# Nonadiabatic Molecular Dynamics with Kohn-Sham DFT: Modeling Nanoscale Materials

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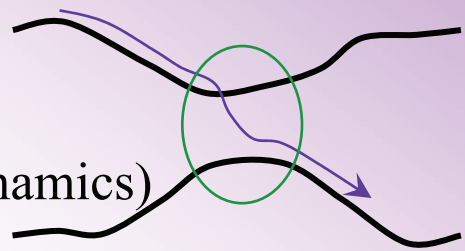
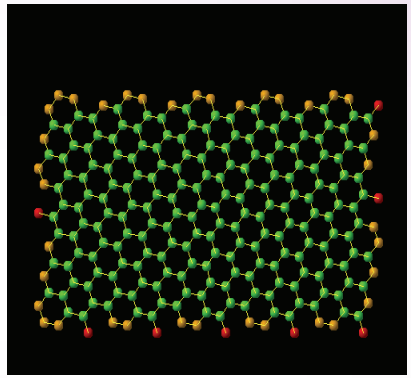
**CSCAMM – Mar 11, 2010**

# Outline

- Nonadiabatic MD with Kohn-Sham DFT
  - Advantages & Validity
  - Quantum Backreaction & Branching (Nuclear Dynamics)
  - Decoherence & Zero-Point Energy

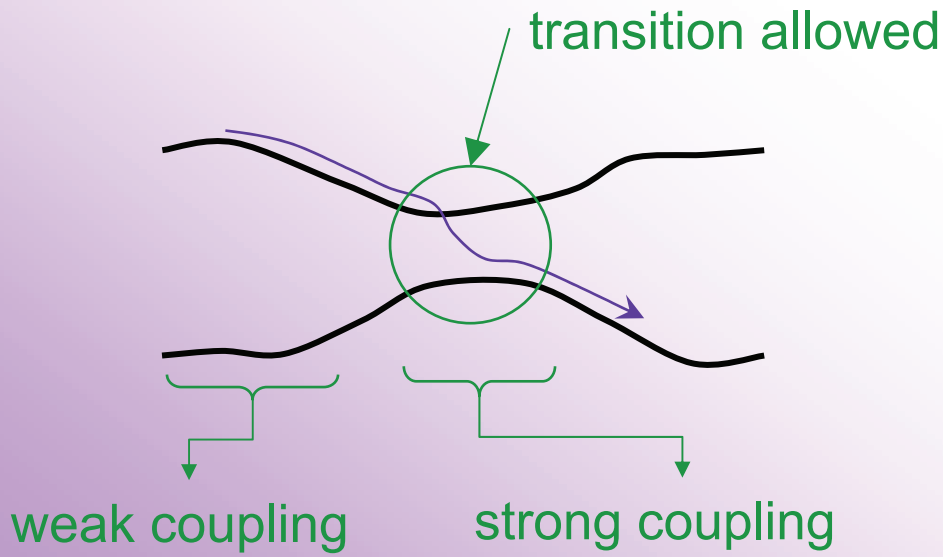


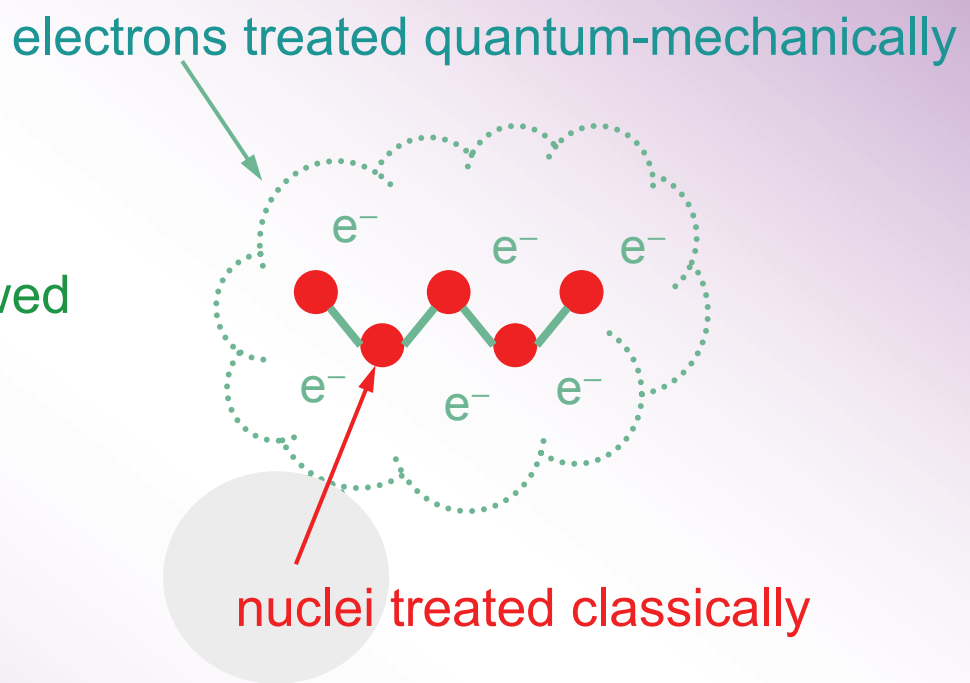
- Carbon Nanotubes & Nanoribbons
  - Luminescence Quenching
  - Singlet-Triplet Transitions
  - Structural Defects



# Adiabatic vs. Nonadiabatic MD

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



# Time-Domain DFT for Nonadiabatic Molecular Dynamics

Electron density derives from Kohn-Sham orbitals

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

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 $$\varphi_p(x,t)=\sum_\alpha c_p^\alpha(t)\chi^\alpha(x)$$

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

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

# Time-Domain DFT in Many-Body Kohn-Sham Basis

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

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

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

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

non-zero only if different in one orbital

# Open Theoretical Questions

- ✓ 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

# Nuclear Evolution: Ehrenfest

"Interfacial ET" Stier, Prezhdo *JPC* ***B*** **106** 8047 (2002)

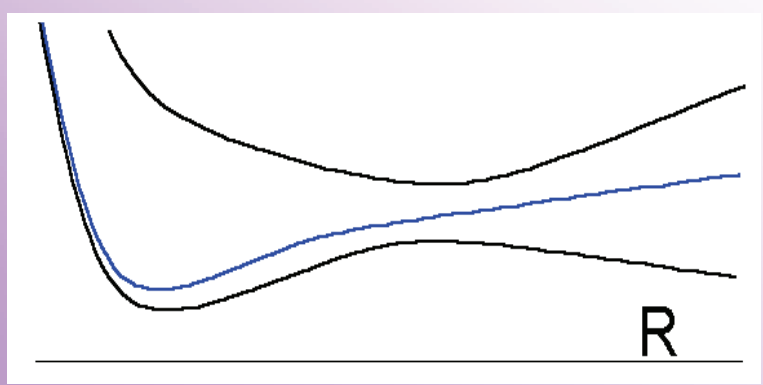
Total energy of electrons and nuclei

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

is conserved

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

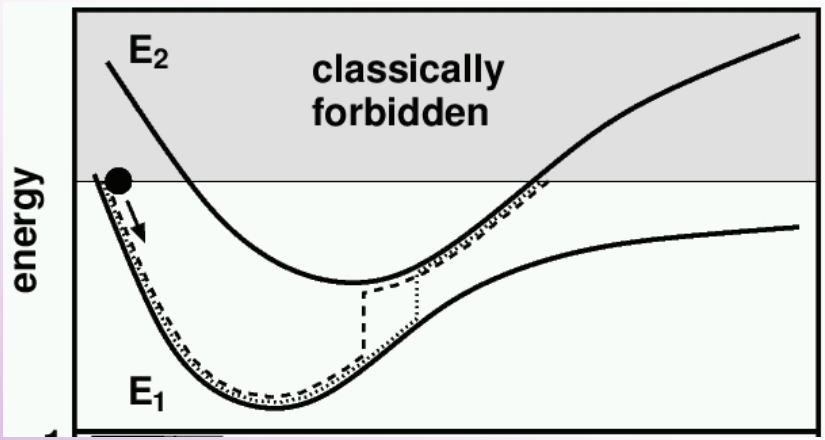
time-dependent Hellmann-Feynman theorem gives Newton equation




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

quantum force

# Nuclear Evolution: 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);

Velocity Rescaling:
Tully, Hammes-Schiffer
*JCP*. **101**, 4657 (1994).

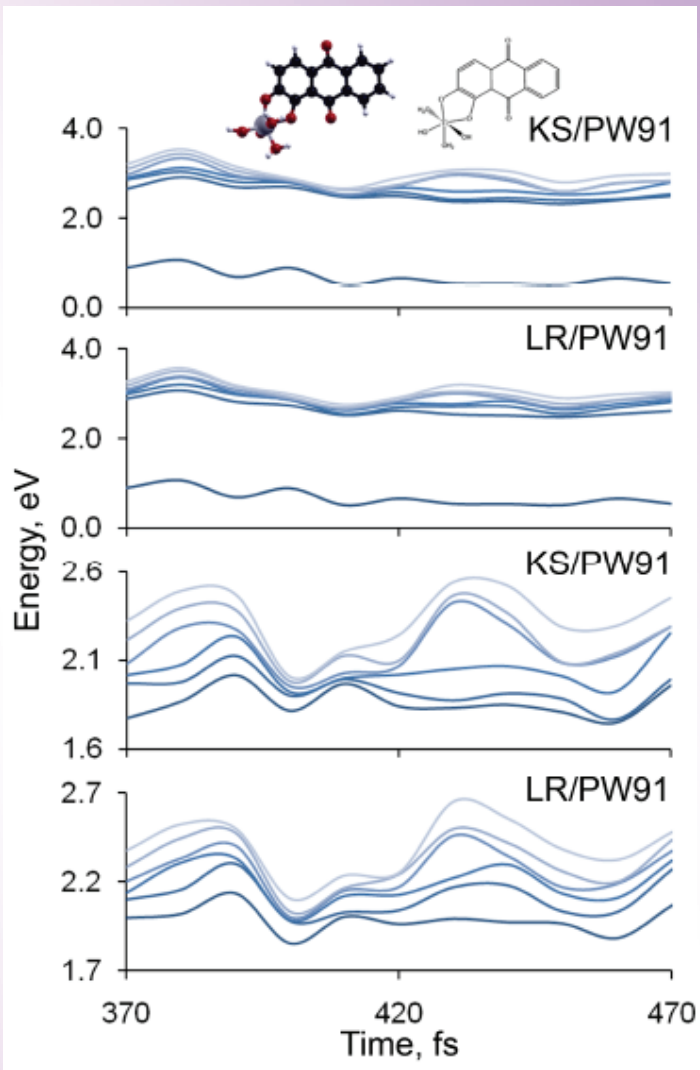
Detailed balance:
Parahdekar, Tully *JCP* **122**, 094102 (2005)

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

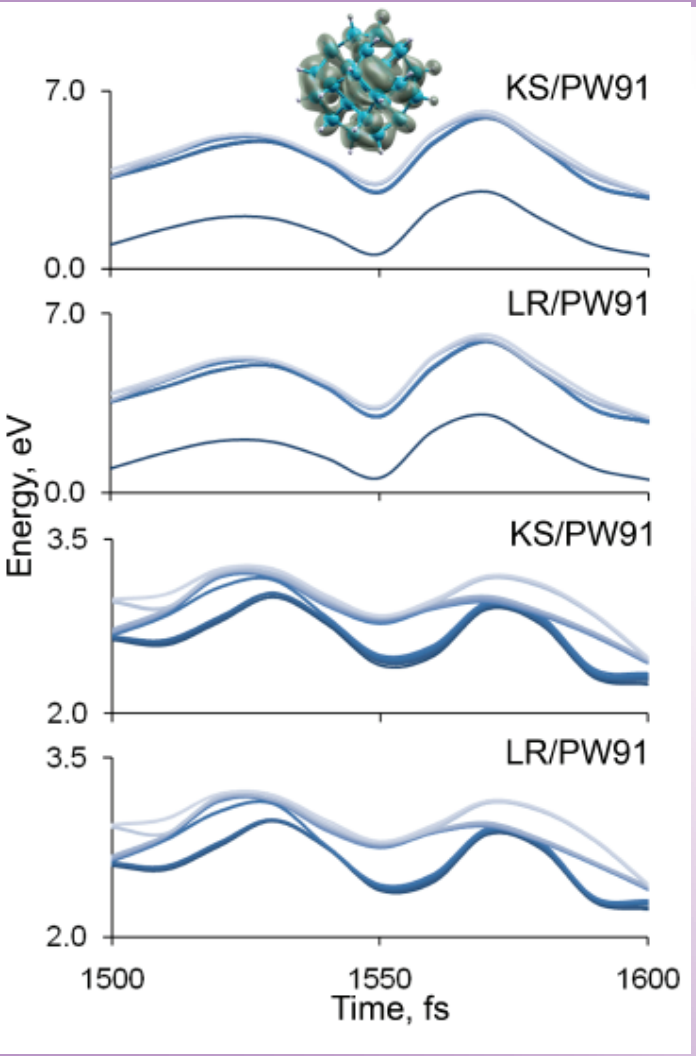
# Why Kohn-Sham Basis Works with Our Systems

