Inverse quantum confinement in luminescent Silicon quantum dots

Thomas Niehaus

Bremen Center for Computational Materials Science

Electron Dynamics in Complex Systems

4th Time-Dependent Density-Functional Theory: Prospects and Applications
Benasque – January 2010
Outline

1 Motivation

2 Theoretical Methods
   - Approximate TDDFT $\Rightarrow$ TD-DFTB

3 Application to Silicon Nanostructures
   - Hydrogenated SiQD - Simple and boring?
   - Functionalization of Dots - Making them useful
   - Surface reconstruction - Energetics and Spectra
   - Silicon nanowires - Confinement in radial and axial dimensions

4 Summary and Outlook
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4 Summary and Outlook
What is a Quantum Dot?

Characteristics

- An object that confines electrons in all three dimensions
- Made mostly from semiconductor material.
- Extension of nanometers
- Electronic level spacing comparable to $k_B T$
Properties of Quantum Dots – Size dependent Emission

Fluorescence of Cadmium Selenide Quantum Dots
www.chemie.uni-hamburg.de/pc/weller/

Range of Emission Wavelength
 Michalet Science (2005)
Properties of Quantum Dots – Advantages over Dyes

Dye

Dot

Mouse intestinal section
http://probes.invitrogen.com

Multi-color labelling possible
Properties of Quantum Dots – Advantages over Dyes


*top:* Nucleus labelled with Dot, microtubules with Dye

*bottom:* vice versa

Quantum dots show only limited photobleaching
Quantum dots as markers in biology

Functionalization with antibodies or aptamers

In vitro

Mouse cerebellum
http://probes.invitrogen.com

In vivo

Rat tumor
Biocompatibility of Cadmium based Dots

Probing the Cytotoxicity of Semiconductor Quantum Dots

Austin M. Derfus, Warren C. W. Chan,† and Sangeeta N. Bhatia∗

Department of Bioengineering, University of California at San Diego, La Jolla, California 92093

Received September 3, 2003; Revised Manuscript Received November 7, 2003

ABSTRACT

With their bright, photostable fluorescence, semiconductor quantum dots (QDs) show promise as alternatives to organic dyes for biological labeling. Questions about their potential cytotoxicity, however, remain unanswered. While cytotoxicity of bulk cadmium selenide (CdSe) is well documented, a number of groups have suggested that CdSe QDs are cytocompatible, at least with some immortalized cell lines. Using primary hepatocytes as a liver model, we found that CdSe-core QDs were indeed acutely toxic under certain conditions. Specifically, we found that the cytotoxicity of QDs was modulated by processing parameters during synthesis, exposure to ultraviolet light, and surface coatings. Our data further suggest that cytotoxicity correlates with the liberation of free Cd2+ ions due to deterioration of the CdSe lattice. When appropriately coated, CdSe-core QDs can be rendered nontoxic and used to track cell migration and reorganization in vitro. Our results provide information for design criteria for the use of QDs in vitro and especially in vivo, where deterioration over time may occur.
Silicon

- Bulk Silicon
  - phonon assisted emission
  - fundamental band gap of 1.13 eV
Silicon

Bulk Silicon
- phonon assisted emission
- fund. band gap of 1.13 eV

Silicon Quantum Dots
- Dipole-allowed transition
- Bright emission in the visible

Emission from SiH nanoparticles under UV excitation, Belomin APL (2002)
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4 Summary and Outlook
Solution strategies in TDDFT

**Time domain**

\[
i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left[ -\frac{1}{2} \nabla^2 + v_{\text{KS}}[\rho](\mathbf{r}) \right] \phi_i(\mathbf{r}, t)
\]

- Valid for strong fields
- Full spectrum at once
- Only occ. orbitals required
- No information on *dark* states

Formally $N^3$, can be made $N$

**Frequency domain**

\[\sum_{kl} \Omega_{ijkl} F^l_{kl} = \omega_I^2 F^l_{ij}\]

