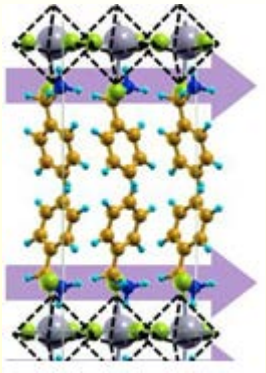
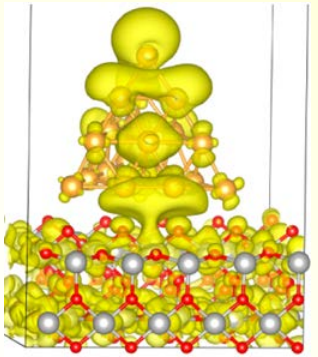
Nonadiabatic Dynamics for Nanoscale Materials

Oleg Prezhdo

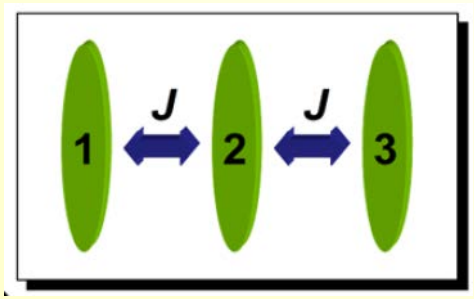
U. Southern California

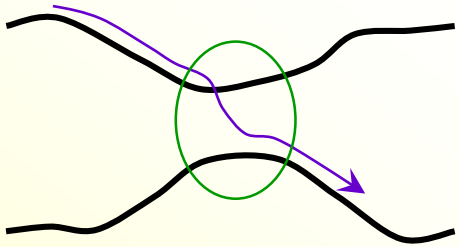


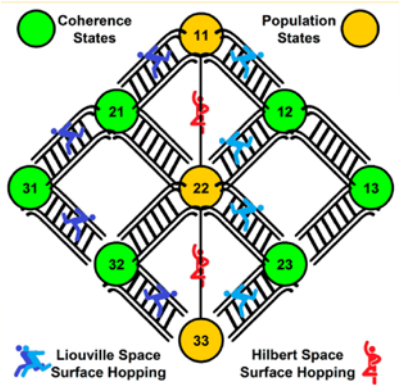


U Buffalo

June 10, 2018







Ehrenfest Dynamics

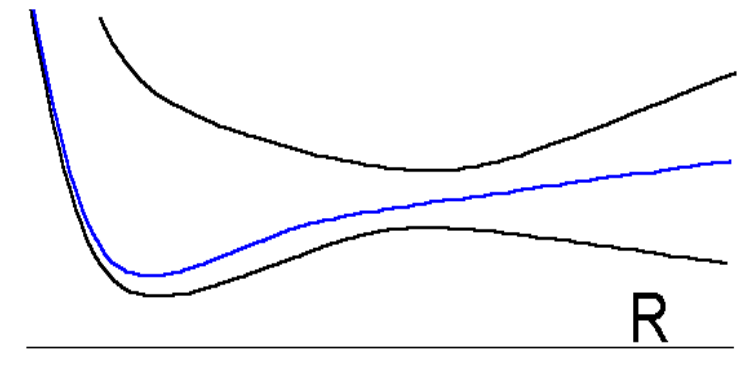
Total energy of electrons and nuclei

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

is conserved

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

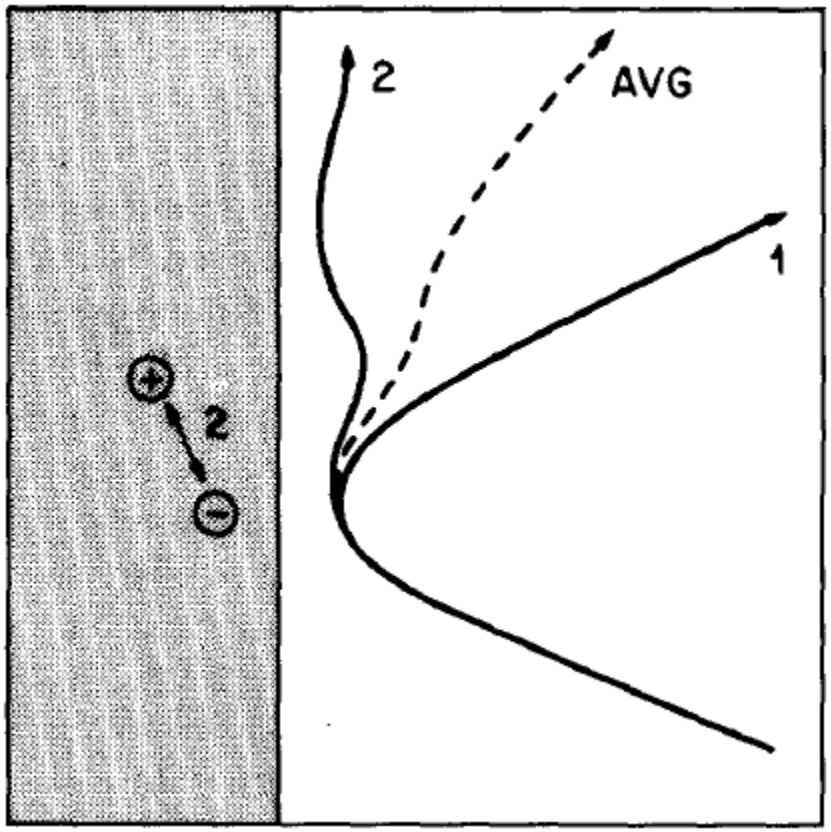
time-dependent Hellmann-Feynman theorem gives Newton equation



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

quantum force
(time-dependent Hellmann-Feynman theorem)

Why Surface Hopping Needed?



Average surface is not physical

Fewest Switches Surface Hopping

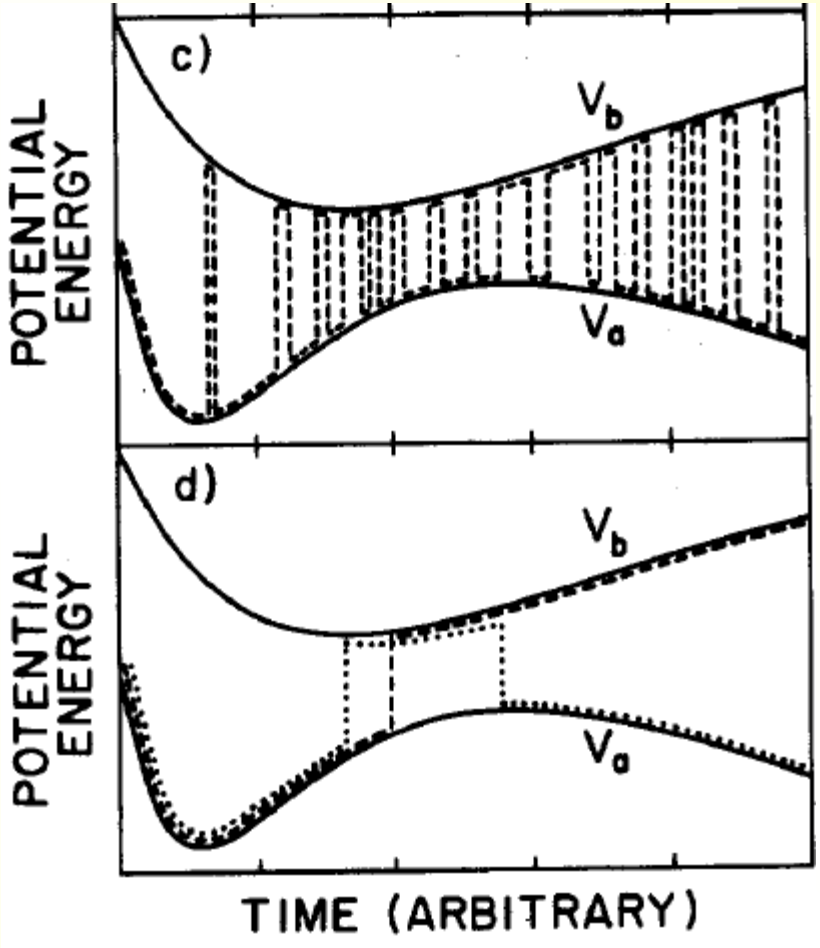
Tully, *JCP* **93**, 1061 (1990)

Based on probability $|c_i|^2$

(becomes effectively Ehrenfest)

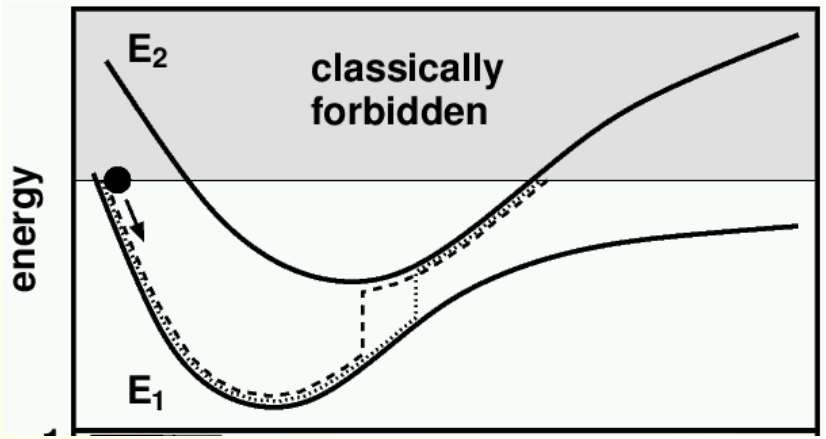
Fewest Switches

based on flux, $d|c_i|^2/dt$



Fewest Switches Surface Hopping

Tully, *JCP* **93**, 1061 (1990)



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, due to hop rejection,
needed for thermodynamic equilibrium:
Parahdekar, Tully *JCP* **122**, 094102 (2005)

Time-Domain DFT for Nonadiabatic Molecular Dynamics

Craig, Duncan, Prezhdo *Phys. Rev. Lett.* **95,** 163001 (2005)

Electron density derives from Kohn-Sham orbitals

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

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

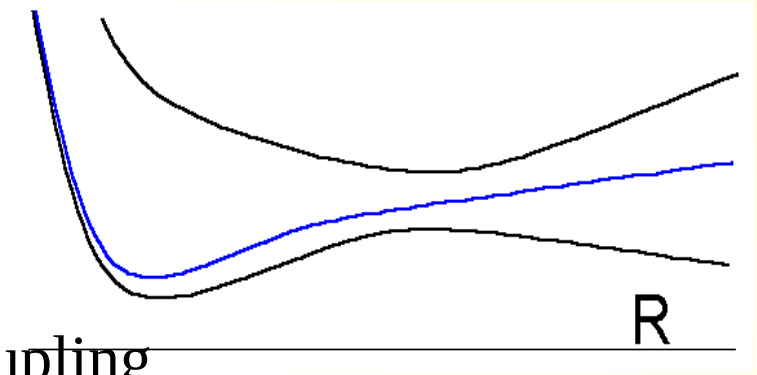
Variational principle gives $i\hbar\dfrac{\partial\varphi_p(x,t)}{\partial t}=H\varphi_p(x,t) \quad p=1,2\ldots$

