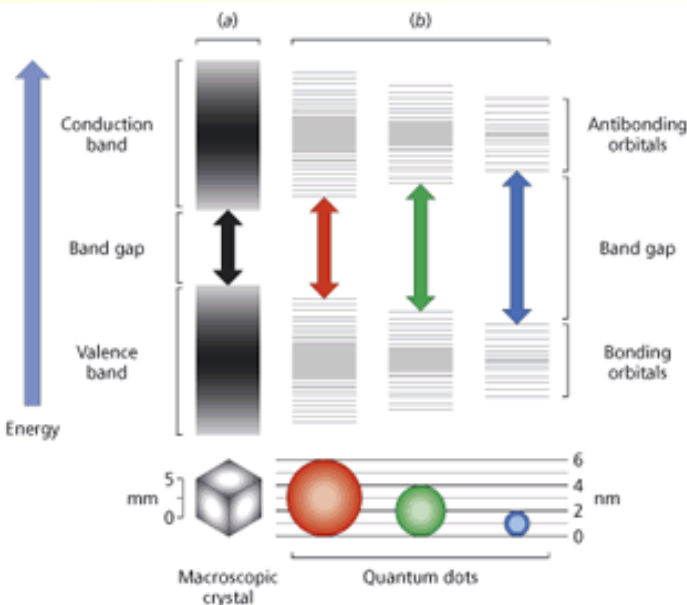
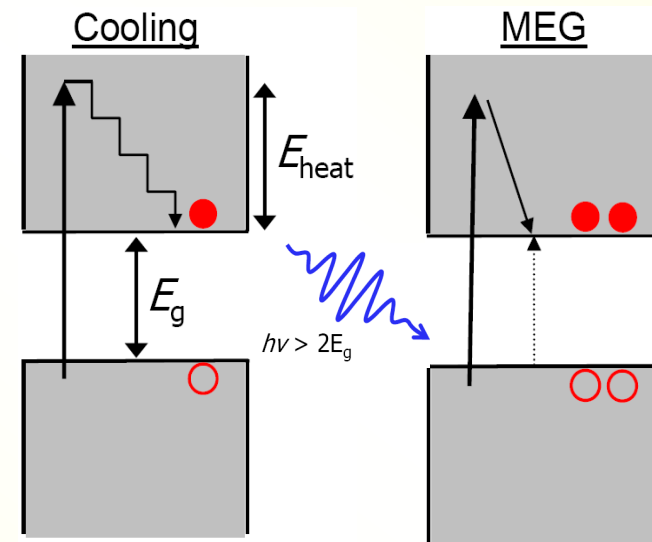


# Elastic and Inelastic Electron-Phonon Scattering in Quantum Dots

*Oleg Prezhd*  
U. Rochester

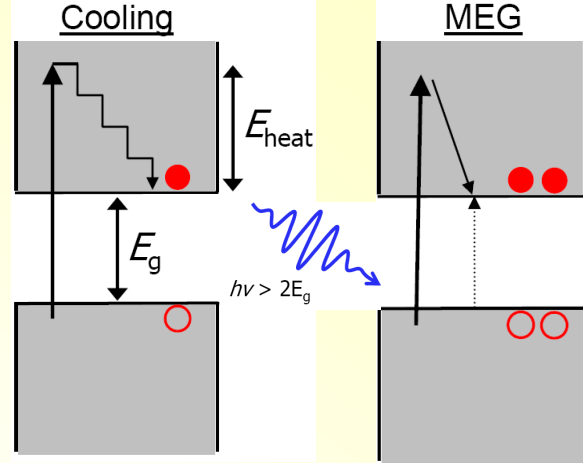


CECAM  
Nov 7-9, 2012





# 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  $\text{TiO}_2$   
Photochemistry on QD surface (e.g. water splitting)

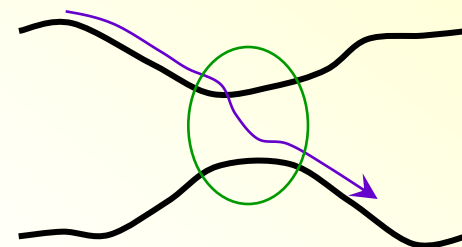
We study these processes in other nanoscale materials as well



# Outline

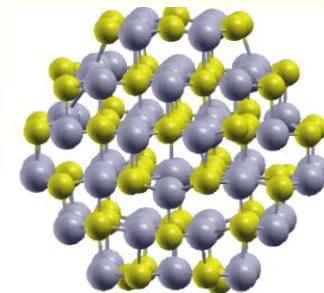
## ➤ Nonadiabatic Molecular Dynamics with TDDFT

- Quantum-classical approximations
- Decoherence & zero-point energy corrections



## ➤ Quantum Dots

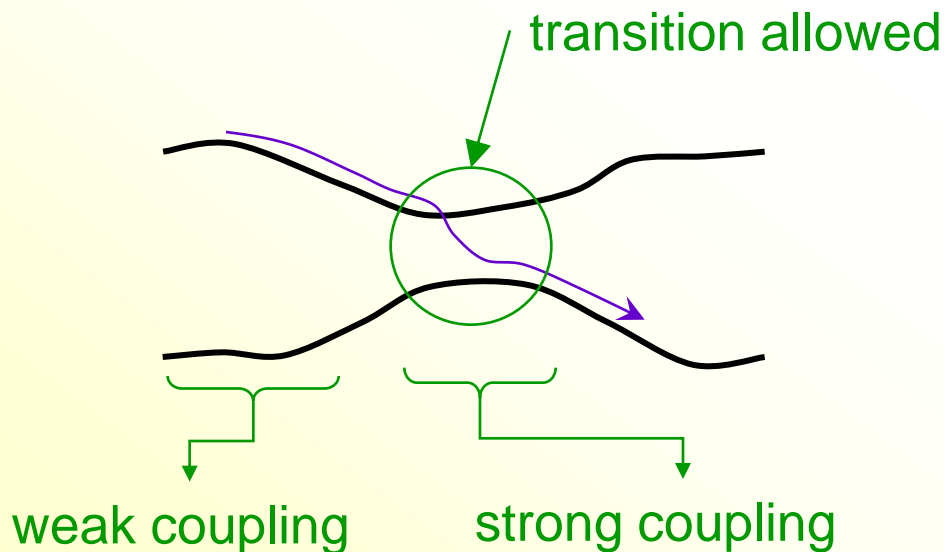
- Electron-Phonon Relaxation & Phonon Bottleneck
- Multiple Exciton Generation and Recombination



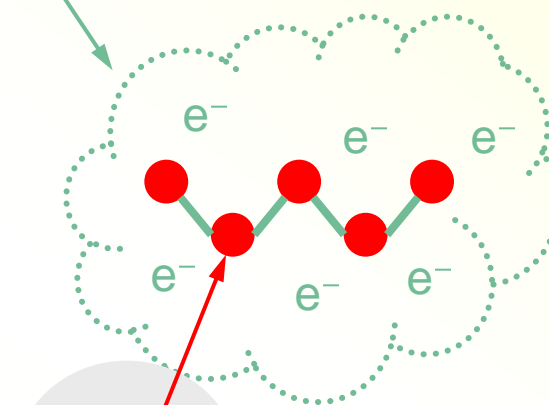


# Nonadiabatic Molecular Dynamics

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



electrons treated quantum-mechanically



nuclei treated classically



# Time-Domain DFT for Nonadiabatic Molecular Dynamics

Electron density derives from Kohn-Sham orbitals

$$\rho(x) = \sum_p |\varphi_p(x)|^2 \quad |\Psi\rangle = |\varphi_p(x_1, t) \varphi_q(x_2, t) \dots \varphi_v(x_N, t)\rangle_{SD}$$

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

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

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

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

$$i\hbar \dot{c}^\alpha = \sum_\beta c^\beta \left( \varepsilon^\beta \delta_{\alpha\beta} - i\hbar \langle \chi^\alpha | \vec{\nabla}_R | \chi^\beta \rangle \cdot \dot{\vec{R}} \right)$$



# Time-Domain DFT

## in Many-Body Kohn-Sham Basis

C. Craig, W. Duncan, O. V. Prezhdo *Phys. Rev. Lett.* **95**, 163001 (2005)

**Need to define states to hop between**

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

$$i\hbar \frac{\partial}{\partial t} C_{q \cdots v}(t) = \sum_{a \cdots p}^{N_e} C_{a \cdots p}(t) [E_{q \cdots v} \delta_{aq} \cdots \delta_{pv} + \mathbf{D}_{a \cdots p; q \cdots r} \cdot \dot{\mathbf{R}}].$$

$$\mathbf{D}_{a \cdots p; q \cdots r} \cdot \dot{\mathbf{R}} = -i\hbar \langle \tilde{\varphi}_a \tilde{\varphi}_b \cdots \tilde{\varphi}_p | \frac{\partial}{\partial t} | \tilde{\varphi}_q \tilde{\varphi}_r \cdots \tilde{\varphi}_v \rangle$$

non-zero only if different in one orbital



# Why KS Representation Works

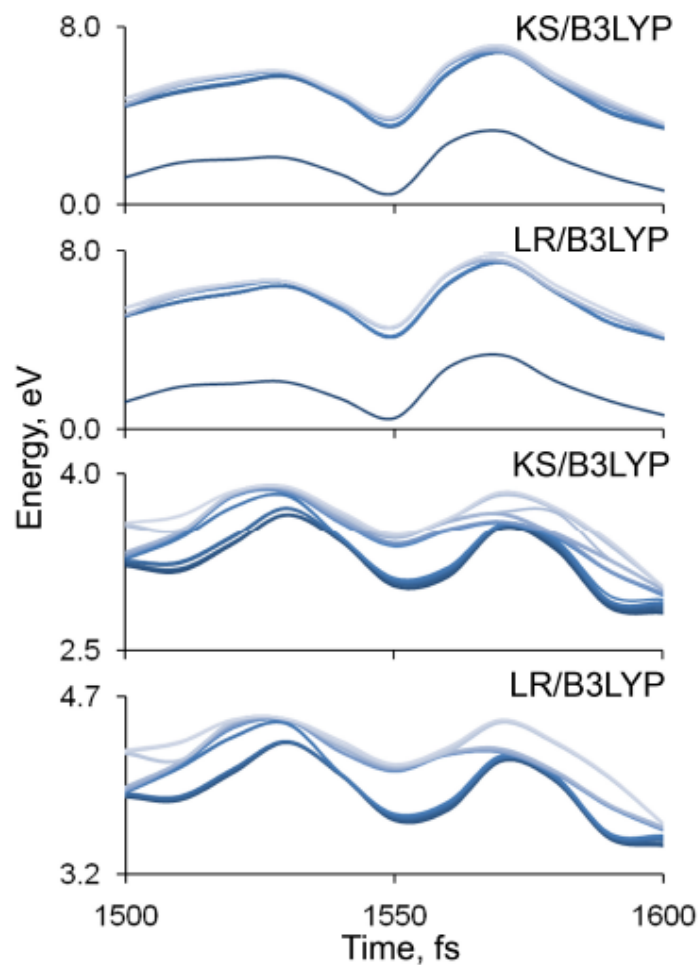
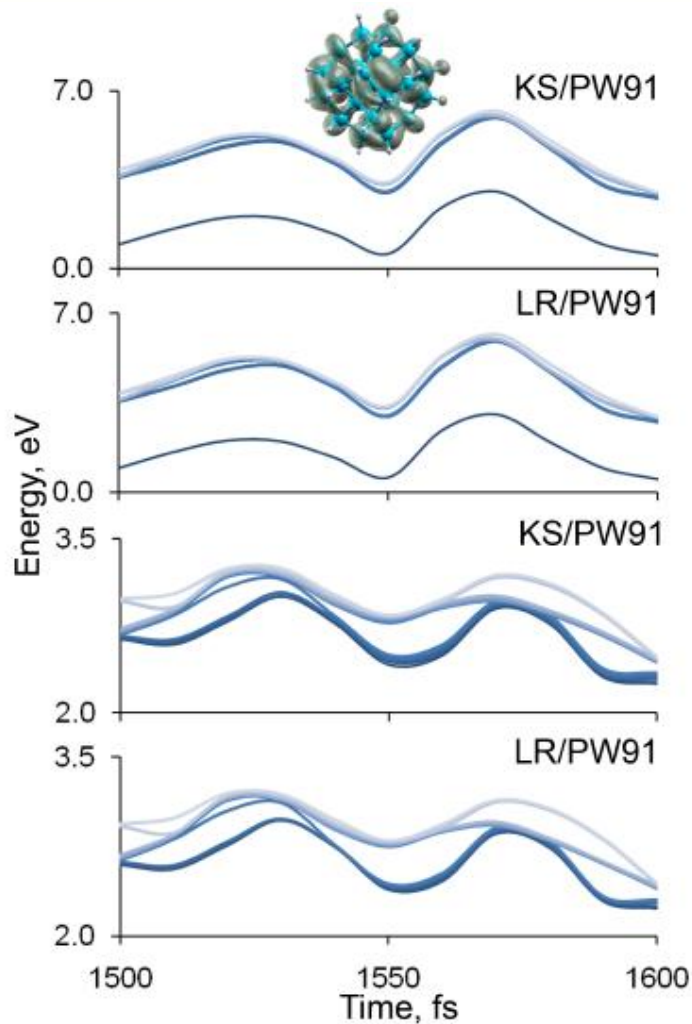
S. Fischer, B. Habenicht, A. Madrid, W. Duncan,  
O. V. Prezhdo, *J. Chem. Phys.* **134**, 024102 (2011)

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

S. Fischer, B. Habenicht, A. Madrid, W. Duncan,  
O. V. Prezhdo, *J. Chem. Phys.* **134**, 024102 (2011)



KS and LR  
agree  
better for

PW91  
(pure DFT)

than  
B3LYP  
(hybrid)

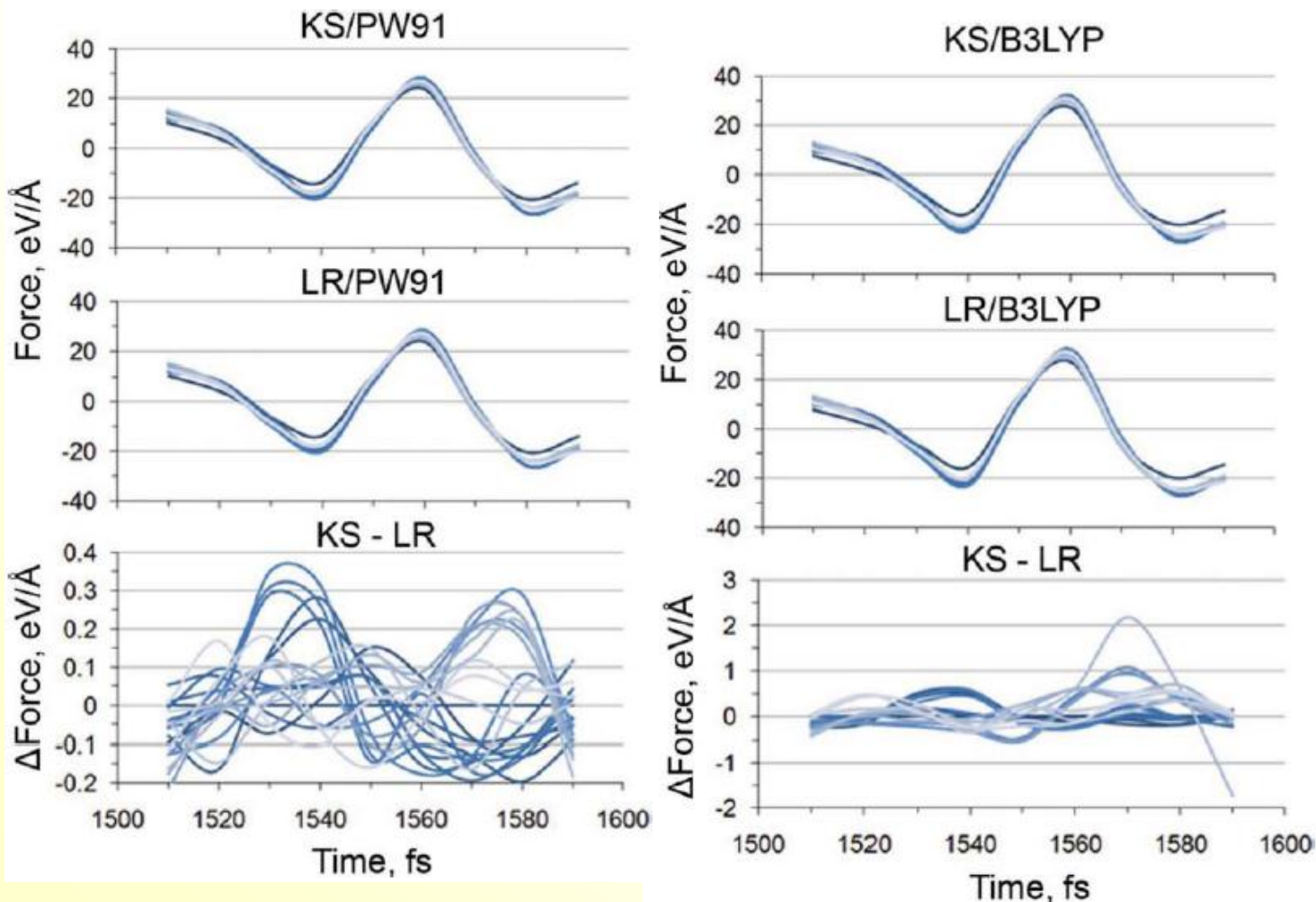




# Silicon Quantum Dot

S. Fischer, B. Habenicht, A. Madrid, W. Duncan,  
O. V. Prezhdo, *J. Chem. Phys.* **134**, 024102 (2011)

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





# Silicon Quantum Dot

S. Fischer, B. Habenicht, A. Madrid, W. Duncan,  
O. V. Prezhdo, *J. Chem. Phys.* **134**, 024102 (2011)

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

W. H. Miller, T. F. George,  
*J. Chem. Phys.* **56**, 5637 (1972)

$$P_{i \rightarrow j}^{tot} = 1 - \prod_n (1 - P_{n,i \rightarrow j})$$

Transition	KS/B3LYP			LR/B3LYP		
	Probabilities (Time, fs)		Total	Probabilities (Time, fs)		Total
S <sub>2</sub> -S <sub>1</sub>	0.887 (1526)	0.766 (1569)	0.974	0.981 (1535)	0.946 (1576)	0.999
S <sub>3</sub> -S <sub>2</sub>	0.572 (1541)		0.572	0.851 (1536)	0.850 (1589)	0.978
S <sub>4</sub> -S <sub>3</sub>	0.709 (1546)	0.759 (1576)	0.930	0.965 (1531)	0.402 (1579)	0.979
S <sub>5</sub> -S <sub>4</sub>	0.936 (1536)	0.713 (1575)	0.982	0.955 (1536)	0.925 (1576)	0.997
S <sub>6</sub> -S <sub>5</sub>	0.961 (1533)	0.477 (1574)	0.980	0.967 (1534)	0.892 (1565)	0.996
S <sub>7</sub> -S <sub>6</sub>	0.484 (1550)		0.484	0.580 (1549)	0.993 (1581)	0.997
S <sub>8</sub> -S <sub>7</sub>	0.906 (1536)		0.906	0.867 (1534)		0.867
S <sub>9</sub> -S <sub>8</sub>	0.830 (1543)	0.887 (1572)	0.981	0.897 (1539)	0.803 (1587)	0.980
S <sub>10</sub> -S <sub>9</sub>	0.894 (1521)	0.674 (1576)	0.966	0.963 (1518)	0.495 (1576)	0.981



# 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

O. V. Prezhdo, V. V. Kisil *Phys. Rev. A* **56** 162 (1997)

O. V. Prezhdo *J. Chem. Phys.* **124** 201104 (2006)

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

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



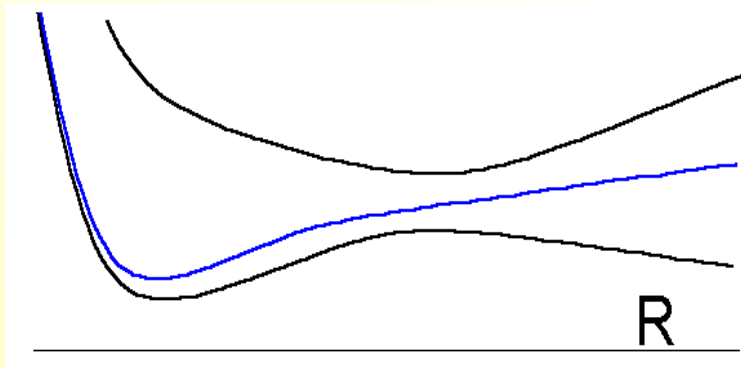
# Ehrenfest (mean-field)

Total energy of electrons and nuclei

$$E_{tot} = \frac{M \dot{R}^2}{2} + V(R) + Tr_x \rho(x) H(x; R)$$

is conserved  $\frac{dE_{tot}}{dt} = 0$

time-dependent Hellmann-Feynman theorem gives Newton equation



$$M \ddot{R} = -\vec{\nabla}_R V - Tr_x \rho(x) \vec{\nabla}_R H(x; R)$$

quantum force

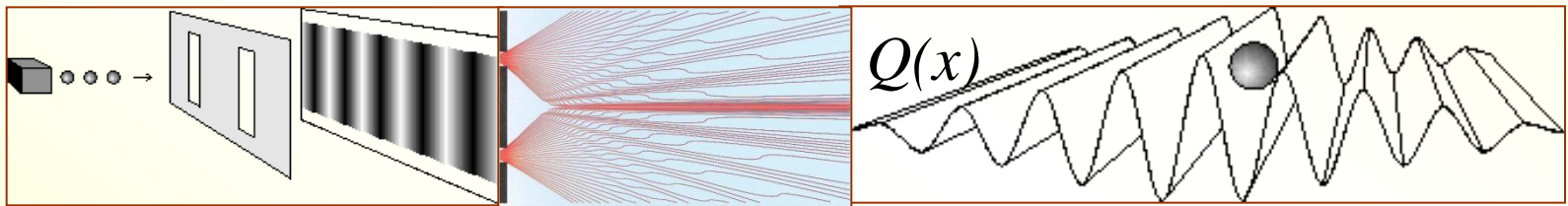


# Bohmian Quant.-Class. Mechanics

C. Brooksby, O. V. Prezhdo *Phys. Rev. Lett.* **86**, 3215 (2001); *ibid* **90**, 118902 (2003)

$\psi(x,t) = \sqrt{\rho(x,t)} e^{iS(x,t)/\hbar}$  gives Newton eq.  $m\ddot{x} = -\nabla_r [V(x) + Q(x)]$

with non-local quantum potential  $Q(x) = -\frac{\hbar^2}{2m} \frac{\nabla_x^2 \sqrt{\rho(x)}}{\sqrt{\rho(x)}}$



Quantum (x) – Classical (R)

$$M\ddot{R} = -\nabla_R [V_R(R) + V_{xR}(x, R)] \quad \text{drop } Q(R)$$

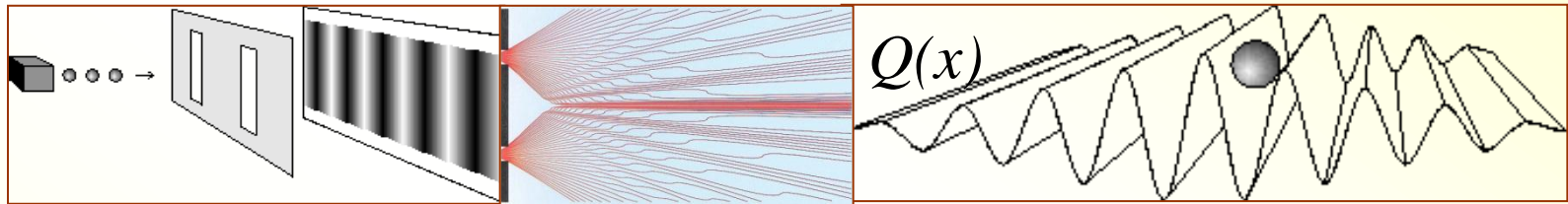
$$m\ddot{x} = -\nabla_x [V_x(x) + V_{xR}(x, R) + Q(x)]$$





# Bohmian Quant.-Class. Mechanics

C. Brooksby, O. V. Prezhdo *Phys. Rev. Lett.* **86**, 3215 (2001); *ibid* **90**, 118902 (2003)



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

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

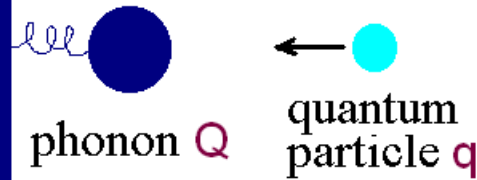
Advantage: correlation between quantum and classical particles (branching)

In practice, Bohmian trajectories are obtained from Schrodinger eq.