- Detailed information on the excited state
- Singlet and Triplet
- Both occ. and virt. orbitals required

Formally $N^6$, can be made $N^3$
Main approximations - Ground state

- Minimal AO basis: $\psi_i(r) = \sum_{\mu} c_{\mu i} \phi_{\mu}(r - R_A)$
- Density divided into reference density ($\rho_0$) and fluctuation: $\rho = \rho_0 + \delta \rho$
- Total energy:

$$E_{\text{tot}} = \sum_i \sum_{\mu \nu} c_{\mu i} H_{\mu \nu}^0[\rho_0] c_{\nu i} + \sum_{AB} \gamma_{AB} \Delta q_A \Delta q_B + U_{\text{rep}}$$

- Two-center approximation, matrix elements calculated not fitted
- $\gamma_{AB}$ represents e-e interaction (including xc)

**Variational principle yields molecular orbitals and energies**

- Elstner et al. PRB **58** 7260 (1998)
DFTB approximation of TDDFT = TD-DFTB

Equation to solve (Singlets):

\[
\sum_{kl} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 2 \sqrt{\omega_{ij}} K_{ij,kl} \sqrt{\omega_{kl}} \right] F_{kl}^l = \omega_i^2 F_{ij}^l
\]

Couplingmatrix $K$ leads to correction of single-particle picture

DFT: $K_{ij,kl} = 2 \int \int \psi_i(r) \psi_j(r) \left( \frac{1}{|r - r'|} + \frac{\delta v_{xc}(r)}{\delta \rho(r')} \right) \psi_k(r') \psi_l(r') \, dr \, dr'$

Niehaus, *PRB* 63 085108 (2001)
DFTB approximation of TDDFT = TD-DFTB

Equation to solve (Singlets):

\[
\sum_{kl} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 2 \sqrt{\omega_{ij} K_{ij,kl} \sqrt{\omega_{kl}}} \right] F_{kl}^l = \omega_i^2 F_{ij}^l
\]

Get single particle energies \( \{ \epsilon_i \} \) from DFTB

Coupling matrix \( K \) leads to correction of single-particle picture

DFT: \( K_{ij,kl} = 2 \int \int \psi_i(\mathbf{r}) \psi_j(\mathbf{r}) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta v_{xc}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \right) \psi_k(\mathbf{r}') \psi_l(\mathbf{r}') \, d\mathbf{r} \, d\mathbf{r}' \)

DFTB: \( K_{ij,kl} = 2 \sum_{AB} q_A^{ij} \gamma_{AB}(|\mathbf{R}_A - \mathbf{R}_B|, U_A, U_B) \, q_B^{kl} \)

Niehaus, *PRB* 63 085108 (2001)
## TD-DFTB performance

### Excitation energies (eV)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>State</th>
<th>Exp.</th>
<th>TD-DFTB</th>
<th>TDDFT$^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\omega_I$</td>
<td>$\omega_{ij}$</td>
</tr>
<tr>
<td>Ethylen</td>
<td>$^3B_{1u}(\pi \to \pi^*)$</td>
<td>4.40</td>
<td>5.47</td>
<td>6.30</td>
</tr>
<tr>
<td></td>
<td>$^1B_{1u}(\pi \to \pi^*)$</td>
<td>7.65</td>
<td>7.81</td>
<td>6.30</td>
</tr>
<tr>
<td>Propynal</td>
<td>$^3A''(n \to \pi^*)$</td>
<td>2.99</td>
<td>4.04</td>
<td>4.04</td>
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<td>$^1A''(n \to \pi^*)$</td>
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[1] BPW91//6-311+G**
### TD-DFTB performance

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<tr>
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<sup>[1]</sup> BPW91//6-311+G**