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 Kohn-Sham Equations: Ehrenfest vs. Surface Hopping



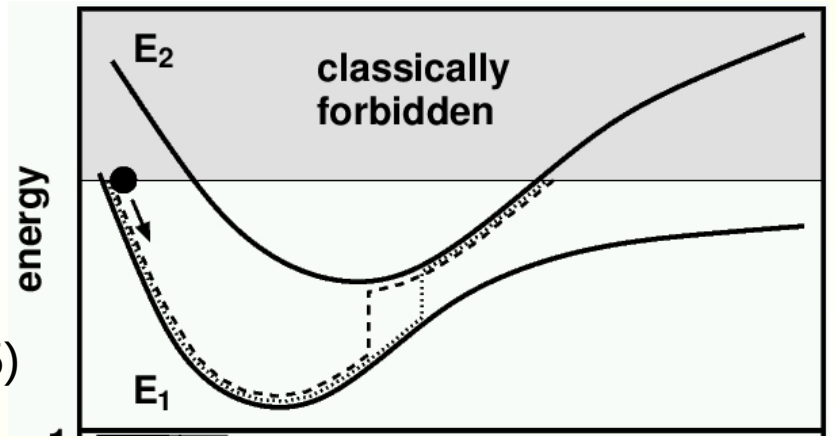
- ✓ Ehrenfest: adiabatic KS basis can be viewed as *numerical representation*

  Stier, Prezhdo *JPC-B* **106** 8047 (2002)

  main challenge – evaluation of NA coupling

- ✓ Surface Hopping: requires definition of "states" for hopping; KS basis gives *0th order adiabatic states*

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



Surface Hopping in Many-Body Kohn-Sham Basis

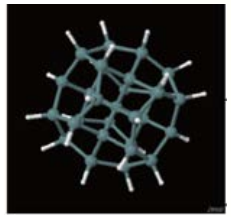
Craig, Duncan, Prezhdo *Phys. Rev. Lett.* **95,** 163001 (2005)
Akimov, Prezhdo, *J. Theor. Comp. Chem.* **9**, 4959 (2013)

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

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

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

D is non-zero only if different in one orbital, very sparse
Multiple excitons in $Si_{29}H_{24}$: 25 VB and 24 CB orbitals
98,101 states = ground+600SE+97,500DE

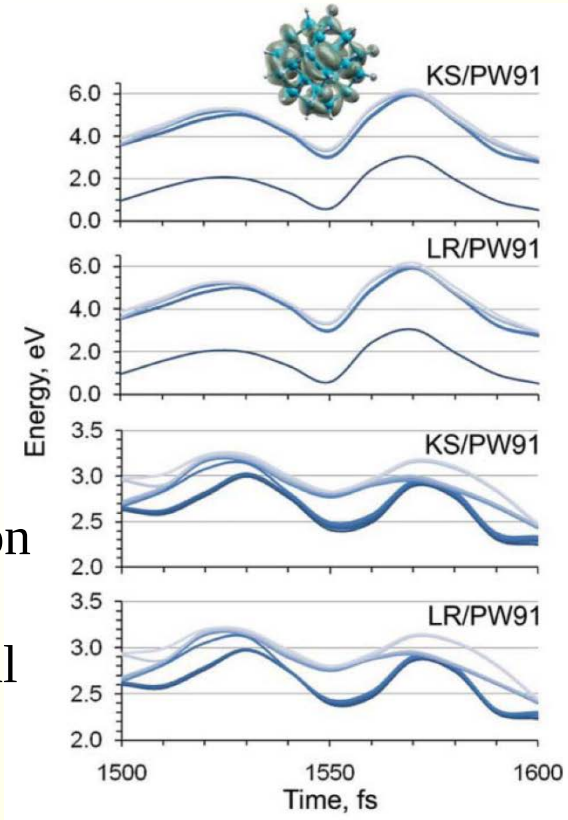


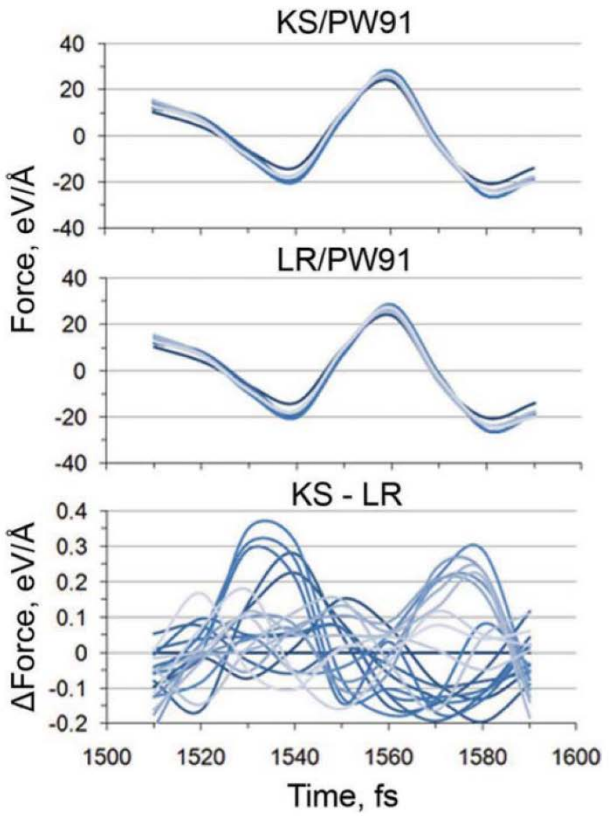
Hyeon-Deuk, Prezhdo *Nano Lett.* **11**, 1845 (2011); *ACS Nano* **6**, 1239 (2012)

Why Surface Hopping in Kohn-Sham Representation Works

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

- KS close to LR/TDDFT (in contrast to HF and CIS)
- No bond-breaking, conformational changes.
- Many-electrons, single excitation small perturbation
- Averaging over many initial conditions and pathways





Classical Path Approximation

Useful for Nanoscale Systems

Prezhdo, Duncan, *Prog. Surf. Sci*. **84**, 30 (2009)
Akimov, Prezhdo, *J. Theor. Comp. Chem*. **9**, 4959 (2013)

1. DFT functional (Hamiltonian) depends on ground state density, even though the true density does evolve
2. Ground and excited state nuclear trajectories are similar

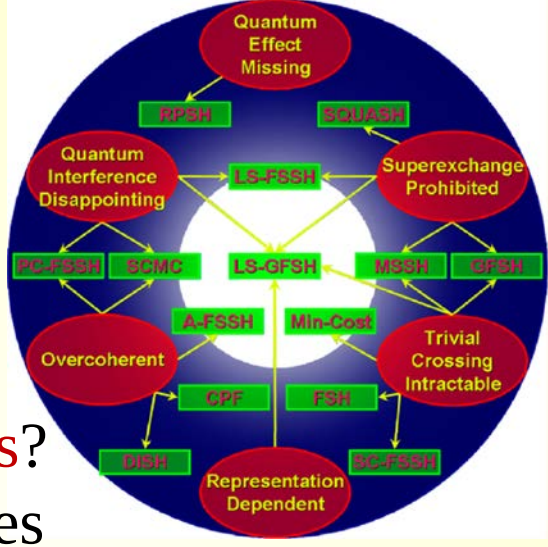
Justification:

1. Excitation of 1 or 2 electrons out of hundreds does not change density and forces much
2. Thermal fluctuations are larger than differences in equilibrium geometries of ground and excited electronic states

Key Advantages – allows use of ground state trajectory, while still performing TDKS & SH for electronic state populations – electronic and nuclear timestep separation (1as & 1fs)

Theoretical Questions

Perspective: *JPC Lett.* **7** 2100 (2016)



- ✓ How to couple quantum and classical dynamics?
  quantum back-reaction on classical variables
- ✓ Can one do better than classical mechanics for nuclear motion?
  zero-point motion, tunneling, branching, loss of coherence

Decoherence induced surface hopping (DISH) *JCP* **137**, 22A545 (2012)
Coherence penalty functional (CPF) *JCP* **140**, 194107 (2014)

Self-consistent FSSH (SC-FSSH) *JPC-L* **5**, 713 (2014)

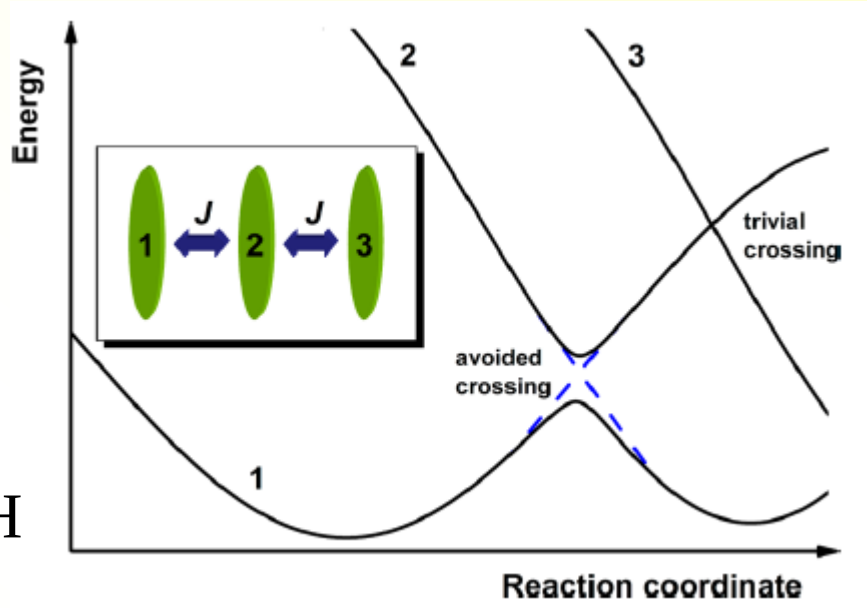
Global flux surface hopping (GFSH) *JCTC* **10**, 3598 (2014)
Second quantized surface hopping (SQUASH) *PRL* **113**, 153003 (2014)
FSSH in Liouville space *JPCL* **6**, 3827 (2015)
GFSH in Liouville space, *JCP-Rapid* **143**, 191102 (2015)

Self-Consistent FSSH

Wang, Prezhdo *J. Phys. Chem. Lett.* **5**, 713 (2014)

FSSH probability depends on NA coupling, which diverges

$$d_{ij}^{k} = \frac{\alpha p_{ki} p_{kj}}{E_j - E_i}$$



Linjun Wang pointed out that in FSSH sum of all hoping probabilities is

$$\sum_{i}^{N} g_i = \mathrm{d}t \cdot \frac{-\mathrm{d}(c_a^* c_a)/\mathrm{d}t}{c_a^* c_a}$$