# Bohmian Quant.-Class.

Brooksby, Prezhdoo *Phys. Rev. Lett.* **86**, 3215 (2001)



Highly simplified representation of O<sub>2</sub> interacting with Pt

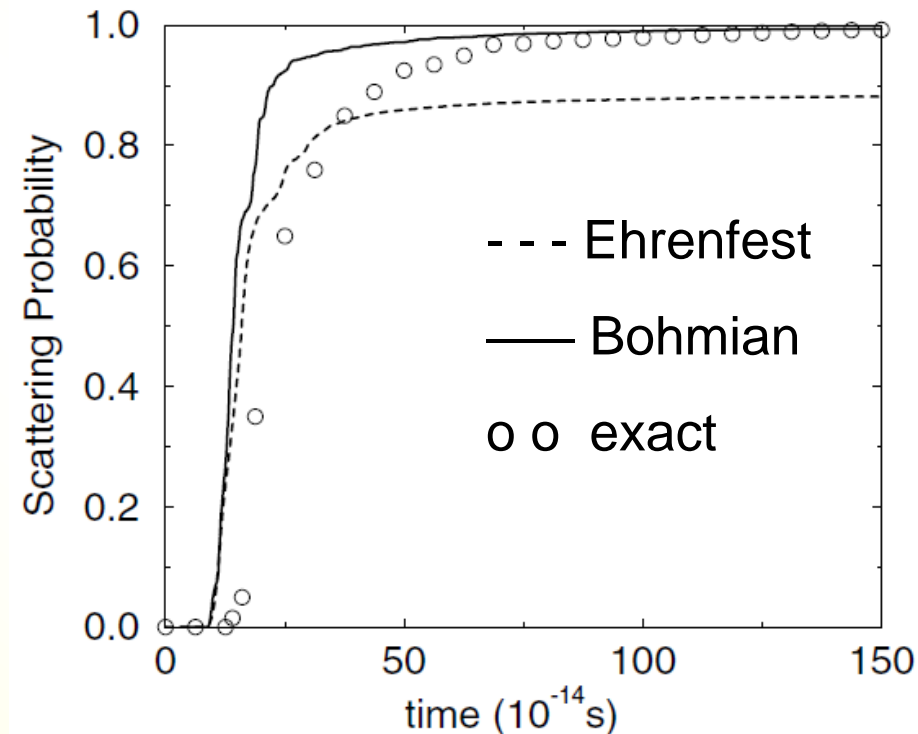
J. Strömquist, S. Gao, *J.Chem.Phys.* **106**, 5751 (1997); D.S. Sholl, J.C. Tully, *J.Chem.Phys.* **109**, 7702 (1998)

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

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

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

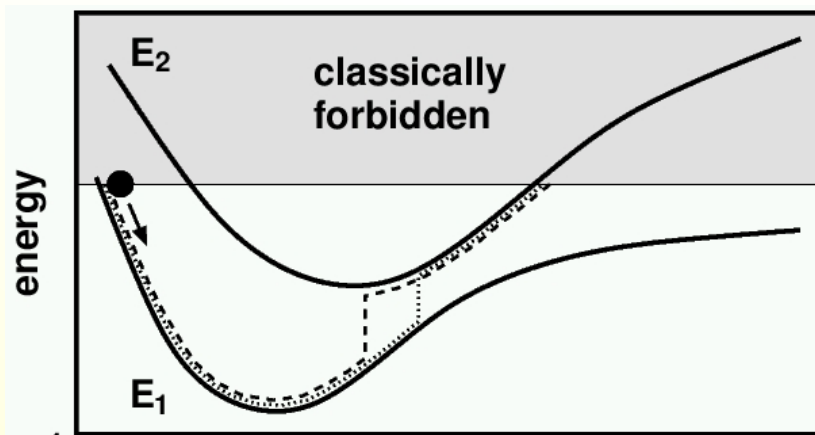
$$V_{qQ}(q,Q) = Ae^{-B(q-Q)}$$







# 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:

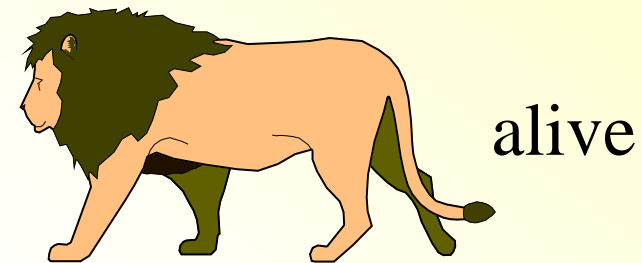
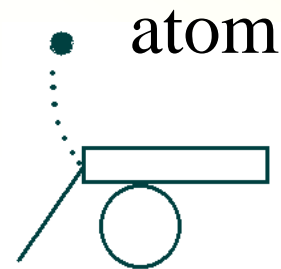
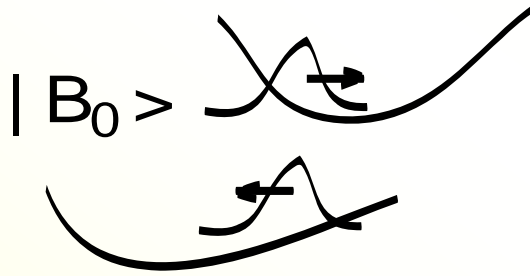
Craig, Duncan, Prezhdo *PRL* **95**, 163001 (2005)

Detailed balance / thermal equilibrium (due to hop rejection):

Parahdekar, Tully *JCP* **122**, 094102 (2005)



# Schrodinger Cat and Decoherence



alive

cat



dead

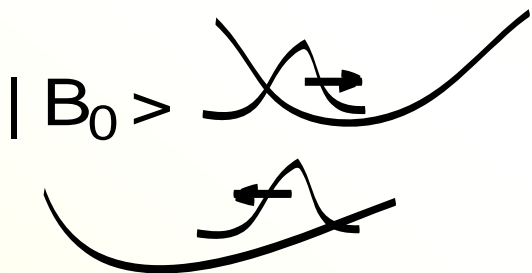
**System** - radioactive atom; **Bath** - cat

In Nanomaterials

**System** - electrons, spins; **Bath** - phonons

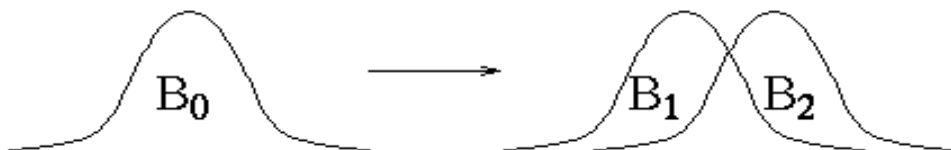


# Franck-Condon Factor and Decoherence



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

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



Bath (vibrational) wave  
functions diverge

This affects evolution of (electronic) system



# Decoherence and Surface Hopping

O. V. Prezhdo, P. J. Rossky, *Phys. Rev. Lett.* **81**, 5294 (1998)

O. V. Prezhdo, *Phys. Rev. Lett.* **85**, 4413 (2000)

Reduced density matrix:

$$\left\| \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \right\| \rightarrow \left\| \begin{pmatrix} \rho_{11} & \rho_{12} \langle B_2 | B_1 \rangle \\ \rho_{21} \langle B_1 | B_2 \rangle & \rho_{22} \end{pmatrix} \right\|$$

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

$\rho_{12} \rightarrow 0$  on decoherence time scale

hopping probability  $P_{12} \sim \rho_{12}$



# Decoherence and Surface Hopping

O. V. Prezhdo, P. J. Rossky, *Phys. Rev. Lett.* **81**, 5294 (1998)

O. V. Prezhdo, *Phys. Rev. Lett.* **85**, 4413 (2000)

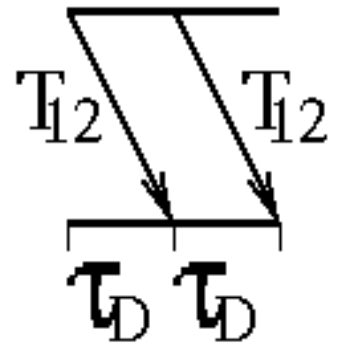
Reduced density matrix:  $\rho = \langle B | \rho^{S-B} | B \rangle$

$$\left\| \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \right\| \rightarrow \left\| \begin{pmatrix} \rho_{11} & \rho_{12} \langle B_2 | B_1 \rangle \\ \rho_{21} \langle B_1 | B_2 \rangle & \rho_{22} \end{pmatrix} \right\| \quad \begin{array}{l} \rho_{12} \rightarrow 0 \text{ on decoherence} \\ \text{time scale} \\ \text{hopping probability } P_{12} \sim \rho_{12} \end{array}$$

## Quantum Zeno Effect

With decoherence:  $P_{12} = |T_{12}|^2 + |T_{12}|^2 + \dots$

Without decoherence  $P_{12} = |T_{12} + T_{12} + \dots|^2$



Decoherence makes transitions less likely

$$|0.1|^2 + |0.1|^2 < |0.1 + 0.1|^2$$



# Stochastic Mean-Field (SMF)

O. V. Prezhdo *J. Chem. Phys.* **111**, 8366 (1999); *Phys. Rev. Lett.* **85**, 4413 (2000)

Stochastic Schrodinger equation  
in place of regular SE in Ehrenfest

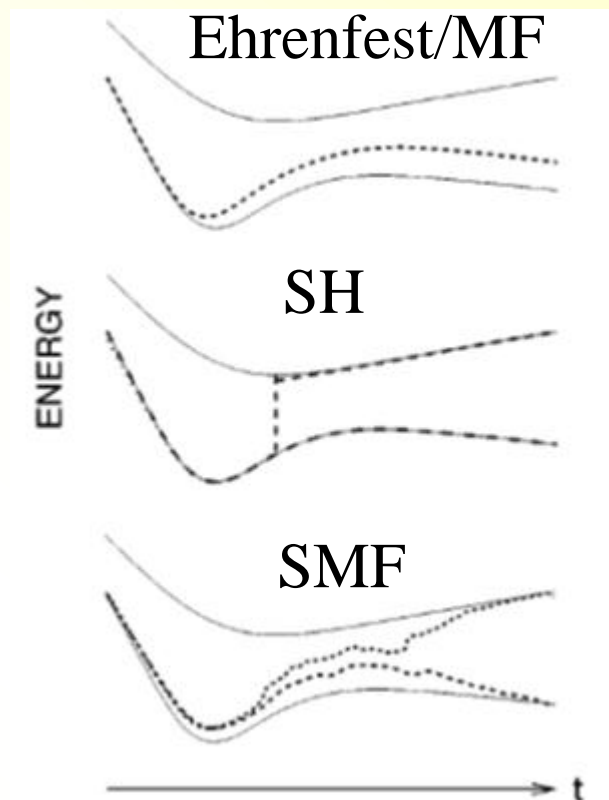
$$|d\Psi\rangle = -iH|\Psi\rangle dt - \frac{\gamma}{2} L^+ L |\Psi\rangle dt + \sqrt{\gamma} L |\Psi\rangle dW$$

$L$  – 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)

H. Jaeger, S. Fisher, O. V. Prezhdo *J. Chem. Phys.* **137**, 22A545 (2012)

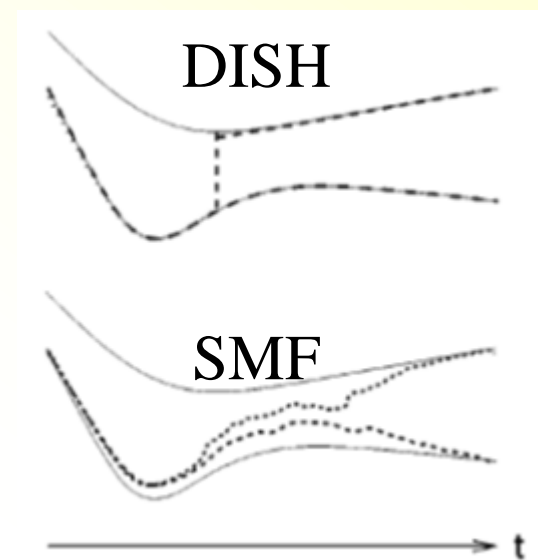
Evolve in an adiabatic state.

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

Kamisaka, Kilina, Yamashita, Prezhdo, *Nano Lett.* **6**, 2295 (2006)

## Optical response function

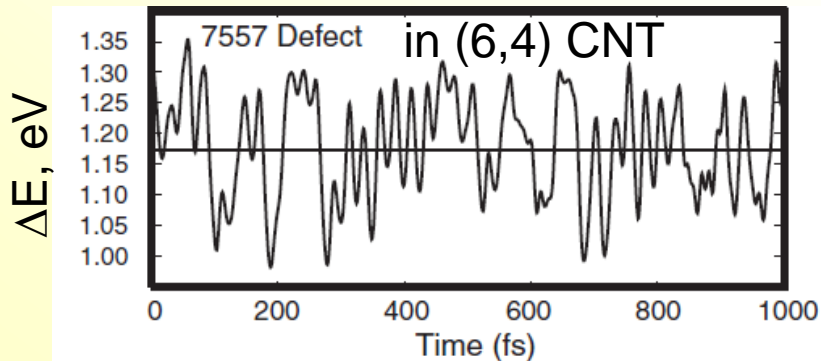
$$D(t) = \exp(i\omega t) \left\langle \exp \left[ -\frac{i}{\hbar} \int_0^t \Delta E(\tau) d\tau \right] \right\rangle_T$$

2<sup>nd</sup> order cumulant approximation

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

$$g(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 C(\tau_2)$$

$$C(t) = \langle \Delta E(t) \Delta E(0) \rangle_T$$







# Evaluating Decoherence Times

Kamisaka, Kilina, Yamashita, Prezhdo, *Nano Lett.* **6**, 2295 (2006)

## Optical response function

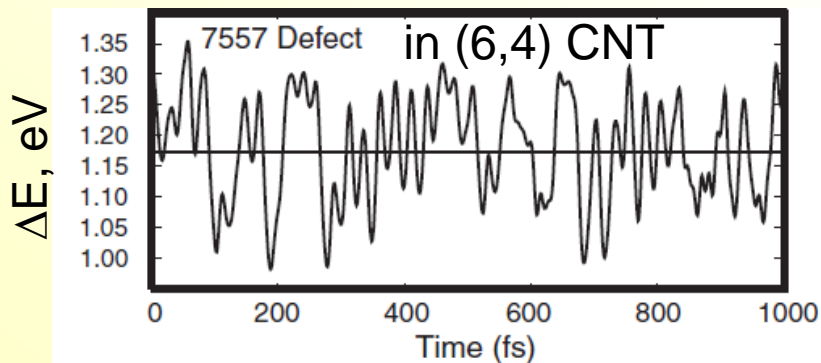
$$D(t) = \exp(i\omega t) \left\langle \exp \left[ -\frac{i}{\hbar} \int_0^t \Delta E(\tau) d\tau \right] \right\rangle_T \tau_D =$$

2<sup>nd</sup> order cumulant approximation

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

$$g(t) = \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 C(\tau_2)$$

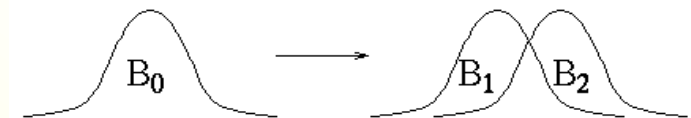
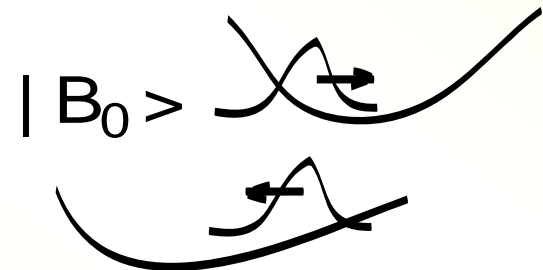
$$C(t) = \langle \Delta E(t) \Delta E(0) \rangle_T$$



## Gaussian approximation

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

$$a_n = \frac{6mk_B T}{\hbar^2} \text{ thermal de Broglie width}$$

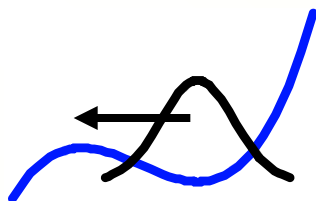




# Quantized Hamilton Dynamics

O. V. Prezhdo, Y. V. Pereverzev *J. Chem. Phys.* **113**, 6557 (2000)

O. V. Prezhdo *Theor. Chem. Acc.* **116**, 206 (2006)



$$V = \frac{q^2}{2} + \frac{q^3}{3}$$

$$\frac{d \langle q \rangle}{dt} = \langle p \rangle; \quad \frac{d \langle p \rangle}{dt} = - \langle q \rangle - \langle q^2 \rangle$$

but  $\langle q^2 \rangle \neq \langle q \rangle \langle q \rangle$  and

$$\frac{d \langle q^2 \rangle}{dt} = \langle pq + qp \rangle \equiv 2 \langle pq \rangle_s$$

$$\frac{d \langle pq \rangle_s}{dt} = \langle p^2 \rangle - \langle q^2 \rangle - \langle q^3 \rangle$$

the infinite hierarchy is  
terminated by a **closure**

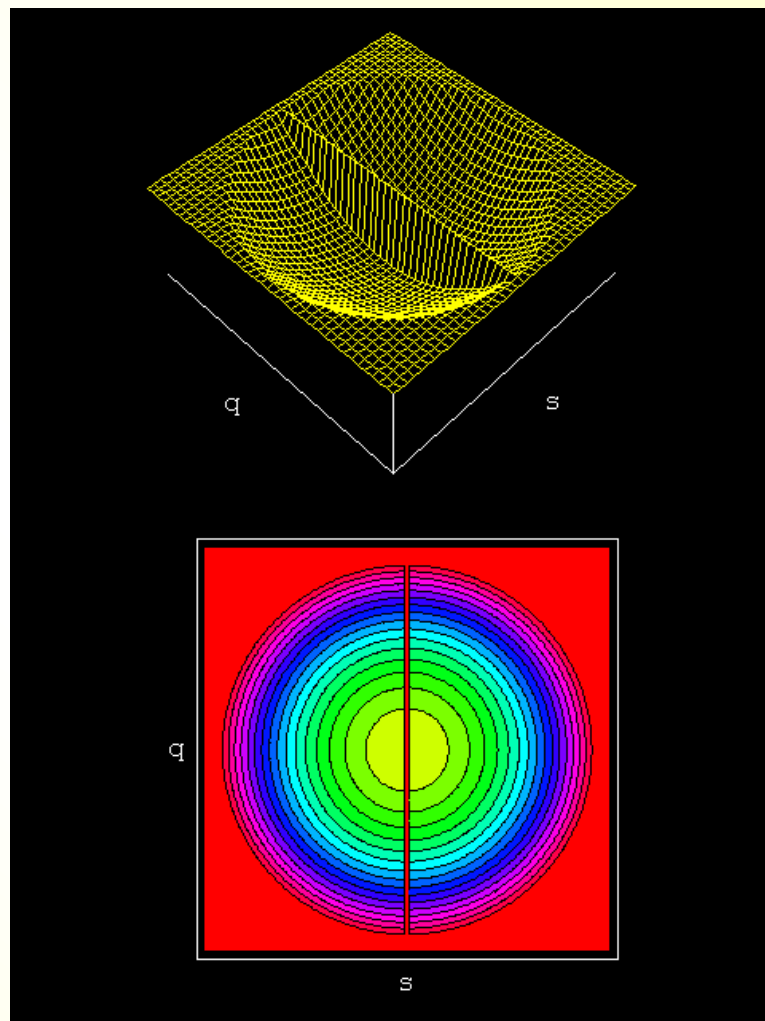
$$\langle q^3 \rangle \approx 3 \langle q^2 \rangle \langle q \rangle - 2 \langle q \rangle^3$$



# Harmonic Oscillator in Mapped QHD-2

$$\begin{matrix} \hbar \\ \text{mass} \end{matrix} \Rightarrow \begin{matrix} \hbar \\ \text{mass} \end{matrix}$$