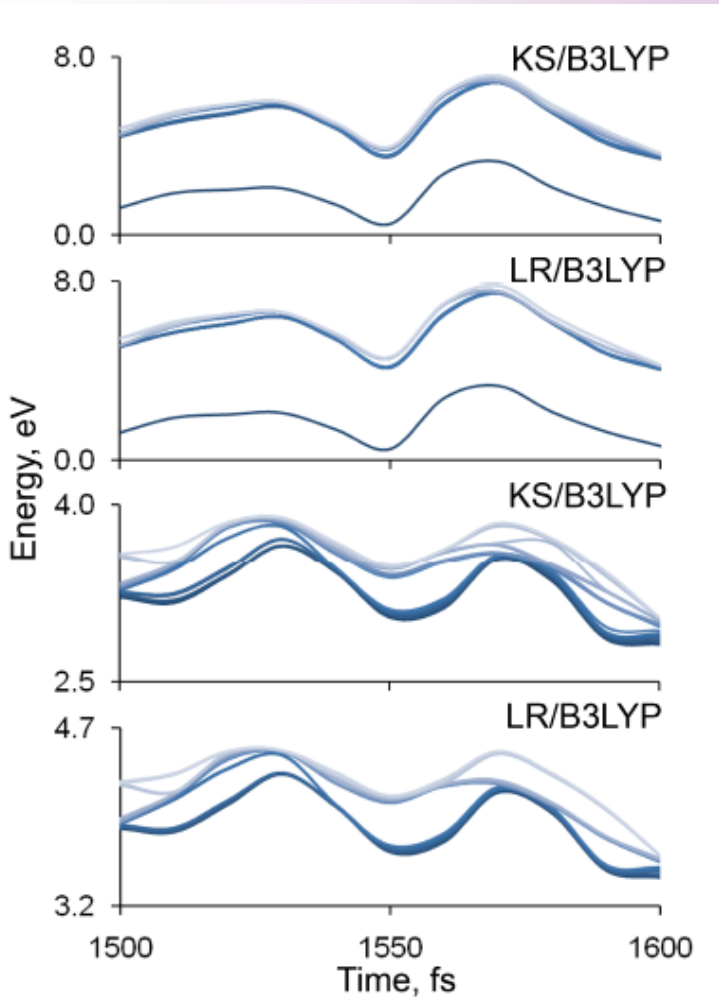
1. KS excitations close to LR/TDDFT (in contrast to HF and CIS)
2. No bond-breaking, conformational changes, etc.
3. Many-electron systems, single excitation is a small perturbation
4. Averaging over many initial conditions and pathways

<u>Electron Transfer Example:</u>



# Silicon Quantum Dot



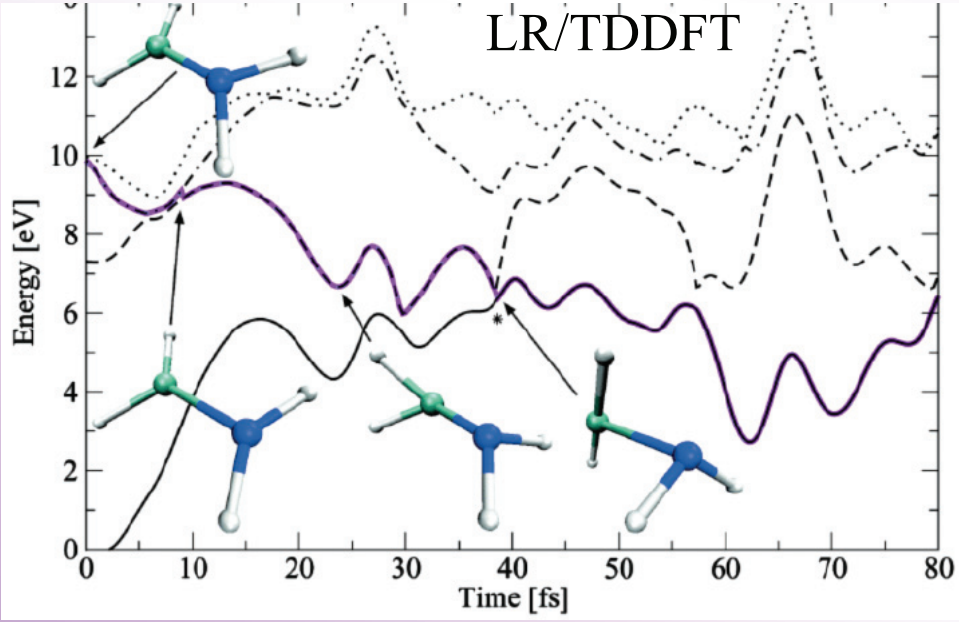




KS and LR agree better for

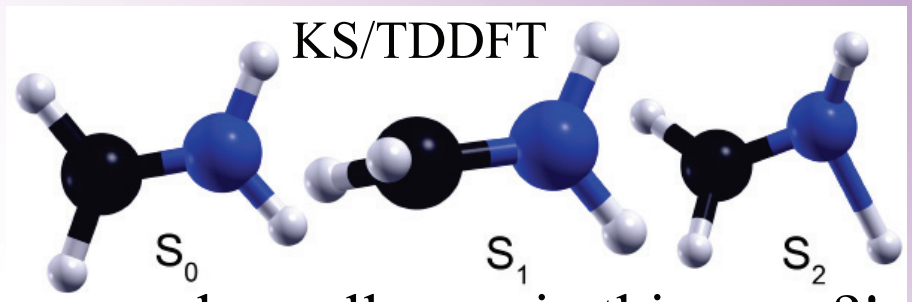
PW91 (pure DFT)

than B3LYP (hybrid)

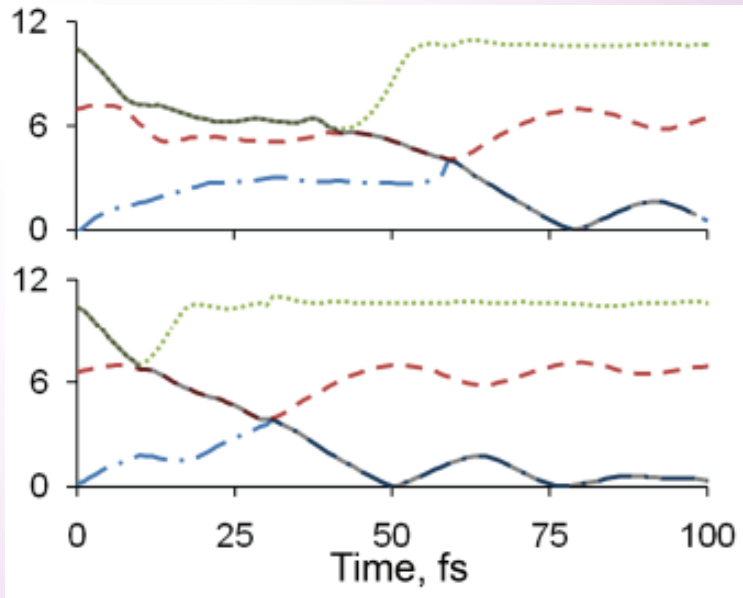
# Small Molecule With Isomerization



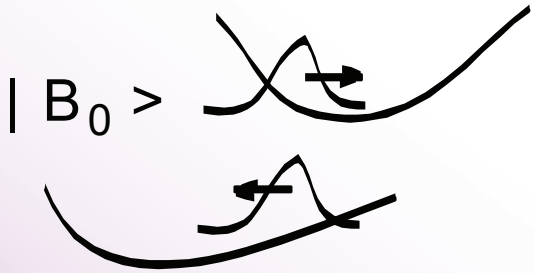

Tapavicza, Tavernelli, Rothlisberger
*PRL* **98,** 023001(2007): LR/TDDFT

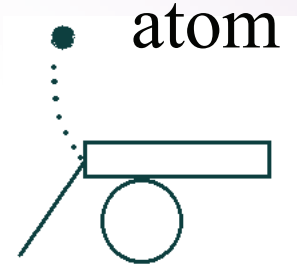


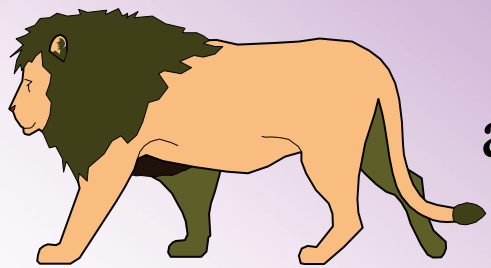

works well even in this case ?!



# Schrodinger Cat and Decoherence



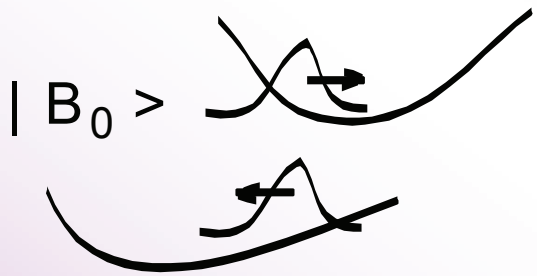

cat


System - radioactive atom; Bath - cat

In Nanomaterials

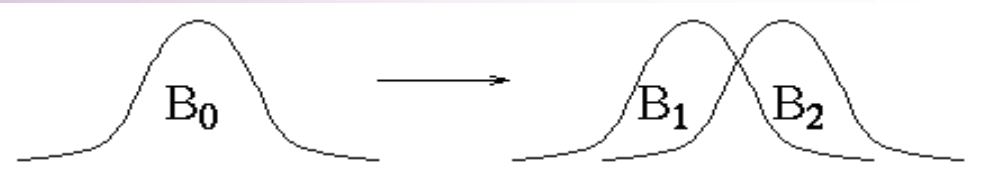
System - electrons, spins; Bath - phonons

# Franck-Condon Factor and Decoherence




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

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




Bath (vibrational) wave functions diverge

This affects evolution of (electronic) system

# Decoherence and Surface Hopping

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

$$\begin{Vmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{Vmatrix} \rightarrow \begin{Vmatrix} \rho_{11} & \rho_{12}\left\langle B_2 \middle| B_1 \right\rangle \\ \rho_{21}\left\langle B_1 \middle| B_2 \right\rangle & \rho_{22} \end{Vmatrix} \quad \rho_{12} \rightarrow 0$$

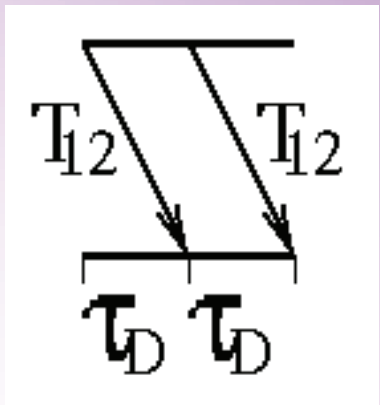
on decoherence time scale

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

# Quantum Zeno Effect

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

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




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

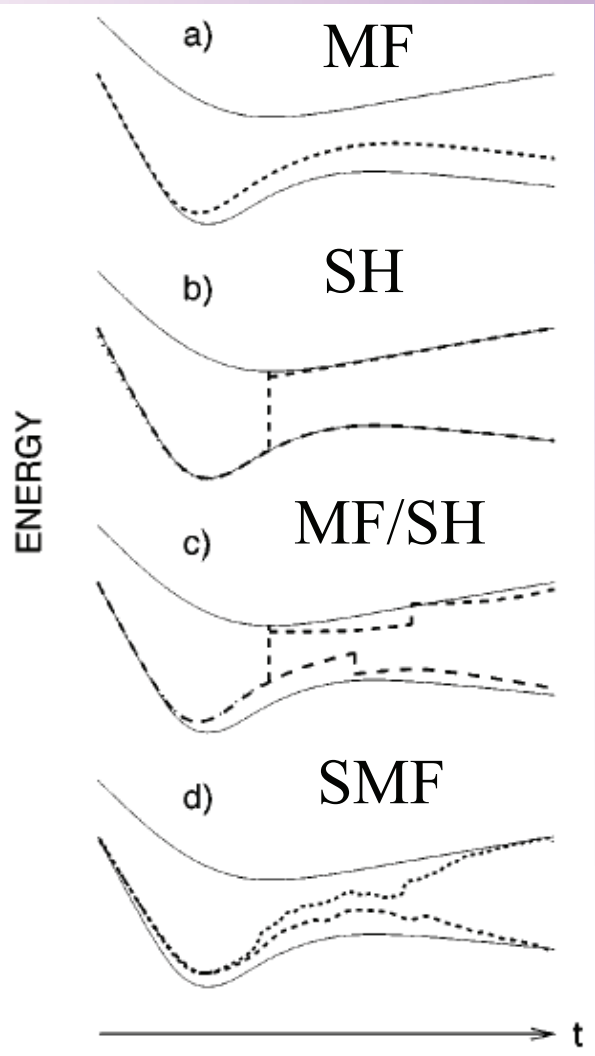
$$|d\Psi\rangle = -iH|\Psi\rangle dt - \frac{\gamma}{2} L^{+}L|\Psi\rangle dt + \sqrt{\gamma}L|\Psi\rangle dW$$

$L$ – system-bath interaction

$\gamma$ – decoherence rate

<u>Advantages</u>

1. Includes decoherence
2. Gives branching
3. Infinitesimal velocity rescalings

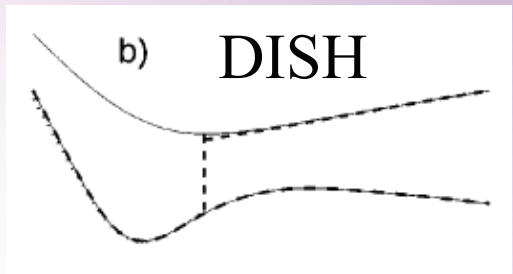


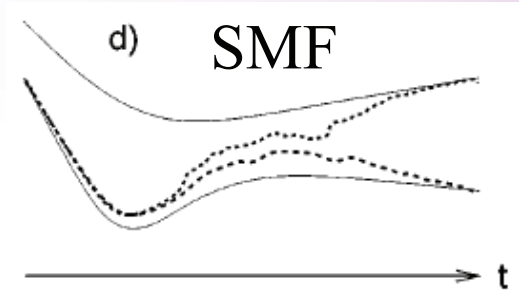
# Decoherence Induced Surface Hopping (DISH)

Evolve in an adiabatic state.

