Elastic and Inelastic Electron-Phonon Scattering in Quantum Dots

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CECAM
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Electron-Phonon Dynamics in QDs

Elastic
Luminescence linewidths
Coherences between single and multiple excitons, etc.
Semiclassical corrections to quantum-classical simulations

Inelastic
Charge cooling
Phonon-assisted Auger processes
Electron transfer from QD to TiO$_2$
Photochemistry on QD surface (e.g. water splitting)

We study these processes in other nanoscale materials as well.
Outline

- Nonadiabatic Molecular Dynamics with TDDFT
  - Quantum-classical approximations
  - Decoherence & zero-point energy corrections
- Quantum Dots
  - Electron-Phonon Relaxation & Phonon Bottleneck
  - Multiple Exciton Generation and Recombination
Nonadiabatic Molecular Dynamics

**Nonadiabatic MD:** Coupling between potential surfaces opens channels for system to change electronic states.

- **transition allowed**
- **weak coupling**
- **strong coupling**

- **electrons treated quantum-mechanically**
- **nuclei treated classically**
Time-Domain DFT for Nonadiabatic Molecular Dynamics

Electron density derives from Kohn-Sham orbitals

$$\rho(x) = \sum_p |\varphi_p(x)|^2$$

$$|\Psi\rangle = |\varphi_p(x_1,t)\varphi_q(x_2,t)\ldots\varphi_v(x_N,t)\rangle_{SD}$$

DFT functional $H$ depends on nuclear evolution $R(t)$

Variational principle gives

$$i\hbar \frac{\partial \varphi_p(x,t)}{\partial t} = H\varphi_p(x,t) \quad p = 1, 2 \ldots$$

Orbitals are expanded in adiabatic KS basis $\varphi_p(x,t) = \sum c^\alpha_p(t)\chi^\alpha(x)$

$$H(x; R(t))\chi^\alpha(x; R(t)) = \varepsilon^\alpha(R(t))\chi^\alpha(x; R(t))$$

$$i\hbar \dot{c}^\alpha = \sum_\beta c^\beta \left( \varepsilon^\beta \delta_{\alpha\beta} - i\hbar \langle \chi^\alpha | \nabla_R | \chi^\beta \rangle \cdot \dot{R} \right)$$
Time-Domain DFT in Many-Body Kohn-Sham Basis


Need to define states to hop between

\[ |\varphi_a \varphi_b \cdots \varphi_p \rangle = \sum_{j \neq k \neq \cdots \neq l}^{N_e} C_{j\cdots l}(t) |\bar{\varphi}_j \bar{\varphi}_k \cdots \bar{\varphi}_l \rangle \]

\[ \text{i}\hbar \frac{\partial}{\partial t} C_{q\cdots v}(t) = \sum_{a\cdots p}^{N_e} C_{a\cdots p}(t) [E_{q\cdots v} \delta_{aq} \cdots \delta_{pv} \]

\[ + D_{a\cdots p; q\cdots r} \cdot \dot{\mathbf{R}} ] \]

\[ D_{a\cdots p; q\cdots r} \cdot \dot{\mathbf{R}} = -\text{i}\hbar \langle \bar{\varphi}_a \bar{\varphi}_b \cdots \bar{\varphi}_p | \frac{\partial}{\partial t} | \bar{\varphi}_q \bar{\varphi}_r \cdots \bar{\varphi}_v \rangle \]

non-zero only if different in one orbital
1. KS excitations close to LR/TDDFT (in contrast to HF and CIS)
2. Typically, no bond-breaking, conformational changes, etc.
3. Many-electron systems, single excitation is a small perturbation
4. Averaging over many initial conditions and pathways
Silicon Quantum Dot


KS and LR agree better for PW91 (pure DFT) than B3LYP (hybrid)
Silicon Quantum Dot


KS and LR agree better for PW91 (pure DFT) than B3LYP (hybrid)
Silicon Quantum Dot


\[
P_{i \rightarrow j} = \exp \left[ -\frac{4U_{ij}}{3\hbar} \left( \frac{2U_{ij}}{d^2U_{ij}/dt^2} \right)^{1/2} \right]
\]


\[
P_{i \rightarrow j}^{tot} = 1 - \prod_{n} (1 - P_{n, i \rightarrow j})
\]

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<th>LR/B3LYP</th>
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<td>S₁₀–S₉</td>
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<td>(1521)</td>
<td>(1576)</td>
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Theoretical Questions our group is interested in

