frac{1}{2} \frac{\partial \gamma_{AA}}{\partial U_A} \frac{\partial U_A}{\partial q_A} \right|_{q_A^0}$$

Damping of $\gamma_{AB}$ for hydrogen interactions:

$$\tilde{\gamma}_{AB} = \frac{1}{R_{AB}} - s(R_{AB}, U_A, U_B)e^{-\left(\frac{U_A+U_B}{2}\right)^{\zeta} R_{AB}^2}$$

DFTB3-QM/MM correct performance for treating water in different chemical environments

Minor changes in DFTB3 substantially improve the structural properties of bulk water under ambient conditions
Water Multilayers on TiO$_2$ (101) Anatase Surface: Assessment of a DFTB-Based Method

Daniele Selli,† Gianluca Fazio,†‡ Gotthard Seifert,‡ and Cristiana Di Valentin*†
Many-body dispersion interaction for DFTB

Communication: Charge-population based dispersion interactions for molecules and materials

Martin Stöhr,1,2 Georg S. Michelitsch,2 John C. Tully,1 Karsten Reuter,2 and Reinhard J. Maurer1,a)

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2Department Chemie, Technische Universität München, Lichtenbergstr. 4, D-85748 Garching, Germany

(Received 3 March 2016; accepted 8 April 2016; published online 19 April 2016)

The DFT+vdW(TS), or in short DFT+TS, scheme2 represents a particularly simple and accurate method to derive dispersion interactions directly from the electron density. The dispersion interaction as given by Eq. (1) is defined via effective atom-wise dispersion parameters such as static atomic polarizabilities $\alpha_A^0, C_6^{AA}$ coefficients, and van der Waals radii $R_A$

$$E_{\text{disp}} = - \sum_{A<B} f_{\text{damp}}(R_{AB}, R_A, R_B) \frac{C_6^{AB}}{R_{AB}^6},$$

(2)

$$C_6^{AB} = \frac{2 C_6^{AA} C_6^{BB}}{\frac{\alpha_B^0}{\alpha_A^0} C_6^{AA} + \frac{\alpha_A^0}{\alpha_B^0} C_6^{BB}}.$$
Many-body dipersion method for DFTB

FIG. 2. Left: MADs in binding energies (in kcal/mol) for a selected subset of S12L complexes as obtained by different dispersion corrected approaches with respect to DQMC calculations. Right: Graphical depiction of the S12L subset considered in this work. H (white), C (black), N (blue), O (red).
Extended Lagrangian Born-Oppenheimer MD: XLBOMD

http://www.dftb-plus.info

MD propagation without SCF cycles → speedup 1 orders of magnitude
DFTB-XLBOMD speedup 3 orders speedup versus conventional DFTB-BO-MD

In progress for release in 2018

• density matrix via a recursive expansion of the Fermi operator
• series of generalized sparse matrix algorithms
• Linear scaling matrix inversion
• efficient parallelisation using graph-based theory

DFTB+ 3 more orders speedup

• 1 time step $10^4$ atoms in 0.1 sec
  • 100 ps QM-MD for $10^6$ atoms
  • Micro-second MD-simulations $10^4$ atoms
  • .........
Outline of the Talk

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3. Ways to improve ground state accuracy for H-bonds and dispersion
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Approximate time-dependent density functional theory

T.A. Niehaus *

Bremen Center for Computational Materials Science, Am Fallturm 1a, 28359 Bremen, Germany

Linear response treatment in the frequency domain
direct propagation in the time domain - Ehrenfest MD and an O(N) implementation in the density matrix formalism

Dr. rer. nat. UPB 2001: Professorship in Lyon
In linear response TD-DFT

Casida’s equation

\[ \Omega F_I = \omega_I^2 F_I \]

\[ \sum_{jb} \left[ \omega_{ia}^2 \delta_{ij} \delta_{ab} + 4 \sqrt{\omega_{ia}K_{ia,jb}^\Sigma \omega_{jb}} \right] F_{jb}^{I\Sigma} = \Omega_{I\Sigma}^2 F_{ia}^{I\Sigma} \]

\[ \omega_I \]