Hop when a decoherence event occurs.

Rescale velocity as before in SH.



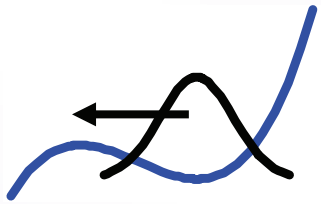




## Advantages

1. Includes decoherence
2. Gives branching
3. Nuclear evolution in pure states

# 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

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

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

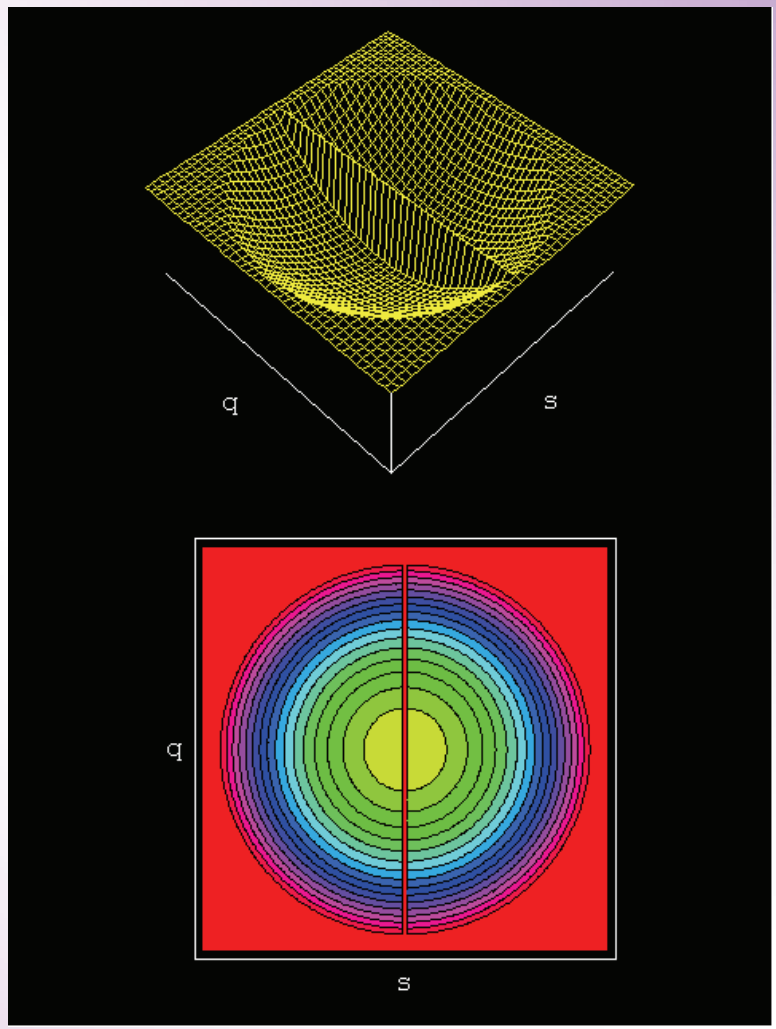
the infinite hierarchy is terminated by a closure

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

# Harmonic Oscillator
## in Mapped QHD-2

hbar
mass
$\Longrightarrow$
hbar
mass

QHD-2 takes care of
zero-point-energy

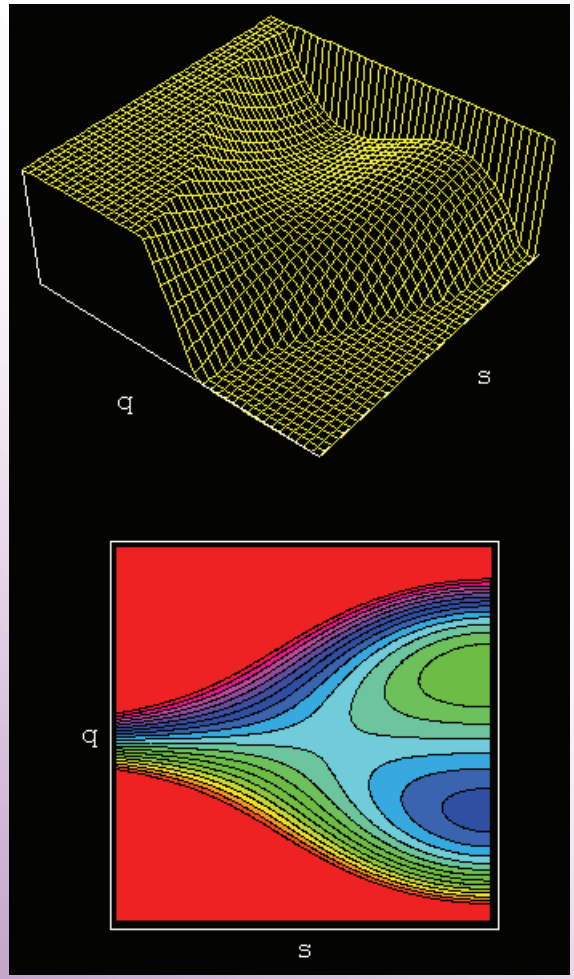


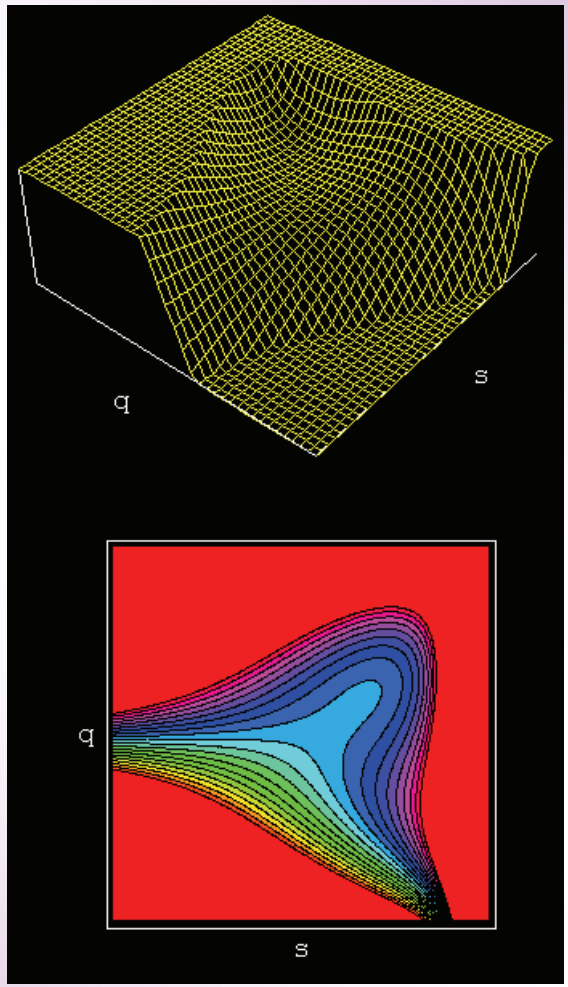
# Metastable Cubic Potential

## in Mapped QHD-2

hbar

mass




QHD-2 gives tunneling

hbar

mass

# 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

starting point for many methods:
Ehrenfest, multiconfiguration quantum-classical

problems with Jacobi identity:

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

Alternative definition:

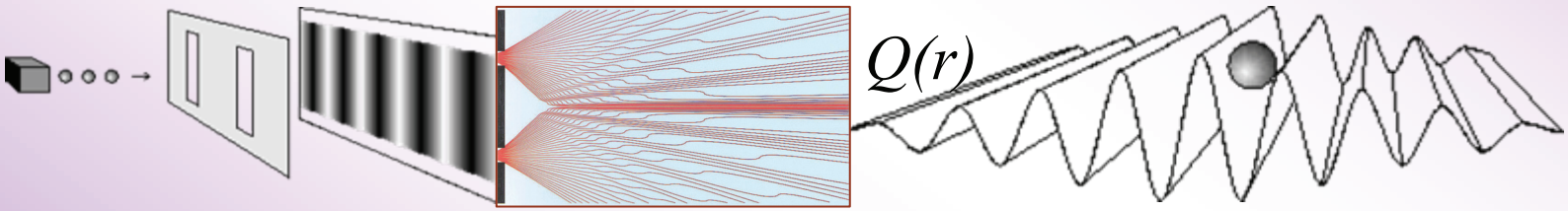
$$[A,B]_{\mathrm{qc}} = -\frac{i}{\hbar}[A,B] - i\left.\frac{\partial[A,B]}{\partial\hbar}\right|_{\hbar=0}$$

# Bohmian Quantum-Classical Mechanics

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

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

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




Quantum (r) – Classical (R)