- How to couple quantum and classical dynamics?
  quantum influence on classical trajectory

- Can one do better than classical mechanics for nuclear motion?
  zero-point motion, tunneling, branching, loss of coherence
Quantum-Classical Lie Bracket


\[
[A, B]_{qc} = -\frac{i}{\hbar} [A, B] + \frac{1}{2} (\{A, B\} - \{B, A\})
\]

quantum commutator + classical Poisson bracket

problems with Jacobi identity:

\[
[[[A, B]_{qc}, C]_{qc} + [[[B, C]_{qc}, A]_{qc} + [[[C, A]_{qc}, B]_{qc} = 0
\]

Practical solution: derive everything quantum mechanically, take classical limit at the end
Ehrenfest (mean-field)

Total energy of electrons and nuclei

\[ E_{tot} = \frac{M \ddot{R}}{2} + V(R) + Tr_x \rho(x) H(x; R) \]

is conserved

\[ \frac{dE_{tot}}{dt} = 0 \]

time-dependent Hellmann-Feynman theorem gives Newton equation

\[ M \dddot{R} = -\nabla_R V - Tr_x \rho(x) \nabla_R H(x; R) \]

quantum force
\[ \psi(x, t) = \sqrt{\rho(x, t)} e^{iS(x, t)/\hbar} \]
gives Newton eq.
\[ m\ddot{x} = -\nabla_r [V(x) + Q(x)] \]
with non-local quantum potential
\[ Q(x) = -\frac{\hbar^2}{2m} \frac{\nabla_x^2 \sqrt{\rho(x)}}{\sqrt{\rho(x)}} \]

\[ M\ddot{R} = -\nabla_R [V_R(R) + V_{xR}(x, R)] \quad \text{drop } Q(R) \]
\[ m\ddot{x} = -\nabla_x [V_x(x) + V_{xR}(x, R) + Q(x)] \]
Bohmian Quant.-Class. Mechanics


\[ M\ddot{R} = -\nabla_R \left[ V_R(R) + V_{xR}(x, R) \right] \quad \text{– Bohmian} \]

\[ M\ddot{R} = -\nabla_R \left[ V_R(R) + \text{Tr}_x \rho(x)V_{xR}(x, R) \right] \quad \text{– Ehrenfest} \]

**Advantage:** correlation between quantum and classical particles (branching)

In practice, Bohmian trajectories are obtained from Schrodinger eq.
Bohmian Quant.-Class.

Highly simplified representation of $O_2$ interacting with Pt

$$H(q,Q) = T_q + T_Q + V_q(q) + V_q(Q) + V_{qQ}(q,Q)$$

$$V_Q(Q) = \frac{M\Omega^2Q^2}{2}$$

$$V_q(q) = a(e^{-b(q-c)} - 2e^{-b(q-c)})$$

$$V_{qQ}(q,Q) = Ae^{-B(q-Q)}$$
Surface Hopping

a.k.a., quantum-master equation with time-dependent transition rates:
- non-perturbative
- correct short time dynamics

Trajectory branching: Tully, *JCP* 93, 1061 (1990);

Within TDDFT:
Craig, Duncan, Prezhdo *PRL* 95, 163001 (2005)

Detailed balance / thermal equilibrium (due to hop rejection):
Parahdekar, Tully *JCP* 122, 094102 (2005)
Schrodinger Cat and Decoherence

System - radioactive atom; Bath - cat

In Nanomaterials
System - electrons, spins; Bath - phonons
Franck-Condon Factor and Decoherence

\[ \sum_{\{B_2\}} \left| \langle B_1 | B_2 \rangle \right|^2 \delta(E_1 - E_2) \]

\[ = \int e^{i(E_1 - E_2)t/\hbar} \langle B_1(t) | B_2(t) \rangle \, dt \]