#### Mean absolute error (eV)

<table>
<thead>
<tr>
<th></th>
<th>TD-DFTB</th>
<th>BPW91 6-311+G**</th>
<th>STO-3G</th>
<th>INDO/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sing. (16 Com.)</td>
<td>0.38</td>
<td>0.36</td>
<td>1.19</td>
<td>0.56</td>
</tr>
<tr>
<td>Trip. (13/11 Com.)</td>
<td>0.64</td>
<td>0.37</td>
<td>0.49</td>
<td>1.38</td>
</tr>
</tbody>
</table>
Sum of CPU times (ground + excited state) for test set of 10 organic molecules (< 10 atoms). TDDFT results are for the BPW91 functional.
Numerical issues

Scaling

- Iterative subspace methods for diag.
- Formal scaling of $N^6$ reduced to $N^3$

$$\sum_{kl} \Omega_{ij,kl} v_{kl} =$$

$$\omega_{ij}^2 v_{ij} + 4 \sqrt{\omega_{ij}} \sum_{\mu} q_{ij}^{\mu} \left( \sum_{\nu} \gamma_{\mu\nu} \left( \sum_{kl} q_{\nu}^{kl} \sqrt{\omega_{kl} v_{kl}} \right) \right)$$

Analytical excited state gradients from auxiliary Lagrangian approach (Furche and Ahlrichs)

⇒ Heringer et al. JCC 28 2589 (2007)
1 Motivation

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   • Approximate TDDFT ⇒ TD-DFTB

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   • Hydrogenated SiQD - Simple and boring?
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4 Summary and Outlook
Generation of models

- Spherical fragments $\text{Si}_{1-199}$ from bulk Si
- Passivation with Hydrogen and relaxation
- Si-Si bonds 2.33-2.38 Å
- $T_d$ symmetry
- $d(\text{Si}_5) = 0.45 \text{ nm}$ to $d(\text{Si}_{199}) = 2.0 \text{ nm}$
## Validation of TD-DFTB

<table>
<thead>
<tr>
<th></th>
<th>DFTB</th>
<th>PBE</th>
<th>B3LYP</th>
<th>MR-MP2</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH(_4)</td>
<td>10.3</td>
<td>8.76</td>
<td>9.25</td>
<td></td>
<td>8.8</td>
</tr>
<tr>
<td>Si(<em>5)H(</em>{12})</td>
<td>6.40</td>
<td>6.09</td>
<td>6.66</td>
<td>6.56</td>
<td>6.5</td>
</tr>
<tr>
<td>Si(<em>{29})H(</em>{36})</td>
<td>4.42</td>
<td>3.65</td>
<td>4.52</td>
<td>4.45</td>
<td></td>
</tr>
<tr>
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<td>4.33</td>
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</tr>
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</table>

B3LYP functional of choice for SiQD
DFTB is fine for larger dots
UV-Vis absorption energies of H-SiQD

Anticipated Particle-in-a-box behaviour

Experimental reports on SiQD photoluminescence

Peak PL versus Si nanocrystal size

Wilcoxon et al. PRB 60 2704 (1999)
Luminescence and excited state processes

Jablonski Energy Diagram
- Excitation (Absorption) 10^{-15} Seconds
- Internal Conversion and Vibrational Relaxation (10^{-14} - 10^{-11} Sec)
- Fluorescence (10^{-9} - 10^{-7} Sec)
- Intersystem Crossing
- Quenching
- Non-Radiative Relaxation

Excited Singlet States

Vibrational Energy States

Delayed Fluorescence

Intersystem Crossing

Non-Radiative Relaxation (Triplet)

Phosphorescence (10^{-3} - 10^{2} Sec)

Ground State

Franck-Condon Energy Diagram
- Absorption
- Emission

Figure 1

Figure 2

Internuclear Separation
Luminescence properties of H-SiQD

Huge Stokes shift for small particles

Structure relaxation in the excited state

$S_1$ optimum of $\text{Si}_{35}\text{H}_{36}$

Formation of a self-trapped exciton
Functionalization of dots

Functionalization with allylamine leads to:
- Increased solubility
- Decreased aggregation
- Decreased oxidation

Does coating destroy the optical properties?