excitation energies

\[ K_{ia,jb}^S = \int \int' \psi_i(\mathbf{r})\psi_a(\mathbf{r}) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}[\rho](\mathbf{r}, \mathbf{r}') \right) \psi_j(\mathbf{r}')\psi_b(\mathbf{r}') \]

excitation vectors

\[ K_{ia,jb}^T = \int \int' \psi_i(\mathbf{r})\psi_a(\mathbf{r}) \left( \frac{\delta^2 E_{xc}}{\delta m(\mathbf{r}) \delta m(\mathbf{r}')} \right) \psi_j(\mathbf{r}')\psi_b(\mathbf{r}') \]
TD-DFT: coupling matrix shifts the excitation energies

\[ K_{ia\sigma}^{DFTB} = \sum_{ABll'} q_{Al}^{ia\sigma} \Gamma_{Al,Bl'}^{\sigma\tau} q_{Bl'}^{jb\tau} \]

Mulliken trans. charges

Mulliken approximation for transition dipole

\[ d_{ia\sigma} \approx \sum_A q_A^{ia\sigma} R_A \]
Absorption spectrum of NO with TD-DFTB without corrections
TD-DFTB excitations in the Mulliken approach

\[ \pi = c_{p_{1x}} \pi p_{x}^{(1)} + c_{p_{2x}} \pi p_{x}^{(2)} \]
\[ \pi^* = c_{p_{1x}} \pi^* p_{x}^{(1)} - c_{p_{2x}} \pi^* p_{x}^{(2)} \]
\[ q_{1}\pi\pi^* = \frac{1}{2}(c_{p_{1x}} \pi c_{p_{1x}} \pi^* S_{p_{1x}p_{1x}} - c_{p_{1x}} \pi c_{p_{2x}} \pi^* S_{p_{1x}p_{2x}}) \]
\[ \sigma = c_{p_{1z}} \pi p_{z}^{(1)} + c_{p_{2z}} \pi p_{z}^{(2)} \]
\[ \pi^* = c_{p_{1x}} \pi^* p_{x}^{(1)} - c_{p_{2x}} \pi^* p_{x}^{(2)} \]
\[ q_{1}\sigma\pi^* = \frac{1}{2}(c_{p_{1z}} \sigma c_{p_{1x}} \pi^* S_{p_{1z}p_{1x}} - c_{p_{1x}} \pi c_{p_{2x}} \pi^* S_{p_{1z}p_{2x}}) \]
\[ \omega_I = \omega_{\sigma\pi^*} \quad d_{\sigma\pi^*} = 0 \]

Correct coupling

Transition charges are zero – no coupling even dipole-forbidden
Extensions of the Time-Dependent Density Functional Based Tight-Binding Approach

A. Domínguez, B. Aradi, T. Frauenheim, V. Lutsker, and T. A. Niehaus

†Bremen Center for Computational Materials Science, Universität Bremen, Am Fallturm 1, 28359 Bremen, Germany
‡Department of Theoretical Physics, University of Regensburg, 93040 Regensburg, Germany

Supporting Information

ABSTRACT: The time-dependent density functional based tight-binding (TD-DFTB) approach is generalized to account for fractional occupations. In addition, an on-site correction leads to marked qualitative and quantitative improvements over the original method. Especially, the known failure of TD-DFTB for the description of $\sigma \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitations is overcome. Benchmark calculations on a large set of organic molecules also indicate a better description of triplet states. The accuracy of the revised TD-DFTB method is found to be similar to first principles TD-DFT calculations at a highly reduced computational cost. As a side issue, we also discuss the generalization of the TD-DFTB method to spin-polarized systems. In contrast to an earlier study, we obtain a formalism that is fully consistent with the use of local exchange-correlation functionals in the ground state DFTB method.
Mulliken-approximation for orbital products:

\[ \phi_\mu(r)\phi_\nu(r) \approx \frac{1}{2} S_{\mu\nu}(|\phi_\mu(r)|^2 + |\phi_\nu(r)|^2) \]

Going beyond Mulliken-approximation:

\[
E_2 = \frac{1}{2} \left[ \sum_{\mu\nu} \Delta \tilde{P}_{\mu\mu}(\mu\mu|\nu\nu) \Delta \tilde{P}_{\nu\nu} + \sum_{\mu \neq \nu} \sum_{A} \sum_{\mu,\nu_A} \Delta \tilde{P}_{\mu\nu}(\mu\nu|\mu\nu) \Delta \tilde{P}_{\mu\nu} + \ldots \right] \\
\Delta \tilde{P} = \Delta P S
\]