Obtains problematic probability

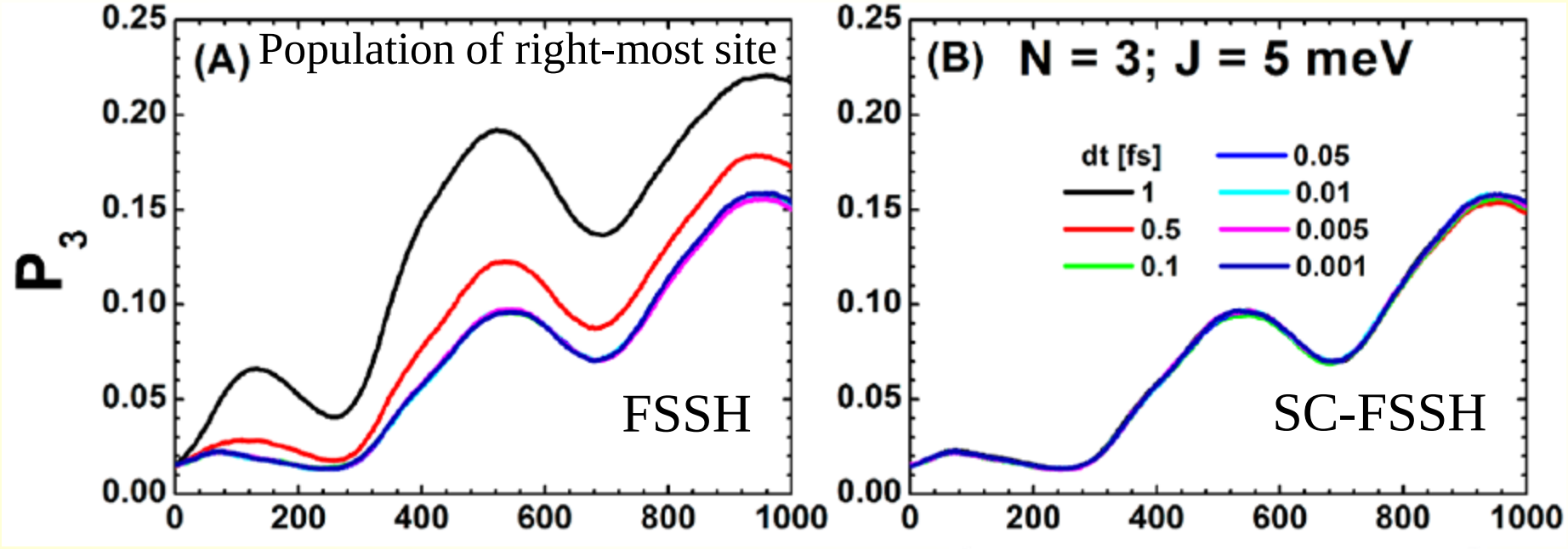
$$g_j = \sum_{i}^{N} g_i - \sum_{i \neq j}^{N} g_i$$

One tests if this is true (self-consistency).

Self-Consistent FSSH

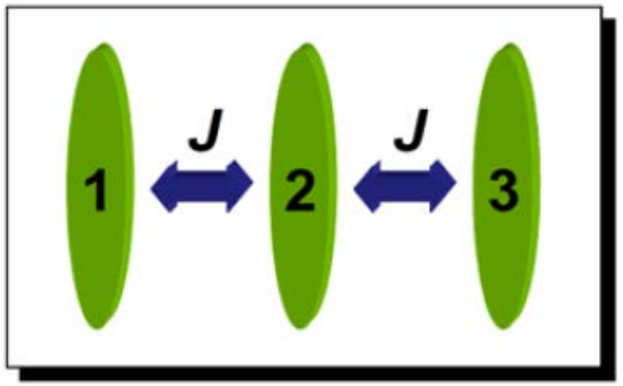
Wang, Prezhdo *J. Phys. Chem. Lett.* **5**, 713 (2014)

FSSH: dt=0.1fs; SC-FSSH: dt=1fs



$$H = H_e + H_n \qquad H_n = \frac{1}{2}\sum_i (Kx_i^2 + mv_i^2)$$

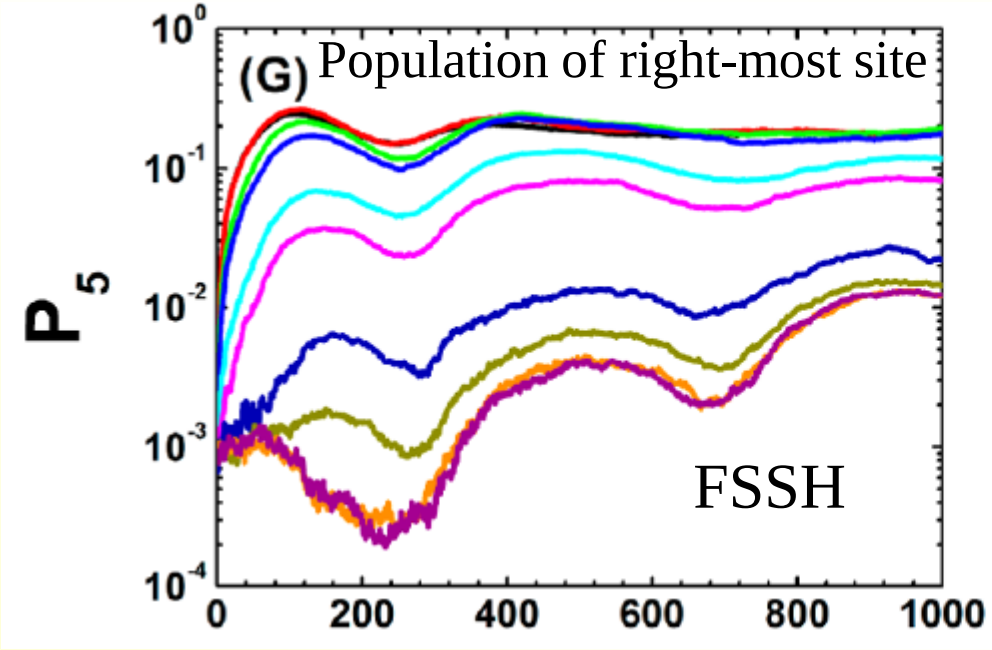
$$H_e = \sum_i^{N-1} J(|i\rangle\langle i+1| + |i+1\rangle\langle i|) + \sum_i^{N} \alpha x_i |i\rangle\langle i|$$

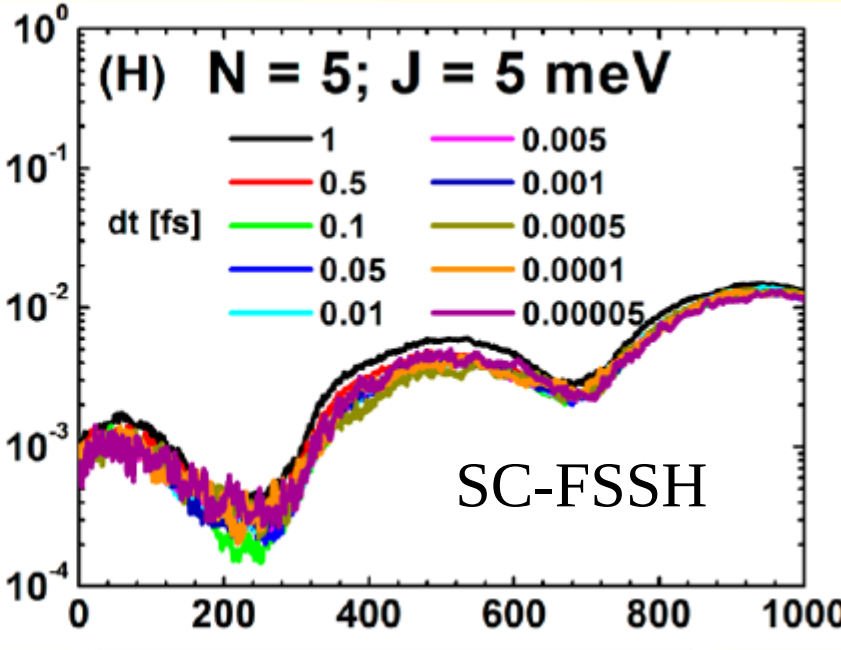


Self-Consistent FSSH

Wang, Prezhdo *J. Phys. Chem. Lett.* **5**, 713 (2014)

FSSH: dt=0.0001fs; SC-FSSH: dt=1fs





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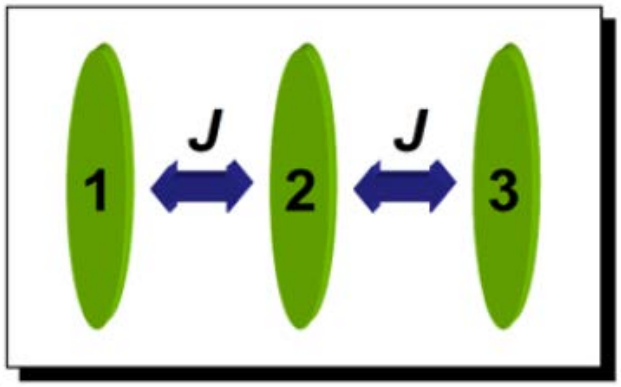
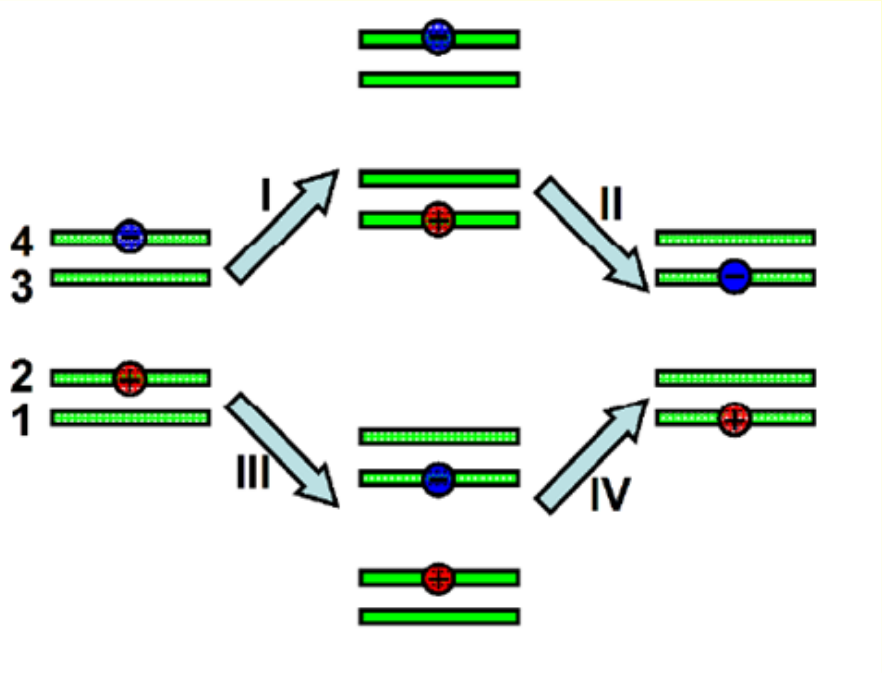


Auger Processes in Nanomaterials

Electron-hole energy exchange
is a 2-particle process,
has super-exchange channel



Also:

- Multiple-exciton generation and recombination
- Singlet fission (via intermediate charge transfer states)
- Auger-assisted electron transfer

Top channel is allowed by Schrodinger equation level,
but forbidden in FSSH due to hop rejection

Global Flux Surface Hopping

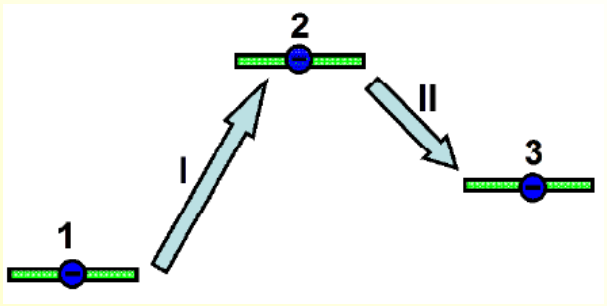
Wang, Trivedi, Prezhdo, *J.Theor.Comp.Chem.* **10**, 3598 (2014)

$$V_{11}(x) = 0\,, \quad V_{22}(x) = 0.01\,, \; V_{33}(x) = 0.005$$

$$V_{12}(x) = V_{21}(x) = 0.001e^{-x^2/2}$$

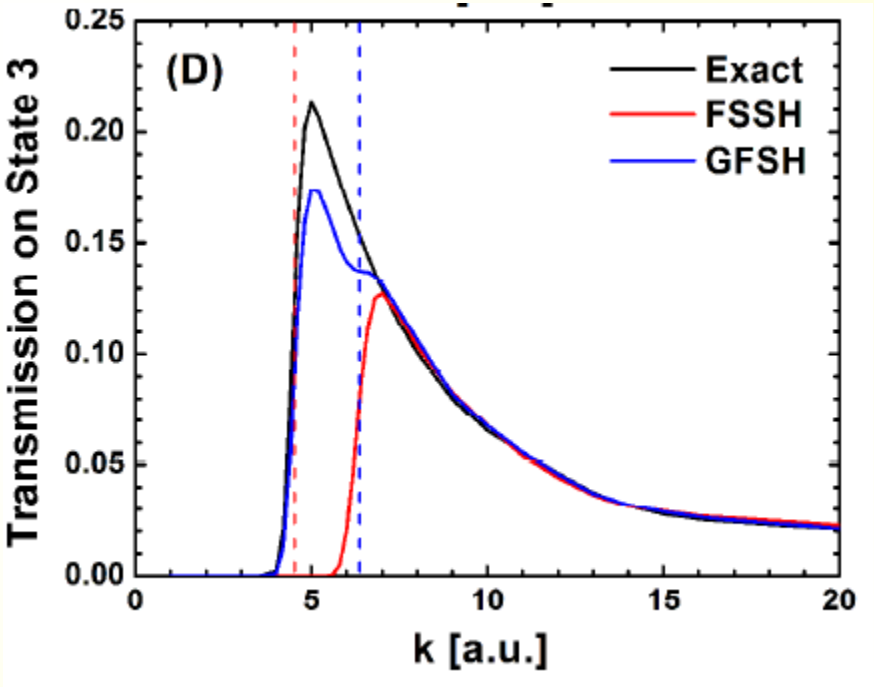
$$V_{23}(x) = V_{32}(x) = 0.01e^{-x^2/2}$$

$$V_{13}(x) = V_{31}(x) = 0$$



Re-sum all fluxes

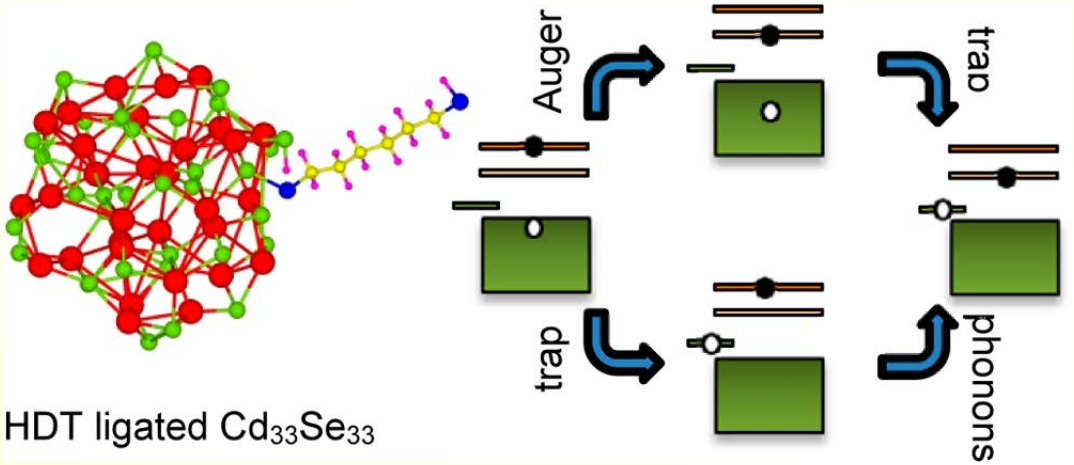
Then 1->2 and 2->3 cancel and 1->3 appears



k=4-7 super-exchange regime

Auger Electron-Hole Relaxation and Hole Trapping in CdSe QD

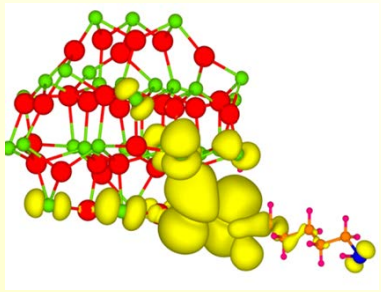
Trivedi, Wang, Prezhdo, *Nano Lett.* **15**, 2086 (2015)



Electron Relaxation
without trap 1.3 ps
with trap 1.8 ps

Hole trapping 1.2 ps

Experiment: Sippel et al. *Nano Lett.* **13** 1655 (2013)



- Hole is localized on surface, ligand tail not important
- Bottleneck not achieved: hole trapping is too slow, not because hole still couples to electron

FSSH underestimates rate by a factor of 4 in this case

FSSH in Liouville Space

L. Wang, A.E. Sifain, O.V.P. *J Phys Chem Lett* **6**, 3827 (2015)

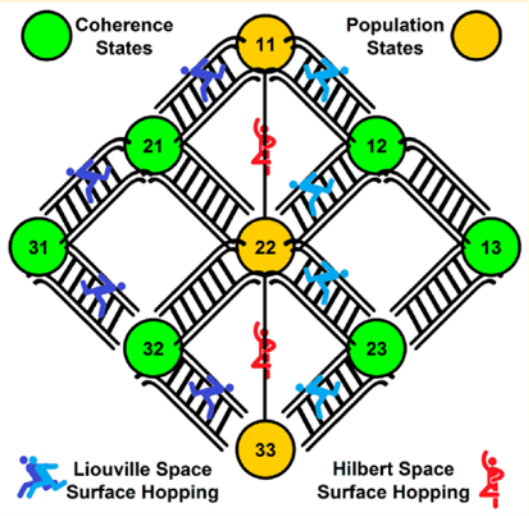
$$\frac{d|\psi(t)\rangle}{dt} = \frac{1}{i\hbar}\hat{H}|\psi(t)\rangle \qquad \hat{\rho}(t) = |\psi(t)\rangle\langle\psi(t)|$$

$$\frac{d\hat{\rho}(t)}{dt} = \frac{1}{i\hbar}[\hat{H}, \hat{\rho}] \qquad |\rho\rangle\rangle = \sum_{ij} \rho_{ij}|ij\rangle\rangle$$

$$\frac{d}{dt}|\rho\rangle\rangle = \frac{1}{i\hbar}\hat{\hat{L}}|\rho\rangle\rangle$$

One trajectory at a time

Normal FSSH



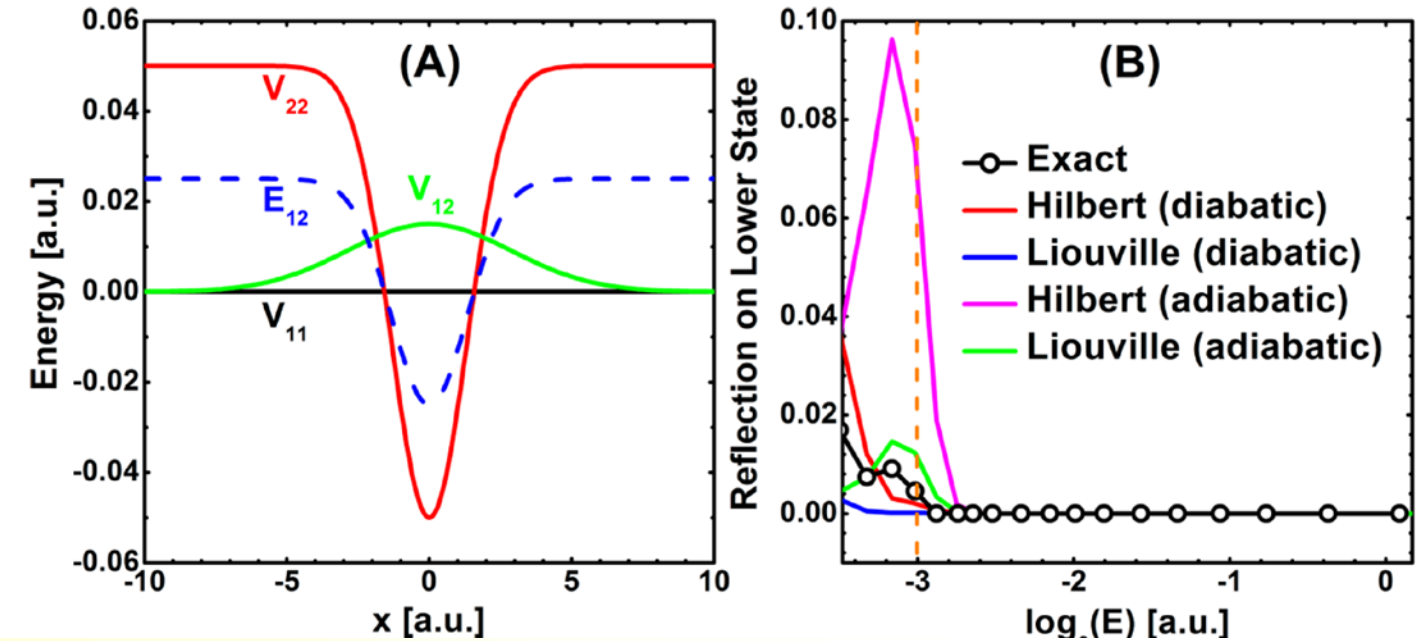
Questions for coherence states, $i \neq j$

- Energy: $E_{ij}=(E_{ii}+E_{jj})/2$, similar to quantum-classical Liouville
- Interpretation of trajectories on *ij*: assign half to *ii*, half to *jj*
- Direction of velocity rescaling for transition $ij \rightarrow kl$:
  add NA coupling vectors $NA_{ik}+NA_{jl}$