**Generation of models**

**No preference in adsorption site**

<table>
<thead>
<tr>
<th>Site</th>
<th>Binding energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Si}<em>{35}\text{H}</em>{36})</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>(\text{Si}<em>{59}\text{H}</em>{60})</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

Complete coverage impossible

Simulated and experimental IR spectrum


Strong quantum size effect – Little dependence on passivation
## Maximum absorption and emission peaks

<table>
<thead>
<tr>
<th>#</th>
<th>Si</th>
<th>allylamine</th>
<th>Absorption [nm]</th>
<th>Emission [nm]</th>
<th>Shift [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0</td>
<td>205</td>
<td>421</td>
<td>216</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>0</td>
<td>281</td>
<td>405</td>
<td>124</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>0</td>
<td>284</td>
<td>429</td>
<td>145</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>284</td>
<td>425</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>297</td>
<td>462</td>
<td>165</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>0</td>
<td>334</td>
<td>390</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>Exp.</td>
<td></td>
<td>320</td>
<td>480</td>
<td>160</td>
<td></td>
</tr>
</tbody>
</table>

### Results
- Good agreement between exp. and theory for Si\textsubscript{35}
- Red light emission requires larger dots as Si\textsubscript{59}
Conclusions on allylamine functionalization

Allylamine is a promising candidate for protection and functionalization of Silicon quantum dots without perturbation of their favorable optical properties.

Wang, Zhang, Niehaus, Frauenheim *JPC C* 111 2394 (2007)
Reconstructed Silicon Quantum Dots

$\text{Si}_{29}\text{H}_{36}$

Dimer formation by $\text{H}_2$ abstraction

$\text{Si}_{29}\text{H}_{24}$
Reconstructed Silicon Quantum Dots

Formation energy:

\[ E_f = E_{re} + (\Delta n/2)E_{H_2} - E_{bl} \]
Optical properties

Inverse quantum confinement effect

Wang, Zhang, Lee, Frauenheim, Niehaus *APL* 93 243120 (2008)
Effects of confinement in radial and axial dimensions

Finite models of SiNW with [110] growth direction

Absorption and emission spectra for SiNW with $d = 0.84$ nm

Excited state relaxation does not quench luminescence
Size dependence of exciton localization

HOMO and LUMO

d=0.84 nm and l=1.17 nm

d=0.84 nm and l=2.32 nm

Exciton delocalizes for rods with \( l > 2 \) nm

Wang, Zhang, Frauenheim, Niehaus *JPC C* **113** 12935 (2009)
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4 Summary and Outlook
### Main findings

- Excited state relaxation is crucial
- Self-trapped excitons form for nanostructures $< 2$ nm
- Oxidation is not the only source of redshifted emission
- Reconstruction has to be considered
Other TD-DFTB implementations

**Linear response O(N)**

Si$_{717}$H$_{300}$

F. Wang et al. PRB 76 045114 (2007)

**TD-DFTB for open systems**

Wang et al., to be published (2010)

**Nonadiabatic Molecular dynamics**

Niehaus et al. EPJD 35 467 (2005)

**NA-MD: Femtochemistry**

Niehaus et al. EPJD 35 467 (2005)

\[ i \frac{\partial}{\partial t} \sigma = [H_{DFTB}, \sigma] \]
Other TD-DFTB implementations

Linear response O(N)

Nonadiabatic Molecular dynamics

TD-DFTB for open systems

NA-MD: Femtochemistry

\[ i \frac{\partial}{\partial t} \sigma_D = [H_D^{\text{DFTB}}, \sigma_D] + i \sum_{\alpha=L,R} Q_\alpha \]
Other TD-DFTB implementations