$M\ddot{R} = -\nabla_R\left[V_R(R) + V_{rR}(r,R)\right]$ drop $Q(R), Q(r,R)$

$m\ddot{r} = -\nabla_r\left[V_r(r) + V_{rR}(r,R) + Q(r)\right]$

Advantage

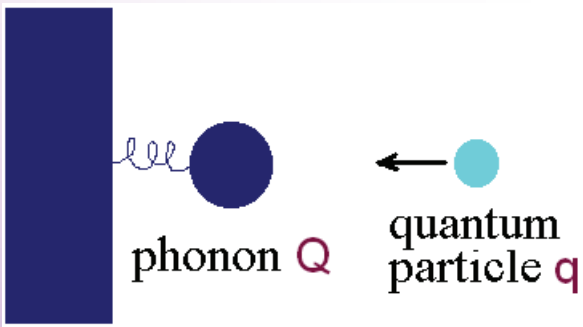
Branching

# Example

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

## Highly simplified representation of $O_2$ 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)

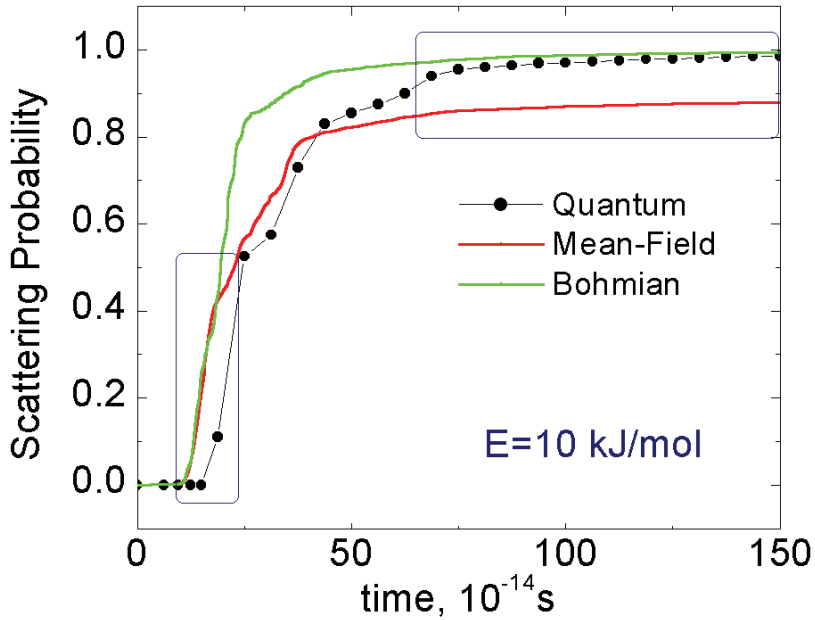



$$H(q,Q) = T_q + T_Q + V_q(q) + V_q(Q) + V_{qQ}(q,Q)$$

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

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

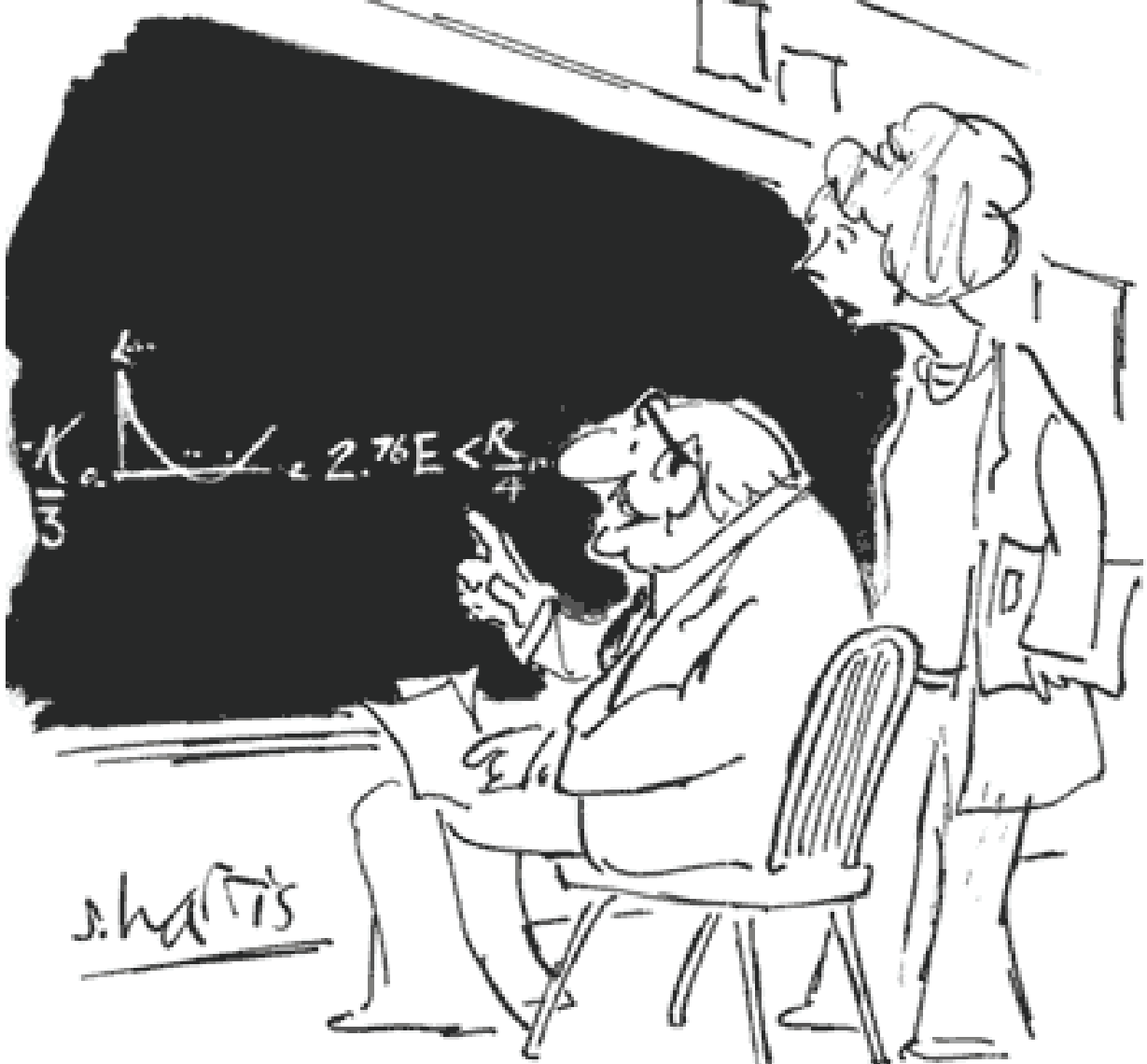
$$V_{qQ}(q,Q) = Ae^{-B(q-Q)}$$



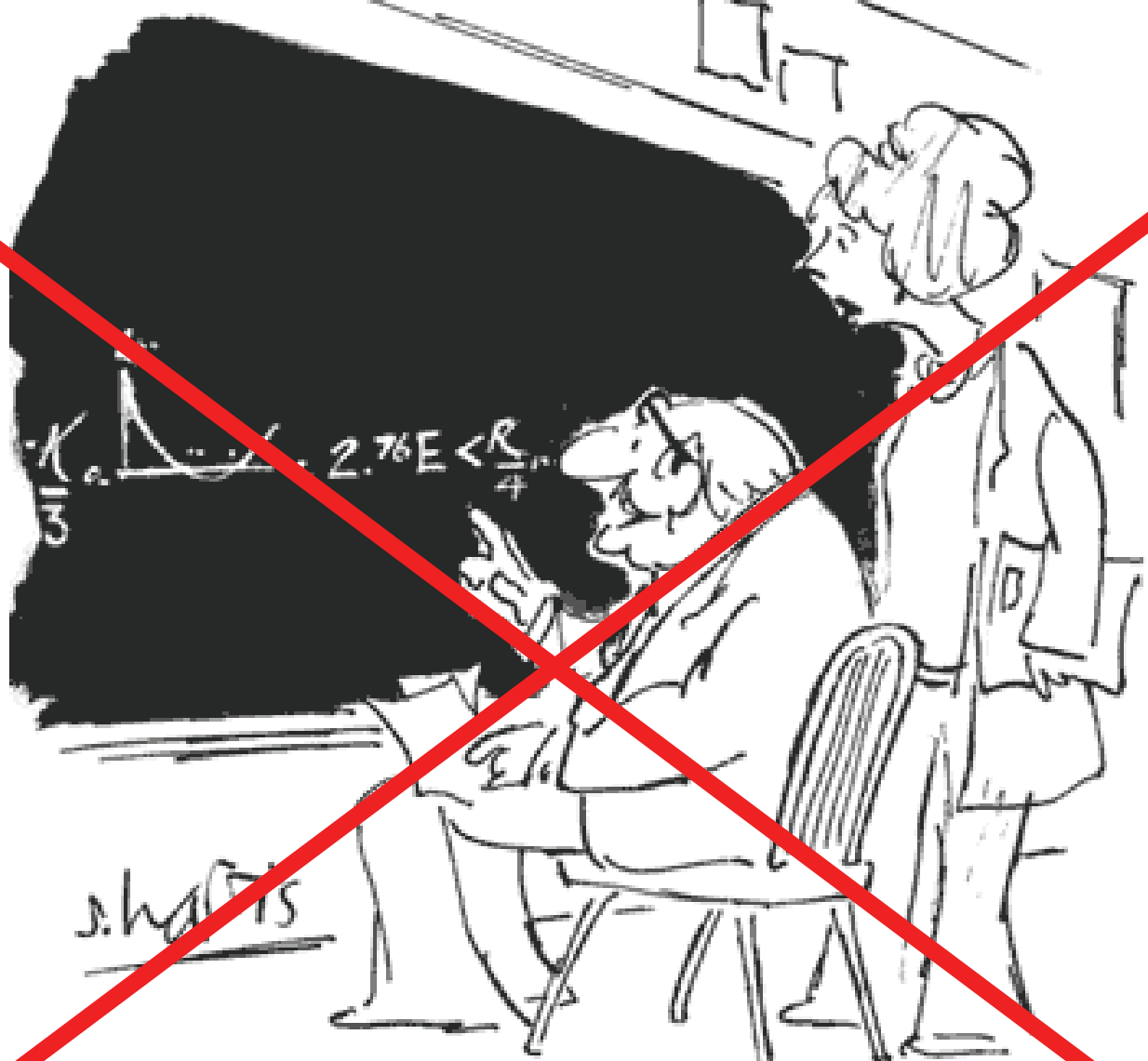

1. Bohmian approach fixes asymptotic behavior
2. Bohmian and MF err at short times due to ZPE

# Summary for Kohn-Sham SH

- ✓ KS-SH works well with nanoscale materials, even small molecules
  - KS excitations are close to LR/TDDFT (in contrast to HF and CIS)
  - Usually no bond-breaking, conformational changes, etc.
  - Many-electron systems, single excitation is a small perturbation
  - Averaging over many initial conditions and pathways
- ✓ FSSH gives (approx.) detailed balance, essential in applications
- ✓ Decoherence effects are essential in many-atom systems
- ✓ Stochastic Mean-Field (SMF) and Decoherence Induced SH (DISH) “derive” a SH algorithm from decoherence
- ✓ Zero-point-energy, tunneling and decoherence are included in Quantized Hamilton Dynamics (QHD)
- ✓ Bohmian quantum-classical formulation naturally gives branching

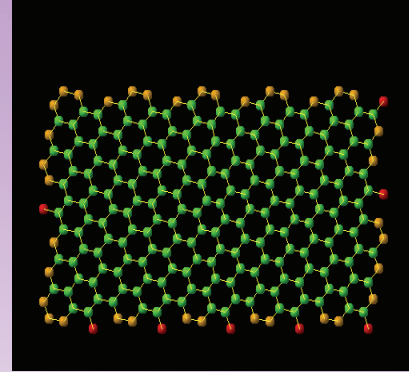



*"The beauty of this is that it is only of theoretical importance, and there is no way it can be of any practical use whatsoever."*



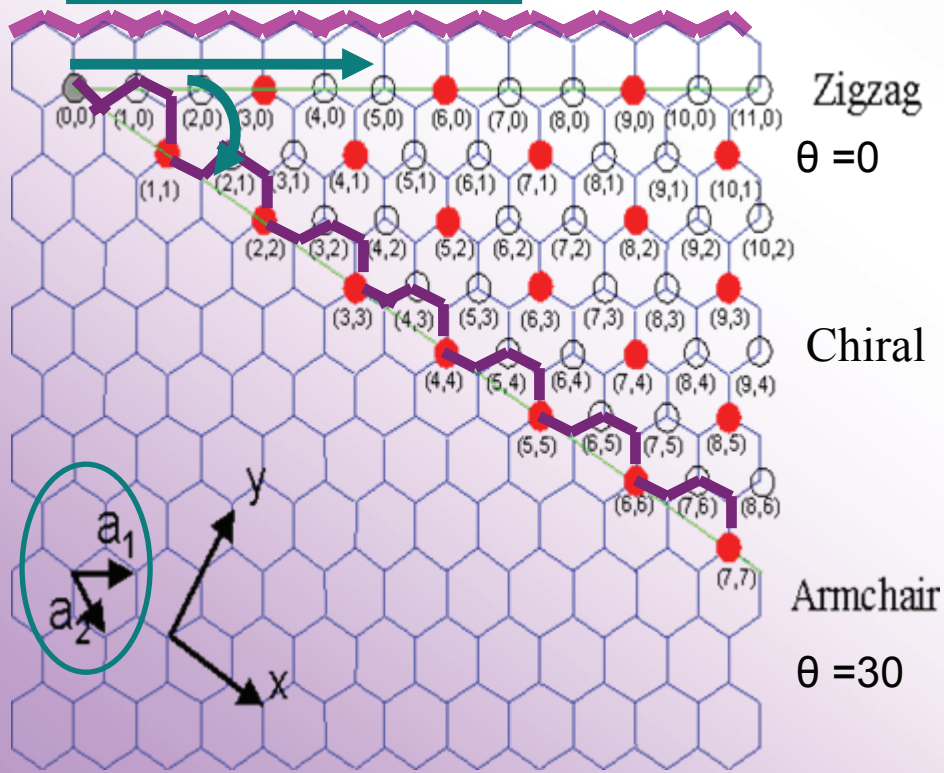

"The beauty of this is that it is only of theoretical importance, and there is no way it can be of any practical use whatsoever."

# Carbon Nanotubes Electronic Structure



$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$

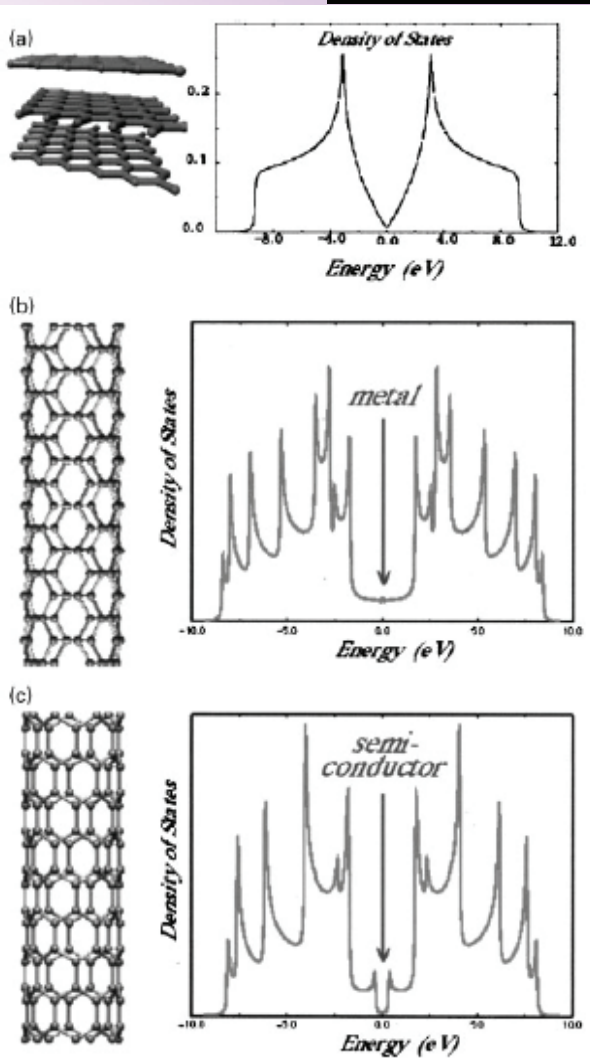
Metallic (red dots)
if n-m = 0 (mod 3)