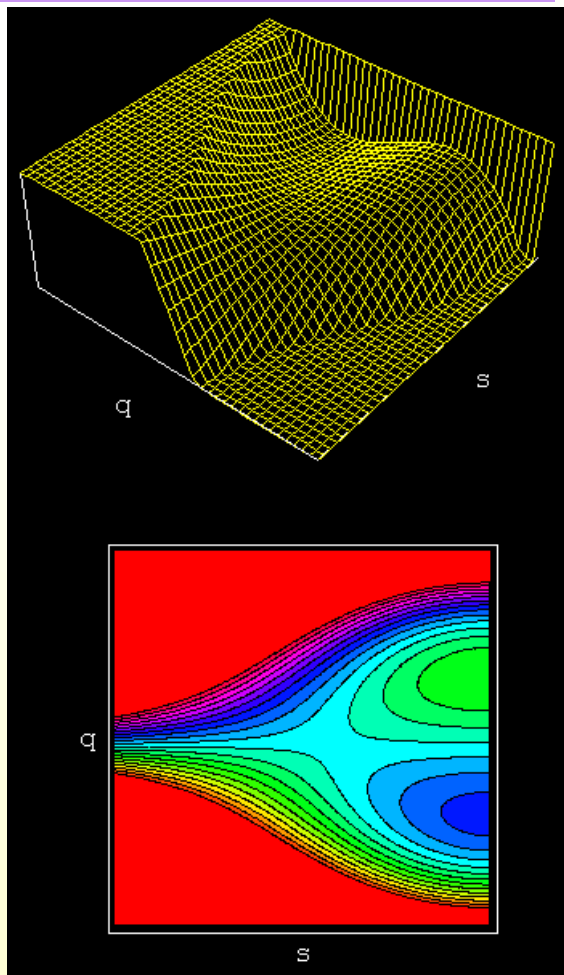
QHD-2 takes care of  
zero-point-energy





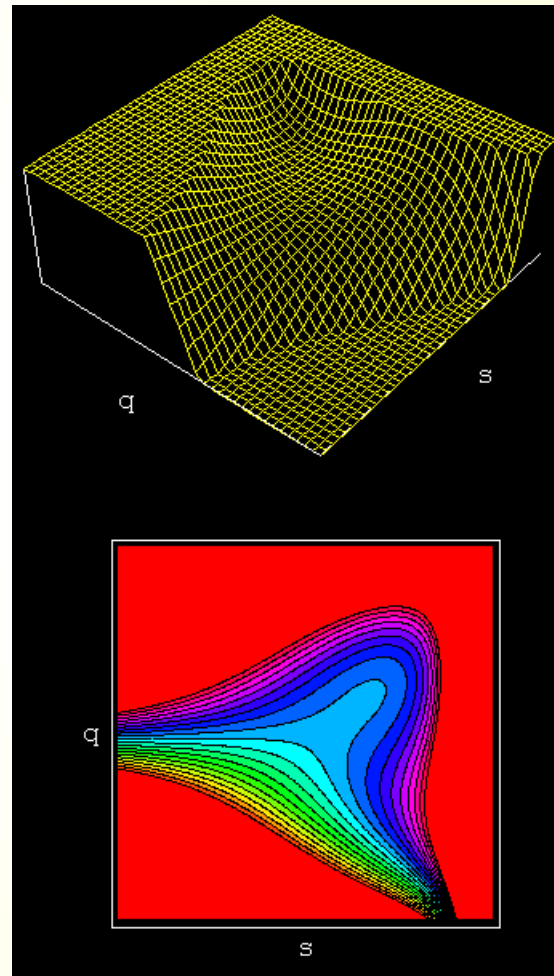
# Metastable Cubic Potential in Mapped QHD-2

$\hbar$  mass



QHD-2  
gives  
tunneling

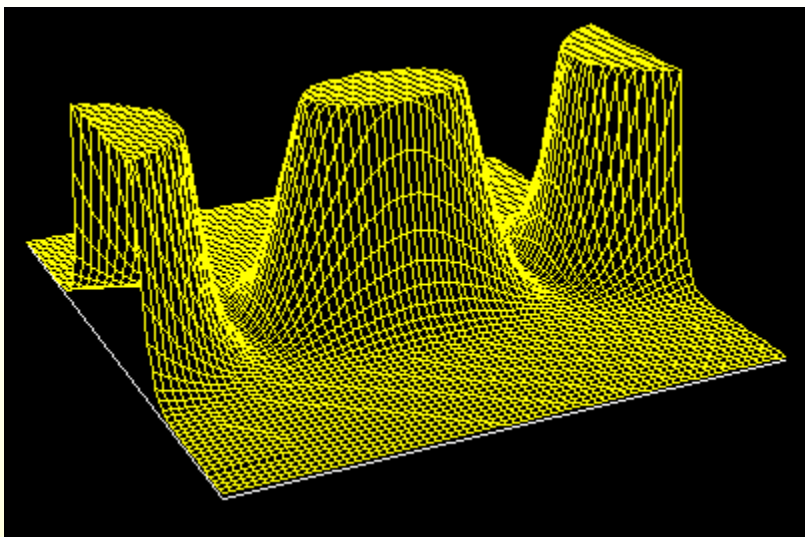
$\hbar$  mass



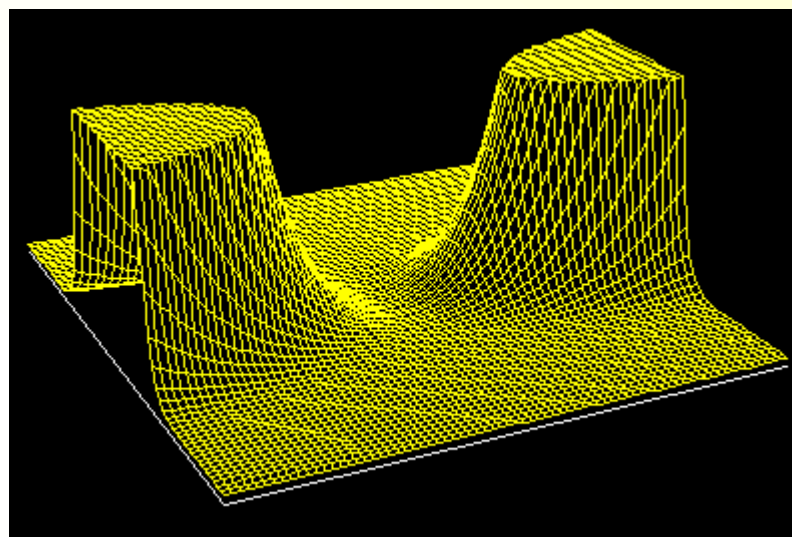


# Double-Slit Potential

## in Mapped QHD-2



potential seen by  
a **narrow** wavepacket



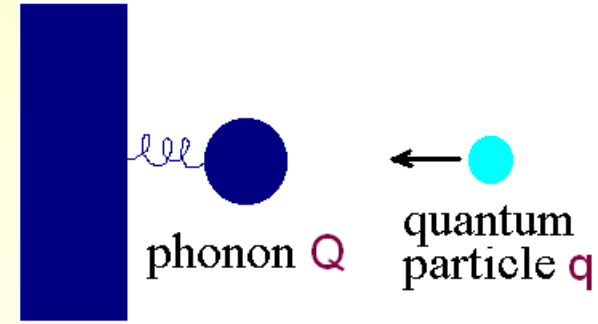
potential seen by  
a **wide** wavepacket

$$v(\mathbf{q}) + \frac{1}{2} v^{(2)}(\mathbf{q}) s^2$$



# Quantized Ehrenfest

C. Brooksby, O. V. Prezhdo,  
*Chem. Phys. Lett.*, **346** 463 (2001)



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

Ordinary

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

Mean-Field

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

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

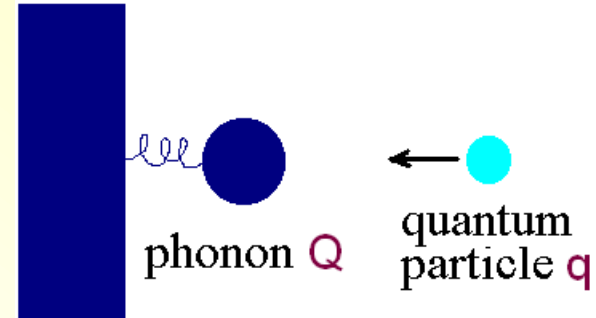
$$\frac{d \langle PQ \rangle_s}{dt} = \frac{\langle P^2 \rangle}{M} - M\Omega^2 \langle Q^2 \rangle - \langle Q \rangle \langle \Psi(q) | \nabla_Q V(q, \langle Q \rangle) | \Psi(q) \rangle$$

QMF-2 equations require **no new quantum calculation** !



# Quantized Ehrenfest

C. Brooksby, O. V. Prezhdo,  
*Chem. Phys. Lett.*, **346** 463 (2001)



Highly simplified representation of O<sub>2</sub> interacting with Pt

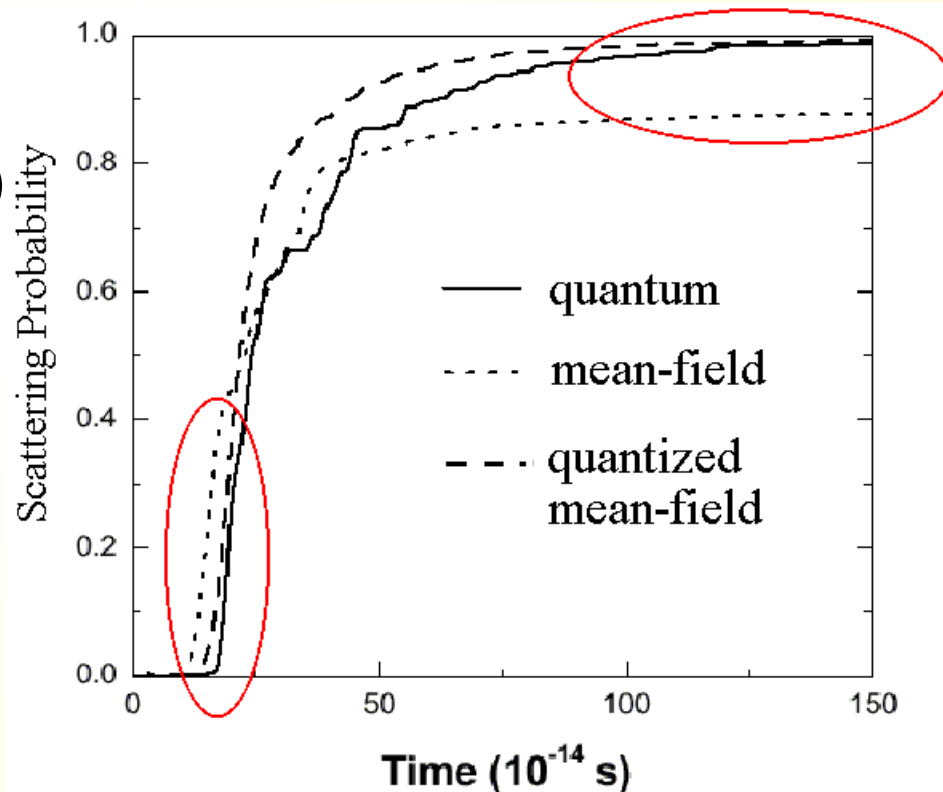
J. Strömquist, S. Gao, *J.Chem.Phys.* **106**, 5751 (1997); D.S. Sholl, J.C. Tully, *J.Chem.Phys.* **109**, 7702 (1998)

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

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

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

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

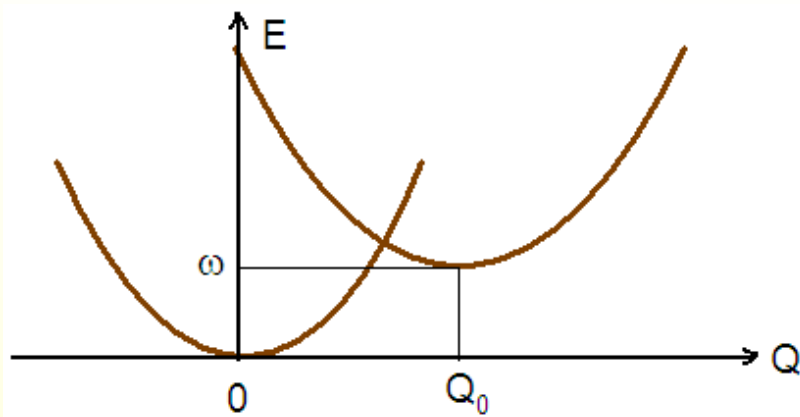






# Energy Transfer (Tunneling) and Dephasing

D.S. Kilin, Yu.V. Pereverzev, O.V. Prezhdo, *J. Chem. Phys.*, **120** 11209 (2004)



Spin-Boson/Marcus Model

Jaynes-Cummings Model

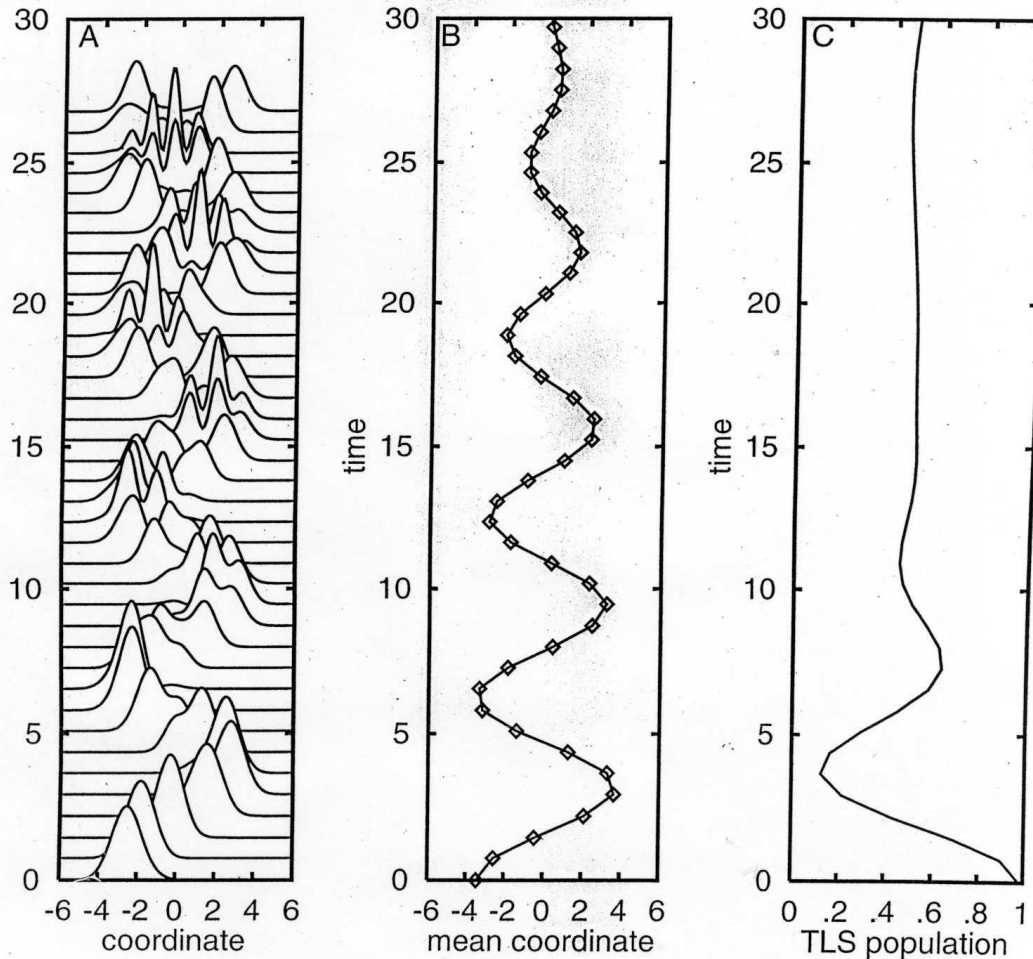
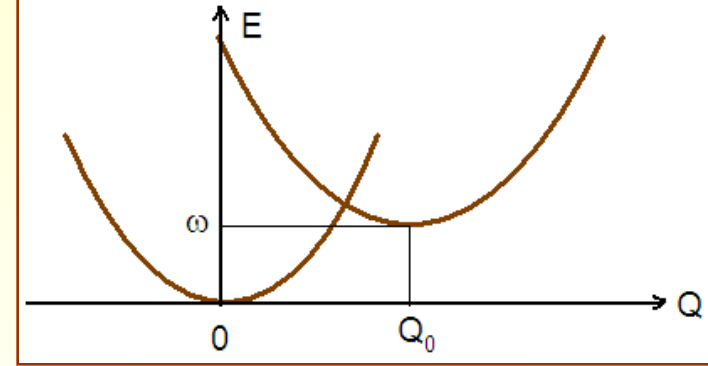
$$H = \Omega \left( a^+ a + \frac{1}{2} \right) + \omega S_z + g(a^+ S_- + a S_+)$$

- 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

$$\alpha = a^+ S_- + a S_+$$

$$\beta = a^+ S_- - a S_+$$

$$\gamma = \left( a^+ a + \frac{1}{2} \right) + S_z$$

$$\frac{d\langle \alpha \gamma^n \rangle}{dt} = -\delta \langle \beta \gamma^n \rangle$$

$$\frac{d\langle \beta \gamma^n \rangle}{dt} = -\delta \langle \alpha \gamma^n \rangle + g \langle S_z \gamma^{n+1} \rangle \quad n=0,1,2,\dots$$

$$\frac{d\langle S_z \gamma^n \rangle}{dt} = g \langle \beta \gamma^n \rangle$$

$$\text{closure: } \langle S_z \gamma^2 \rangle \approx 2\langle S_z \gamma \rangle \langle \gamma \rangle + \langle S_z \rangle \langle \gamma^2 \rangle - 2\langle S_z \rangle \langle \gamma \rangle^2$$

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

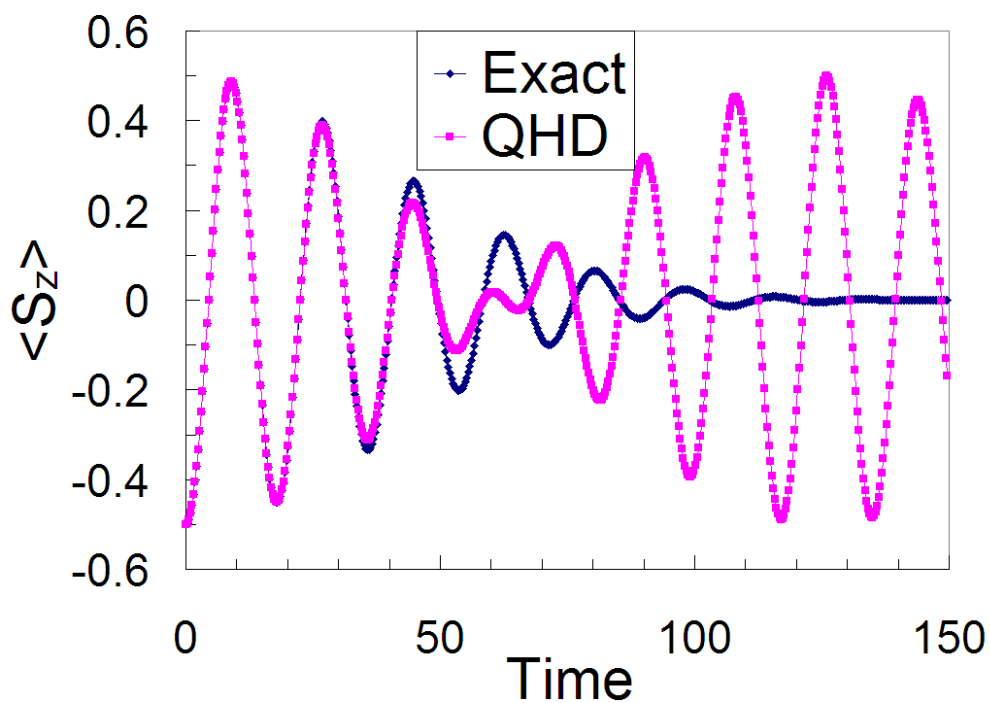
$\langle S_z \rangle, \langle \alpha \rangle, \langle \beta \rangle, \langle S_z \gamma \rangle, \langle \alpha \gamma \rangle, \langle \beta \gamma \rangle$  - 6 variables



# Evolution of $\langle S_z \rangle$ by QHD

D.S. Kilin, Yu.V. Pereverzev, O.V. Prezhdo, *J. Chem. Phys.*, **120** 11209 (2004)

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



Multiple transfer events

Dephasing envelope



# State-Specific Dynamics

## a.k.a. multi-configuration mean-field

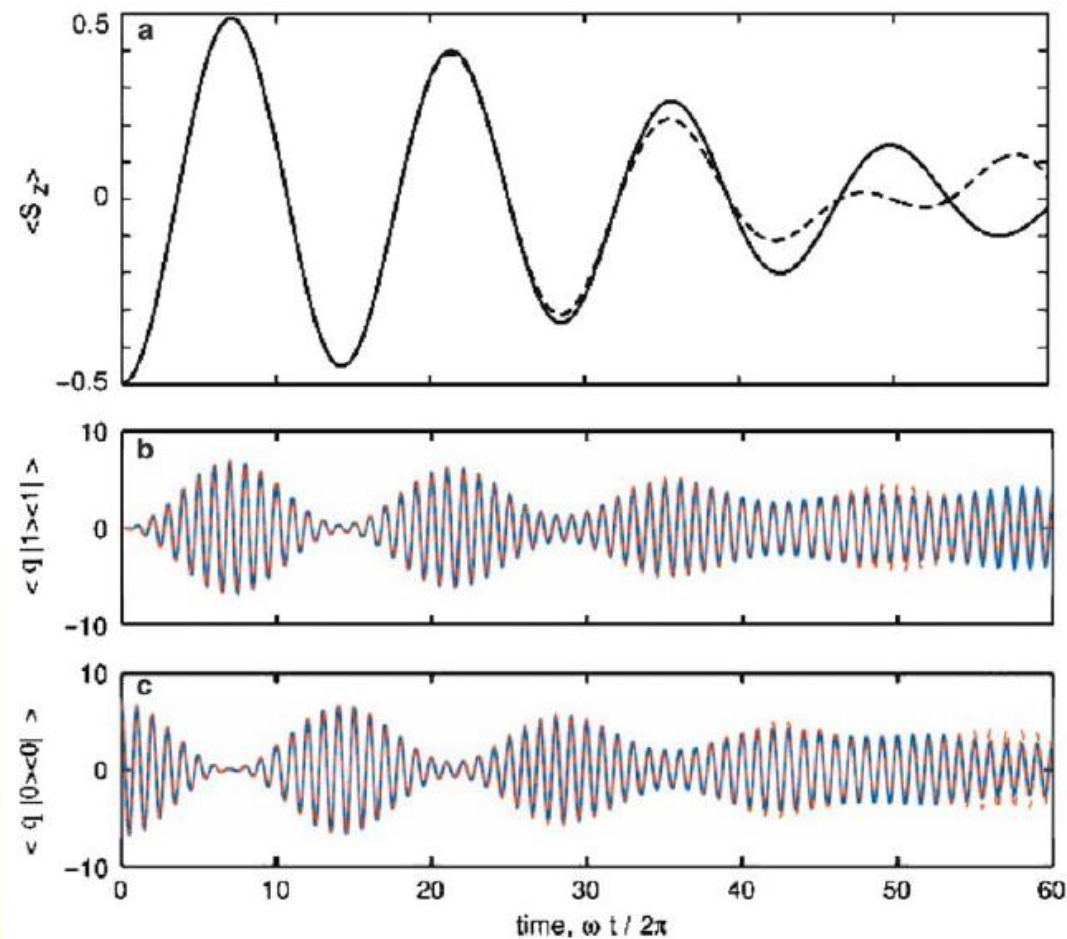
D.S. Kilin, Yu.V. Pereverzev, O.V. Prezhdo, *J. Chem. Phys.*, **120** 11209 (2004)

$$\langle q | 0 \rangle \langle 0 | \rangle \simeq \langle q \rangle (1/2 + \langle S_z \rangle)$$

$$\langle q | 1 \rangle \langle 1 | \rangle \simeq \langle q \rangle (1/2 - \langle S_z \rangle)$$

closure:  $\langle \tilde{a} S_z \rangle \simeq \langle \tilde{a} \rangle \langle S_z \rangle$