A. Dominguez et. al, JCTC 9, 4901 (2013)
Absorption spectrum of NO with onsite corrections
Performance – Thiel’s benchmark set

Singlet and triplet vertical excitations compared to TD-DFT PBE, PBE0, CAM-B3LYP
RMS error and MSD for singlet-triplet transition energies

<table>
<thead>
<tr>
<th>Method</th>
<th>RMS (eV)</th>
<th>MSD (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD-DFTB (new)</td>
<td>0.33</td>
<td>0.07</td>
</tr>
<tr>
<td>TD-DFTB (old)</td>
<td>0.63</td>
<td>0.50</td>
</tr>
<tr>
<td>PBE</td>
<td>0.38</td>
<td>-0.27</td>
</tr>
<tr>
<td>PBE0</td>
<td>0.46</td>
<td>-0.38</td>
</tr>
<tr>
<td>CAM-B3LYP (RPA)</td>
<td>0.43</td>
<td>-0.31</td>
</tr>
<tr>
<td>CAM-B3LYP (TDA)</td>
<td>0.21</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Thiel’s benchmark set compared to experimental data.
RMS error and MSD for singlet-singlet transition energies

Thiel’s benchmark set compared to experimental data
Total wall clock time Thiel’s set singlet and triplets excitations

Thiel’s benchmark subset
Nitrogen(II) Oxide Charge Transfer Complexes on TiO$_2$: A New Source for Visible-Light Activity

J. Freitag,† A. Domínguez,*‡ T. A. Niehaus,‖ A. Hülsewig,§ R. Dillert,† T. Frauenheim,‡ and D. W. Bahnemann†,⊥
Photonic efficiencies of four TiO$_2$ powders under UV and VIS

<table>
<thead>
<tr>
<th>TiO$_2$ powder</th>
<th>Selectivity (UV) /%</th>
<th>Selectivity S (Visible) /%</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>23.44</td>
<td>67.03</td>
</tr>
<tr>
<td>UV100</td>
<td>56.75</td>
<td>83.62</td>
</tr>
<tr>
<td>PP10</td>
<td>51.51</td>
<td>41.15</td>
</tr>
<tr>
<td>VLP 7000</td>
<td>53.51</td>
<td>79.77</td>
</tr>
</tbody>
</table>

Pollutant – TiO$_2$ hybrid complexes are photo-active in the visible light.
Two stable NO adsorption sites on anatase TiO$_2$

Scanning NO-adsorption for most stable sites on anatase (110)
Two stable NO adsorption sites on anatase TiO$_2$

Strongly enhanced visible light activity
NO adsorption spectra on anatase TiO$_2$ (001) surface

Charge transfer from TiO$_2$ valence band to NO-$\pi^*$ molecular orbital
NO adsorption spectra on anatase TiO$_2$ surface

Charge transfer from NO-$\pi$ orbital to TiO$_2$ conduction band

Outline of the Talk

1. Brief introduction of the DFTB-method
2. Examples for device modeling
3. Ways to improve ground state accuracy for H-bonds and dispersion
4. TD-DFTB properties in linear response
5. NO-reduction on TiO$_2$ surfaces
6. Charge transfer excitations using pp-DFTB
7. Non-adiabatic molecular dynamics
Nonadiabatic Molecular Dynamics for Thousand Atom Systems: A Tight-Binding Approach toward PYXAID

Sougata Pal, † Dhara J. Trivedi, ‡ Alexey V. Akimov, § Bálint Aradi, ‡ Thomas Frauenheim, ‡ and Oleg V. Prezhdo*, †

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ABSTRACT: Excited state dynamics at the nanoscale requires treatment of systems involving hundreds and thousands of atoms. In the majority of cases, depending on the process under investigation, the electronic structure component of the calculation constitutes the computation bottleneck. We developed an efficient approach for simulating nonadiabatic molecular dynamics (NA-MD) of large systems in the framework of the self-consistent charge density functional combined with self-hybridization (SH) and for the Python implementation. The developed approach is tested with ab initio DFT and experimental data, by simulation of nonradiative electron–hole recombination in a CdSe quantum dot and unique is capable of treating accurately and efficiently excitation dynamics in high computational resources.
DFTB+ as electronic structure driving engine for NAMD in PYXAID