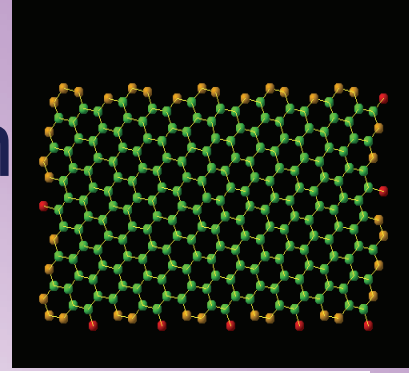

Zigzag
θ =0

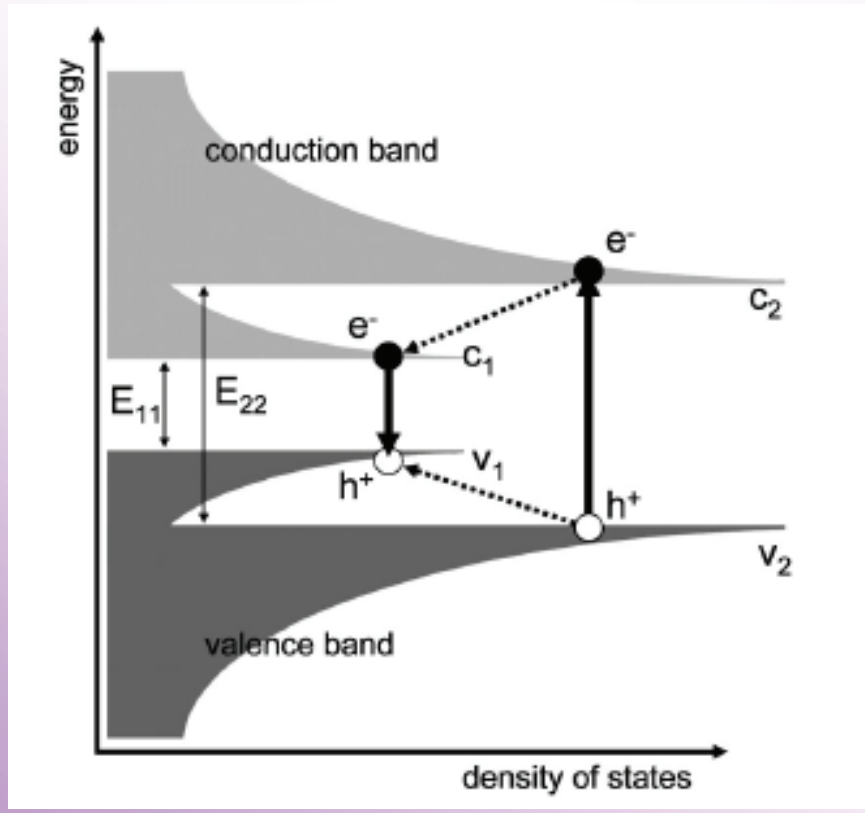
Chiral

Armchair
θ =30

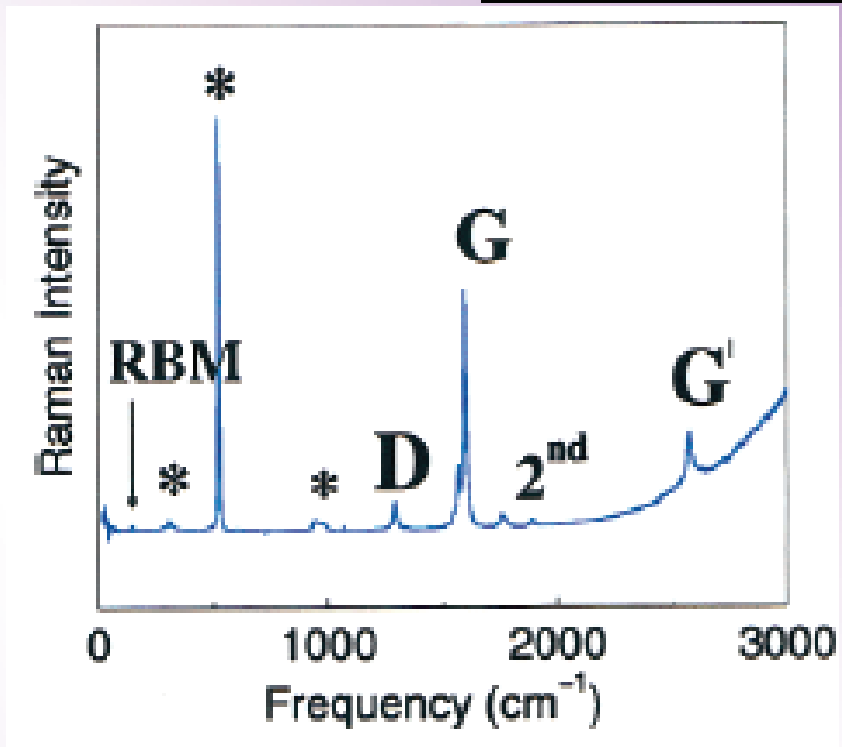


# Electron-Phonon Relaxation and Phonon Modes






Ma, Valkunas, Dexheimer, Bachilo, Fleming
*PRL* **94**, 157402 (2005)



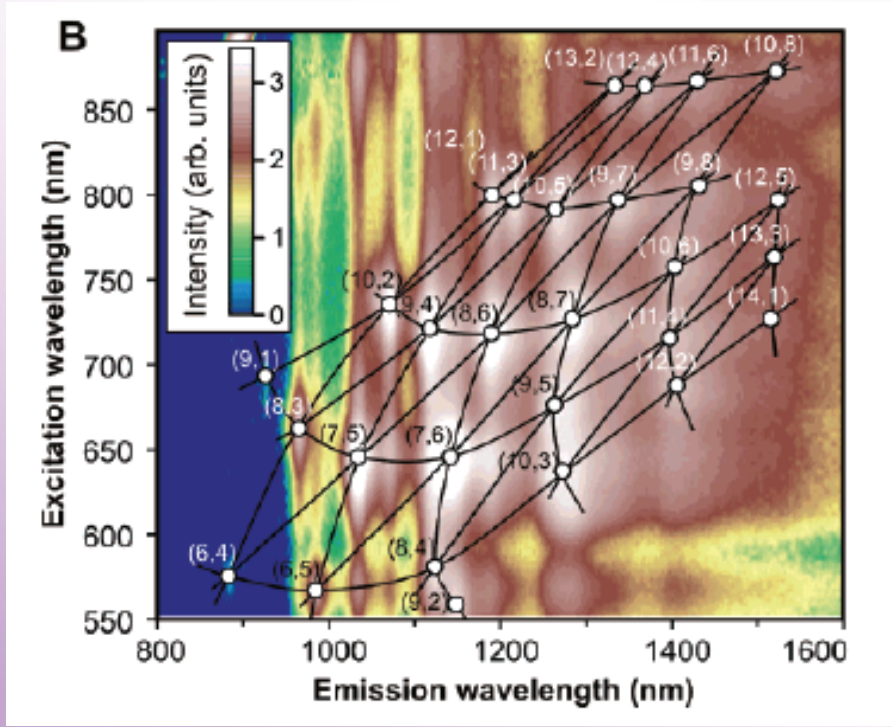

High frequency optical G-modes

Low frequency acoustic
radial breathing modes (RBM)

* – graphite background

# Luminescence Quenching and Ground State Recovery

Hertel et al. *Nano Lett.* **5**, 511 (2005)



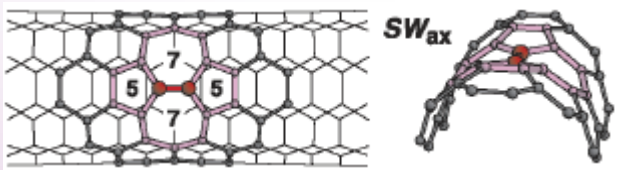

Multiple luminescence quenching timescales in literature:
~20ps, 200ps and 10ns

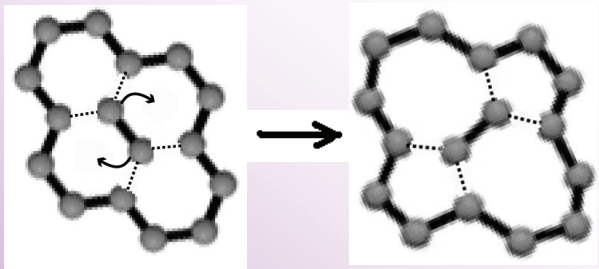
Luminescence yields are generally low <1%, i.e. quenching is efficient

# Defects

## Stone-Wales defect

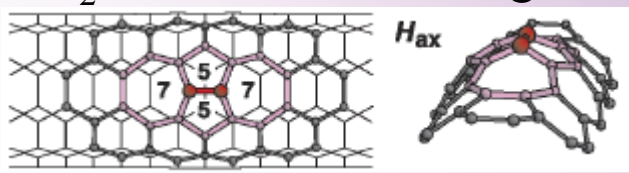
bond rotation

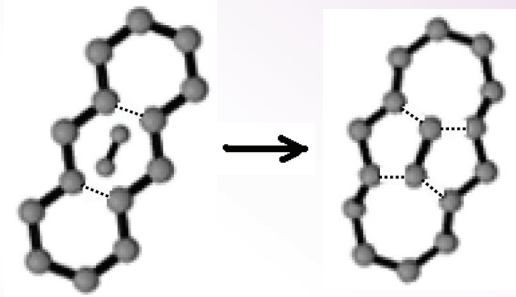


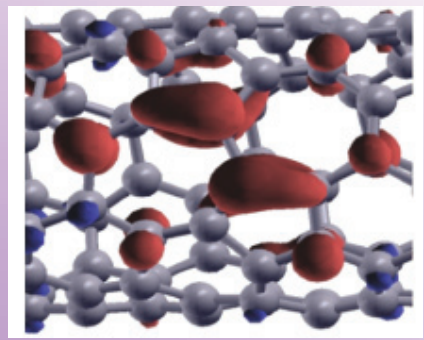



## 7557 defect

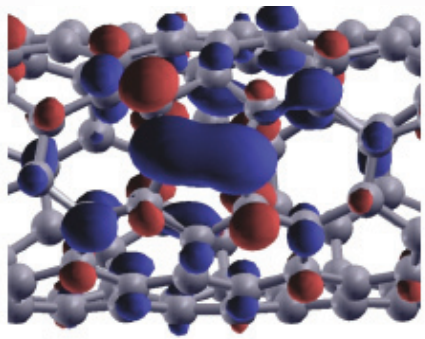
$C_2$ inserts across hexagon





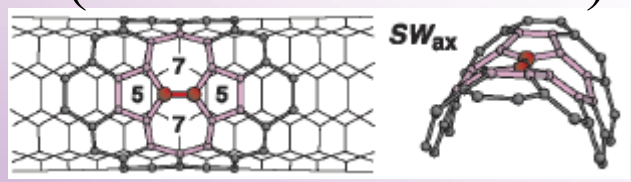
transition density



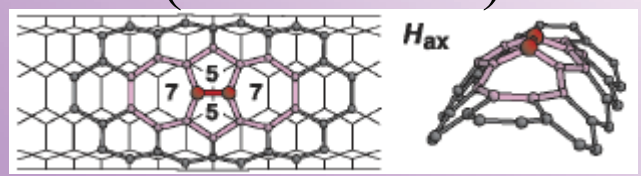
# Defects and Density of States

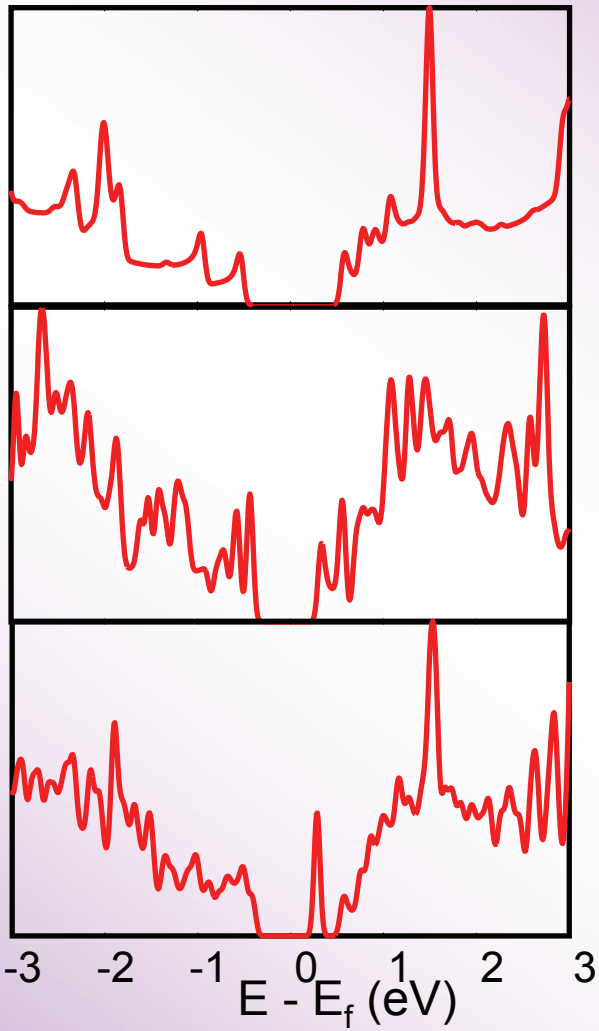
Ideal (6,4) tube

bond rotation
(Stone-Wales defect)




$C_2$ inserts across hexagon
(7557 defect)