$\langle S_z \rangle$  – as before



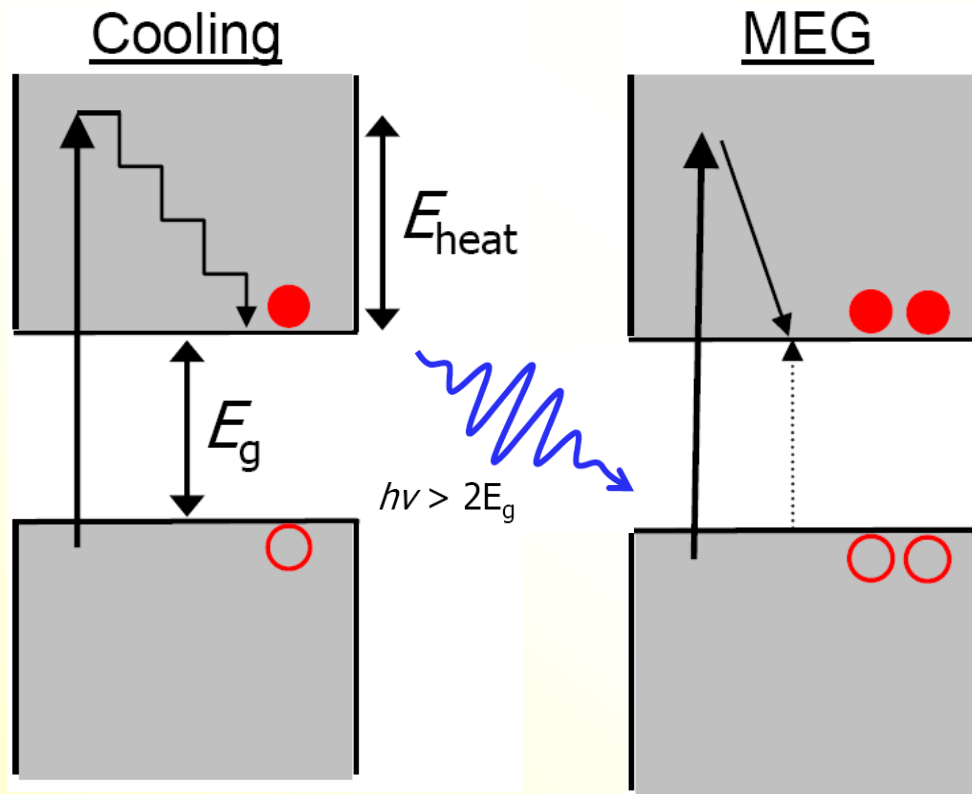


# Summary for TDDFT / NAMD

- ✓ **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

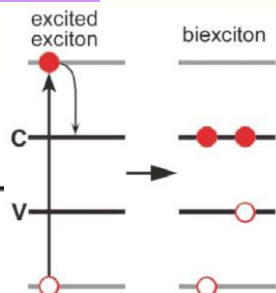
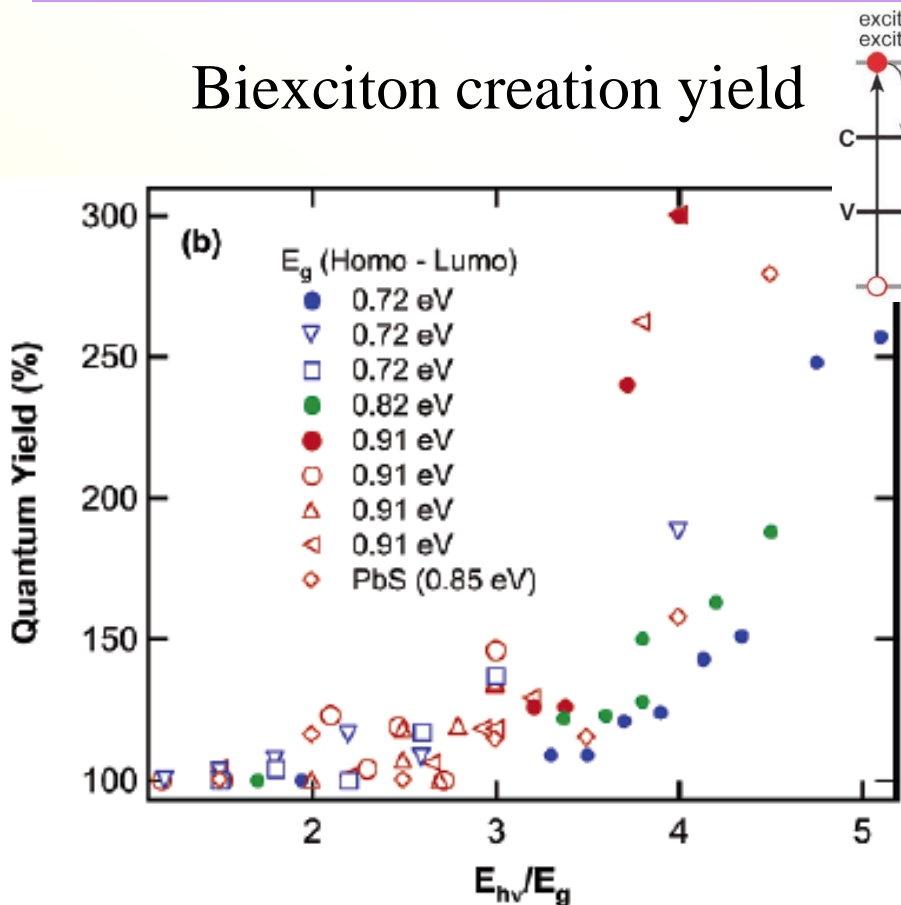
mechanisms for carrier multiplication



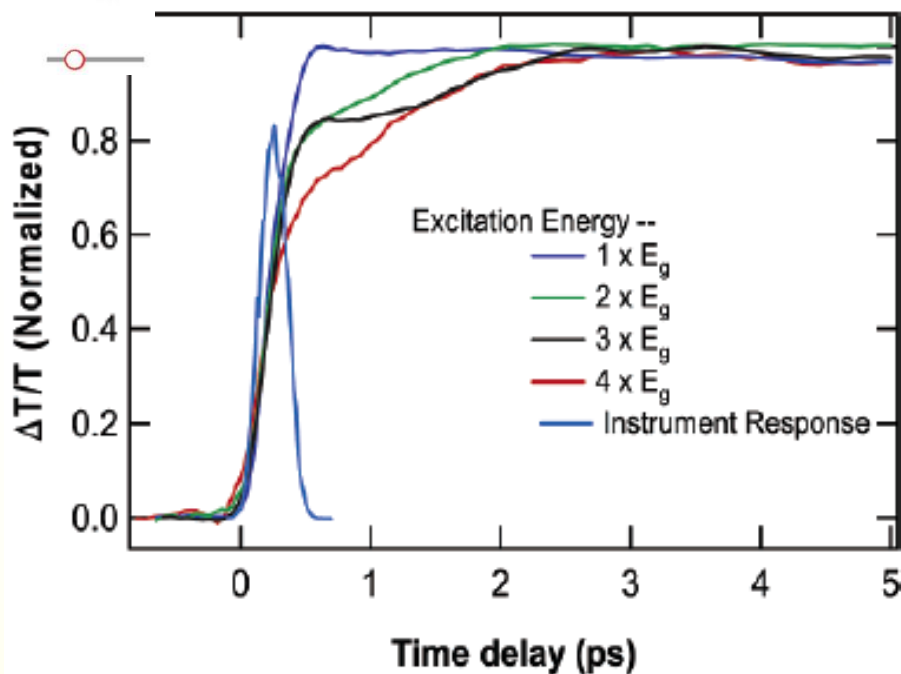
# Excitons in QDs: 2005

Shaller, Klimov *PRL* **92** 186601 (2004); Ellingson, Beard, Johnson, Yu, Micic, Nozik, Shabaev, Efros, *Nano Lett.* **5** 865 (2005)

## Biexciton creation yield



## Exciton to biexciton time under 0.25ps







# Excitons in QDs: 2005

Schaller, Pietryga, Goupalov, Petruska, Ivanov, Klimov

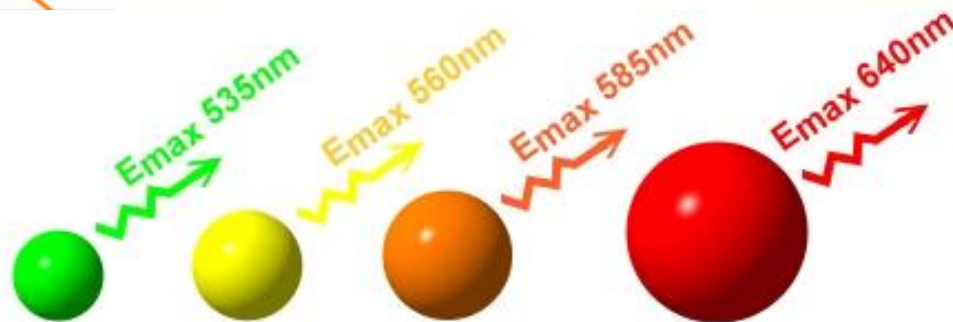
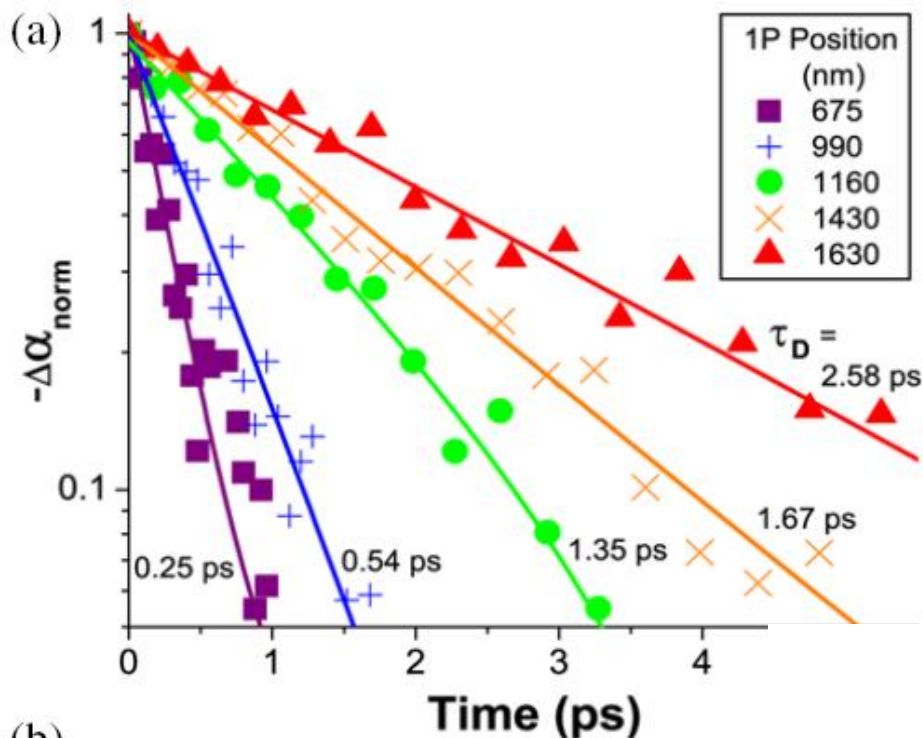
*Phys. Rev. Lett.* **95** 196401 (2005)

## Electron-Phonon Relaxation

No phonon bottleneck.

Times are similar to  
biexciton creation times

Larger dots relax more slowly ?!

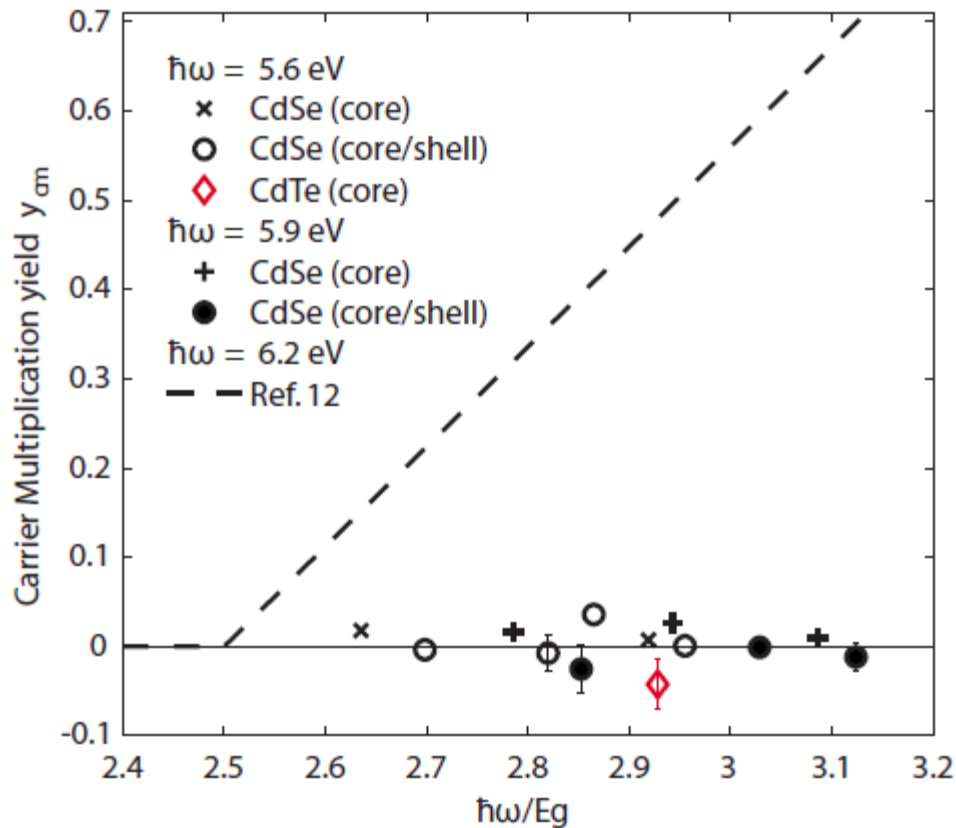






# Excitons in QDs: 2007

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



Original multiplication experiments could not be reproduced by other groups.

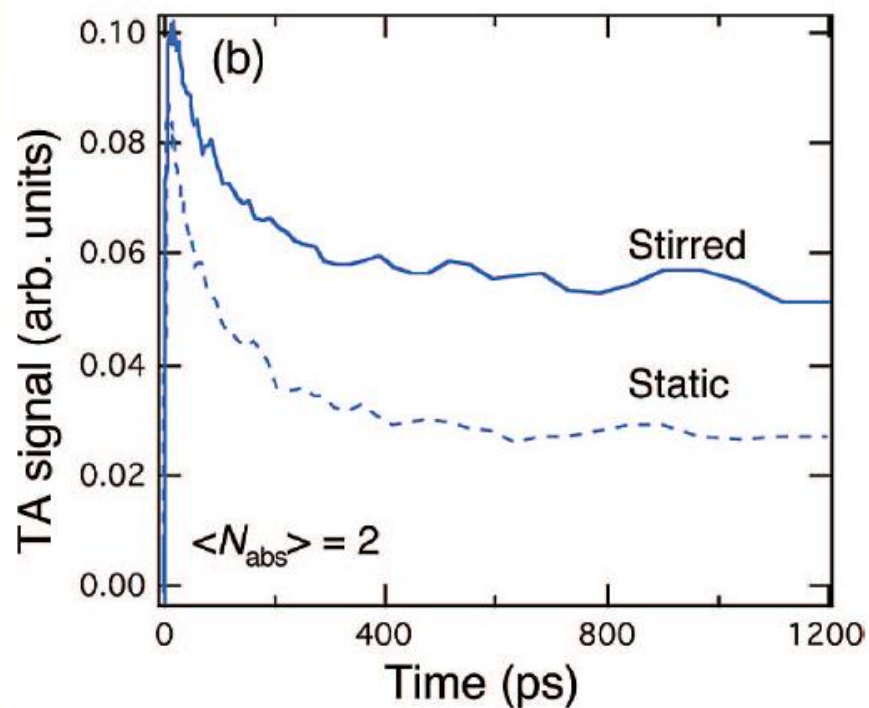
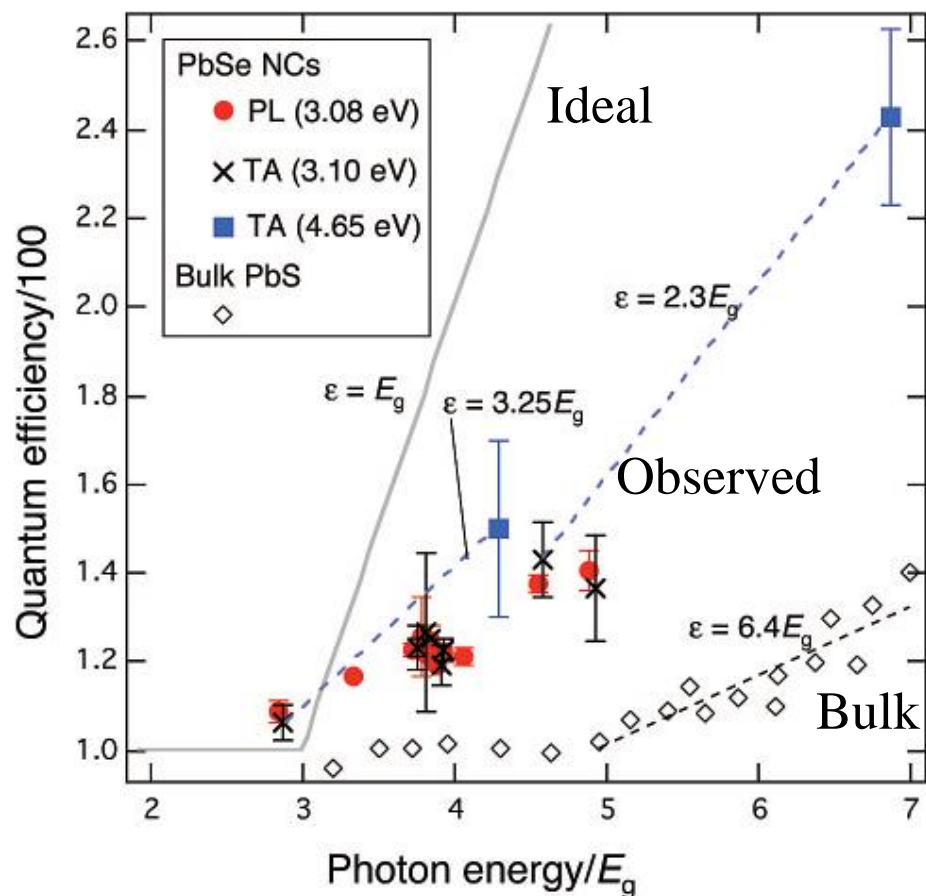
Experimental conditions and data interpretation are very important.



# Excitons in QDs: 2008

McGuire, Joo, Pietryga, Schaller, Klimov

*Acc. Chem. Res.* **41** 1810 (2008)



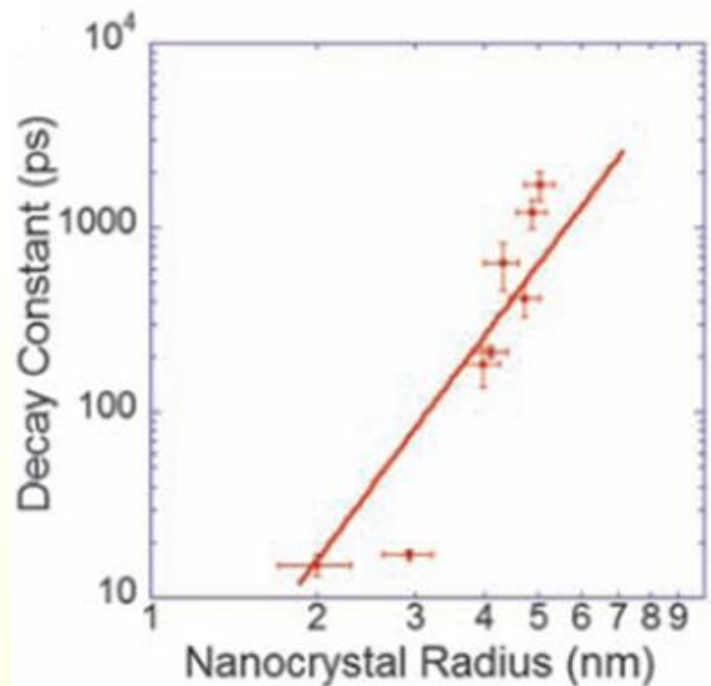
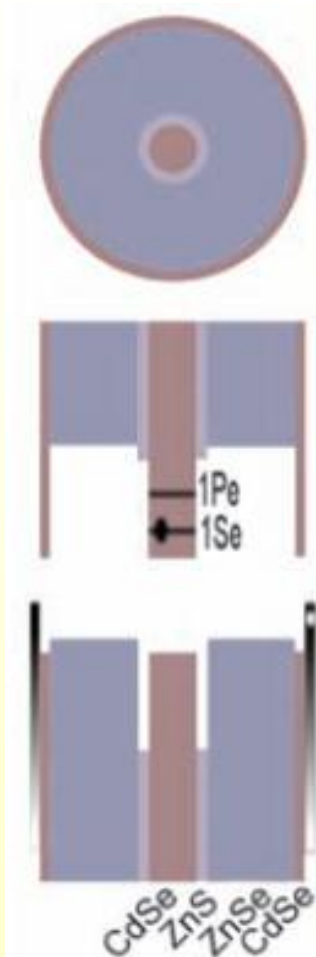
Efficiency estimates are significantly lowered