FSSH in Liouville Space

L. Wang, A.E. Sifain, O.V.P. *J Phys Chem Lett* **6**, 3827 (2015)

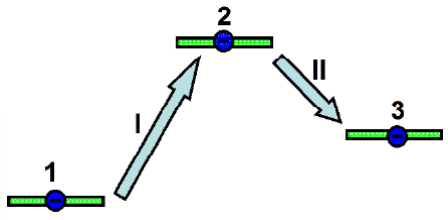
Dual avoided crossing

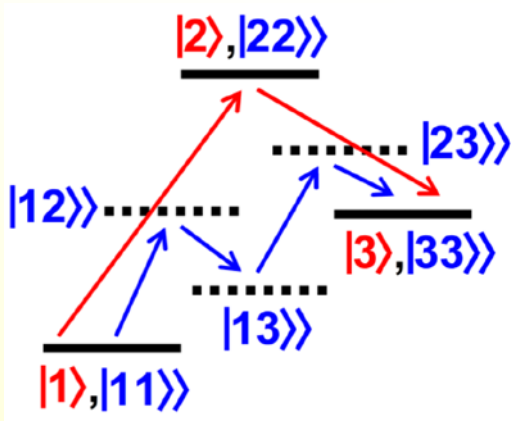


- FSSH in diabatic representation is better than adiabatic
- Big improvement in adiabatic using Liouville (better treatment of coherence)

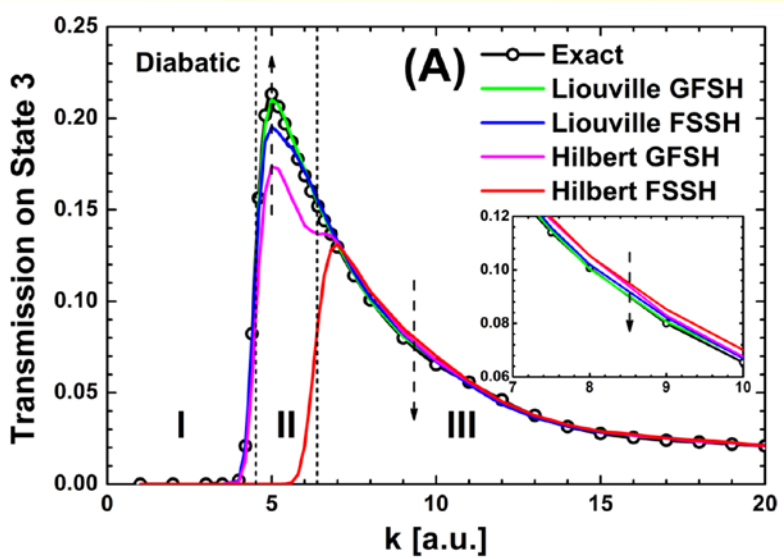
FSSH & GFSH in Liouville Space

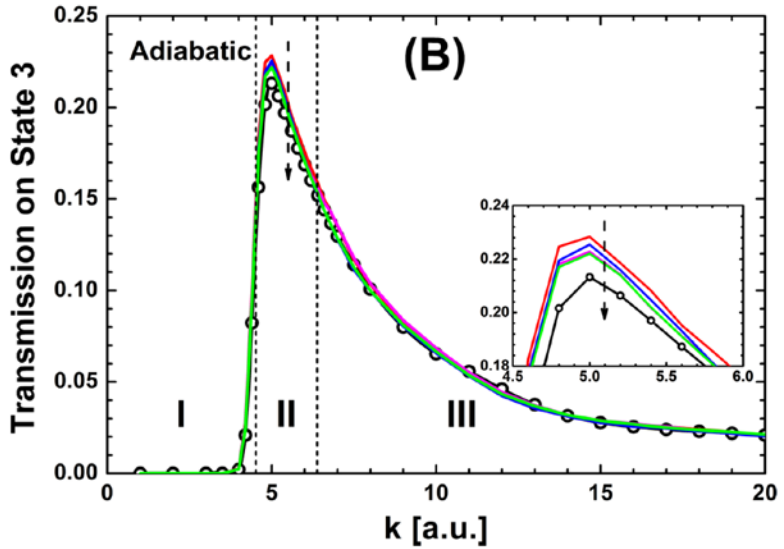
L. Wang, A.E. Sifain, O.V.P. *JCP-Rapid* **143**, 191102 (2015)





Super-exchange is obtained



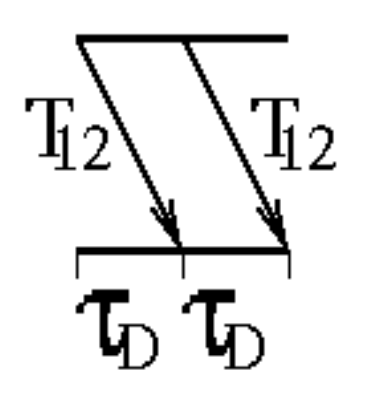


Decoherence & Quantum Zeno Effect

O. V. Prezhdo, P. J. Rossky, *Phys. Rev. Lett.* **81**, 5294 (1998)
O. V. Prezhdo, *Phys. Rev. Lett.* **85**, 4413 (2000)

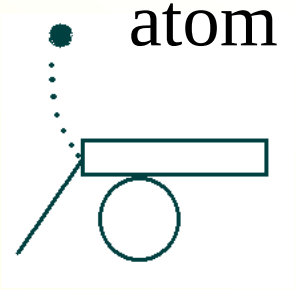
With decoherence: $P_{12} = |T_{12}|^2 + |T_{12}|^2 + \ldots$

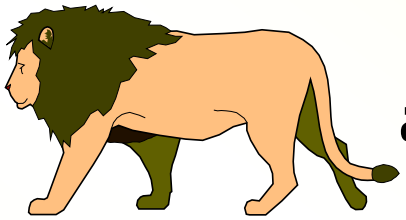
Without decoherence $P_{12} = |T_{12} + T_{12} + \ldots|^2$

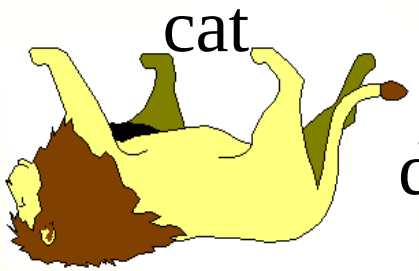


Decoherence makes transitions less likely

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





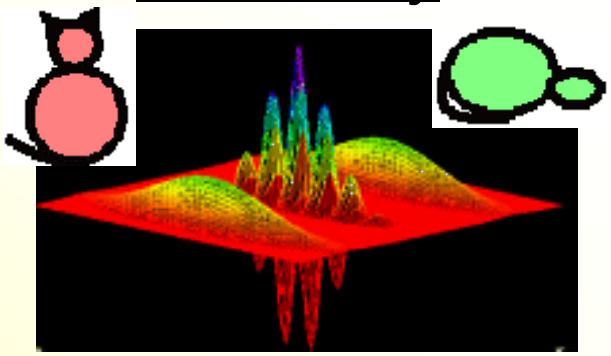


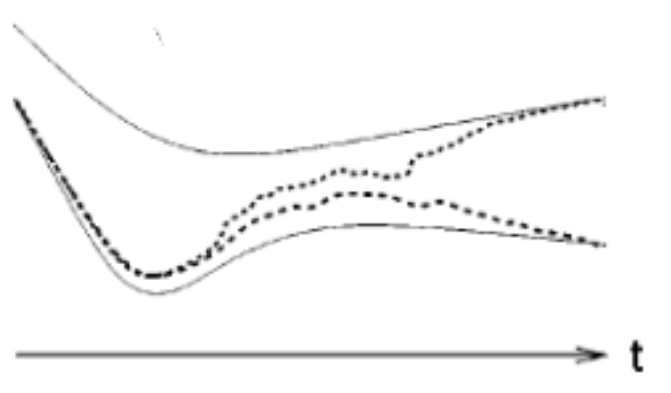
Stochastic Mean-Field
(decoherence gives branching)

O. V. Prezhdo *J. Chem. Phys.* **111**, 8366 (1999)

No ad hoc expressions for hopping probability

Cat Density





dead cat 

alive cat 

quantum Brownian motion

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

friction noise

Decoherence Induced Surface Hopping (DISH)

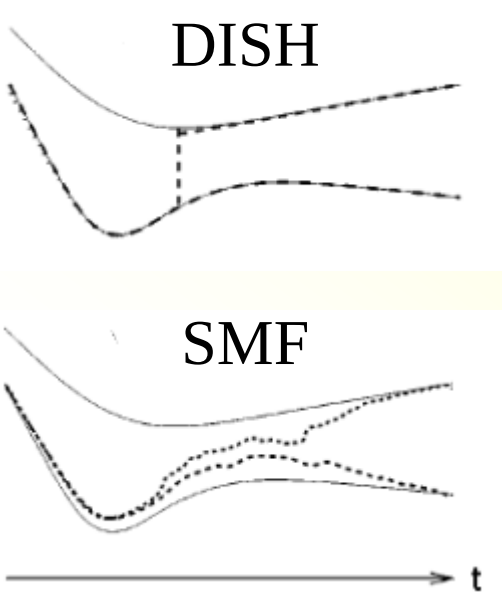
Jaeger, Fisher, Prezhdo *J. Chem. Phys.* **137**, 22A545 (2012)

Evolve in an adiabatic state.

Hop when a decoherence event occurs.

Use normal quantum probabilities.

Rescale velocity as before in SH.



Advantages

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

Corresponds to a piece-wise continuous stochastic Schrodinger equation

Coherence Penalty Functional

Akimov, Long, Prezhdo, *J. Chem. Phys.* **140**, 194107 (2014)

- Retain computational efficiency of Ehrenfest – no stochastic sampling: 1 trajectory, ordinary differential equations
- Penalize development of coherence

$$i\hbar\frac{\partial c_i(t)}{\partial t} = \sum_i \left[E_i(R(t))\,\delta_{i,j} - i\hbar\frac{P}{M}d_{ij} \right] c_j(t) \qquad \begin{aligned} q_i &= \mathrm{Re}(c_i) \\ p_i &= \mathrm{Im}(c_i) \end{aligned}$$

$$H = \sum_i \frac{E_i}{2\hbar}\left(q_i^2 + p_i^2\right) - \frac{P}{M}\sum_{i,j} d_{ij}\,p_i q_j \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i} \quad \dot{q}_i = -\frac{\partial H}{\partial p_i}$$