Defect states both in the gap and inside bands

$C_2$ addition creates a distinct state

# Decoherence Times & Fluorescence Linewidth

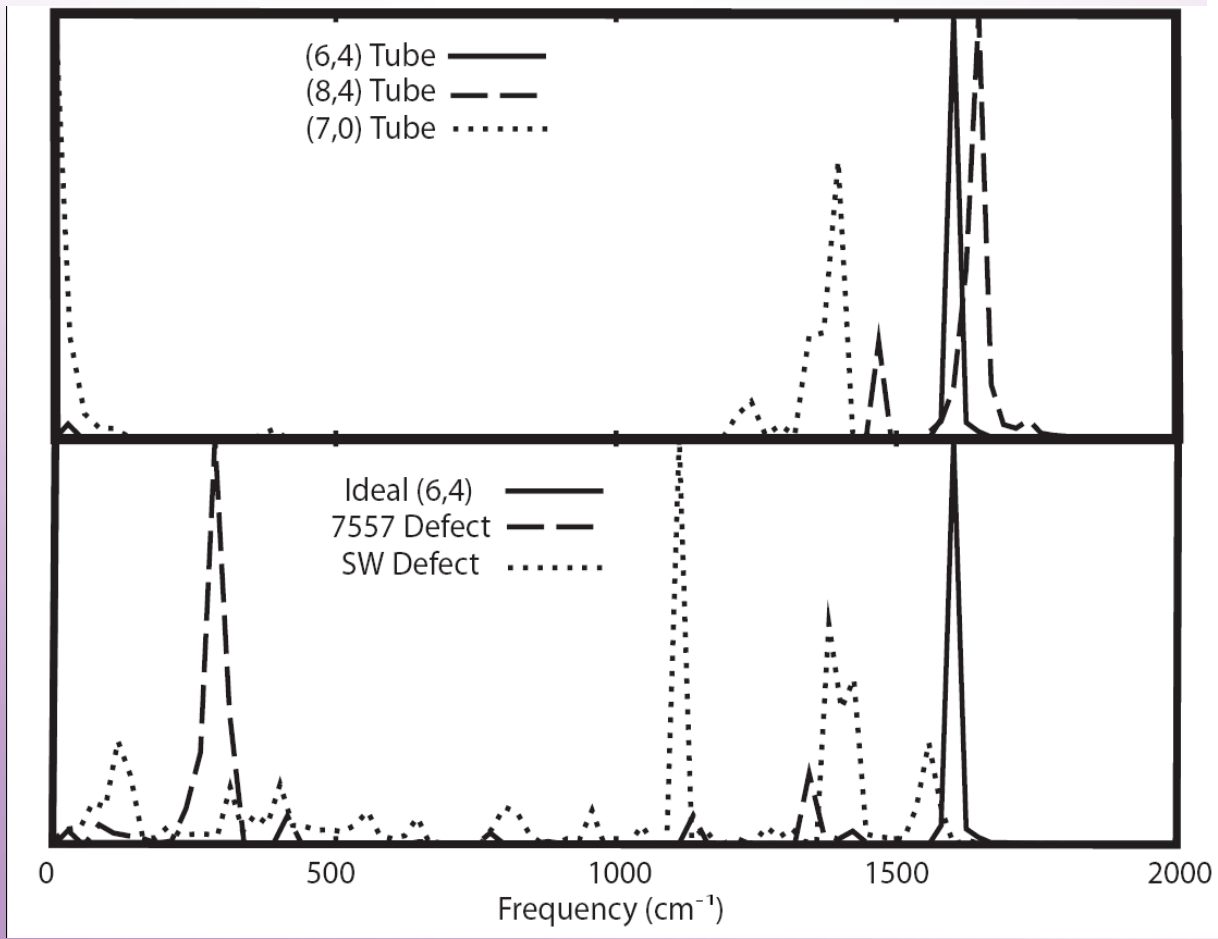
| Tube | $\tau$ (fs) | $A$ | $\omega$ (fs$^{-1}$) | linewidth (meV) |
|---|---|---|---|---|
| (6,4) | 59.6 | 0.086 | 0.32 | 11.0 |
| (8,4) | 51.2 | 0.061 | 0.30 | 12.8 |
| (7,0) | 24.5 | - | 0 | 26.9 |
| 7557 | 18.4 | 0.88 | 0.12 | 35.8 |
| SW | 48.0 | 0.062 | 0.25 | 13.7 |
| 50K | 955 | 0.0056 | 0.30 | 0.69 |

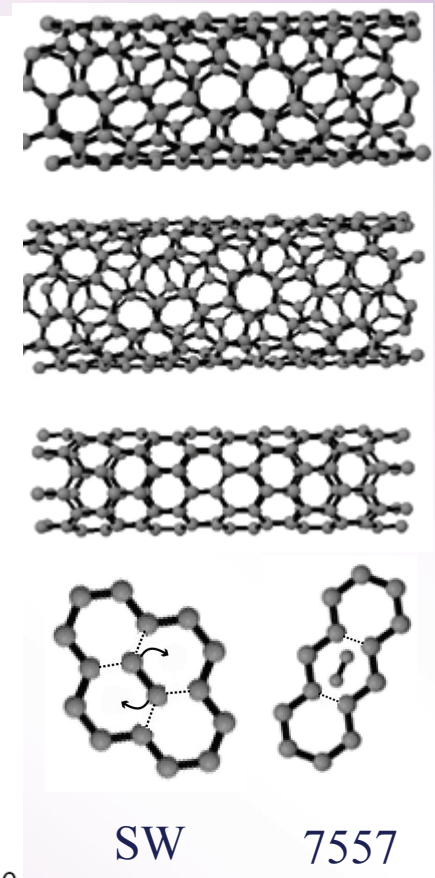
$$f(t) = exp(\frac{-t}{\tau})\frac{1 + Acos(\omega t)}{1 + A}$$

Experiment
10 meV (suspended)
25 meV (surfactant)

Defects create stronger electron-phonon coupling and can be detected by broader lines

# Active Phonon Modes



(8,4)

n-m=1 mod3

(6,4)

n-m=2 mod3

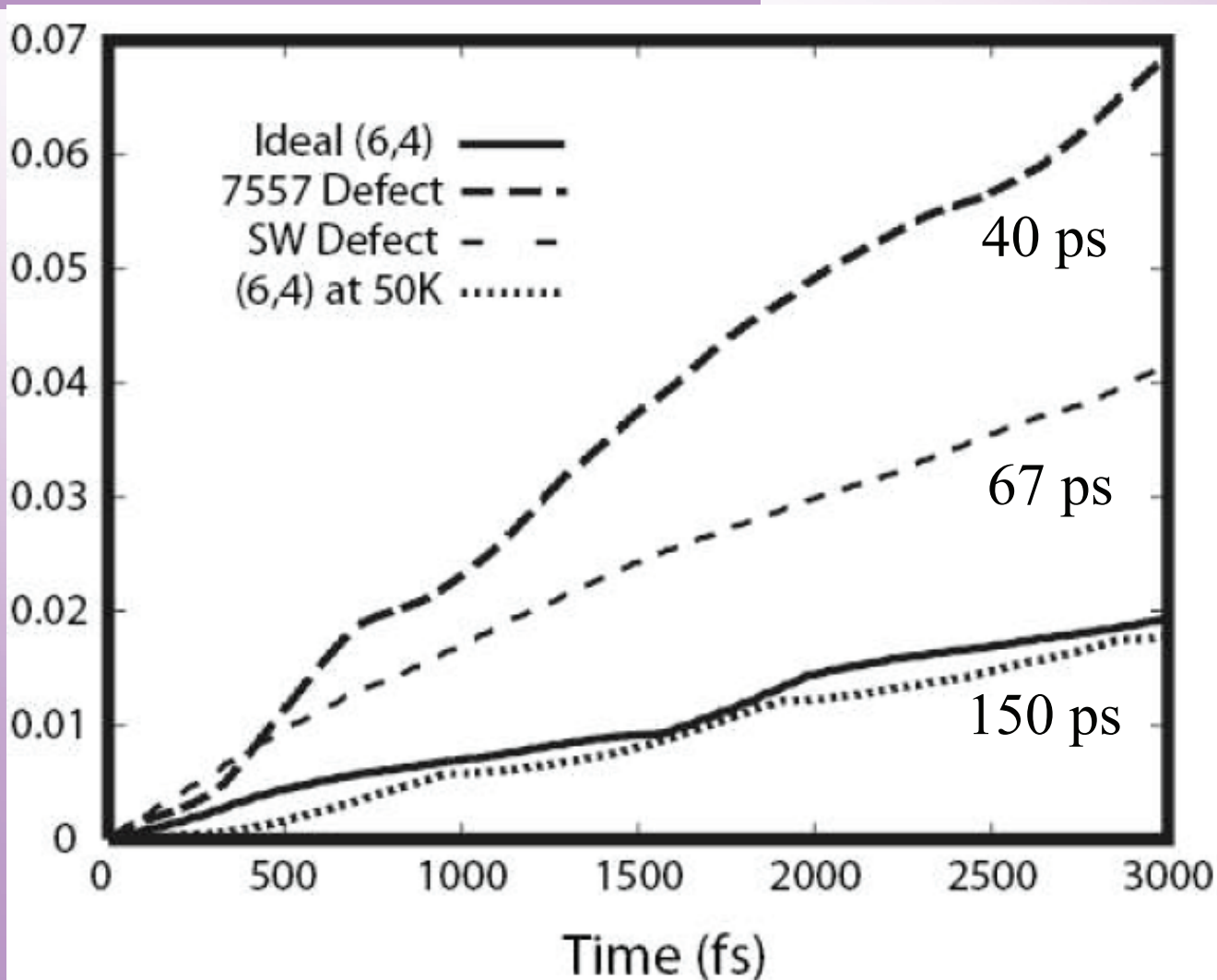
(7,0)

n-m=1 mod3

SW

7557

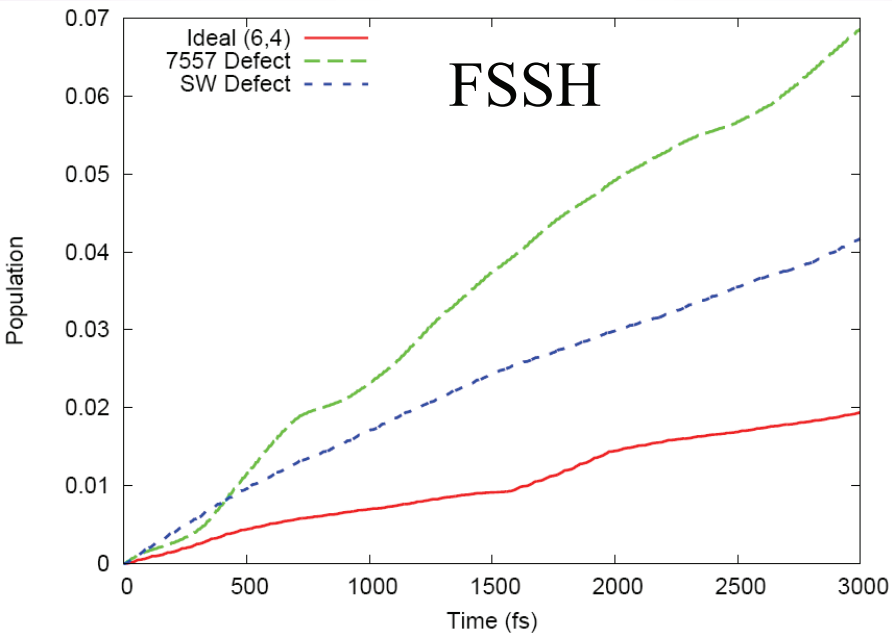
# Fluorescence Decay (FSSH)