# Excitons in QDs: 2008

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

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

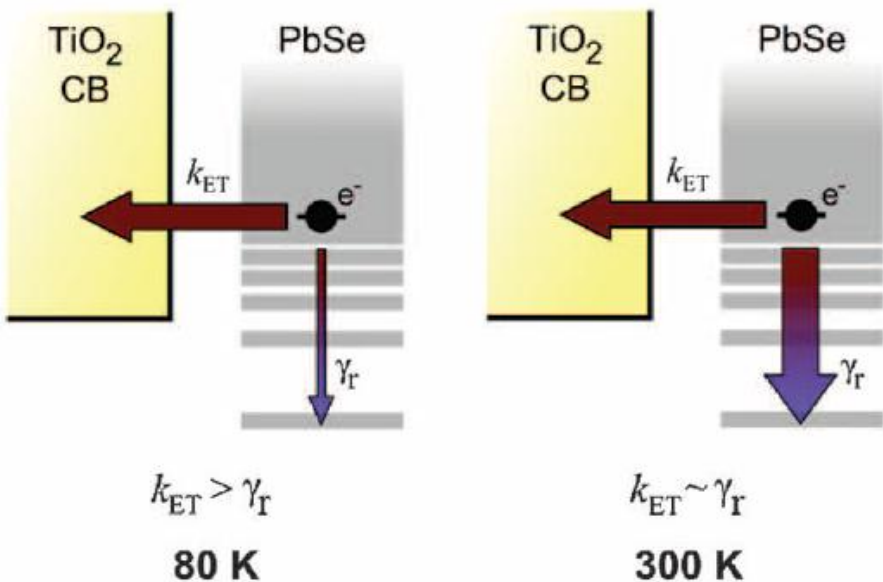


(shell thickness)

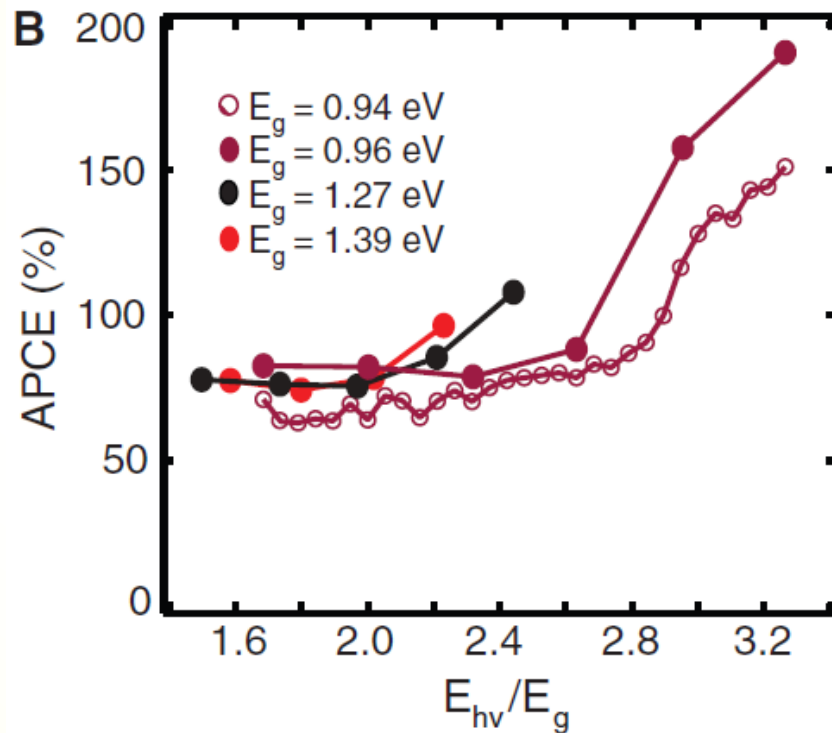


# Excitons in PbSe QDs: 2010

Zhu group, *Science* **328** 1543 (2010); Parkinson group, *Science* **330** 63 (2010); Nozik group, *Science* **334** 1530 (2011)



50 fs injection time



absorbed photon-to-current efficiency



# Structural Relaxation PbSe QDs

Kilina, Kilin, Prezhd, *ACS Nano*, **3**, 93 (2009)

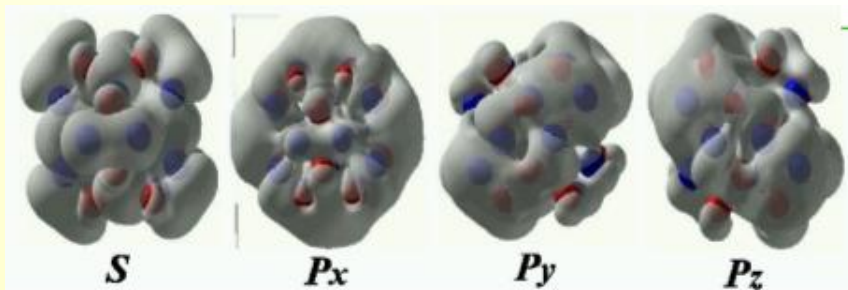
Kilina, Craig, Kilin, Prezhd, *J. Phys. Chem. C* **111** 4871 (2007)

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

Bulk,  $T=0\text{ K}$     Relaxed,  $T=0\text{ K}$     Heated,  $T=300\text{ K}$

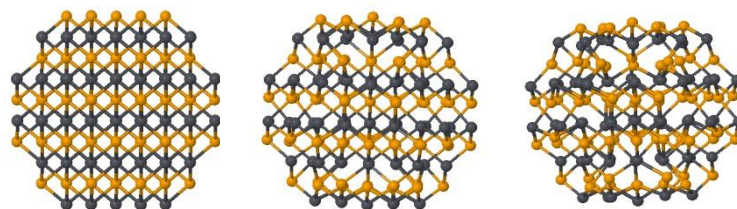


(LUMO) (LUMO+1) (LUMO+2) (LUMO+3)

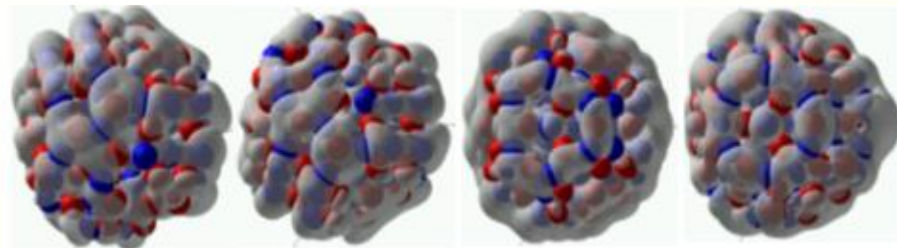


**136 atoms**  $\text{Pb}_{68}\text{Se}_{68}$   $d=1.4\text{nm}$

Bulk,  $T=0\text{ K}$     Relaxed,  $T=0\text{ K}$     Heated,  $T=300\text{ K}$



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



states mix

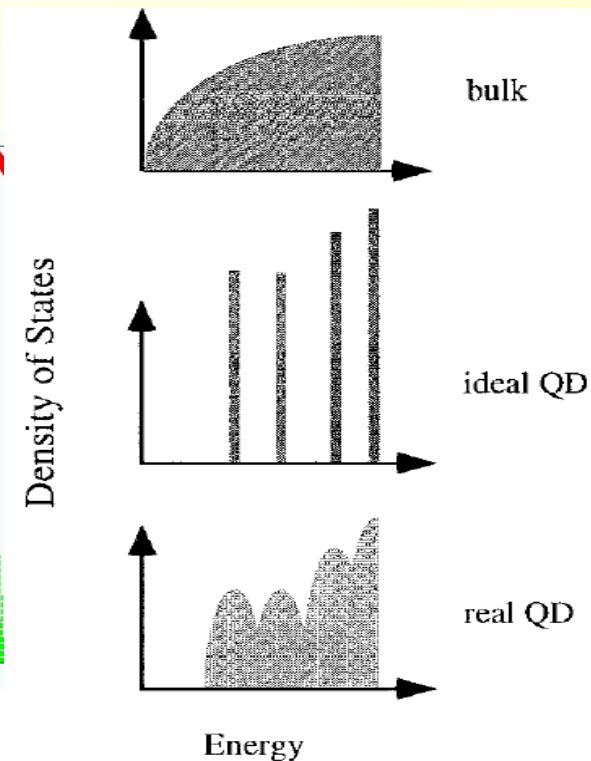
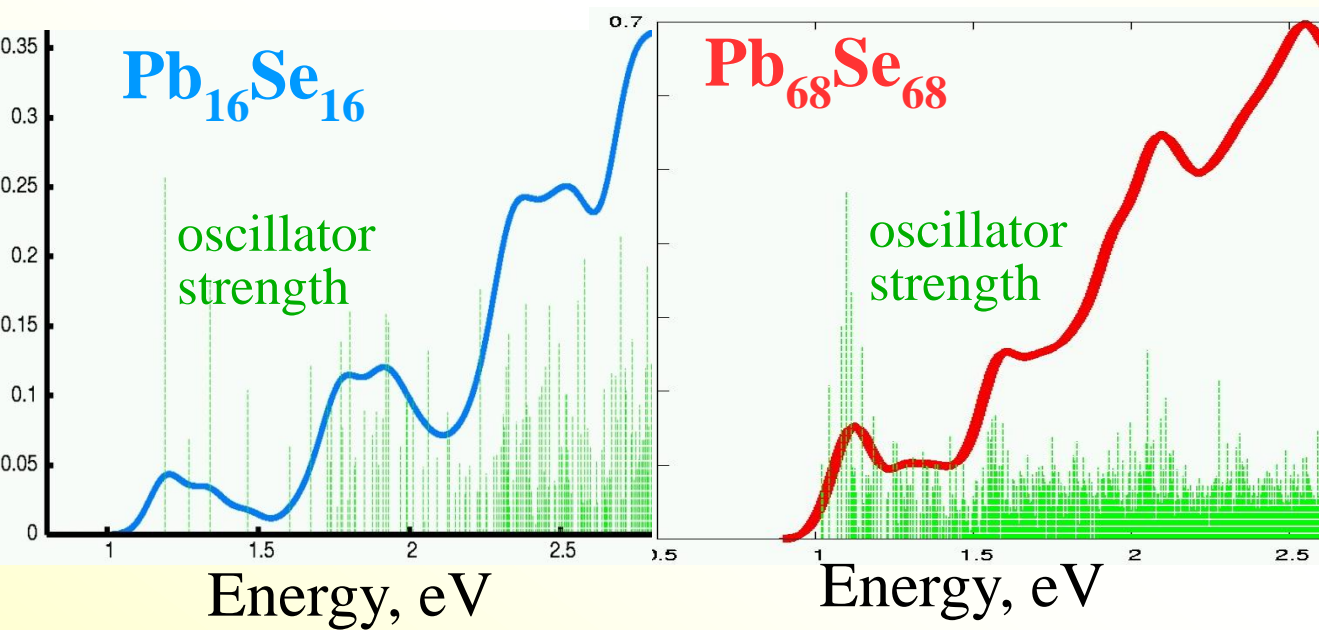




# Absorption Spectra of PbSe QDs

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

Kilina, Craig, Kilin, Prezhdo, *J. Phys. Chem. C* **111** 4871 (2007)

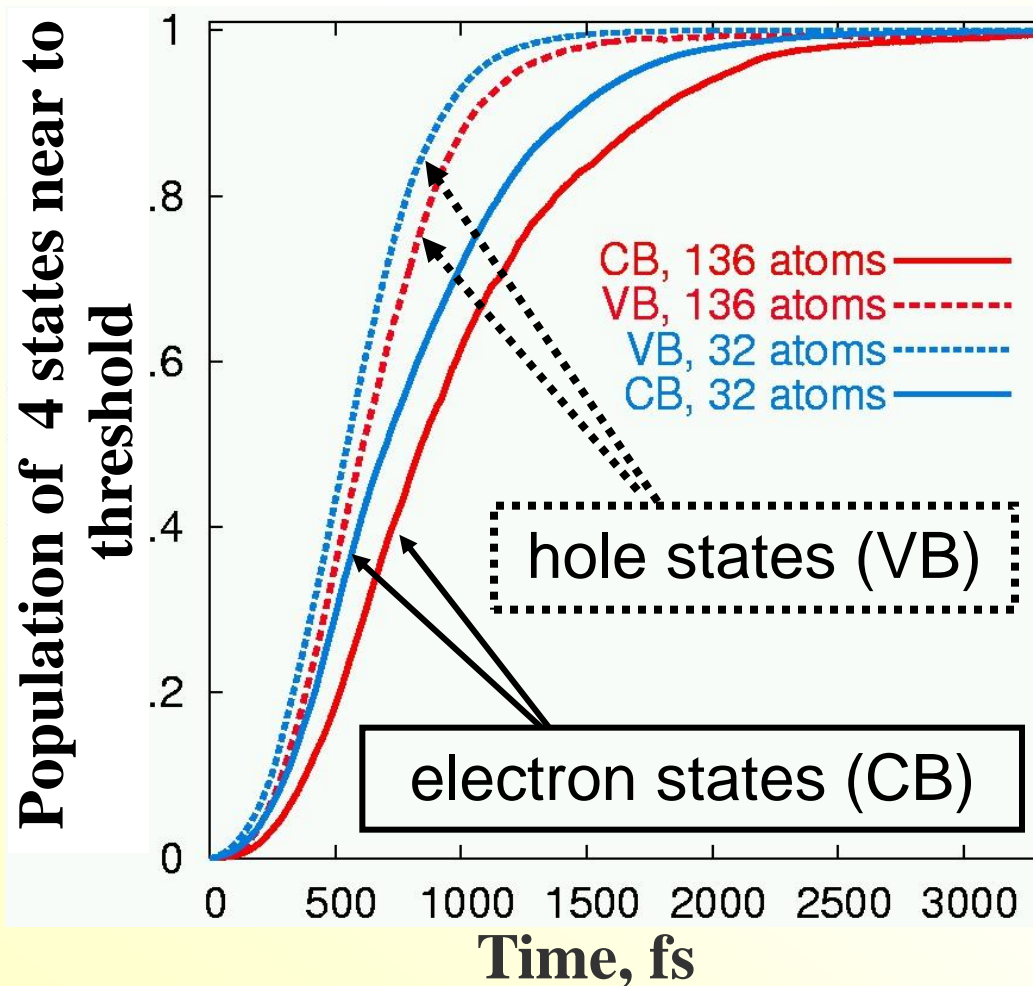




# Comparison of Relaxation, PbSe

Kilina, Kilin, Prezhd, *ACS Nano*, **3**, 93 (2009)

Kilina, Craig, Kilin, Prezhd, *J. Phys. Chem. C* **111** 4871 (2007)



Sub-picosecond times agree with experiment

e.g. Gdor et al.

*ACS Nano* **6**, 3269 (2012)

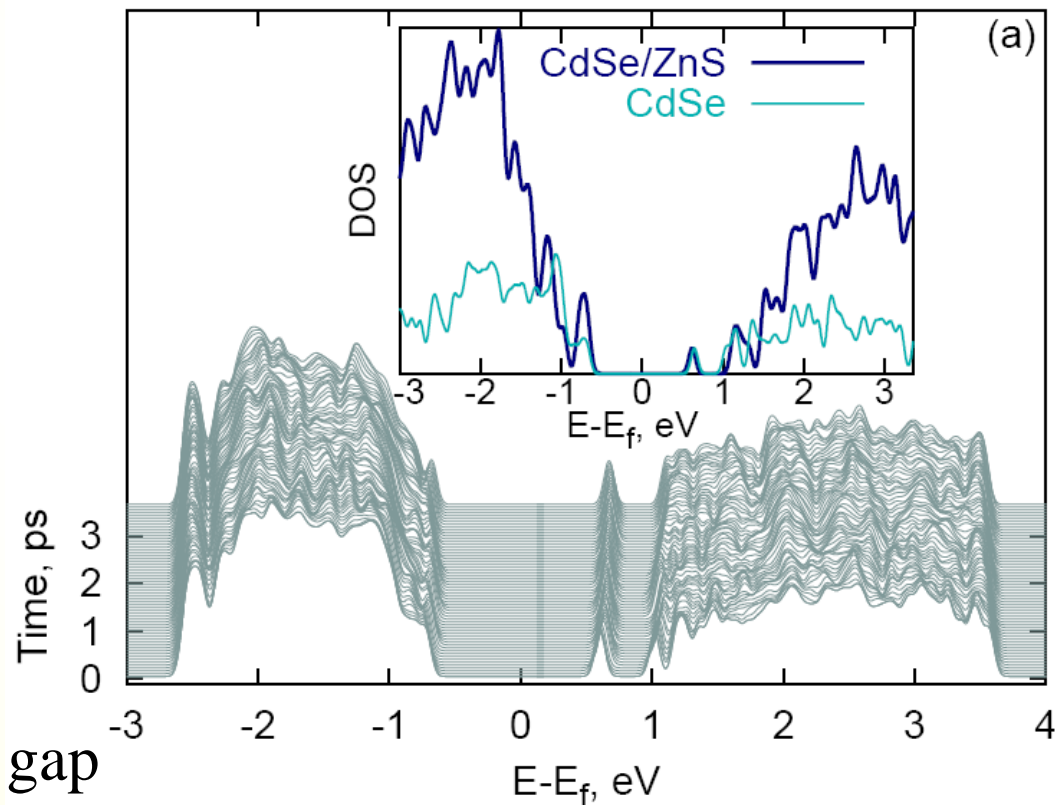
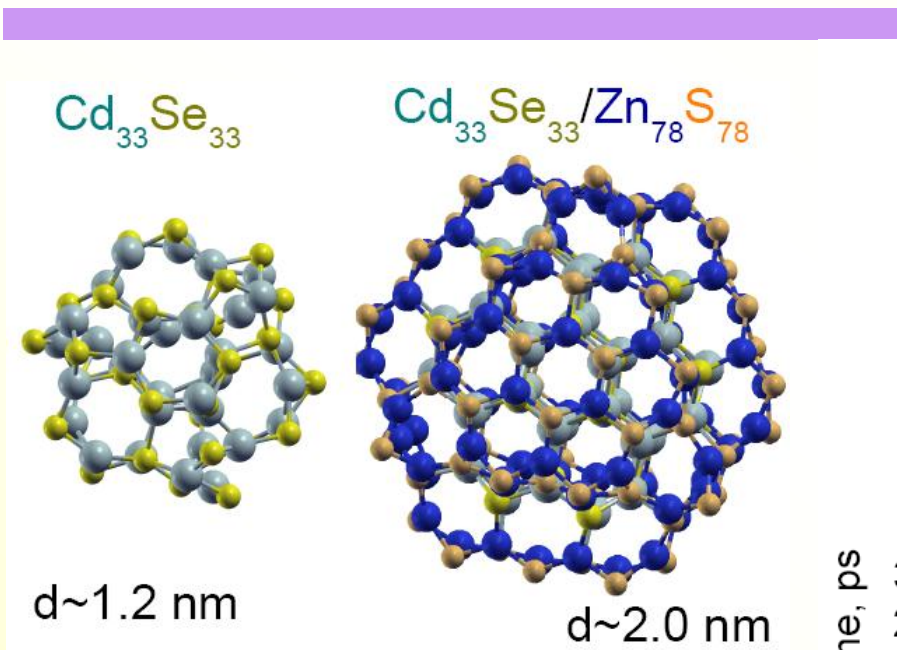
Similar relaxation times for electrons and holes

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

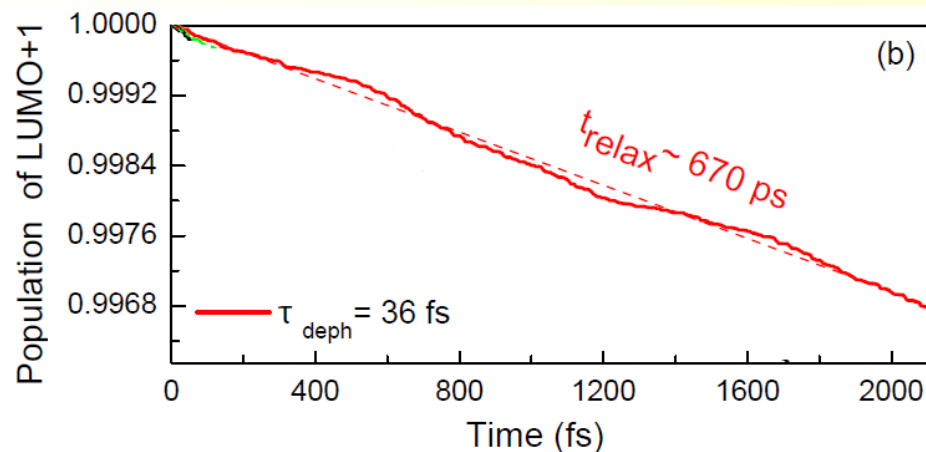
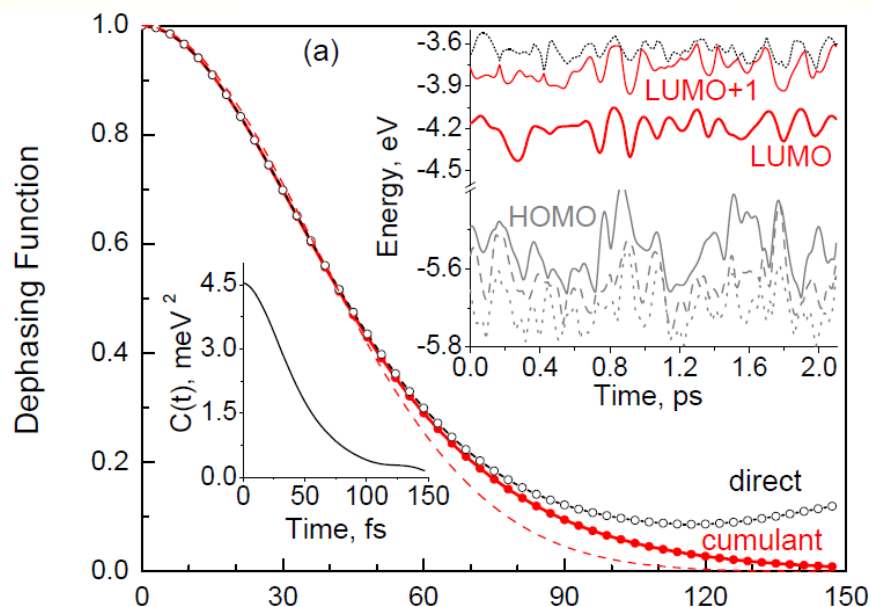
Relaxation time  $\sim 1 \text{ ns}$

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

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



# Phonon Bottleneck for 1P Electron in CdSe Quantum Dots



Simulation shows bottleneck

Relaxation time  $\sim 1 \text{ ns}$

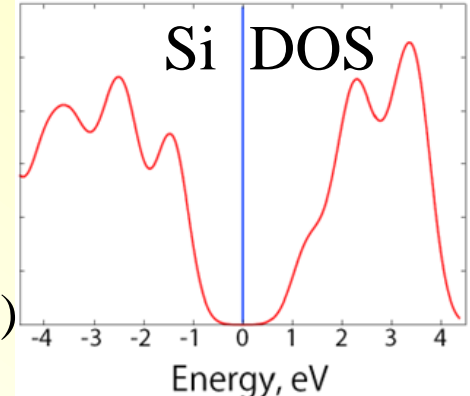
Pandey, Guyot-Sionnest, *Science* **322** 929 (2008)