Linear response $O(N)$

Si$^{717}$H$^{300}$

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$i \frac{\partial}{\partial t} |\psi_i\rangle = H^{\text{DFTB}} |\psi_i\rangle \quad \wedge \quad M_\alpha \ddot{R}_\alpha = - \sum_{i}^{\text{occ}} \langle \psi_i | \frac{dH^{\text{DFTB}}}{dR_\alpha} |\psi_i\rangle - \frac{dE_{\text{rep}}}{dR_\alpha}$

TD-DFTB for open systems

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Welcome to DFTB+

The aim of the DFTB+ (DFTB Plus) project is to create a highly modularised, but nevertheless fast and efficient stand alone Density Functional based Tight Binding (DFTB) implementation, containing all useful extensions, which had been implemented in several separate programs before now, and adding new useful features. The project is already in a very advanced state, learn more about the DFTB+ code and its features.

DFTB+ is free for non-commercial use. If you are interested to try it, you can download it. In the case you are not a registered user yet, you will have to register first, though. If you are interested in commercial use, please contact us.

For help in using DFTB+, check out the appropriate subpage for its documentation, especially the manual of the current version and the available howtos.

Orbital visualisation with Waveplot and VMD

A step by step mini-howto “First steps with Waveplot” had been uploaded, which gives a compact introduction into the use of Waveplot and the visualisation of the created data with VMD.

New release DFTB+ 1.0.1 available

A new release of the DFTB+ code is available. In version 1.0.1, few minor bugs had been fixed. See the release notes for a detailed list of changes. The source code and binaries can be downloaded from the download area.

Tools and howto for calculating band structures added

A howto containing a detailed description about band structure and density of states calculation with DFTB+ had been added. The download file of the howto contains useful scripts helper scripts.

[News archive]
Xian Wang, Quan-Song Li, Chensheng Lin and Ruiqin Zhang

- The EDiCS group at BCCMS

Bernhard Grundkötter

ChiYung Yam

Setianto

Yong Wang
Atomic DFT calculations ⇒ $\rho_A(r)$, $\phi_\mu(r)$, $\epsilon_\mu$ ⇒ $\rho_0 = \sum_A \rho_A$
Density Functional based Tight-Binding

- Atomic DFT calculations \( \Rightarrow \rho_A(r), \phi_\mu(r), \epsilon_\mu \Rightarrow \rho_0 = \sum_A \rho_A \)

- Construction of molecular Hamiltonian \( H^0_{\mu\nu}[\rho_0] \)

\[
H^0_{\mu\nu} = \begin{cases} 
\epsilon_\mu & : \mu = \nu \\
\langle \phi_\mu | H_{KS}[\rho_A + \rho_B] | \phi_\nu \rangle & : \mu \in A, \nu \in B \\
0 & : \text{otherwise}
\end{cases}
\]

Density Functional based Tight-Binding

- Atomic DFT calculations \( \Rightarrow \rho_A(r), \phi_\mu(r), \epsilon_\mu \Rightarrow \rho_0 = \sum_A \rho_A \)

- Construction of molecular Hamiltonian \( H_{\mu\nu}^0[\rho_0] + H_{\mu\nu}^1[\rho - \rho_0] \)

\[
H_{\mu\nu}^0 = \begin{cases} 
\epsilon_\mu & : \mu = \nu \\
\langle \phi_\mu | H_{KS}[\rho_A + \rho_B] | \phi_\nu \rangle & : \mu \in A, \nu \in B \\
0 & : \text{otherwise}
\end{cases}
\]

\[
H_{\mu\nu}^1 = \frac{1}{2} S_{\mu\nu} \sum_\alpha (\gamma_{\mu\alpha} + \gamma_{\nu\alpha}) \Delta q_\alpha
\]

\[
\gamma_{\mu\nu} = \iint |\phi_\mu(r)|^2 \left( \frac{1}{|r - r'|} + f_{xc}[\rho_0] \right) |\phi_\nu(r')|^2 drdr'
\]