Bath (vibrational) wave functions diverge

This affects evolution of (electronic) system
Decoherence and Surface Hopping

Reduced density matrix:

\[
\begin{pmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{pmatrix}
\rightarrow
\begin{pmatrix}
\rho_{11} & \rho_{12}\langle B_2 | B_1 \rangle \\
\rho_{21}\langle B_1 | B_2 \rangle & \rho_{22}
\end{pmatrix}
\]

\[
\rho = \langle B | \rho^{S-B} | B \rangle
\]

\[
\rho_{12} \rightarrow 0 \quad \text{on decoherence time scale}
\]

hopping probability \( P_{12} \sim \rho_{12} \)
Decoherence and Surface Hopping


Reduced density matrix:
\[
\rho = \langle B \mid \rho^{S-B} \mid B \rangle
\]

\[
\begin{pmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{pmatrix}
\rightarrow
\begin{pmatrix}
\rho_{11} & \rho_{12} \langle B_2 \mid B_1 \rangle \\
\rho_{21} \langle B_1 \mid B_2 \rangle & \rho_{22}
\end{pmatrix}
\]

\begin{align*}
\rho_{12} & \to 0 \quad \text{on decoherence time scale} \\
\text{hopping probability } P_{12} & \sim \rho_{12}
\end{align*}

Quantum Zeno Effect

With decoherence: 
\[
P_{12} = \left| T_{12} \right|^2 + \left| T_{12} \right|^2 + \ldots
\]

Without decoherence 
\[
P_{12} = \left| T_{12} + T_{12} + \ldots \right|^2
\]

Decoherence makes transitions less likely
\[
\left| 0.1 \right|^2 + \left| 0.1 \right|^2 < \left| 0.1 + 0.1 \right|^2
\]
Stochastic Schrödinger equation in place of regular SE in Ehrenfest

\[ \langle d\Psi \rangle = -iH\Psi dt - \frac{\gamma}{2} L^* L\Psi dt + \sqrt{\gamma} L\Psi dW \]

- \( L \) – system-bath interaction
- \( \gamma \) – decoherence rate

**Advantages**

1. Includes decoherence
2. Gives branching
3. Infinitesimal velocity rescaling, (but every time-step)
Decoherence Induced Surface Hopping (DISH)


Evolve in an adiabatic state.
Hop when a decoherence event occurs.
Rescale velocity as before in SH.

**Advantages**

1. Includes decoherence
2. Gives branching
3. Nuclear evolution in pure states
4. Gives detailed balance / thermal equilibrium
Evaluating Decoherence Times

**Optical response function**

\[
D(t) = \exp(i\omega t) \exp\left[-\frac{i}{\hbar} \int_0^t \Delta E(\tau) \, d\tau\right]_T
\]

**2nd order cumulant approximation**

\[
D(t) = \exp(-g(t))
\]

\[
g(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, C(\tau_2)
\]

\[
C(t) = \langle \Delta E(t) \, \Delta E(0) \rangle_T
\]

**Graph:**

- **\(\Delta E, \text{ eV}\)**
- **7557 Defect**
- **in (6,4) CNT**

**Axes:**
- **Time (fs)** from 0 to 1000
- **\(\Delta E, \text{ eV}\)** from 1.00 to 1.35
Evaluating Decoherence Times

Optical response function

\[
D(t) = \exp(i\omega t) \left\langle \exp \left[ -\frac{i}{\hbar} \int_0^t \Delta E(\tau) \, d\tau \right] \right\rangle_T
\]

2\textsuperscript{nd} order cumulant approximation

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D(t) = \exp(-g(t))
\]

\[
g(t) = \int_0^t \, d\tau_1 \int_0^{\tau_1} \, d\tau_2 \, C(\tau_2)
\]

\[
C(t) = \langle \Delta E(t) \, \Delta E(0) \rangle_T
\]

Gaussian approximation

\[
\tau_D = \left[ \left\langle \sum_n \frac{1}{2a_n \hbar^2} (F_{1n} - F_{2n})^2 \right\rangle_T \right]^{-1/2}
\]

\[
a_n = \frac{6mk_B T}{\hbar^2}
\]

thermal de Broglie width

\[| B_0 > \]

in (6,4) CNT

\[\Delta E, \text{ eV} \]

\[7557 \text{ Defect} \]

\[\text{Time (fs)} \]

\[1.35 \quad 1.30 \quad 1.25 \quad 1.20 \quad 1.15 \quad 1.10 \quad 1.05 \quad 1.00 \]

\[0 \quad 200 \quad 400 \quad 600 \quad 800 \quad 1000 \]
Quantized Hamilton Dynamics


\[ V = \frac{q^2}{2} + \frac{q^3}{3} \]

\[
\frac{d < q >}{dt} = < p >; \quad \frac{d < p >}{dt} = - < q > - < q^2 >
\]

but \[ < q^2 > \neq < q > < q > \] and

\[
\frac{d < q^2 >}{dt} = < pq + qp > \equiv 2 < pq >_s
\]

\[
\frac{d < pq >_s}{dt} = < p^2 > - < q^2 > - < q^3 >
\]

the infinite hierarchy is terminated by a closure

\[ < q^3 > \approx 3 < q^2 > < q > - 2 < q >^3 \]
Harmonic Oscillator in Mapped QHD-2

\[ \hbar \overset{\text{mass}}{\rightarrow} \hbar \text{mass} \]