Neukirch, Kilina, Kilin, Prezhdov,  
in preparation



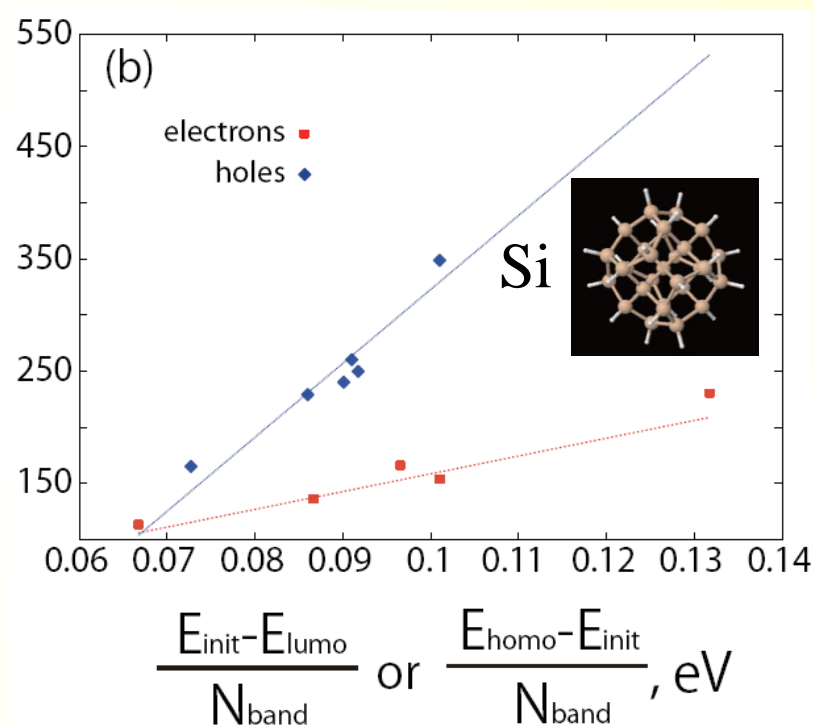
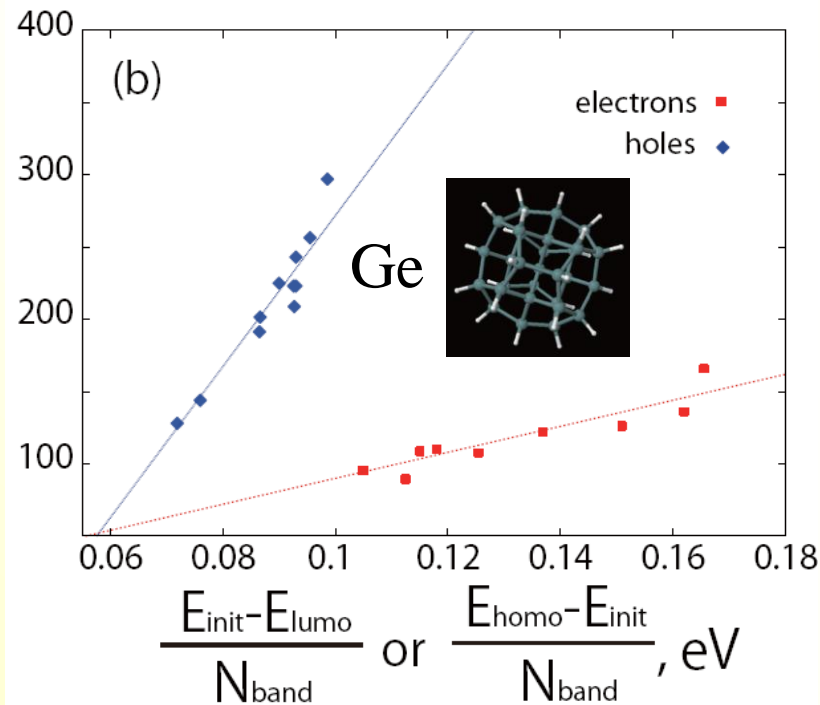
# Enhanced Energy Losses due to Ligands

Kim, Madrid, Prezhdo, *Dalton Trans.*, **45**, 10069 (2009)



Electrons relax much faster than holes ! (despite nearly symmetric DOS)

Relaxation Time, fs



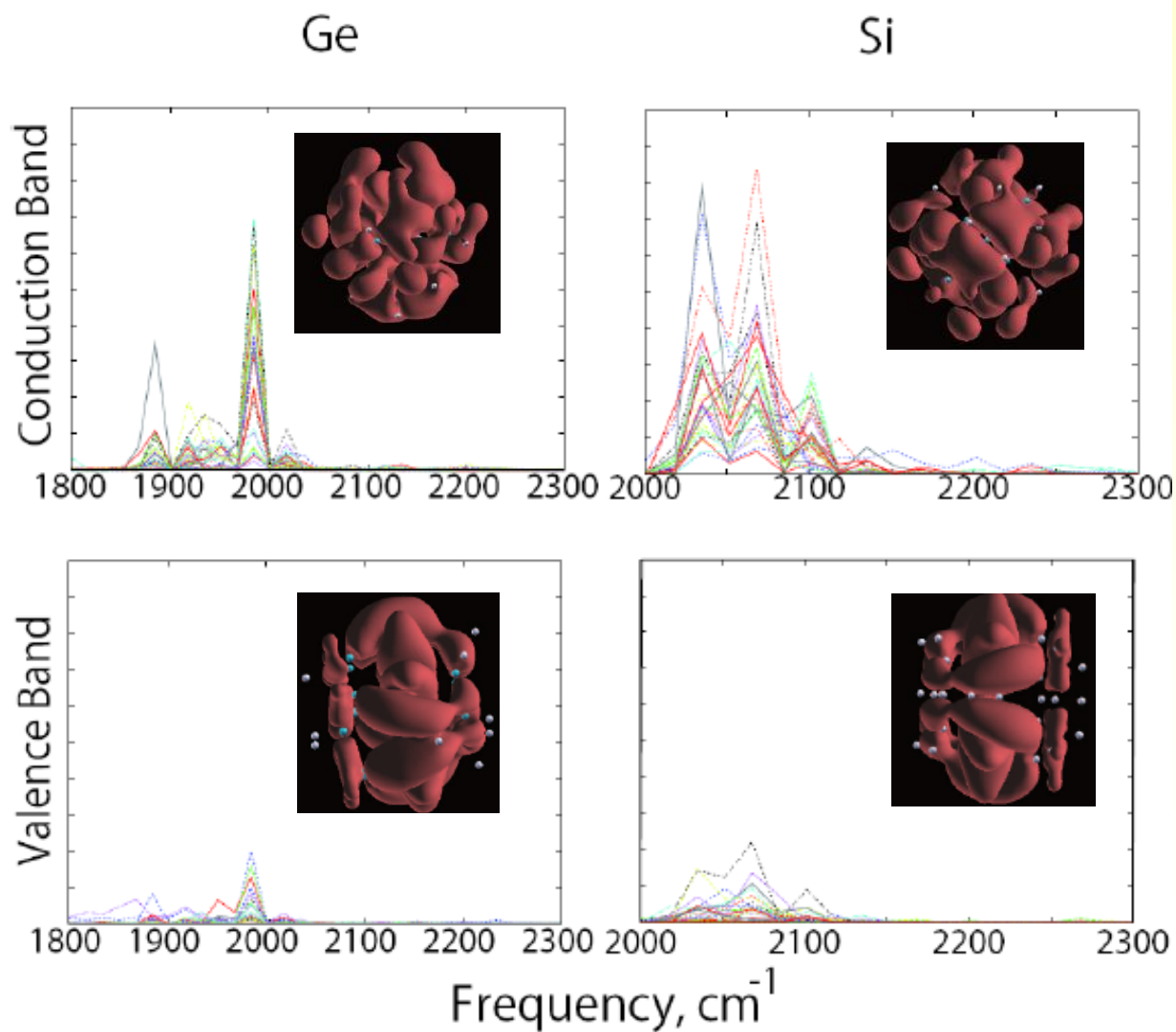


# Enhanced Energy Losses due to Ligands: Active Phonon Modes

Kim, Madrid, Prezhdoo, *Dalton Trans.*, **45**, 10069 (2009)

Low frequency modes  
are active for both  
electrons and holes

However,  
high frequency  
(ligand)  
modes are active  
only for electrons





# Phonon-Assisted Auger Processes

Kim, Prezhdo, *Nano Lett.*, **11**, 1845 (2011)

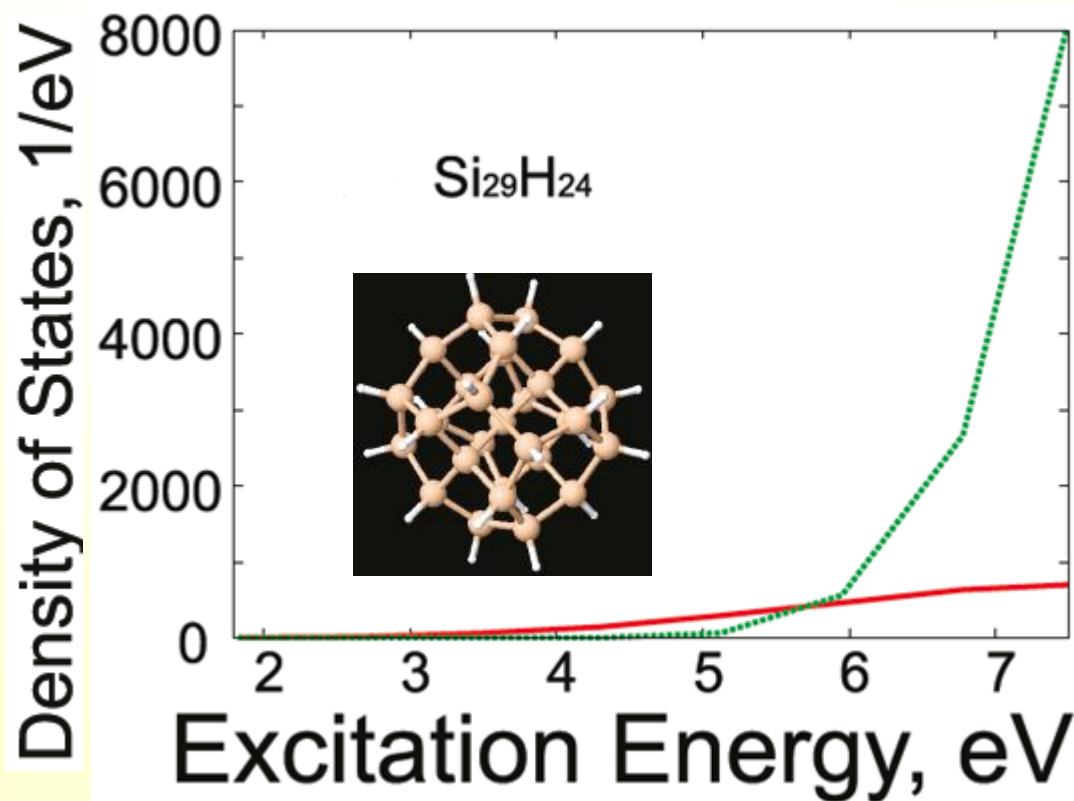
Kim, Prezhdo, *ACS Nano*, **6**, 1239 (2012)

25 VB and 24 CB orbitals

**98,101 states** =

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

$E_g = 2.1$  eV



SE — SE & DE DOS  
DE - - - cross at 5.8 eV

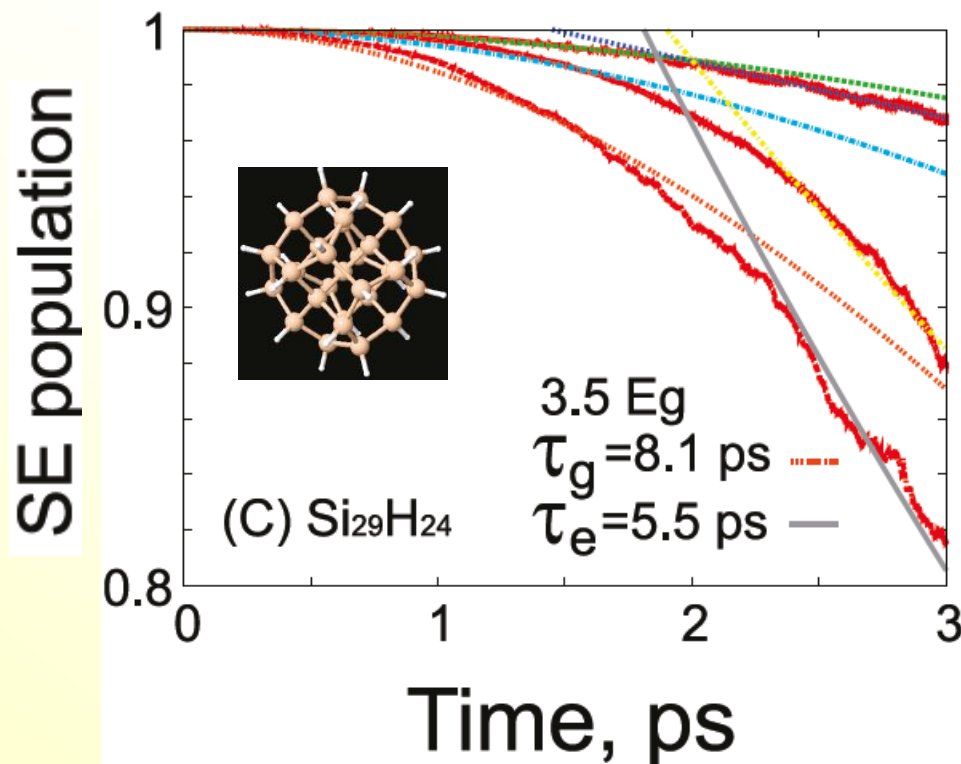
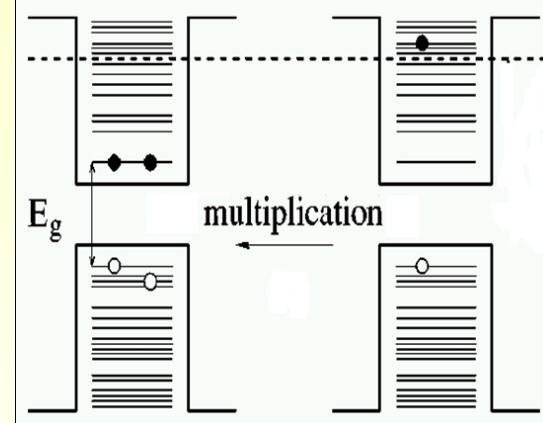




# ME Generation

Kim, Prezhd, *Nano Lett.*, **11**, 1845 (2011)

Kim, Prezhd, *ACS Nano*, **6**, 1239 (2012)



Gaussian + Exponential

Rates increase  
with energy

Phonon-assisted  
Auger at energies  
less than  $2E_g$

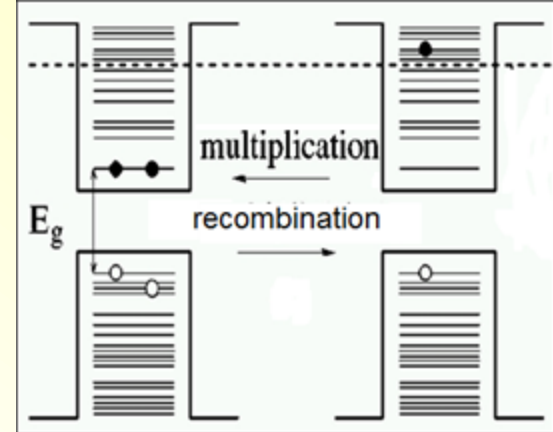
Auger processes are slower than electron-phonon relaxation,  
multiple excitons are created while interacting with light



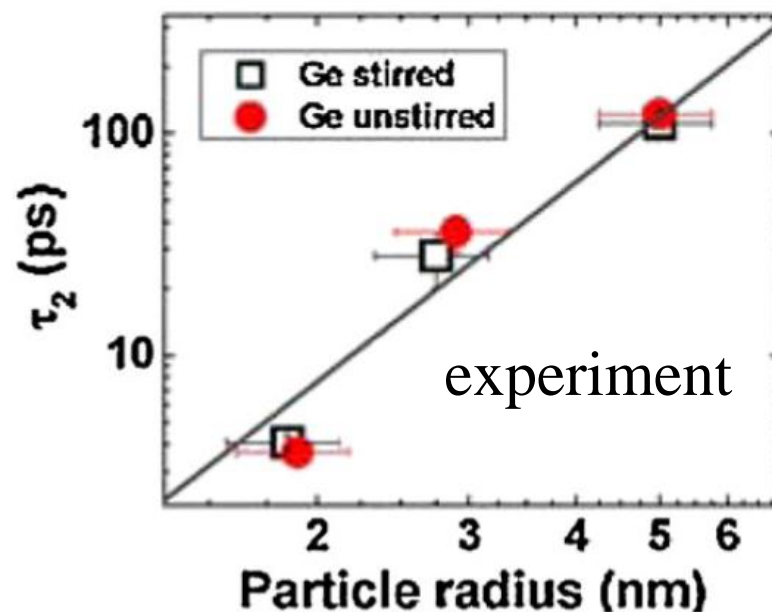
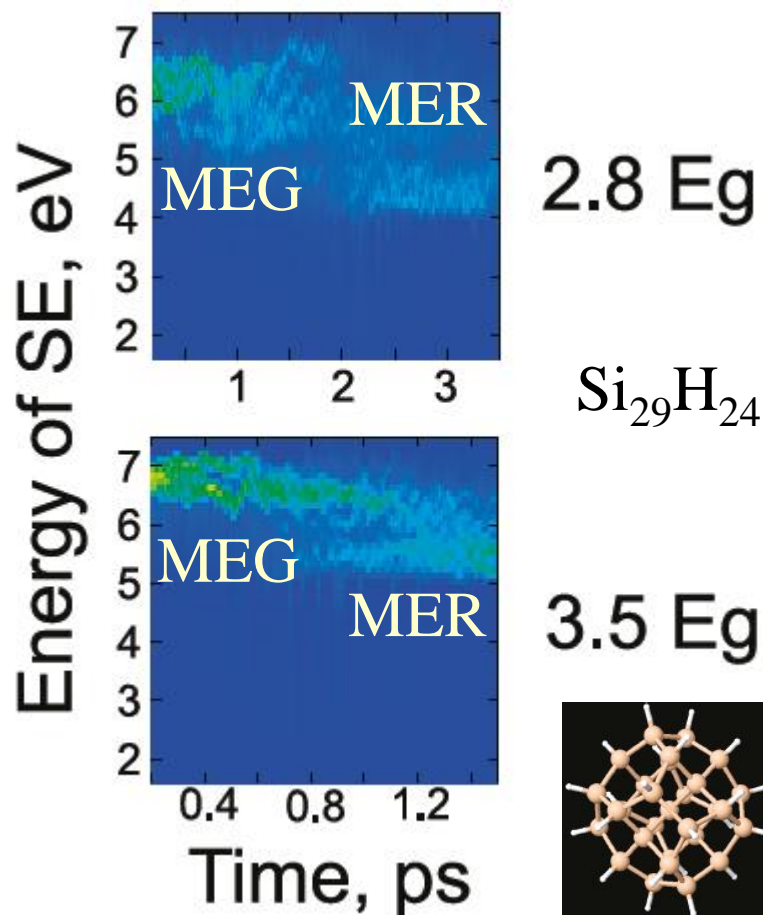
# ME Recombination

Kim, Prezhd, *Nano Lett.*, **11**, 1845 (2011)

Kim, Prezhd, *ACS Nano*, **6**, 1239 (2012)



## SE population



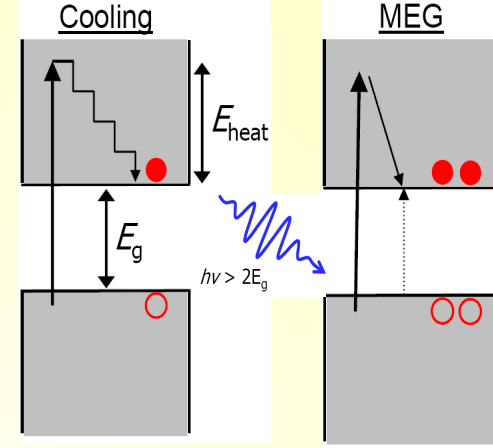
Robel et al. *PRL* **102** 177404 (2009)

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/  
*Phys. Rev. Lett.* **100**, 197402 (2008) /decoherence corrected/  
*J. Am. Chem. Soc.*, **134**, 15648 (2012) /spin-orbit interactions/

## Decoherence based surface hopping/

*J. Chem. Phys.* **111**, 8366 (1999) /stochastic mean-field/  
*Phys. Rev. Lett.* **85**, 4413 (2000) /anti-Zeno effect/  
*J. Chem. Phys.* **137**, 22A545 (2012) /decoherence induced SH/

## Quantum dots

*Chem. Phys. Lett. – Frontier* **460** 1 (2008)  
*Acc. Chem. Res* **42** 2005 (2009)  
*Chem. Science* **2** 400 (2011)

## Quantized Hamilton dynamics

*J. Chem. Phys.* **113**, 6557 (2000)  
*Theor. Chem. Acc.* **116**, 206 (2006)

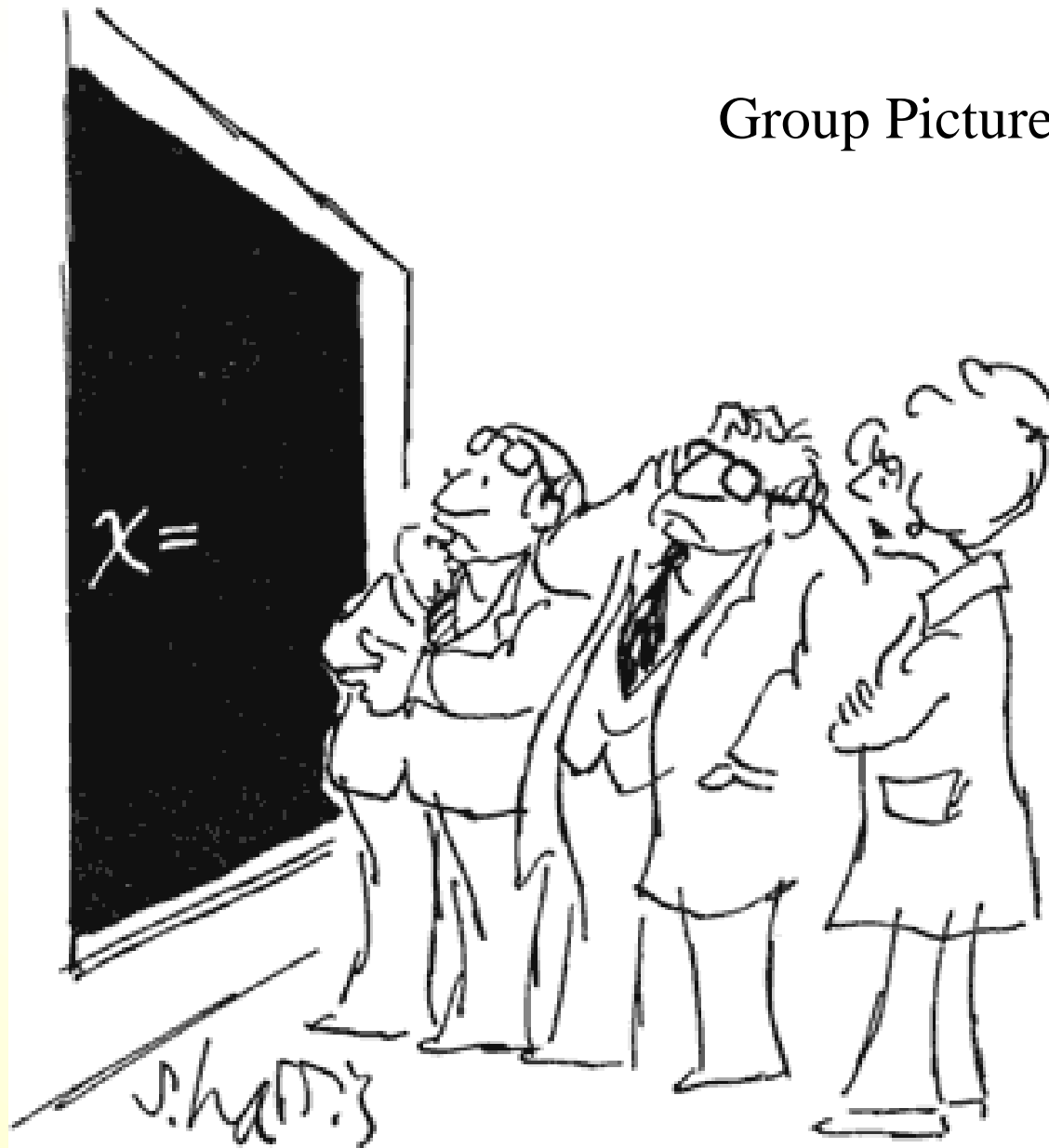
## Quantum-classical Lie bracket

*Phys. Rev. A* **56** 162 (1997)  
*J. Chem. Phys.* **124** 201104 (2006)