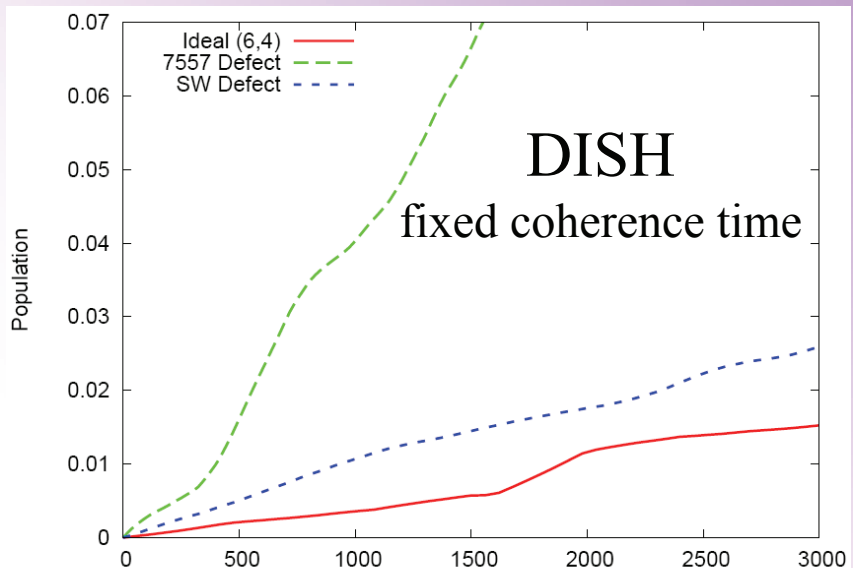


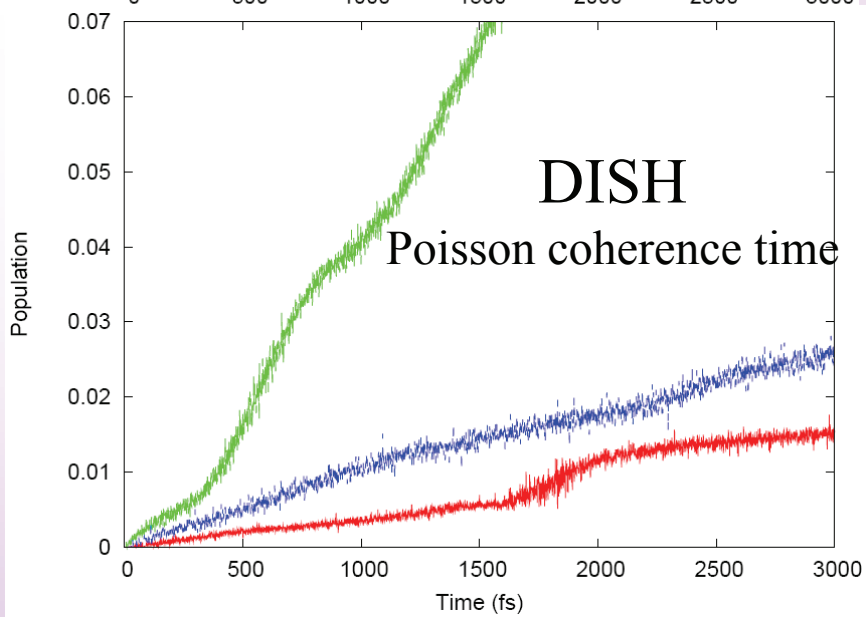

Defects notably decrease lifetime, explain multiple decay components

No T-dependence: cancellation of changes in NA coupling and decoherence

# Comparison of FSSH with DISH



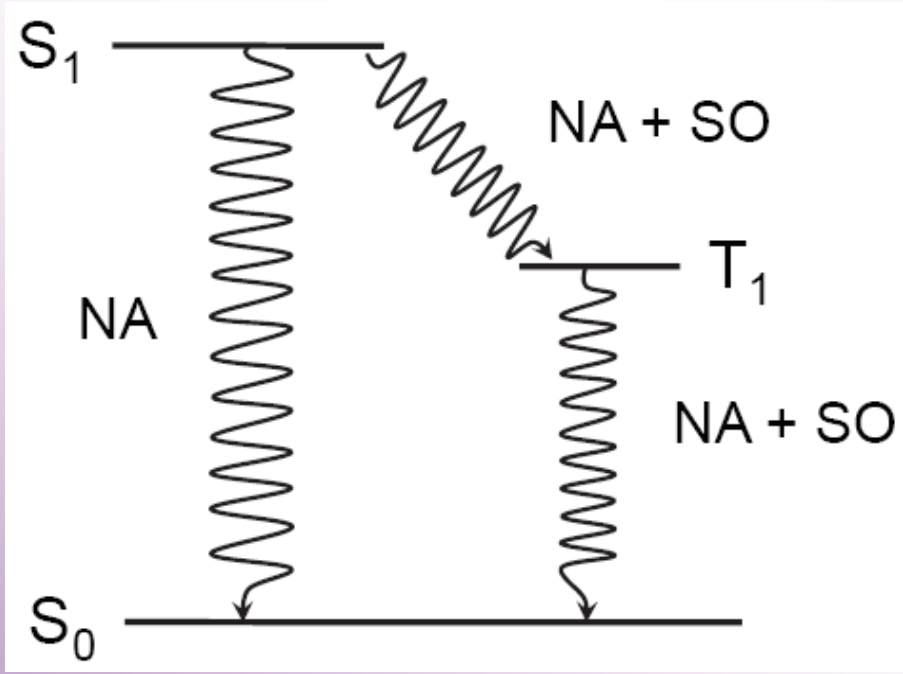




FSSH and DISH give similar results

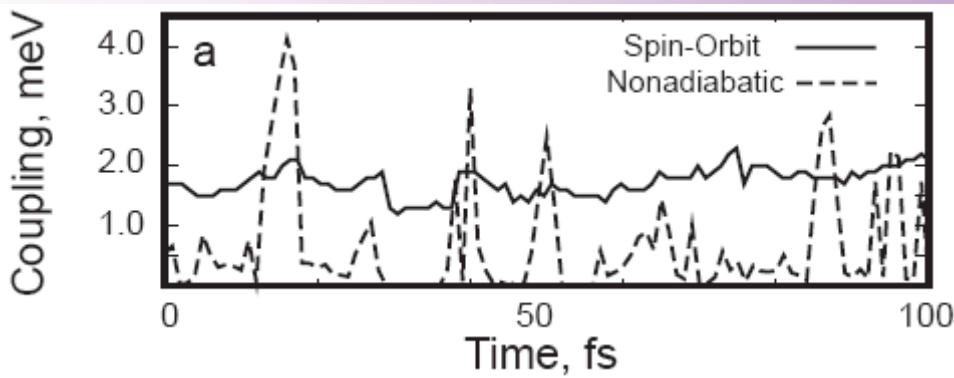
DISH uses decoh. as SH algorithm

Poisson and fixed coh. times similar

# Triplets & Phosphorescence Decay




Jablonsky diagram




Triplets provide new decay pathway

Spin-Orbit (SO) coupling is on the same order as NA coupling, but SO coupling fluctuates less

# Triplets & Phosphorescence Decay

| Transition | Gap (eV) | Coupling (meV) | ISC Time (ps) |
|---|---|---|---|
| $S_1$-$T_1$ | 0.35 | 1.0 | 362 |
| | | 1.6 | 139 |
| | | 2.4 | 62.2 |
| $T_1$-$S_0$ | 1.05 | 1.0 | 1,082 |
| | | 1.6 | 430 |
| | | 2.4 | 189 |
| | 1.30 | 1.0 | 1,392 |
| | | 1.6 | 548 |
| | | 2.4 | 238 |

Triplets decay ~5 times more slowly than singlets

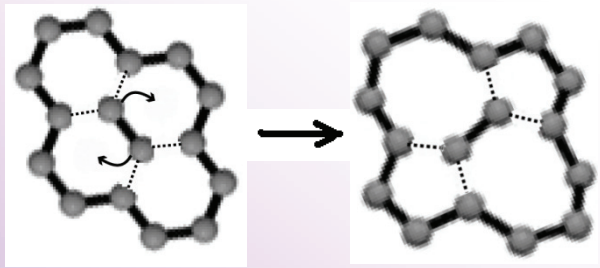
Decay rate is proportional to square of SO coupling and inverse energy gap

Larger tubes – weaker coupling (due to smaller curvature), but also smaller energy gaps