Elstner et al. PRB 58 7260 (1998)
Density Functional based Tight-Binding

- Atomic DFT calculations $\Rightarrow \rho_A(r), \phi_\mu(r), \epsilon_\mu \Rightarrow \rho_0 = \sum_A \rho_A$

- Construction of molecular Hamiltonian $H^0_{\mu\nu}[ho_0] + H^1_{\mu\nu}[ho - \rho_0]$

$$H^0_{\mu\nu} = \begin{cases} 
\epsilon_\mu & : \mu = \nu \\
\langle \phi_\mu | H_{KS} [\rho_A + \rho_B] | \phi_\nu \rangle & : \mu \in A, \nu \in B \\
0 & : \text{otherwise}
\end{cases}$$

$$H^1_{\mu\nu} = \frac{1}{2} S_{\mu\nu} \sum_\alpha (\gamma_{\mu\alpha} + \gamma_{\nu\alpha}) \Delta q_\alpha$$

$$\gamma_{\mu\nu} = \int \int |\phi_\mu(r)|^2 \left( \frac{1}{|r - r'|} + f_{xc}[\rho_0] \right) |\phi_\nu(r')|^2 dr dr' \approx \gamma_{\mu\nu}(U_A, U_B, |R_A - R_B|)$$

Elstner et al. PRB 58 7260 (1998)
Density Functional based Tight-Binding

- Atomic DFT calculations \( \Rightarrow \rho_A(r), \phi_\mu(r), \epsilon_\mu \Rightarrow \rho_0 = \sum_A \rho_A \)

- Construction of molecular Hamiltonian \( H_{\mu\nu}^0[\rho_0] + H_{\mu\nu}^1[\rho - \rho_0] \)

\[
H_{\mu\nu}^0 = \begin{cases} 
\epsilon_\mu & : \mu = \nu \\
\langle \phi_\mu | H_{KS} [\rho_A + \rho_B] | \phi_\nu \rangle & : \mu \in A, \nu \in B \\
0 & : \text{otherwise}
\end{cases}
\]

\[
H_{\mu\nu}^1 = \frac{1}{2} S_{\mu\nu} \sum_\alpha (\gamma_{\mu\alpha} + \gamma_{\nu\alpha}) \Delta q_\alpha
\]

\[
\gamma_{\mu\nu} = \int \int |\phi_\mu(r)|^2 \left( \frac{1}{|r-r'|} + f_{xc}[\rho_0] \right) |\phi_\nu(r')|^2 \, dr \, dr' \approx \gamma_{\mu\nu}(U_A, U_B, |R_A - R_B|)
\]

- Total energy

\[
E_{\text{tot}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^0 + \frac{1}{2} \sum_{\mu\nu} \gamma_{\mu\nu} \Delta q_\mu \Delta q_\nu + E_{\text{rep}}
\]

Elstner et al. PRB 58 7260 (1998)
Equation to solve (singlets):

\[
\sum_{kl} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 4\sqrt{\omega_{ij}} K_{ij,kl} \sqrt{\omega_{kl}} \right] F_{kl}^I = \omega_i^2 F_{ij}^I
\]

\[
K_{ij,kl}^S = \int \int \psi_i(r) \psi_j(r) \left( \frac{1}{|r-r'|} + f_{xc}[\rho] \right) \psi_k(r') \psi_l(r') drdr'
\]
Linear response in DFTB: TD-DFTB

Equation to solve (singlets):

$$\sum_{kl} \left[ \omega_{ij} \delta_{ik} \delta_{jl} + 4 \sqrt{\omega_{ij} K_{ij,kl} \sqrt{\omega_{kl}}} \right] F^I_{kl} = \omega_i^2 F^I_{ij}$$

$$K^S_{ij,kl} = \int \int \psi_i(r) \psi_j(r) \left( \frac{1}{|r-r'|} + f_{xc}[\rho] \right) \psi_k(r') \psi_l(r') \, dr \, dr'$$