QHD-2 takes care of zero-point-energy
Metastable Cubic Potential
in Mapped QHD-2

QHD-2 gives tunneling

$\hbar \text{mass}$
Double-Slit Potential
in Mapped QHD-2

potential seen by
a narrow wavepacket

\[ v(q) + \frac{1}{2} v^{(2)}(q) s^2 \]

potential seen by
a wide wavepacket
Quantized Ehrenfest

C. Brooksby, O. V. Prezhdo,

\[
\frac{d}{dt} \langle Q \rangle = \frac{\langle P \rangle}{M}
\]

\[
\frac{d}{dt} \langle P \rangle = -M\Omega^2 \langle Q \rangle - \langle \Psi (q) | \nabla_q V (q, \langle Q \rangle) | \Psi (q) \rangle
\]

\[
\frac{d}{dt} \langle Q^2 \rangle = \frac{2 \langle PQ \rangle_s}{M}
\]

\[
\frac{d}{dt} \langle P^2 \rangle = -M\Omega^2 \langle PQ \rangle_s - 2 \langle P \rangle \langle \Psi (q) | \nabla_q V (q, \langle Q \rangle) | \Psi (q) \rangle
\]

\[
\frac{d}{dt} \langle PQ \rangle_s = \frac{\langle P^2 \rangle}{M} - M\Omega^2 \langle Q^2 \rangle - \langle Q \rangle \langle \Psi (q) | \nabla_q V (q, \langle Q \rangle) | \Psi (q) \rangle
\]

QMF-2 equations require no new quantum calculation!
Quantized Ehrenfest

Highly simplified representation of O$_2$ interacting with Pt

\[ H(q,Q) = T_q + T_Q + V_q(q) + V_q(Q) + V_{qQ}(q,Q) \]

\[ V_Q(Q) = \frac{M\Omega^2 Q^2}{2} \]

\[ V_q(q) = a(e^{-2b(q-c)} - 2e^{-b(q-c)}) \]

\[ V_{qQ}(q,Q) = Ae^{-B(q-Q)} \]
Energy Transfer (Tunneling) and Dephasing


Spin-Boson/Marcus Model


$H = \Omega \left( a^+ a + \frac{1}{2} \right) + \omega S_z + g(a^+ S_- + a S_+)$

Jaynes-Cummings Model

- same curvatures
- no displacement
- resonance (rotating wave) approx.
Quantum Result

ENERGY TRANSFER (TUNNELING):
spin oscillation

DEPHASING:
wave-packet splits
spin stops oscillating
Evolution of $\langle S_z \rangle$ by QHD

\[ \alpha = a^+ S_- + a S_+ \]
\[ \beta = a^+ S_- - a S_+ \]
\[ \gamma = \left( a^+ a + \frac{1}{2} \right) + S_z \]

\[
\frac{d\langle \alpha \gamma^n \rangle}{dt} = -\delta \langle \beta \gamma^n \rangle \\
\frac{d\langle \beta \gamma^n \rangle}{dt} = -\delta \langle \alpha \gamma^n \rangle + g \langle S_z \gamma^{n+1} \rangle \\
\frac{d\langle S_z \gamma^n \rangle}{dt} = g \langle \beta \gamma^n \rangle \\
\]

n=0,1,2…

Closure:
\[ \langle S_z \gamma^2 \rangle \approx 2\langle S_z \gamma \rangle \langle \gamma \rangle + \langle S_z \rangle \langle \gamma^2 \rangle - 2\langle S_z \rangle \langle \gamma \rangle^2 \]

\[ \langle \gamma \rangle, \langle \gamma^2 \rangle \] are constants of motion, linear system of ODE

\[ \langle S_z \rangle, \langle \alpha \rangle, \langle \beta \rangle, \langle S_z \gamma \rangle, \langle \alpha \gamma \rangle, \langle \beta \gamma \rangle \] - 6 variables
Evolution of $<S_z>$ by QHD


$$\langle S_z \rangle(t) = -\frac{1}{2} + \frac{g^2 \sqrt{\gamma_0} (\sqrt{\gamma_0} + 1)}{2\omega_1^2} (1 - \cos \omega_1 t) + \frac{g^2 \sqrt{\gamma_0} (\sqrt{\gamma_0} - 1)}{2\omega_2^2} (1 - \cos \omega_2 t)$$