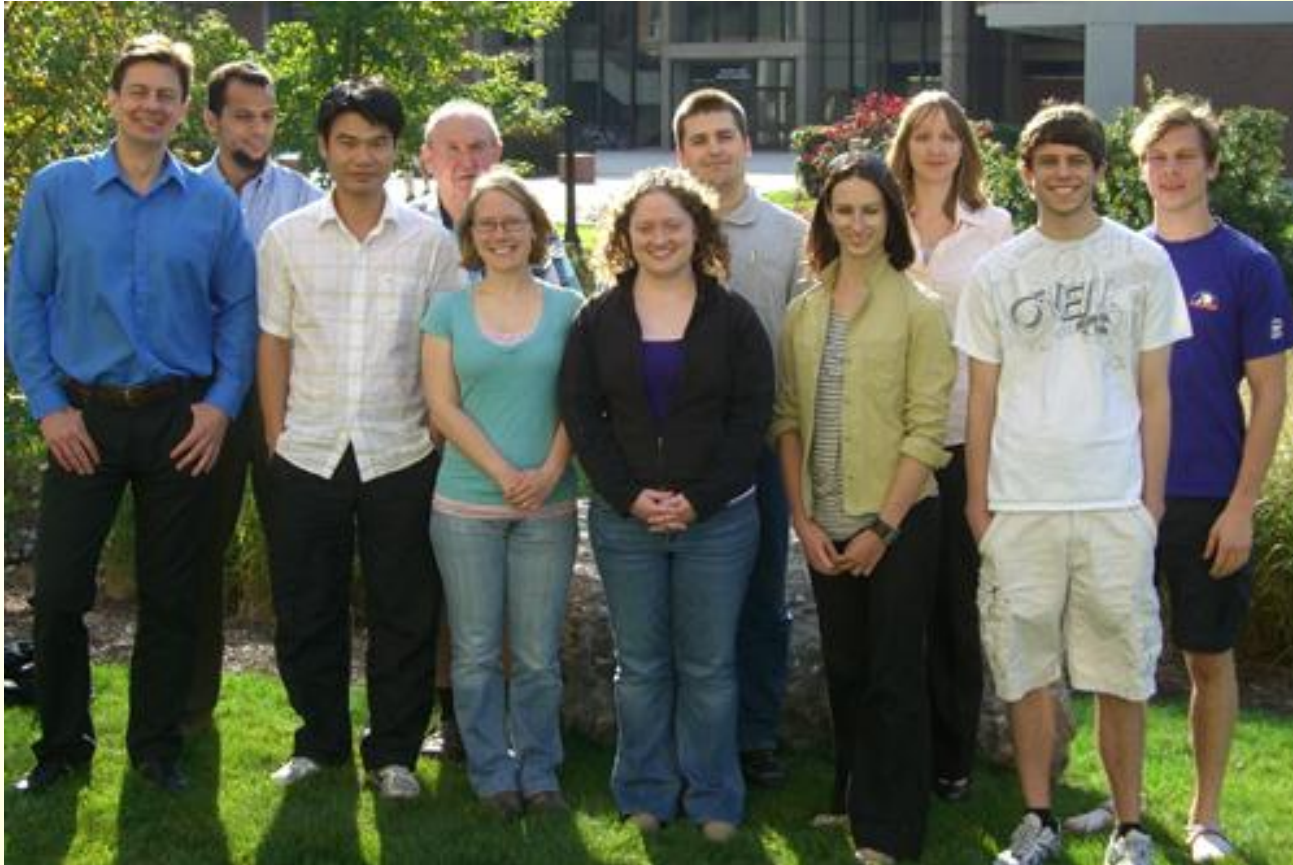
## Bohmian quantum-classical dynamics

*Phys. Rev. Lett.* **86**, 3215 (2001)

## Group Picture



## Group Picture





# 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

Madrid, Hyeon-Deuk, Prezhd, *ACS Nano* **3** 2487 (2009)

Phonon-induced pure-dephasing times, fs

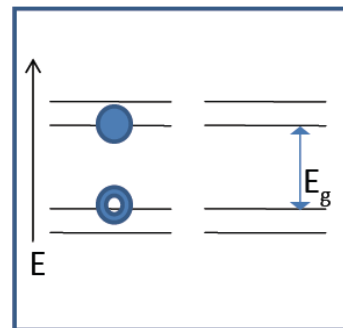
T=300K/100K	Si <sub>29</sub> H <sub>24</sub>	Cd <sub>33</sub> Se <sub>33</sub>	Pb <sub>68</sub> Se <sub>68</sub>	Pb <sub>16</sub> Se <sub>16</sub>
Luminescence	4 / 7	10 / 16	9 / 23	7 / –
ME Generation	4 / 7	5 / 9	5 / 11	4 / –
ME Fission	80 / 310	–	–	–

Luminescence – 50meV linewidth, agree with exp.

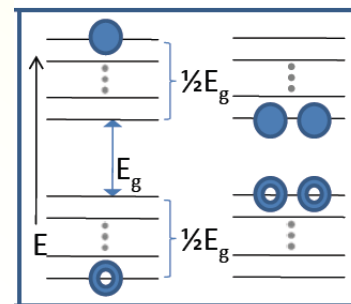
ME Generation – rapid 10fs dephasing

ME Fission – 100fs

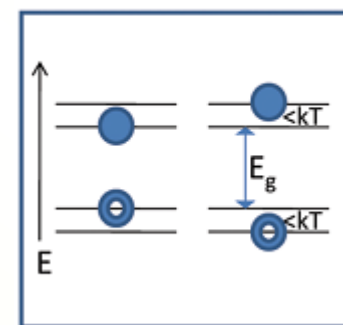
Luminescence



ME Generation



ME Fission



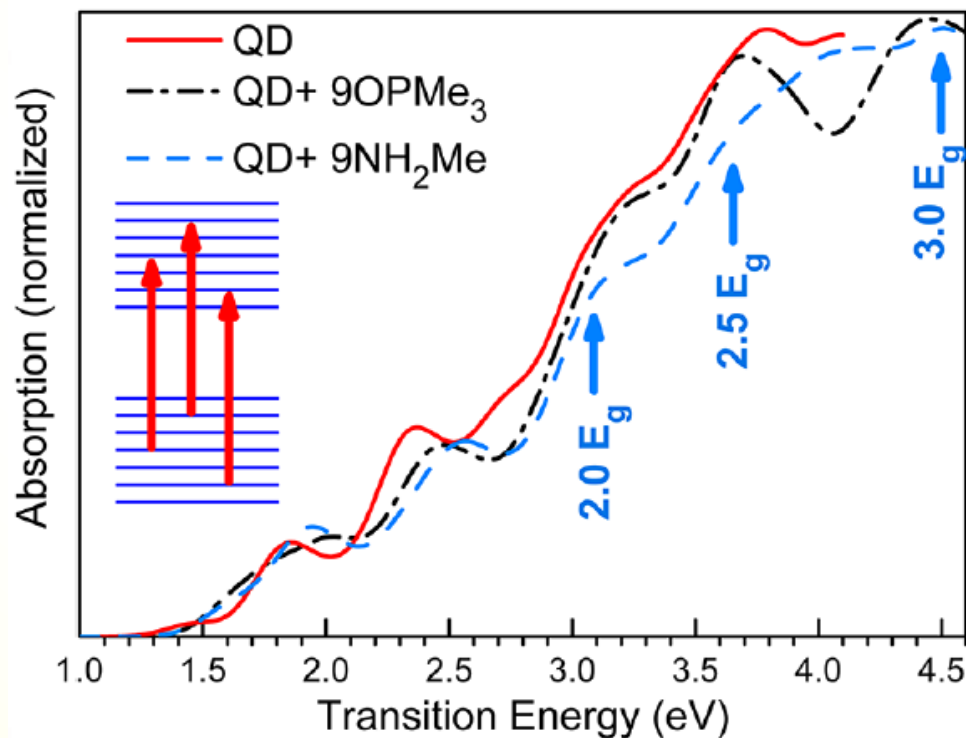
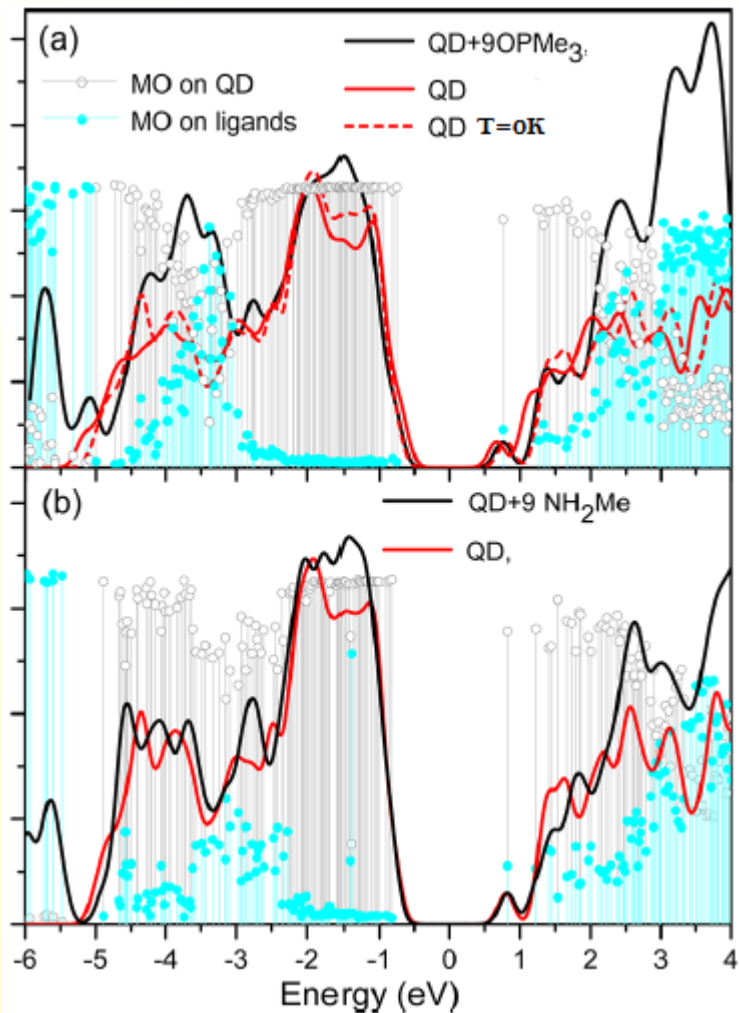






# More Realistic Ligands: Electronic Structure

Kilina, Velizhanin, Ivanov, Prezhdov, Tretiak *ACS Nano*, **6**, 6515 (2012)

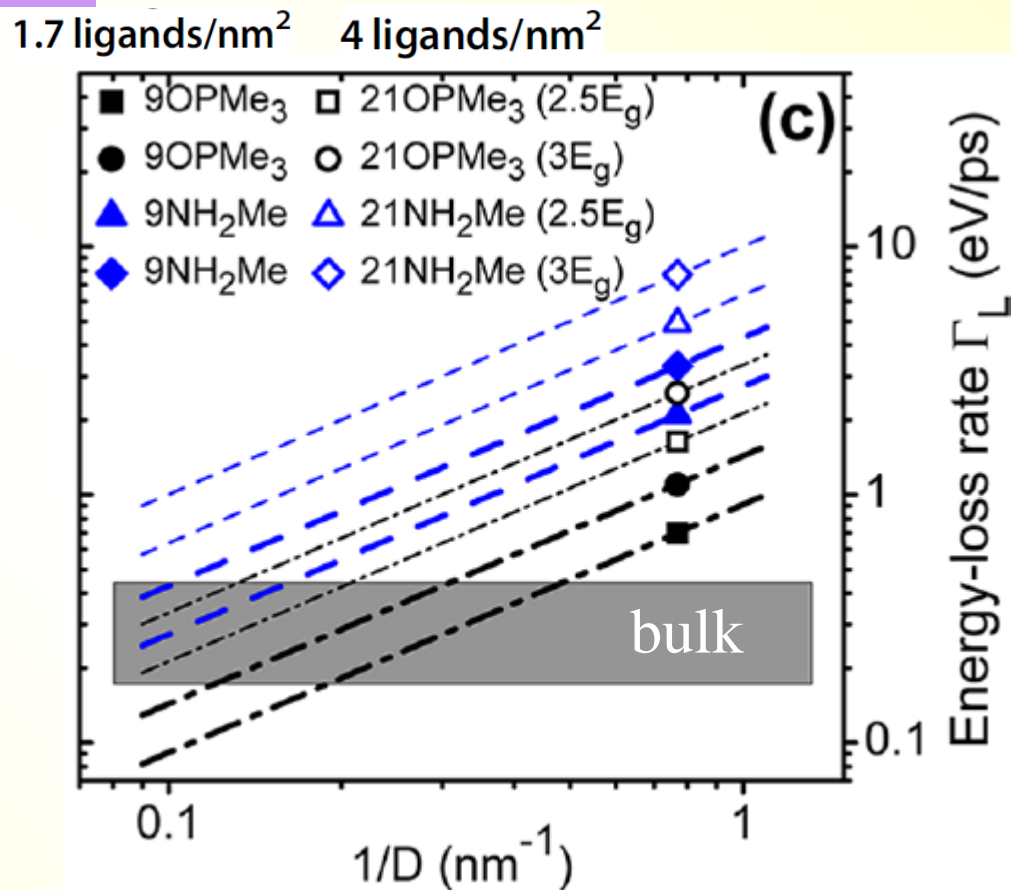
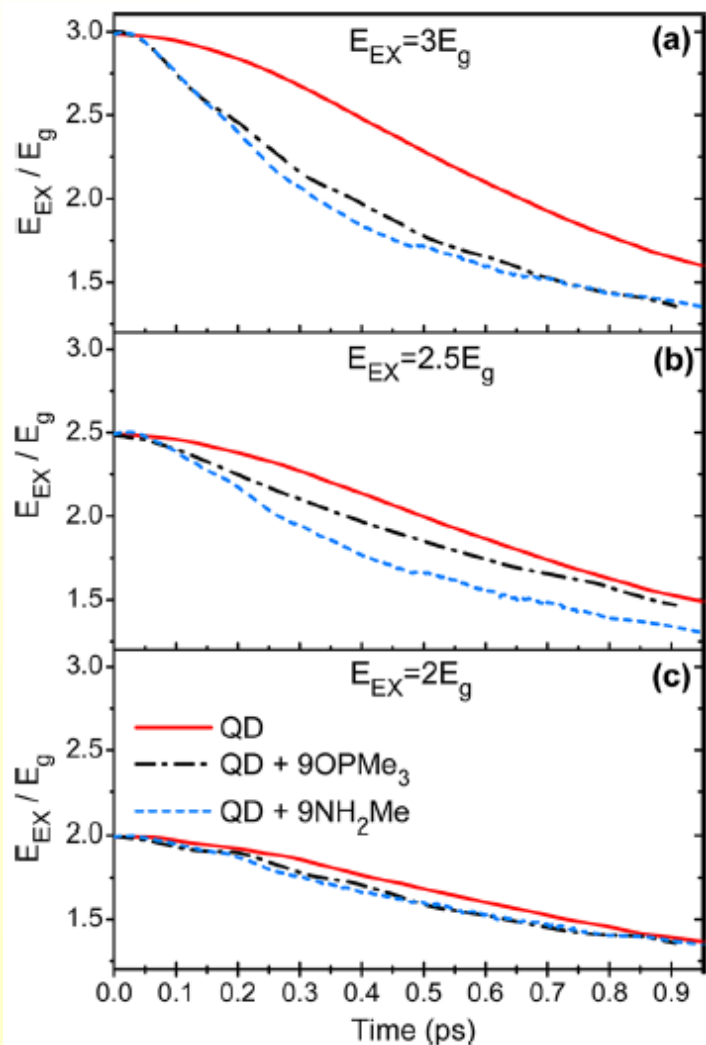


Ligands start contributing  
at energies of 2.5-3 $E_g$



# Ligand Contribution to Electron-Phonon Relaxation

Kilina, Velizhanin, Ivanov, Prezhdov, Tretiak *ACS Nano*, **6**, 6515 (2012)

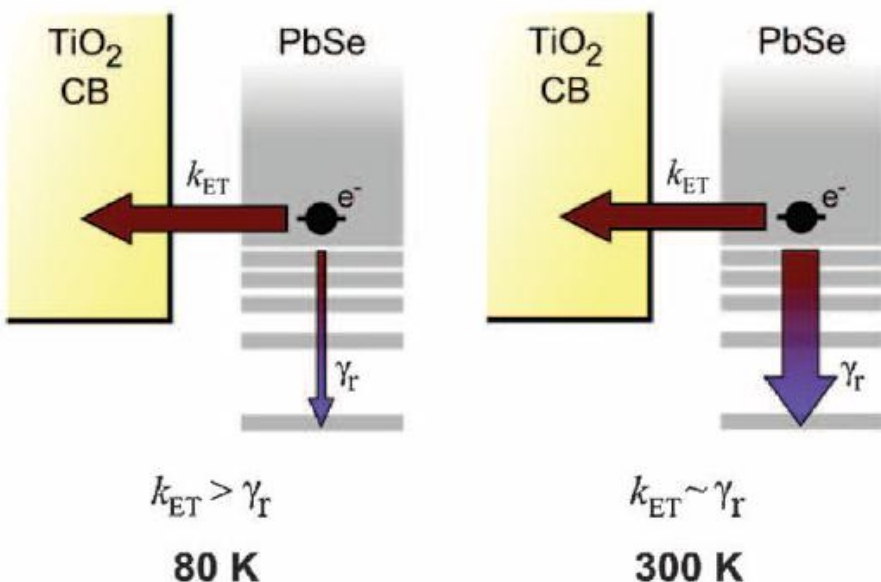


Ligands contribute up to 10nm QDs



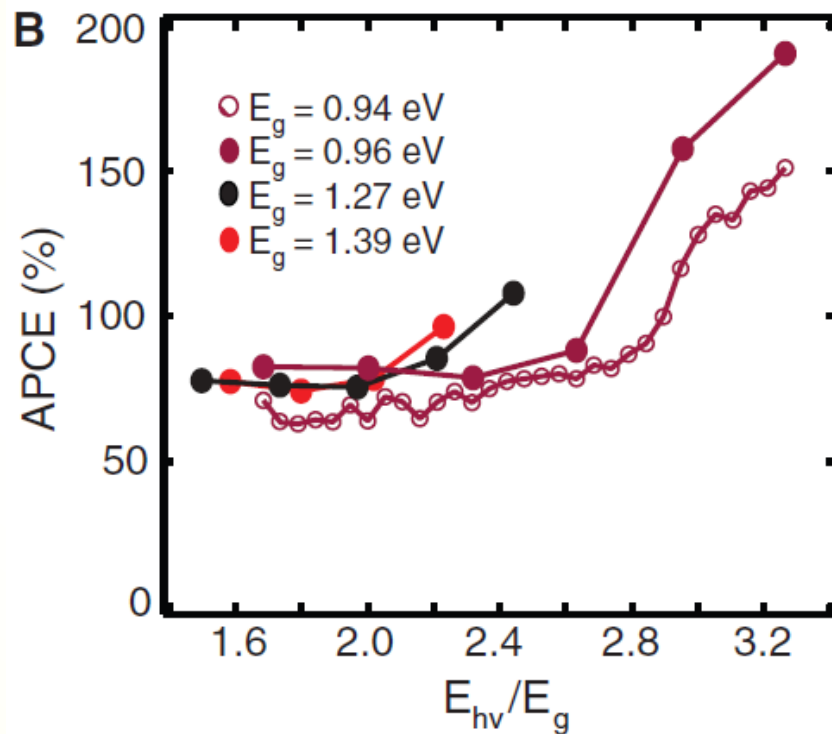


# Electron Transfer from QDs to $\text{TiO}_2$



50 fs injection time

Zhu group, *Science* **328** 1543 (2010)



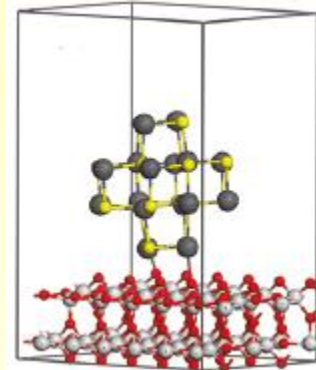
absorbed photon-to-current efficiency

Parkinson group, *Science* **330** 63 (2010)