Approximation:

$$K^S_{ij,kl} = \sum_{\mu \nu \alpha \beta} c_{\mu i} c_{\nu j} c_{\alpha k} c_{\beta l} \int \int \phi_{\mu}(r) \phi_{\nu}(r) \left( \frac{1}{|r-r'|} + f_{xc}[\rho] \right) \phi_{\alpha}(r') \phi_{\beta}(r') \, dr \, dr'$$
Linear response in DFTB: TD-DFTB

Equation to solve (singlets):

\[
\sum_{k,l} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 4 \sqrt{\omega_{ij} K_{ij,kl} \omega_{kl}} \right] F^l_{kl} = \omega_i^2 F^l_{ij}
\]

\[
K^S_{ij,kl} = \int \int \psi_i(r) \psi_j(r) \left( \frac{1}{|r-r'|} + f_{xc} [\rho] \right) \psi_k(r') \psi_l(r') dr dr'
\]

Approximation:

\[
K^S_{ij,kl} = \sum_{\mu \nu \alpha \beta} c_{\mu i} c_{\nu j} c_{\alpha k} c_{\beta l} \int \int \phi_{\mu}(r) \phi_{\nu}(r) \left( \frac{1}{|r-r'|} + f_{xc} [\rho] \right) \phi_{\alpha}(r') \phi_{\beta}(r') dr dr'
\]

Mulliken approximation:

\[
\phi_{\mu}(r) \phi_{\nu}(r) \approx \frac{1}{2} S_{\mu \nu} \left( |\phi_{\mu}(r)|^2 + |\phi_{\nu}(r)|^2 \right)
\]
Linear response in DFTB: TD-DFTB

Equation to solve (singlets):

\[
\sum_{kl} \left[ \omega^2_i \delta_{ik} \delta_{jl} + 4\sqrt{\omega_{ij}} K^S_{ij,kl} \sqrt{\omega_{kl}} \right] F^I_{kl} = \omega^2_i F^I_{ij}
\]

\[
K^S_{ij,kl} = \int \int \psi_i(r) \psi_j(r) \left( \frac{1}{|r - r'|} + f_{xc}[^\rho] \right) \psi_k(r') \psi_l(r') \, dr \, dr'
\]

Approximation:

\[
K^S_{ij,kl} = \sum_{\mu\nu\alpha\beta} c_{\mu i} c_{\nu j} c_{\alpha k} c_{\beta l} \int \int \phi_\mu(r) \phi_\nu(r) \left( \frac{1}{|r - r'|} + f_{xc}[^\rho] \right) \phi_\alpha(r') \phi_\beta(r') \, dr \, dr'
\]

Mulliken approximation:

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

\[
K^S_{ij,kl} \approx \sum_{\mu\nu} q^i_\mu q^k_\nu \int \int |\phi_\mu(r)|^2 \left( \frac{1}{|r - r'|} + f_{xc}[^\rho] \right) |\phi_\nu(r')|^2 \, dr \, dr'
\]
Linear response in DFTB: TD-DFTB

Equation to solve (singlets):

$$
\sum_{kl} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 4 \sqrt{\omega_{ij}} K_{ij,kl} \sqrt{\omega_{kl}} \right] F_{kl}^I = \omega_i^2 F_{ij}^I
$$

$$
K_{ij,kl}^S = \int \int \psi_i(r) \psi_j(r) \left( \frac{1}{|r-r'|} + f_{xc}[\rho] \right) \psi_k(r') \psi_l(r') \, dr \, dr'
$$

Approximation:

$$
K_{ij,kl}^S = \sum_{\mu \nu \alpha \beta} c_{\mu i} c_{\nu j} c_{\alpha k} c_{\beta l} \int \int \phi_{\mu}(r) \phi_{\nu}(r) \left( \frac{1}{|r-r'|} + f_{xc}[\rho] \right) \phi_{\alpha}(r') \phi_{\beta}(r') \, dr \, dr'
$$