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$$\tilde{H} = H + \sum_{\substack{i,j \\ i\neq j}} \lambda_{ij}\left(q_i^2 + p_i^2\right)\left(q_j^2 + p_j^2\right)$$

states with large coherence are energy maxima

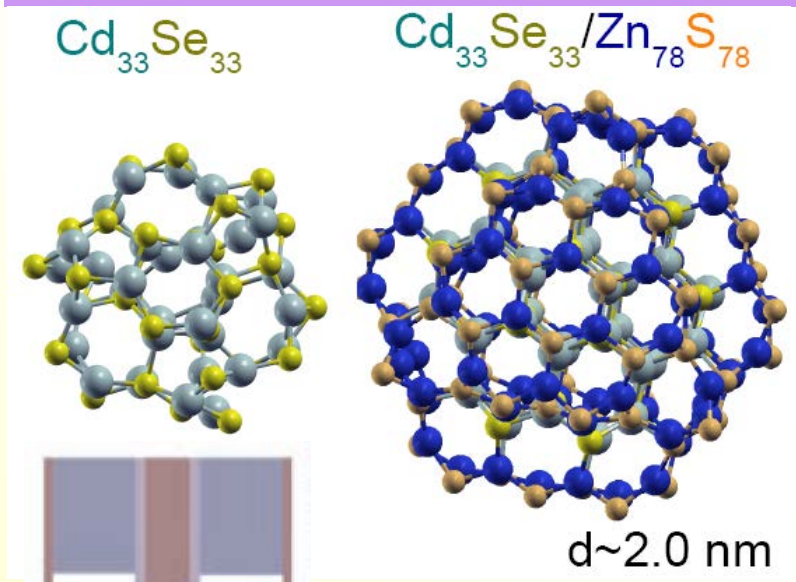
$$\left(q_i^2 + p_i^2\right)\left(q_j^2 + p_j^2\right) = |c_i^* c_j|^2$$

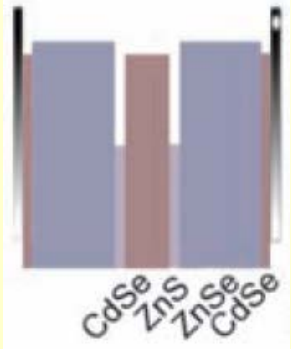
coherence measure

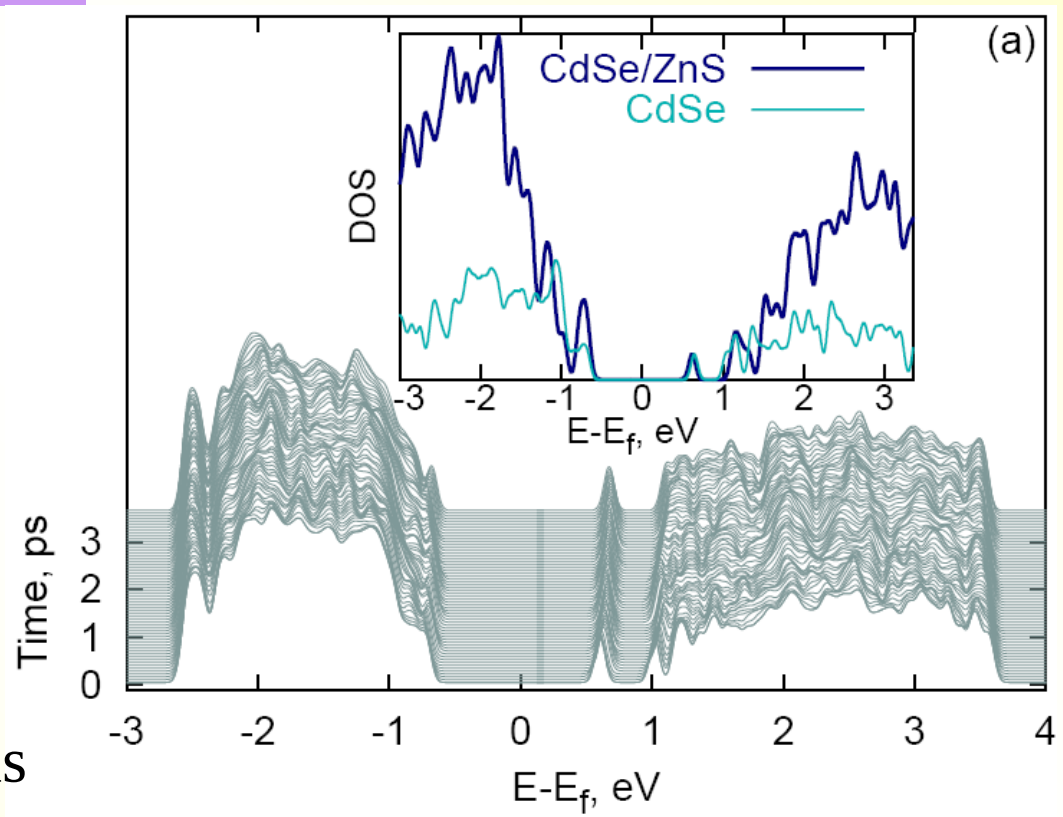
λ_{ij} - decoherence rate

Phonon Bottleneck in CdSe QD

Kilina, Neukirch, Habenicht, Kilin, Prezhdo, *PRL* **110**, 180404 (2013)







Experiment: 1ns

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

Calculation: 0.7ns
without decoherence: 0.003ns

PYXAID: PYthon eXtension of Ab Initio Dynamics

Akimov, Prezhdo, *J. Theor. Comp. Chem.* **9**, 4959 (2013)
ibid. **10**, 789 (2014)

Python interfaced with Quantum Espresso, VASP

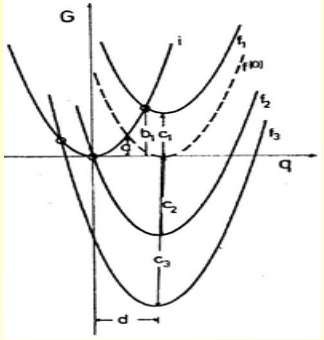
In DFTB+: Pal, Trivedi, Akimov, Aradi, Frauenheim, Prezhdo
JCTC **12** 1436 (2016)

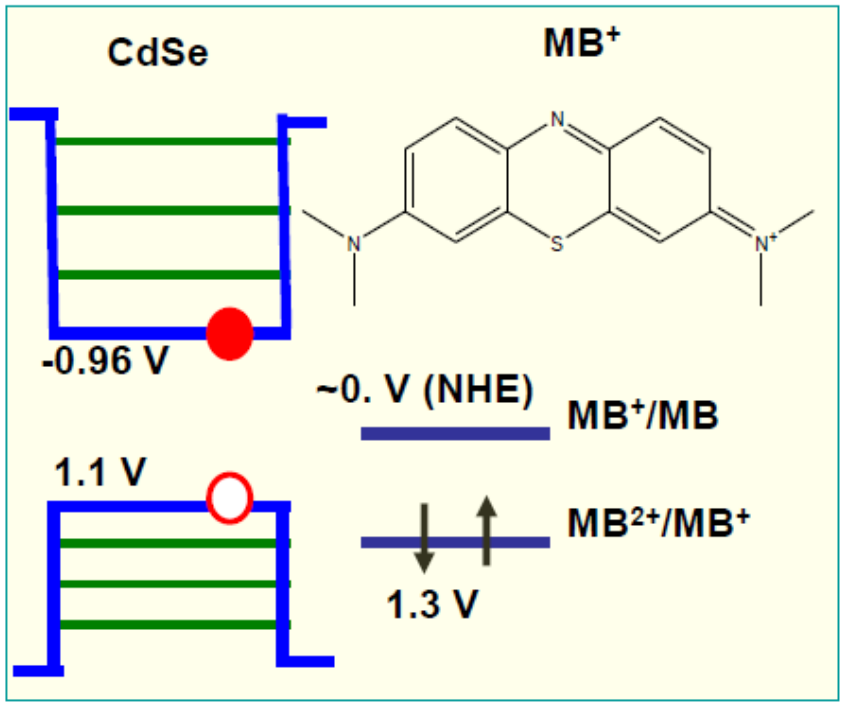
Fragment approach in Gamess: Negben, Prezhdo
JPC A **120** 7205 (2016)

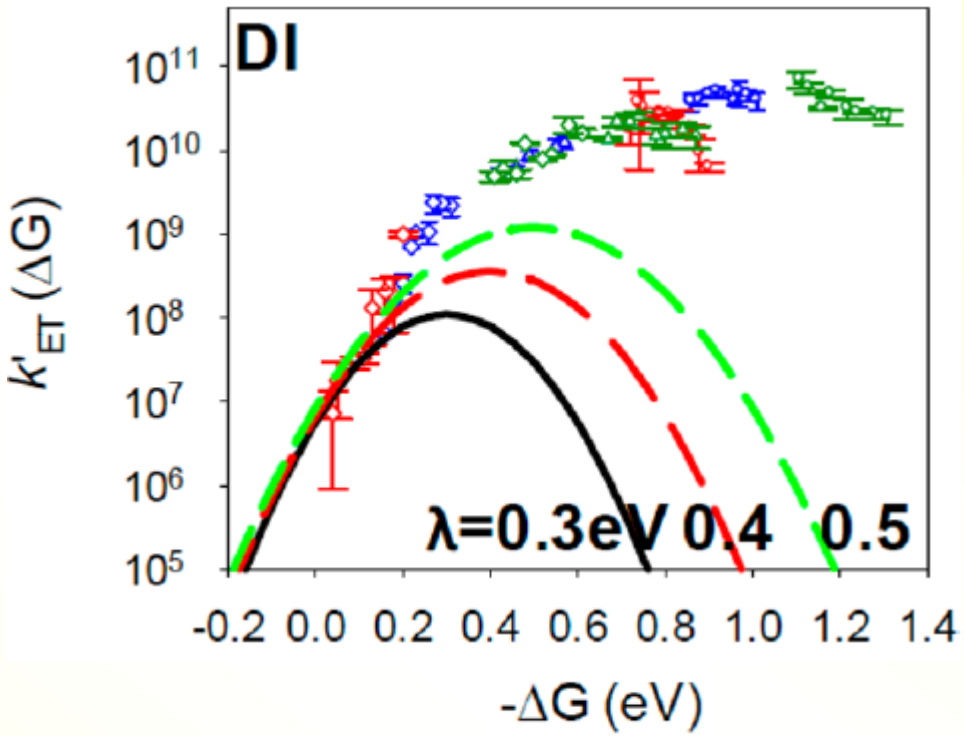
Overview of new methods
Perspective Article in
JPC Lett. **7** 2100 (2016)

Auger-assisted ET

Zhu, Yang, Hyeon-Deuk, Califano, Song, Wang, Zhang, Prezhdo, Lian, *Nano Lett.* **14**, 1263 (2014)