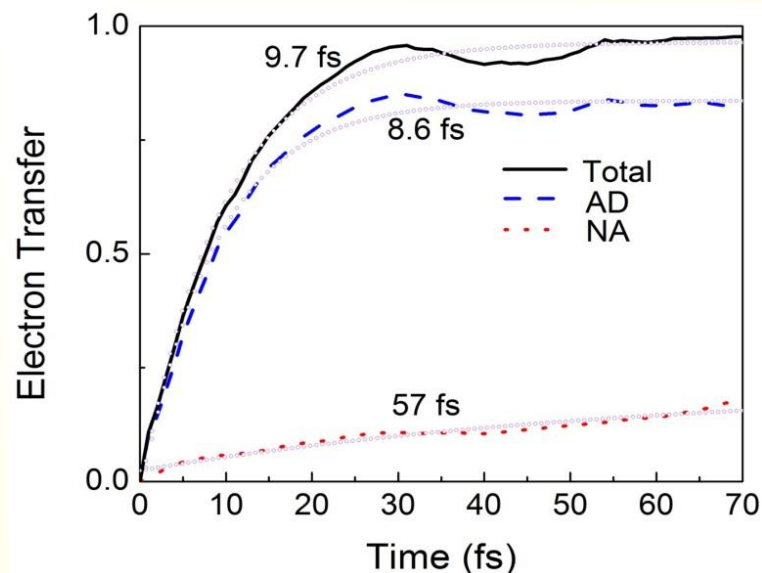
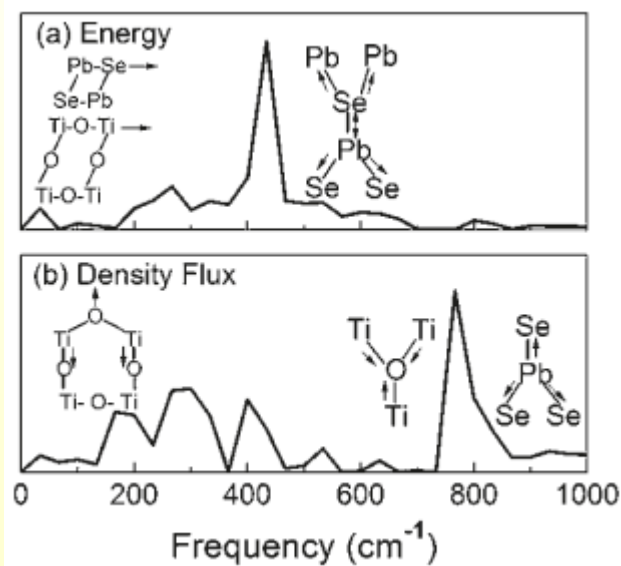
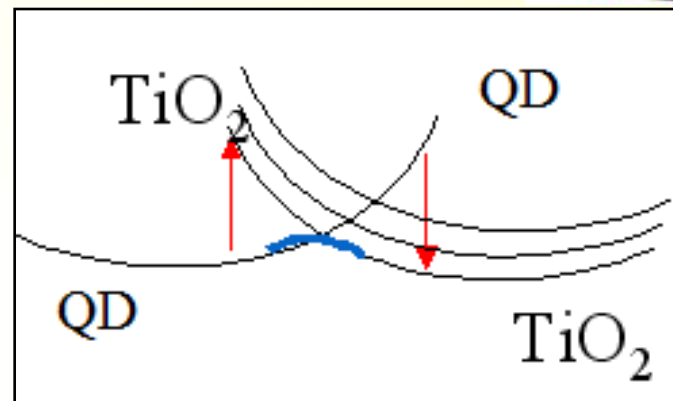


# $e^-$ transfer from QDs to $\text{TiO}_2$

Long, Prezhdo J. Am. Chem. Soc. **133** 19240 (2011)



- 10 fs time; mostly adiabatic ET
- strong donor-acceptor coupling
- ET is driven by high frequency polar phonons





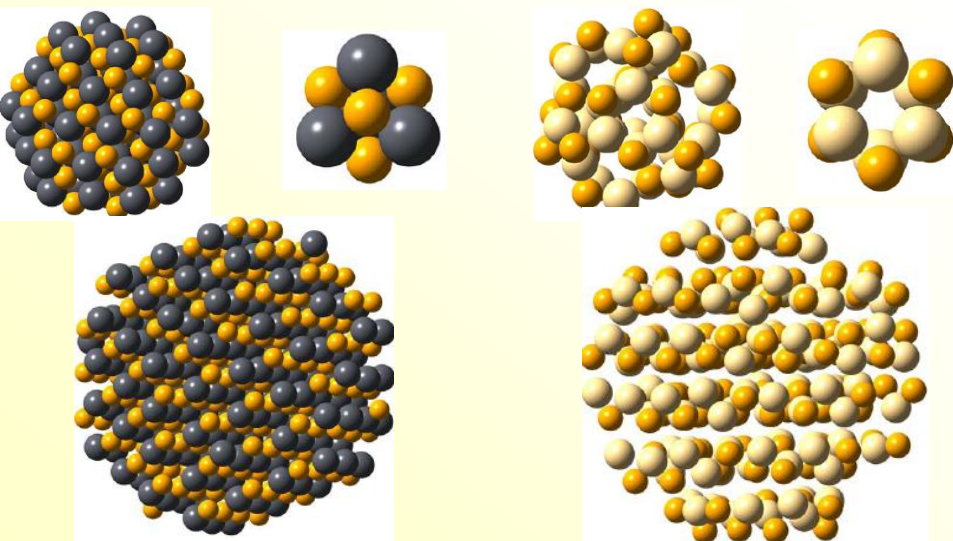
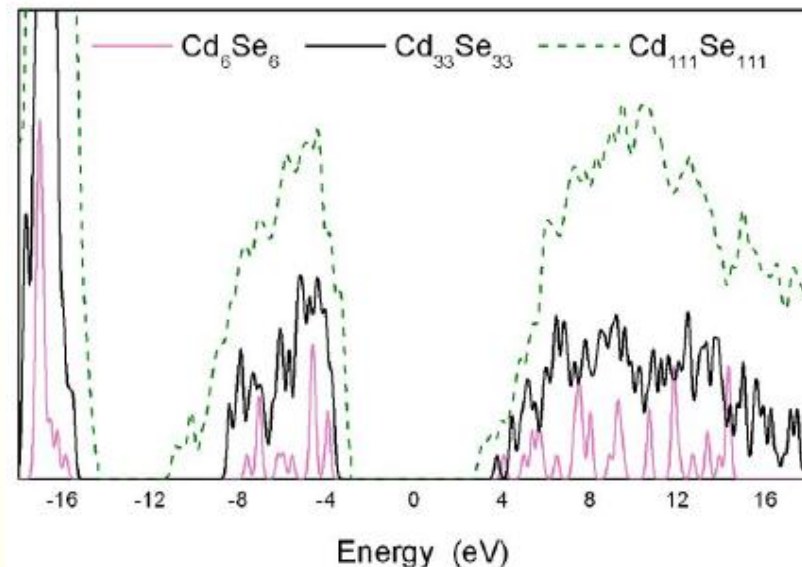
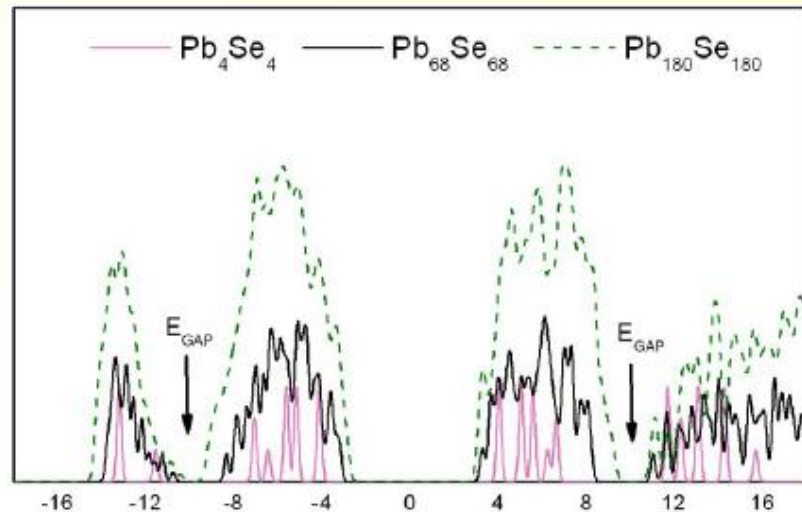




# Hartree-Fock Band Structure

Fischer, Isborn, Prezhd, *Chem. Science*, **2**, 400 (2011)

1. Small dots represent large dot DOS
2. Huge one-electron gap
3. Symmetric vs. asymmetric DOS
4. Secondary gaps in PbSe DOS

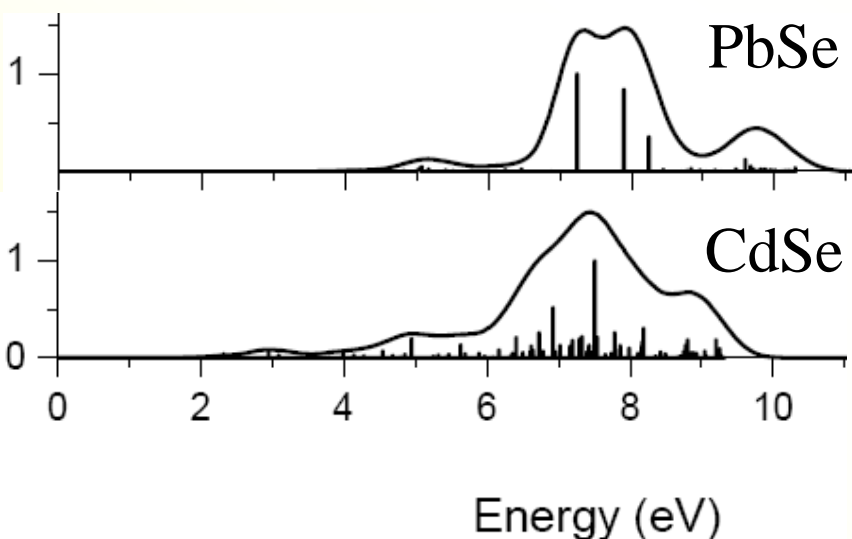




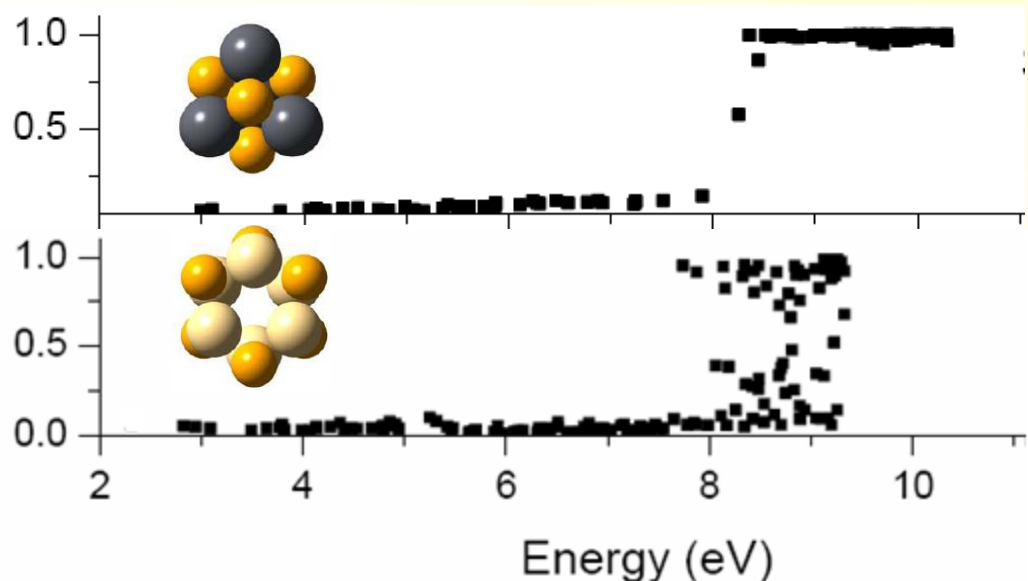
# Spectra and Multiple Excitons

Fischer, Isborn, Prezhdov, *Chem. Science*, **2**, 400 (2011)

spectra (SAC-CI calculations)



fraction of multiple excitons



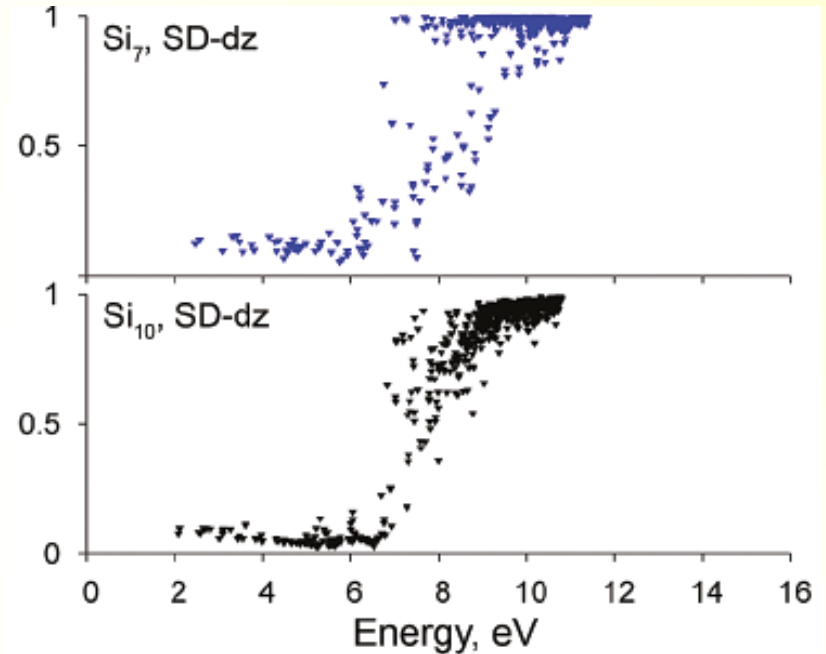
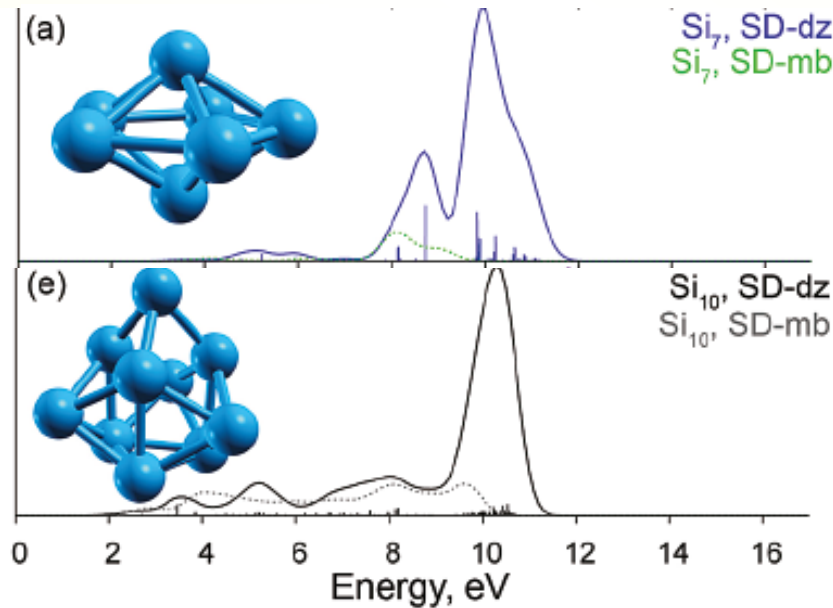
CdSe spectra agree  
with experiment  
*JACS* **128**, 629 (2006)

1. Sharp onset of multiple excitons
2. Above threshold: double excitons in PbSe; single, double and superpositions in CdSe



# Direct Mechanism: Si Clusters

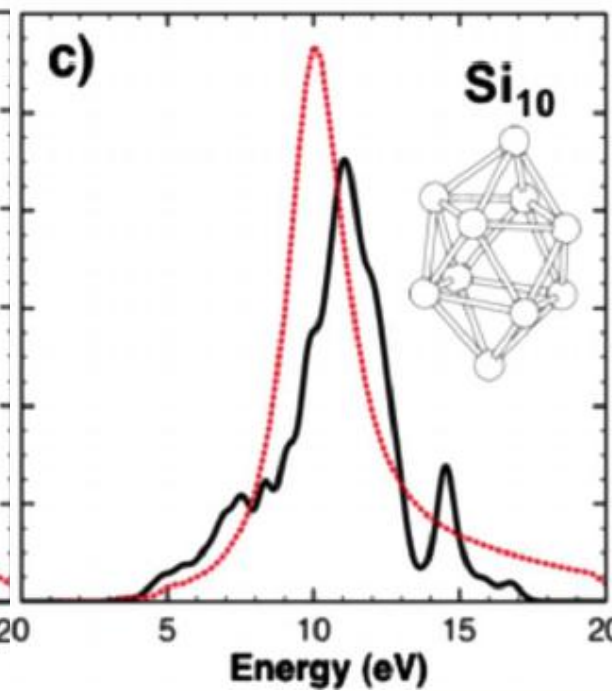
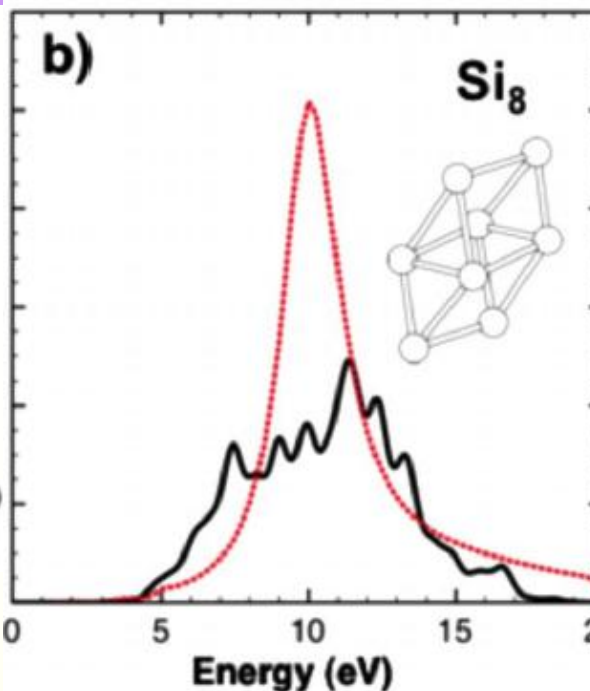
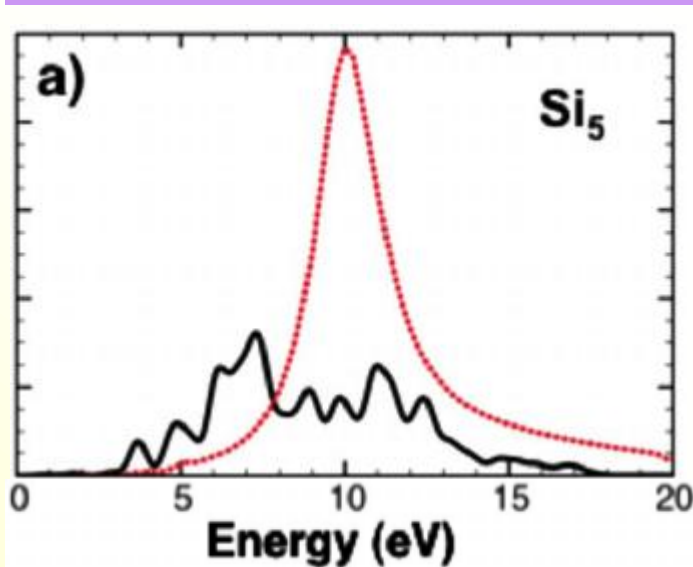
spectra



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



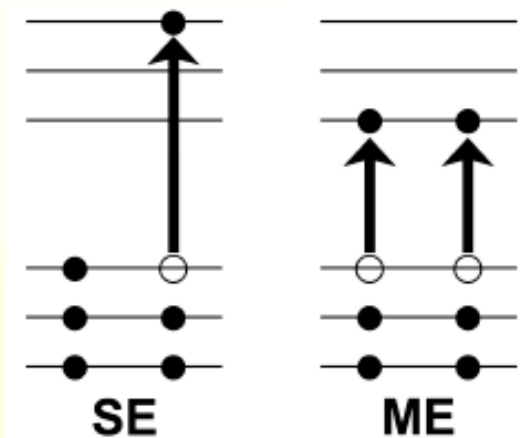
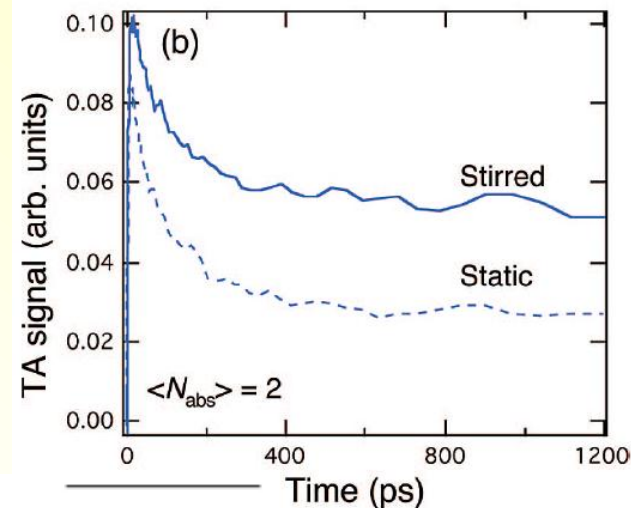
Idrobo et al. *PRB* **79** 125322 (2009)

$$\sigma_{\text{abs}}(\omega) = \frac{9\omega V}{c} \frac{\epsilon_2(\omega)}{[\epsilon_1(\omega) + 2]^2 + \epsilon_2(\omega)^2}$$

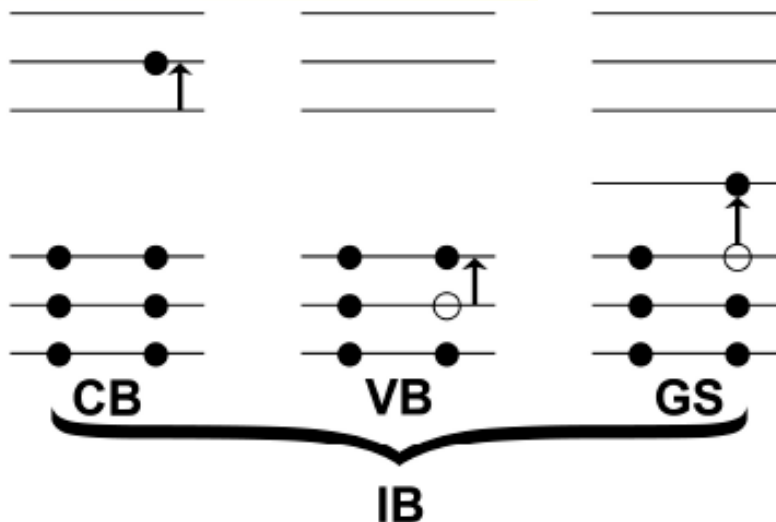
Classical Mie theory matches ab initio calculations on very small clusters, independent of bonding configuration



# Defects Introduce New Transitions



ideal QDs



anion

cation

dopant  
dangling bonds





# Calculations for Charged PbSe Dots

Fischer, Isborn, Prezhd, *Chem. Science*, **2**, 400 (2011)

Conduction band  
transitions  
overwhelm MEs

Much higher  
ME threshold