Mulliken approximation:

$$
\phi_{\mu}(r) \phi_{\nu}(r) \approx \frac{1}{2} S_{\mu \nu} \left( |\phi_{\mu}(r)|^2 + |\phi_{\nu}(r)|^2 \right)
$$

$$
K_{ij,kl}^S \approx \sum_{\mu \nu} q_{\mu i}^j q_{\nu j}^{kl} \gamma_{\mu \nu}(U_A, U_B, |R_A - R_B|)
$$
Linear response in DFTB: TD-DFTB

Equation to solve (triplets):

\[ \sum_{kl} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 4 \sqrt{\omega_{ij} K_{ij,kl}^T \sqrt{\omega_{kl}}} \right] F_{kl}^I = \omega_{ij}^2 F_{ij}^I \]

\[ K_{ij,kl}^T = \int \int \psi_i(r) \psi_j(r) \frac{\partial^2 E_{xc}}{\partial m(r) \partial m(r')} \psi_k(r') \psi_l(r') \, dr \, dr' \]

Niehaus et al. PRB 63 085108 (2001)
Linear response in DFTB: TD-DFTB

Equation to solve (triplets):

\[ \sum_{kl} \left[ \omega_{ij}^2 \delta_{lk} \delta_{jl} + 4 \sqrt{\omega_{ij}} K_{ij,kl} \sqrt{\omega_{kl}} \right] F_{kl}^l = \omega_{i}^2 F_{ij}^l \]

\[ K_{ij,kl} = \int \int \psi_i(r) \psi_j(r) \frac{\partial^2 E_{xc}}{\partial m(r) \partial m(r')} \psi_k(r') \psi_l(r') \, dr \, dr' \]

Approximation:

\[ K_{ij,kl} \approx \sum_{\mu \nu} q_{ij}^{kl} \int \int |\phi_{\mu}(r)|^2 \frac{\partial^2 E_{xc}}{\partial m(r) \partial m(r')} |\phi_{\nu}(r')|^2 \, dr \, dr' \]

Niehaus et al. PRB 63 085108 (2001)
Equation to solve (triplets):

\[
\sum_{kl} \left[ \omega_{ij}^2 \delta_{ik} \delta_{jl} + 4 \sqrt{\omega_{ij} K_{ij,kl}} \sqrt{\omega_{kl}} \right] F_{kl}^l = \omega_i^2 F_{ij}^l
\]

\[
K_{ij,kl}^T = \int \int \psi_i(r) \psi_j(r) \frac{\partial^2 E_{xc}}{\partial m(r) \partial m(r')} \psi_k(r') \psi_l(r') \, dr \, dr'
\]

Approximation:

\[
K_{ij,kl}^T \approx \sum_{\mu \nu} q_{i\mu} q_{j\nu}^{kl} \int \int |\phi_{\mu}(r)|^2 \frac{\partial^2 E_{xc}}{\partial m(r) \partial m(r')} |\phi_{\nu}(r')|^2 \, dr \, dr'
\]

\[
\approx \sum_{\mu} q_{i\mu} q_{j\mu}^{kl} M_{\mu} \quad \text{Onsite only, } M_{\mu} \text{ from atomic DFT}
\]

Niehaus et al. PRB 63 085108 (2001)
Oxidation leads to
- Size-independent emission
- Weak luminescence
SiQD with Si=O bond optimized in $S_0$ and $S_1$.

$\text{Si}_5\text{H}_{12}$ photodissociates.

LUMO strongly localized around Oxygen.

Oxygen stabilizes Silicon core.
Curse and Blessing of Oxygen – The Blessing but ... 

HOMO-LUMO gap of hydrogenated and oxidized SiQD

No size dependence, emission in the IR