Multiple transfer events
Dephasing envelope
State-Specific Dynamics
a.k.a. multi-configuration mean-field


\[
\langle q|0\rangle \langle 0| \simeq \langle q \rangle (1/2 + \langle S_z \rangle)
\]
\[
\langle q|1\rangle \langle 1| \simeq \langle q \rangle (1/2 - \langle S_z \rangle)
\]

**closure:** \(\langle \tilde{a} S_z \rangle \simeq \langle \tilde{a} \rangle \langle S_z \rangle\)

\(\langle S_z \rangle\) – as before
Surface hopping is needed to describe inelastic scattering.

Kohn-Sham representation works well for surface hopping in nanoscale materials.

Decoherence (elastic scattering) is fast in condensed phases.

Stochastic Mean-Field (SMF) and Decoherence Induced Surface Hopping (DISH) “derive” a SH algorithm from decoherence.

Quantized Hamilton Dynamics (QHD) provides models for zero-point energy and decoherence.
Electron-Phonon Dynamics in QDs

rates of carrier cooling
mechanisms for carrier multiplication
Excitons in QDs: 2005


Biexciton creation yield

Exciton to biexciton time under 0.25ps
Excitons in QDs: 2005
Schaller, Pietryga, Goupalov, Petruska, Ivanov, Klimov
*Phys. Rev. Lett.* **95** 196401 (2005)

Electron-Phonon Relaxation

No phonon bottleneck.

Times are similar to biexciton creation times

Larger dots relax more slowly ?!
Excitons in QDs: 2007

Nair, Bawendi *Phys. Rev. B* 76 081304(R) (2007)

Original multiplication experiments could not be reproduced by other groups.

Experimental conditions and data interpretation are very important.
Efficiency estimates are significantly lowered.

Observed vs. Ideal: Excitons in QDs: 2008
McGuire, Joo, Pietryga, Schaller, Klimov
Excitons in QDs: 2008


Electron-phonon bottleneck found for electrons in CdSe QDs, in the absence of holes

(shell thickness)
Excitons in PbSe QDs: 2010


50 fs injection time

absorbed photon–to–current efficiency
Structural Relaxation PbSe QDs

Kilina, Kilin, Prezhdo, ACS Nano, 3, 93 (2009)

32 atoms Pb$_{16}$Se$_{16}$ d=1.0nm

<table>
<thead>
<tr>
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<th>Bulk, T=0 K</th>
<th>Relaxed, T=0 K</th>
<th>Heated, T=300 K</th>
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</table>

136 atoms Pb$_{68}$Se$_{68}$ d=1.4nm

<table>
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<th>Bulk, T=0 K</th>
<th>Relaxed, T=0 K</th>
<th>Heated, T=300 K</th>
</tr>
</thead>
</table>

(LUMO) (LUMO+1) (LUMO+2) (LUMO+3)

states mix
Absorption Spectra of PbSe QDs

Comparison of Relaxation, PbSe


Similar relaxation times for electrons and holes

Larger dot relaxes more slowly due to weaker electron-phonon coupling
Phonon Bottleneck for 1P Electron in CdSe Quantum Dots

1P–1S electron states show big gap
Relaxation time ~ 1ns

Pandey, Guyot-Sionnest, Science 322 929 (2008)

Kilina, Kilin, Prezhdo, ACS Nano, 3, 93 (2009)
Phonon Bottleneck for 1P Electron in CdSe Quantum Dots

Relaxation time ~ 1ns
Pandey, Guyot-Sionnest, Science 322 929 (2008)

Simulation shows bottleneck

Neukirch, Kilina, Kilin, Prezhdo, in preparation
Enhanced Energy Losses due to Ligands


Electrons relax much faster than holes! (despite nearly symmetric DOS)
Low frequency modes are active for both electrons and holes.