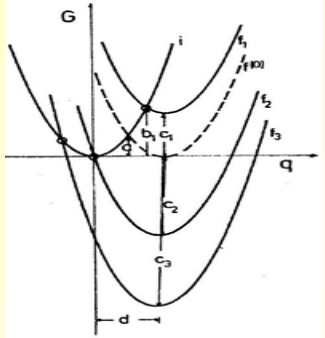


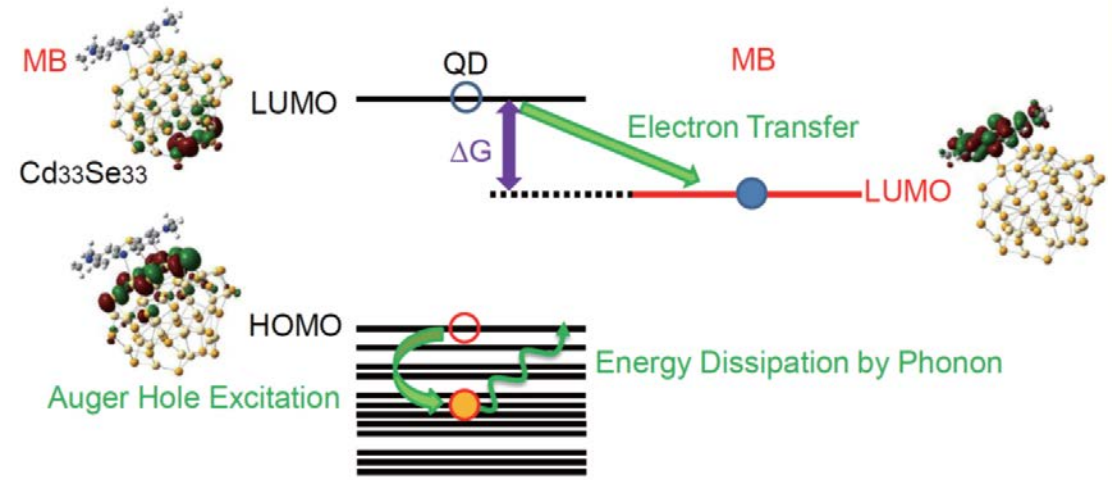


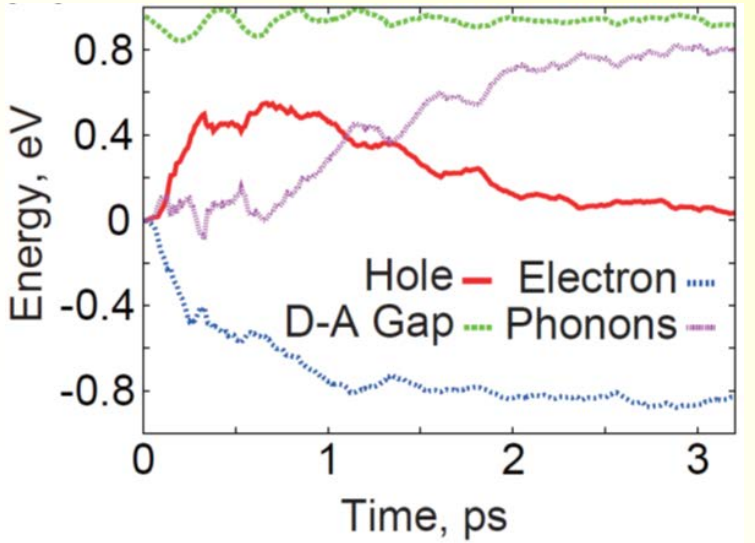
Why is there no Marcus inverted region? $k(r) \propto e^{-\frac{[\Delta G(r)+\lambda]^2}{4\lambda RT}}$

Auger-assisted ET

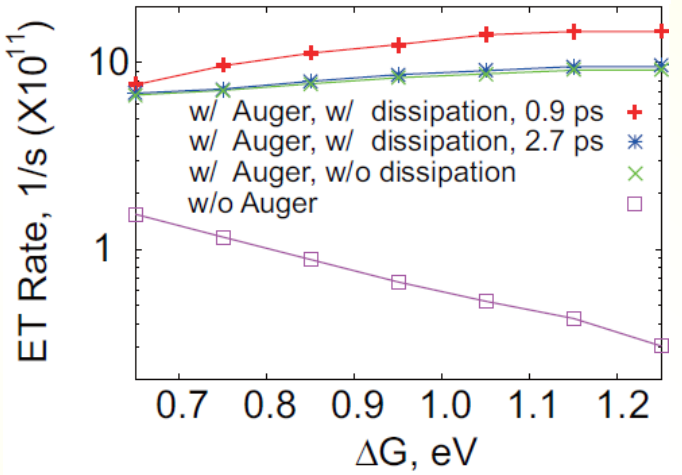
Zhu, Yang, Hyeon-Deuk, Califano, Song, Wang, Zhang, Prezhdo, Lian, *Nano Lett.* **14**, 1263 (2014)





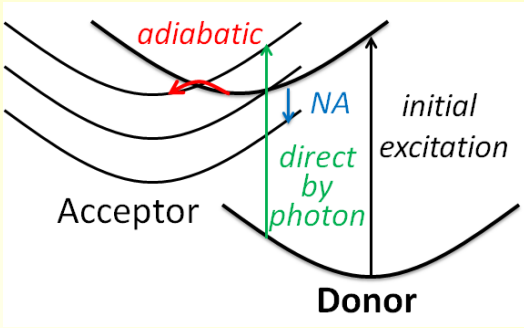


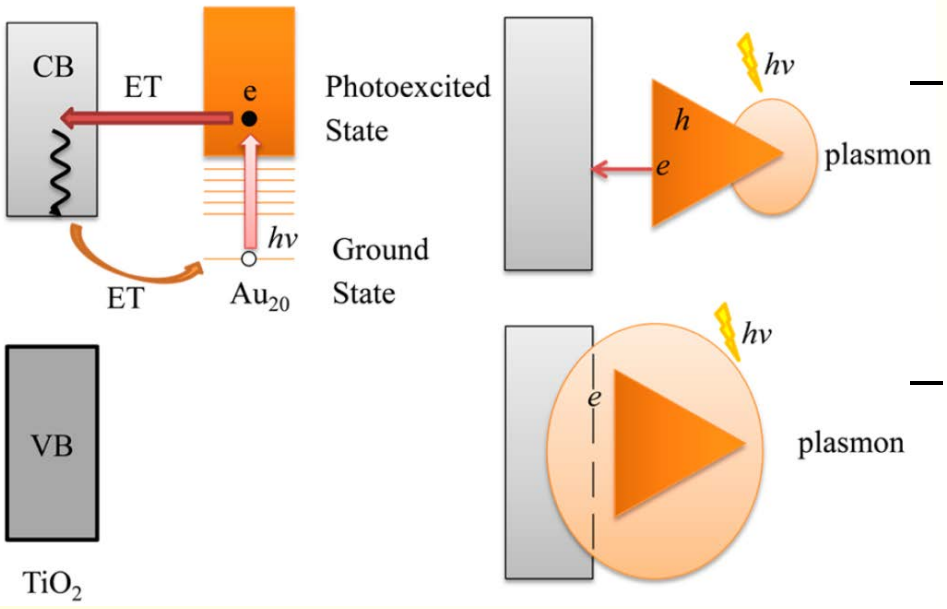
- Normally, excess energy goes to phonons
- In QDs, hole excitation accompanies ET
- Then, hole transfers energy to phonons



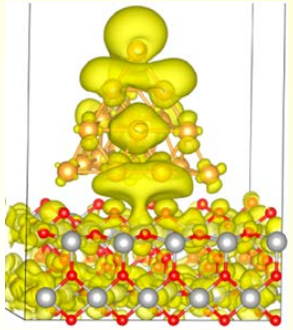
Plasmon-driven ET

Long, English, Prezhdo *JACS* **136**, 4343 (2014)

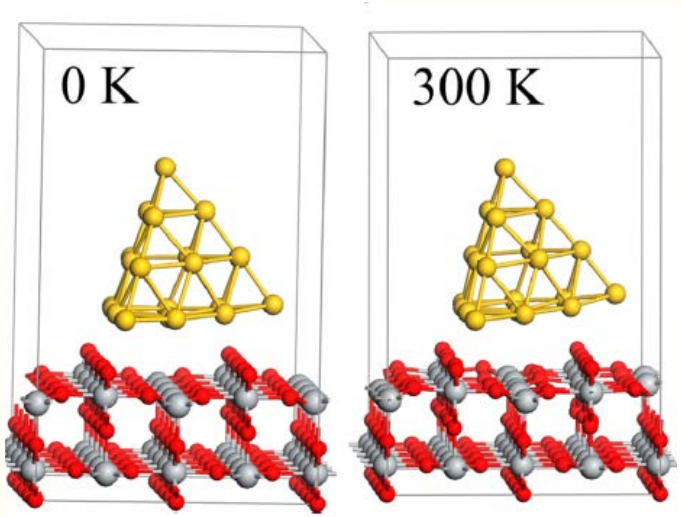


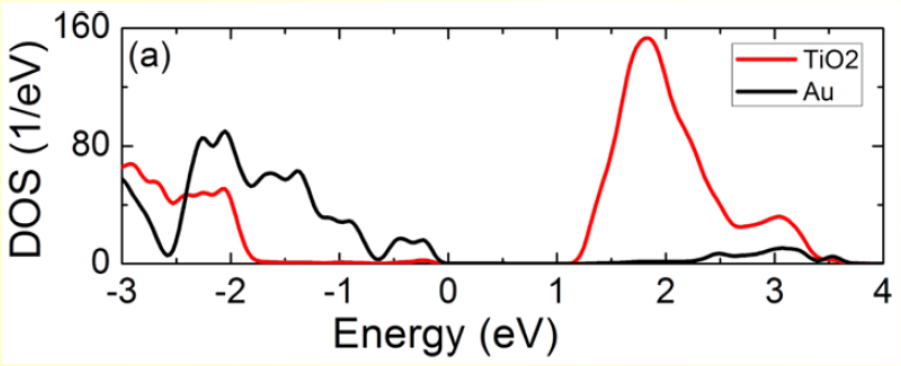


– traditional view



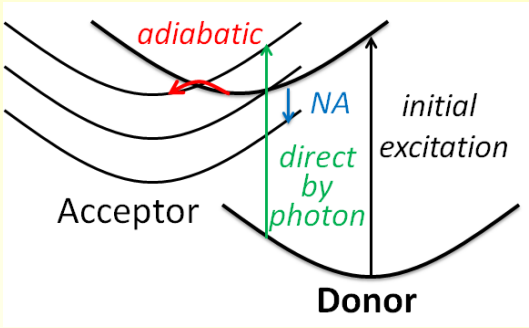
– our calculation

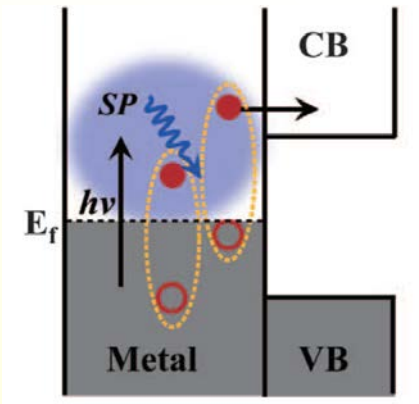




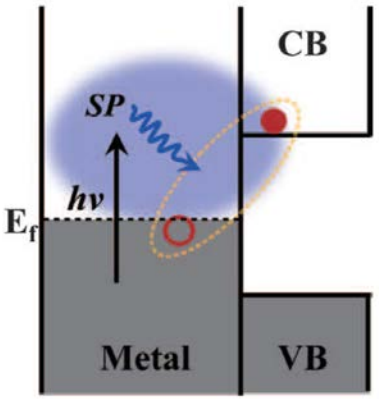
Experimental Evidence

Lian et al, *Science* **349** 632 (2015)