- Adiabatic electronic state energies
- NA couplings, $d_{ki}$,
- Interatomic forces acting on the nuclei

as essential input quantities for NA-MD simulations

\[ i\hbar \frac{dc_k(t)}{dt} = \sum_{i=0}^{N} (\varepsilon_k \delta_{ki} - i\hbar d_{ki})c_i(t) \]

where

\[ d_{ki} = \left\langle \phi_k(r, R(t)) \right| \frac{\partial \phi_i(r, R(t))}{\partial t} \right\rangle \]
DFTB+ as driving engine for NAMD in NEXMD (Los Alamos)

- **NEXMD** with various surface hopping techniques
- Real-time NAMD
- Based on excited state determinants
- Available in combination with SE methods, like AM$_{x}$

**Interface to AMBER force field:** *excited state QM/MM*

Sergei Tretiak LANL

Adrian Roitberg U Florida
**NEW implementation of real time TDDFTB: electron-ion dynamics**

Christian Sanchez (right), Franco Bonafe, University of Cordoba

**Numerical propagation** of density matrix according to Liouville-von Neumann equation

\[ \dot{\rho} = -i(S^{-1}H\rho - \rho HS^{-1}) \rightarrow \rho_{i+1} = \rho_{i-1} + 2\Delta t \dot{\rho}_i \]

\[ H_{\mu\nu} = H_{\mu\nu}^0 + \frac{1}{2}S_{\mu\nu}\sum_K (\gamma_{IK} + \gamma_{JK})\Delta q_K, \quad \mu \in I, \quad \nu \in J. \]

**Absorption spectra** are calculated by the polarizability tensor obtained by Fourier transform of the dipole moment, after a proper perturbation

\[ \mu(t) = \int_{-\infty}^{\infty} \alpha(t-\tau)E(\tau)d\tau \]

\[ E(t) = E_0\delta(t-t_0) \]

**Initial kick** determines type of spectrum:
- Electric field: singlet spectrum
- Magnetic field: triplet spectrum

![Zigzag graphene nanoflake](image-url)
Absorption spectra of photosynthetic pigments

ChlA

ChlB

BChlA

BChlB

BChlC

BChlE

Experimental data in agreement with calculated frequencies and intensities
Non-adiabatic Ehrenfest dynamics

Semi-classical treatment: \textbf{classical nuclei, quantum electrons.}

Equation of motion of density matrices includes \textbf{non-adiabatic coupling matrix and velocity dependent terms}:

\[ \dot{\rho} = -i(S^{-1}H\rho - \rho HS^{-1}) - (S^{-1}\tilde{D}\rho + \rho\tilde{D}S^{-1}) \]

\begin{align*}
\mathbf{R}_A(t + \Delta t) &= \mathbf{R}_A(t) + \dot{\mathbf{R}}_A(t)\Delta t + \frac{1}{2m}\mathbf{F}_A(t)\Delta t^2 \\
\dot{\mathbf{R}}_A(t + \Delta t) &= \dot{\mathbf{R}}(t) + \frac{1}{2m}(\mathbf{F}_A(t) + \mathbf{F}_A(t + \Delta t))\Delta t
\end{align*}

The electric field is added as any external perturbation to the hamiltonian:

\[ H = H^1 + \frac{1}{2}(Sf + fS) \]

where \( f = -e\mathbf{E}(t) \cdot \hat{r} \)

For a \( \sin^2 \) laser pulse of length \( \tau \) with frequency \( \omega \), e.g., the electric field is:

\[ \mathbf{E}(t) = E_0 \sin^2(\pi t / \tau) \sin(\omega t)(1 - \Theta(\tau)) \]
Impulsive breathing mode excitations in Ag and Au NPs

Motivation by experimental studies

Chemical Reviews

Optical Studies of Dynamics in Noble Metal Nanostructures
Gregory V. Hartland
Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556-5670, United States