# Transition Densities

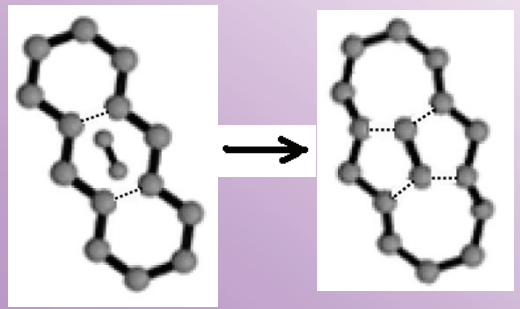
Stone-Wales defect

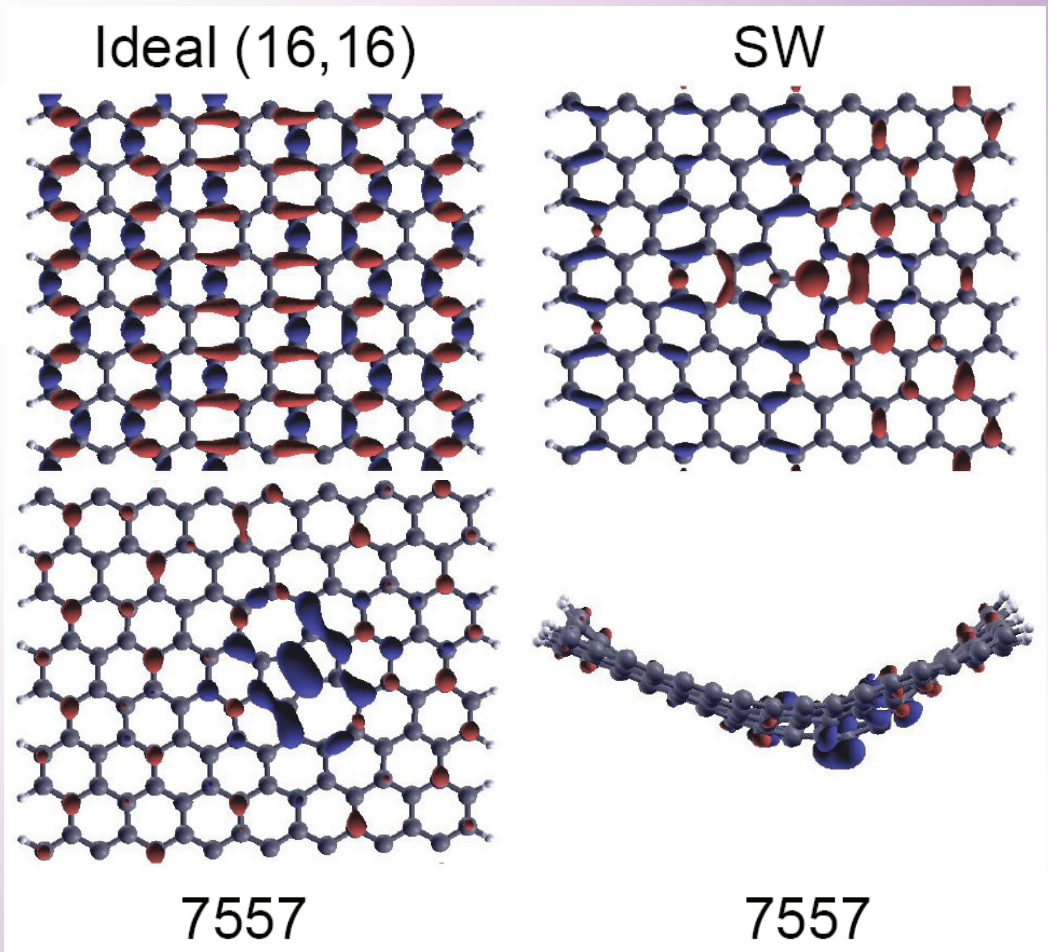
bond rotation



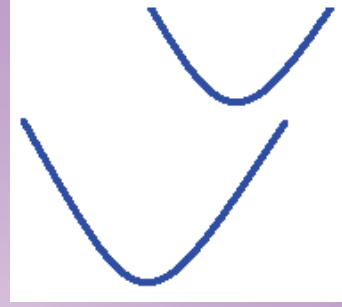
7557 defect

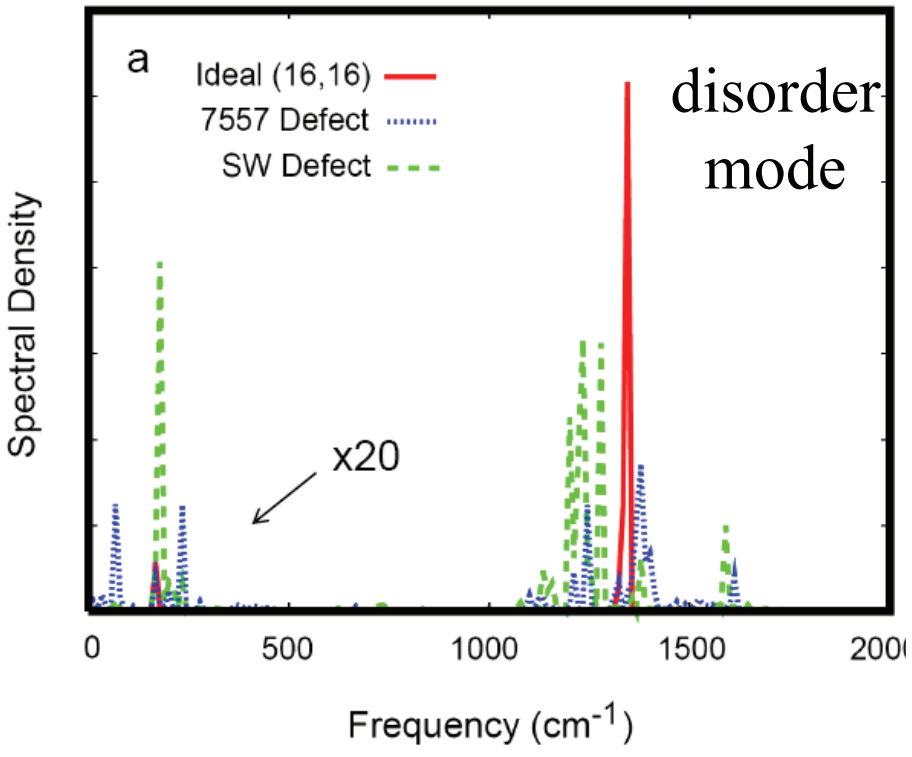
$C_2$ inserts across hexagon

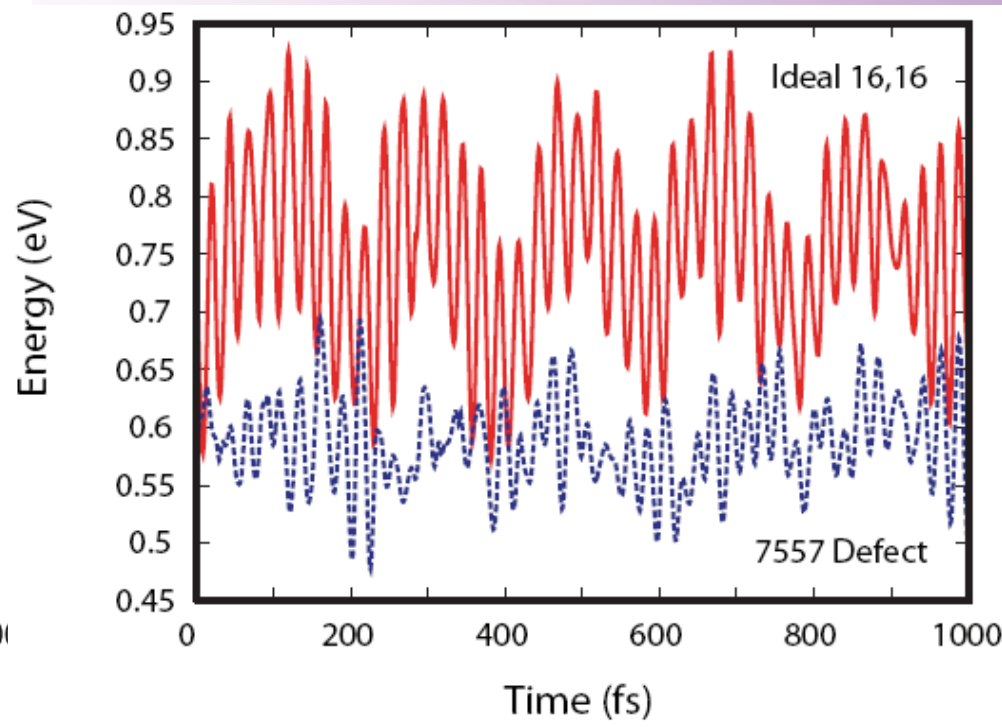




# Phonon Modes





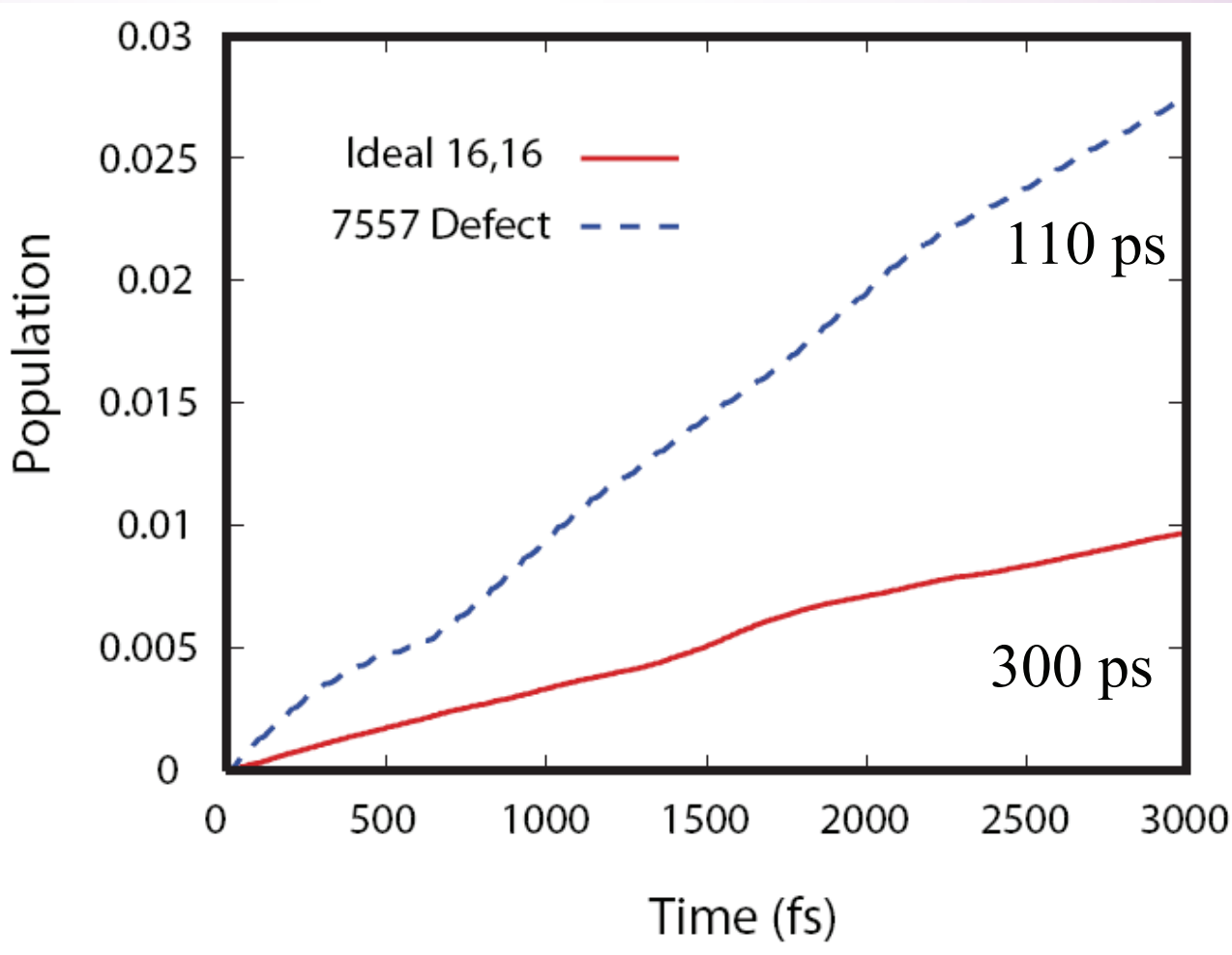

Opposite to tubes: weaker electron-phonon coupling in defects compared to ideal ribbon

# Decoherence Time & Fluorescence Linewidth

| Ribbon | $\tau$ (fs) | $\omega$ (fs$^{-1}$) | $A$ | $\Gamma$ (meV) |
|---|---|---|---|---|
| (16,16) | 23.5/25.8 | 0.259/0.257 | 0.024/0.069 | 28.0/25.5 |
| **Defect** | $\tau_e$ (fs) | $\tau_g$ (fs) | $B$ | $\Gamma$ (meV) |
| 7557 | 41.8/48.9 | 39.9/35.7 | 0.38/0.30 | 16.1/16.5 |
| SW | 69.8/57.3 | 42.3/46.0 | 0.54/0.44 | 11.5/12.9 |

Opposite to tubes: wider lines in ideal ribbon than in defects

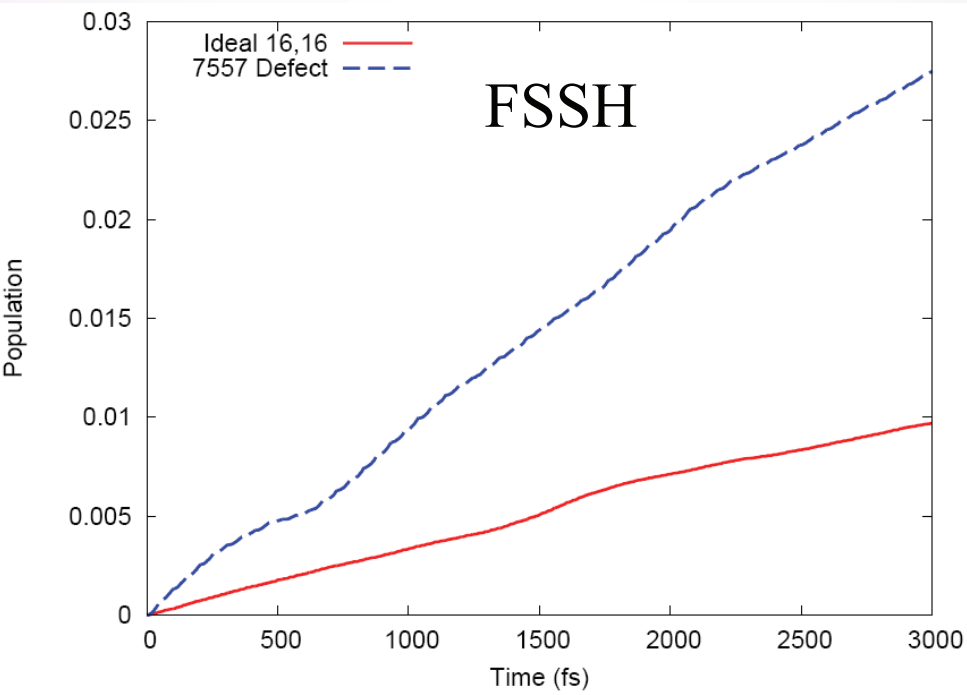
# Fluorescence Decay (FSSH)

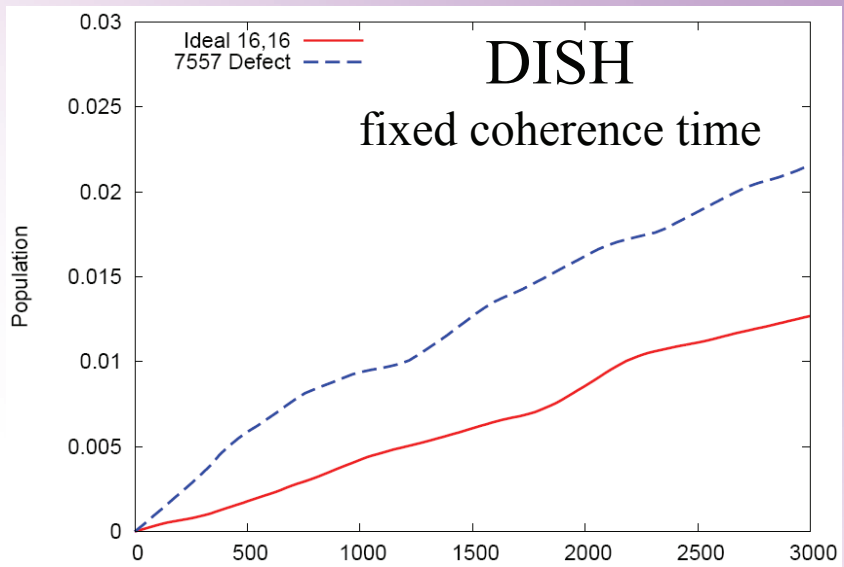


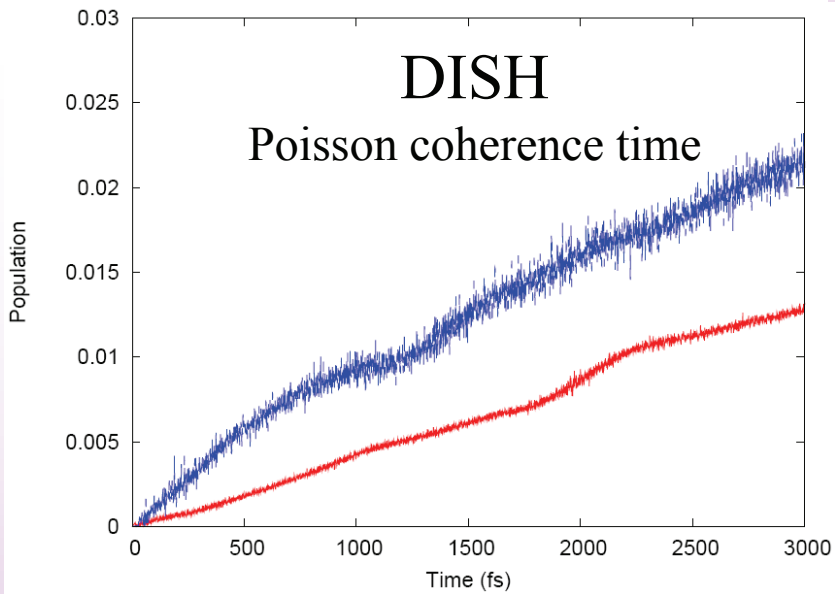

Defects speed up relaxation, same as in tubes

Ribbons decay more slowly than tubes due to smaller electronic overlaps

# Comparison of FSSH with DISH




FSSH and DISH give similar results

DISH uses decoh. as SH algorithm

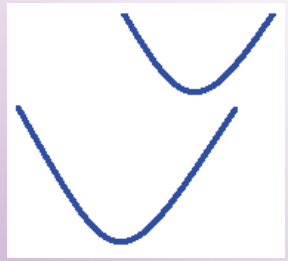
Poisson and fixed coh. times similar

# Apparent Paradoxes

$$k_{1\to 2}^{qm} = \frac{2\pi}{\hbar}\left\langle \left| \sum_n -\frac{i\hbar}{M_n}\langle 1|\nabla_n|2\rangle\langle \hat{p}_n\rangle \right|^2 \times \prod_m |\langle i_m|f_m\rangle|^2 \delta(E_{1i}-E_{2f}) \right\rangle_T$$

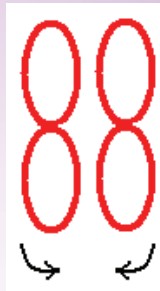
Tubes vs. Ribbons

Ideal ribbons show wider lines, i.e. faster dephasing,
but slower relaxation than ideal tubes ??



Ideal vs. Defects

Defects accelerate relaxation in both tubes and ribbons;
However, defects make lines broader in tubes
and narrower in ribbons ??



# Summary for Carbon Tubes/Ribbons

- ✓ Luminescence quenching – 3 timescales, as in experiment
  Tubes: 150ps ideal, 50ps defects, 700ps triplet channel
  Ribbons: 300ps ideal, 100ps defects
- ✓ Phonons: C-C stretch in ideal systems
  low frequency modes with defects
- ✓ No T-dependence by decoherence correction
- ✓ DISH and FSSH results are similar, DISH is "more justified"

*Phys. Rev. Lett.* **96** 187401 (2006); *Phys. Rev. Lett.* **98** 189901 (2007);
*Nano Lett.* **7** 3260 (2007); *Phys. Rev. Lett.*, **100** 197402 (2008);
*Nature Nanotech*. **4** 190 (2008); *Pure & Appl. Chem.* **80** 1433 (2008);
*Nano Lett.* **8** 2126 (2008); *Nano Lett.* **8** 2510 (2008);
*J. Phys. Chem. C*, **113**, 14067 (2009); *Nano Lett.*, **9**, 12 (2009).