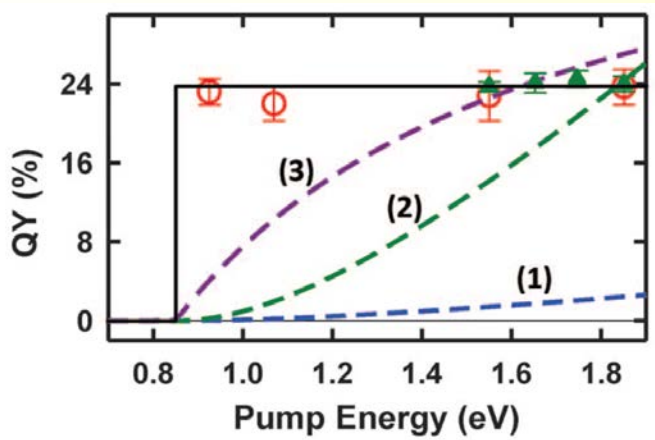




traditional view



this experiment



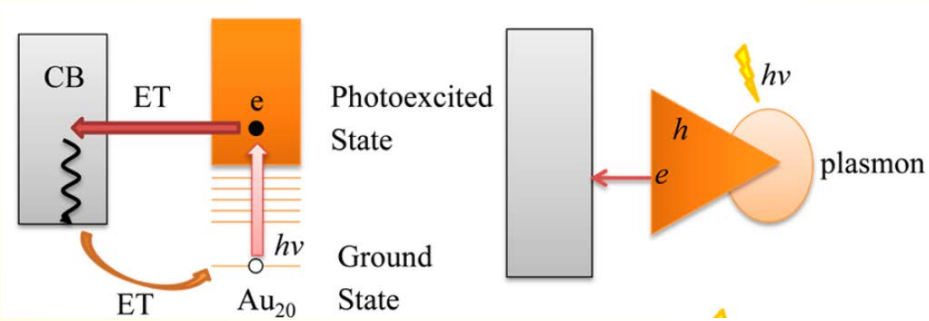
Quantum yield is independent of excitation energy, in contrast to traditional model

$$QY(\omega) = (\hbar\omega - E_B)^2/(4E_F\hbar\omega)$$

Gold Rods on MoS_2

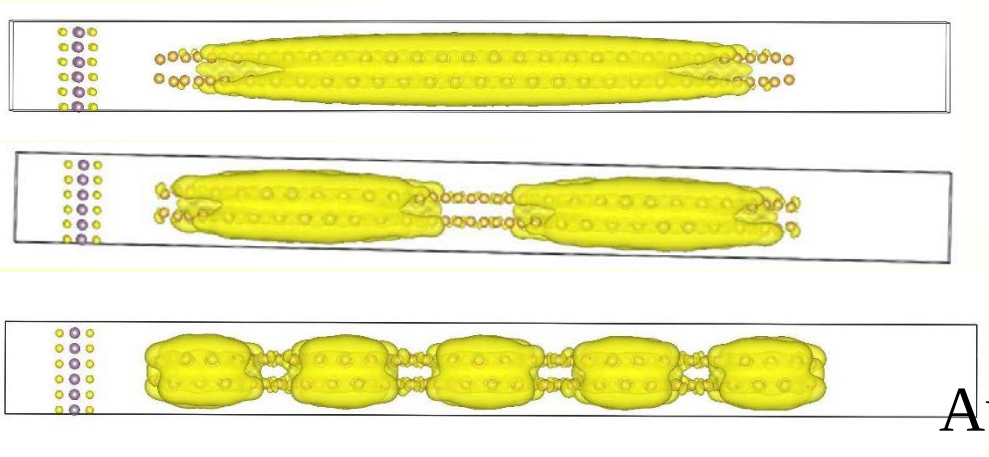
Long, Fang, Prezhdo & co-workers *Chem*, accepted

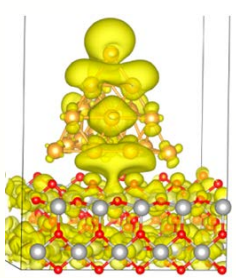
Traditional mechanism holds



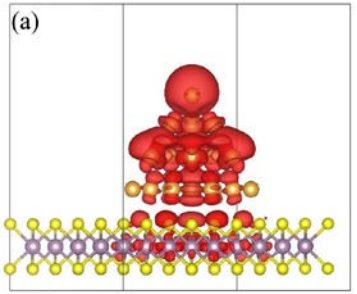
Coupling is weak:

- Plasmon-like excitations have no density on MoS_2
- MoS_2 is fully chemically saturated

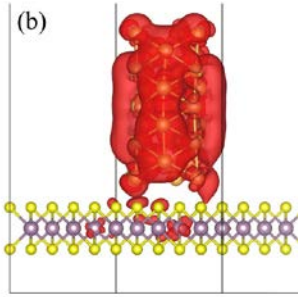




Au pyramid on TiO_2



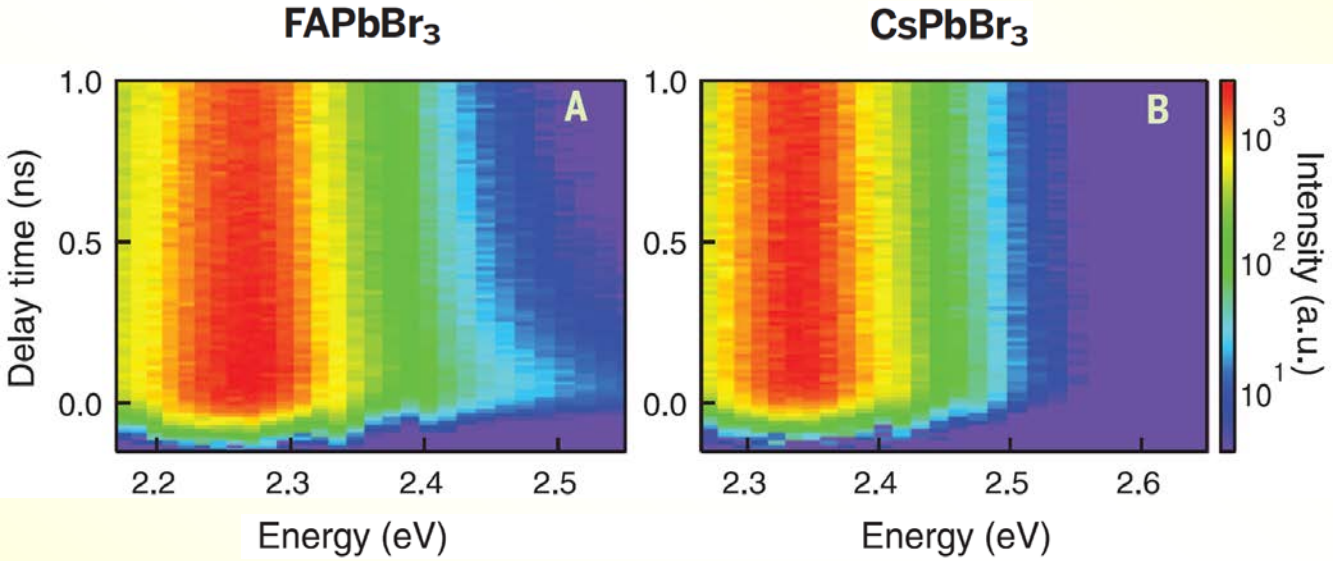
Au pyramid on MoS_2



Au rod on MoS_2

Hot Luminescence in $FAPbBr_3$

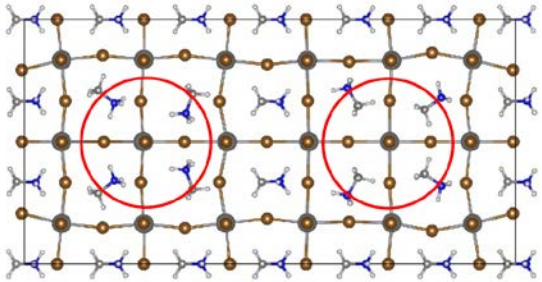
X. Y. Zhu and co-workers,
Science **353** 6306 (2016)



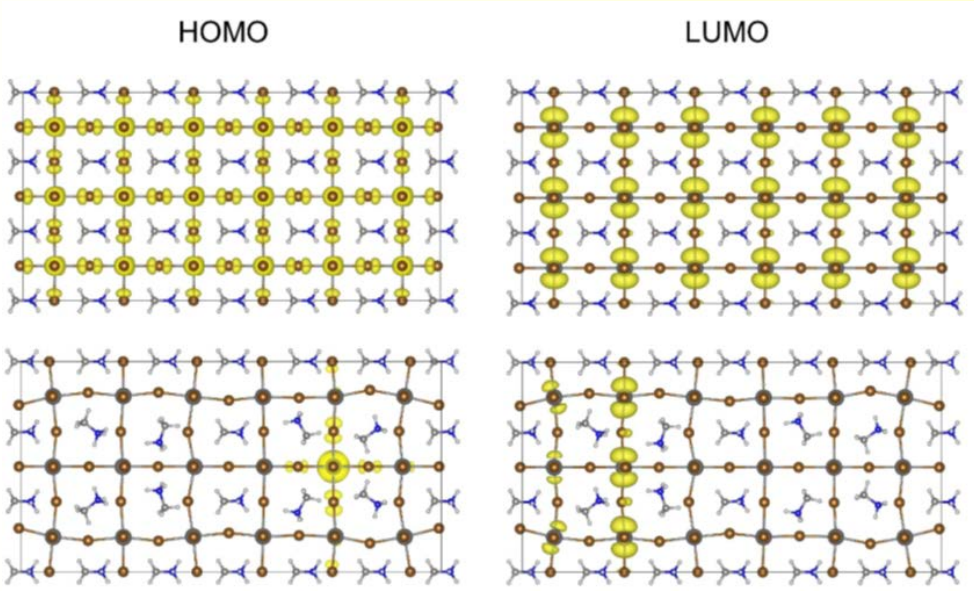
- Organic-inorganic perovskite luminesces at both low (>1ns) and high (200ps) energies
- Purely inorganic perovskite emits only at low energy
- Origin of high energy luminescence?

Hot Luminescence in $FAPbBr_3$

Long, Prezhdo & co-workers *J. Am. Chem. Soc.* **48** 17327 (2017)



	bandgap (eV)	NA coupling (meV)	recombination (ps)
higher E_g	2.01	0.255	465
lower E_g	1.68	0.157	1165



High energy: delocalized (free) carriers, larger coupling, faster decay
Low energy: localized (polaron) carriers, smaller coupling, slower decay

Different “chromophores” can also arise from ion rich phases, electrically ordered phases, grain boundaries, defects, etc.

In Lieu of Conclusions

- Nonadiabatic MD with TDDFT
  - Classical path approximation for SH
  - Self-consistent FSSH (trivial crossings)
  - Global flux surface hopping
  - Surface hopping in Liouville space
  - Decoherence induced surface hopping
  - Coherence penalty functional
- Applications
  - Phonon-bottleneck in QDs
  - Auger assisted ET
  - Plasmon-driven ET
  - Hot luminescence in perovskites