However, high frequency (ligand) modes are active only for electrons.
Phonon-Assisted Auger Processes


25 VB and 24 CB orbitals

98,101 states =
ground+600SE+97,500DE
(9,623,806,201
matrix elements)

Eg = 2.1 eV

SE & DE DOS
cross at 5.8 eV
ME Generation


Auger processes are slower than electron-phonon relaxation, multiple excitons are created while interacting with light.

Gaussian + Exponential

Rates increase with energy

Phonon-assisted Auger at energies less than 2Eg

$E_g$

$\tau_g = 19 \text{ ps}$
$\tau_e = 48 \text{ ps}$

$1.8 E_g$

$3.5 E_g$

$\tau_g = 8.1 \text{ ps}$
$\tau_e = 5.5 \text{ ps}$

$2.8 E_g$

$(C) \text{ Si}_{29}\text{H}_{24}$
ME Recombination


Robel et al. *PRL* 102 177404 (2009)

Sub-10ps for small QDs
Rate theories give much longer times
Electron-Phonon Dynamics in QDs

- Inelastic scattering on 10-100fs timescale (luminescence, single & multiple exciton coherences)
- Electron-phonon relaxation on a picosecond timescale
- Phonon bottleneck in special cases
- Phonon-assisted Auger processes are predicted
- Phonons drive adiabatic and nonadiabatic electron transfer
Selected Publications

Surface hopping within TDDFT

Phys. Rev. Lett. 95, 163001 (2005) /original implementation/

Decoherence based surface hopping/


Quantum dots

Chem. Science 2 400 (2011)

Quantized Hamilton dynamics


Quantum-classical Lie bracket


Bohmian quantum-classical dynamics

Questions Arising in our Research

- When is classical description of phonons valid?
- What quantum corrections are needed and when (zero point energy, decoherence)?
- Are there alternatives to surface hopping; can one “derive” surface hopping?
- Surface hopping requires states, can we use DFT?
- Can we model light-matter interactions separate from electron-phonon dynamics?
Pure-Dephasing: Luminescence, ME Generation & ME Fission


Phonon-induced pure-dephasing times, fs

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<tr>
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<th>Si$<em>{29}$H$</em>{24}$</th>
<th>Cd$<em>{33}$Se$</em>{33}$</th>
<th>Pb$<em>{68}$Se$</em>{68}$</th>
<th>Pb$<em>{16}$Se$</em>{16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Luminescence</td>
<td>4 / 7</td>
<td>10 / 16</td>
<td>9 / 23</td>
<td>7 / –</td>
</tr>
<tr>
<td>ME Generation</td>
<td>4 / 7</td>
<td>5 / 9</td>
<td>5 / 11</td>
<td>4 / –</td>
</tr>
<tr>
<td>ME Fission</td>
<td>80 / 310</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tbody>
</table>

Luminescence – 50meV linewidth, agree with exp.
ME Generation – rapid 10fs dephasing
ME Fission – 100fs
More Realistic Ligands: Electronic Structure


Ligands start contributing at energies of 2.5-3E_g
Ligand Contribution to Electron-Phonon Relaxation


Ligands contributes up to 10nm QDs

Ligands contributes up to 10nm QDs
Electron Transfer from QDs to TiO$_2$

50 fs injection time

absorbed photon–to–current efficiency
e⁻ transfer from QDs to TiO₂


- 10 fs time; mostly adiabatic ET
- Strong donor-acceptor coupling
- ET is driven by high frequency polar phonons
1. Small dots represent large dot DOS
2. Huge one-electron gap
3. Symmetric vs. asymmetric DOS
4. Secondary gaps in PbSe DOS
Spectra and Multiple Excitons


CdSe spectra agree with experiment *JACS* 128, 629 (2006)

1. Sharp onset of multiple excitons
2. Above threshold: double excitons in PbSe; single, double and superpositions in CdSe
1. Complete and fairly sharp transition
2. Si is more similar to PbSe than CdSe due to symmetric band structure
Universal Optical Response in Si Clusters

Classical Mie theory matches ab initio calculations on very small clusters, independent of bonding configuration.

\[
\sigma_{\text{abs}}(\omega) = \frac{9 \omega V}{c} \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2]^2 + \varepsilon_2(\omega)^2}
\]

Idrobo et al. *PRB* 79 125322 (2009)
Defects Introduce New Transitions

ideal QDs

anion  cation  dopant  dangling bonds
Calculations for Charged PbSe Dots


Conduction band transitions overwhelm MEs

Much higher ME threshold