Acoustic Vibration of Metal Films and Nanoparticles
N. Del Fatti, C. Voisin, D. Christofilos, F. Vallée,* and C. Flytzanis
Laboratoire d’Optique Quantique du CNRS, Ecole Polytechnique, 91128 Palaiseau Cedex, France
Received: November 16, 1999; In Final Form: January 27, 2000

Scheme 1. Sequence of Events and Approximate Time Scales Following Absorption of Photons by a Metal Nanoparticle

- Plasmon resonance
- Dephasing (10 fs)
- Non-thermal electron distribution
- e-e scattering (100 fs)
- Hot electron distribution
- e-ph scattering (1 ps)
- Vibrational resonances
- Coupling to the environment (>10 ps)
Impulsive breathing mode excitation in Ag and Au NPs

25 fs pulse
frequency tuned to plasmon excitation
Ag: Change in radius versus field strength
Photo-splitting of CO adsorbed on metal nanoparticles

NEW application

O holds the negative charge in the antibonding state of CO

Work in progress!
Dynamics of charge separation in organic blends

P3HT - PCBM

Chi Yung Yam

Guanhua Chen

BCCMS

CSRC
Absorption spectra of PCBM and P3HT

Figure 1 (A) atomic structures of P3HT:PCBM; (B) experiment absorption spectra; (C) absorption spectra of PCBM and (D) absorption spectra of P3HT using TD-DFTB
Figure 2 (A) and (B): experiment absorption spectra; (C) and (D): corresponding absorption spectra obtained using TD-DFTB, the atomic structure is shown in (E);
Electron Dynamics with and without Ehrenfest MD

- External field is continuous sine function with frequency corresponding to P3HT absorbance peak;
- External field is applied on P3HT;
- With Ehrenfest, charge transfer process is faster and more charge transfers from P3HT to PCBM;
- The change of charge on P3HT has 20-30fs oscillation which is consistent with TD-DFT Ehrenfest results

Figure 3. The change of charge on molecular fragments without (A) and with (B) Ehrenfest dynamics. The initial velocity is random assigned. (C) Movie of atomic movement with Ehrenfest dynamics. (D) TD-DFT-Ehrenfest result for system containing one P3HT and one PCBM.
Figure 4 (A) Atomic structure for simulation containing four P3HT and five PCBM aggregates in X direction. (B) The change of charge on each molecular fragments without Ehrenfest; (C,D,E) Snapshots of induced electron density in real space and real time.
Analysis of charge transfer process in multiple layers of P3HT/PCBM

Movie for induced electron density in real space & real time
Summary: DFTB for nanoscale device simulations
DFTB+ connects to world wide software development
Major collaboration partners

Alessandro Pecchia Rome
Marcus Elstner Karlsruhe
Qiang Cui Boston
Thomas Niehaus Lyon

Christian Sanchez Cordoba

Oleg Prezhdo USC-LA
Sergei Tretiak LANL
Adrian Ronberg U Florida
Bremen Center for Computational Materials Science

http://www.bccms.uni-bremen.de

Acknowledgement – CMS-group

TAB-Building
Technische Akademie Bremen
Am Fallturm 1

Funding agencies: DFG, BMBF, DAAD, AvH, EC,

......

collaborations around the world
Quantum Mechanical Materials Modelling

Research Training Group
DFG - RTG 2247
Speaker/Co-Speaker:
T. Frauenheim; T. Wehling

QM³
Thank You!

Hope to welcome you sometime in Bremen
Since 2009 Transformation of CECAM into a multi-nodal structure with CECAM-EPFL as its Headquarter, meanwhile 21 nodes
International CECAM Workshop

Tackling Complexity of the Nano/Bio Interface - Computational and Experimental Approaches

Bremen June 12-16\textsuperscript{th} 2017
Applications to nanotoxicity

International CECAM Workshop

Charge carrier dynamics in nanostructures: optoelectronic and photo-stimulated processes

Bremen 9-13\textsuperscript{th} October 2017
Applications in photo-catalysis and photovoltaics
International CECAM Workshop
Crystal defects for qubits, single photon emitters and nanosensors
Bremen July 9th to 13th 2018

International CECAM Workshop
Reliable and quantitative prediction of defect properties in Ga-based semiconductors
Bremen October 8th to 12th 2018

International CECAM Workshop
Correlated electron physics beyond the Hubbard model
Bremen February 4th to 8th 2019