Correlated Electron-Ion Dynamics for resonant systems:

High order expansion and applications to simple models

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Motivation

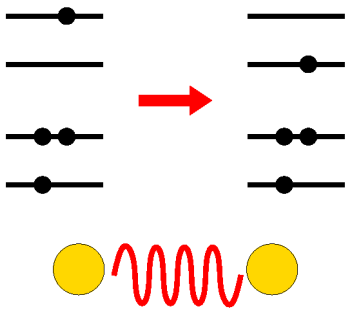
Expand on part of A. Fisher's lectures

A. Horsfield
(Imperial College)

A variant of Correlated Electron-Ion Dynamics (CEID)

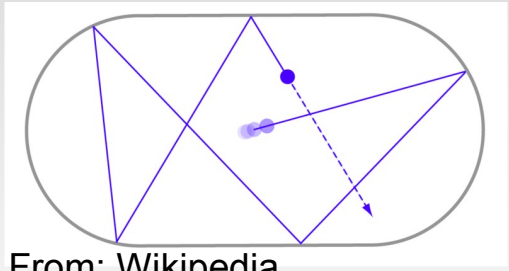
Original CEID: Joule heating in nanowires

Variant of CEID: resonant electron-ion systems



A more general framework to model quantum ions

The nonadiabatic problem



From: Wikipedia

$$\dot{P} = F(R)$$
$$\dot{R} = P/M$$

Newton's eqs. (classical)

- ***Numerically efficient***
- ***No electronic transitions***

No ***quantum*** degrees of freedom

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho]$$

From: Wikipedia

Von Neumann's eq. (quantum)

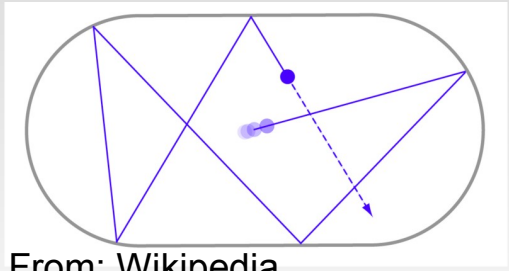
- ***Exact***
- ***Not feasible***

No ***classical*** degrees of freedom

How to ***interpolate*** between these two limits?

The ***CEID*** answer in the first part of this talk...

Ehrenfest Dynamics



From: Wikipedia

$$\dot{P} = F(R)$$
$$\dot{R} = P/M$$

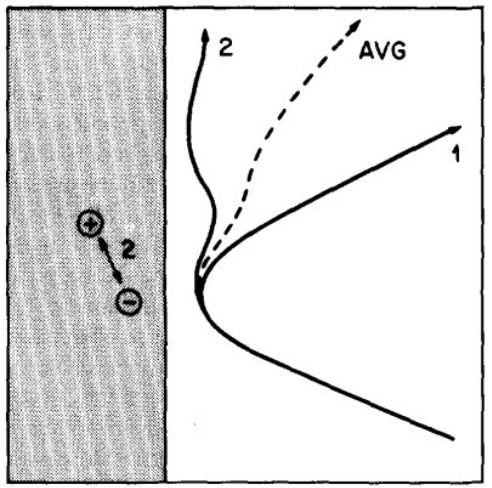
Newton's eqs. (classical)

$$\dot{\rho}_e = \frac{1}{i\hbar}[H_e(R), \rho_e]$$
$$\dot{P} = -\langle \rho_e \frac{\partial H_e}{\partial R} \rangle$$
$$\dot{R} = P/M$$

From: Wikipedia

(Incomplete) ***ED summary***:

- ☑ Energy & normalisation conserved
- ☑ Deterministic
- ☑ Rather efficient
- ☒ Too much *coherent*
- ☒ Hard to thermalise



From: *JCP* **93** 1061 (1990)

$$pure\ \rho_e^{ini} \Rightarrow pure\ \rho_e^{fin}$$

The (semi)classical limit

From: Wikipedia

$$\dot{\rho}_e = \frac{1}{i\hbar}[H_e(R), \rho_e]$$

$$\dot{P} = -\langle \rho_e \frac{\partial H_e}{\partial R} \rangle$$

$$\dot{R} = P/M$$

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho]$$

?

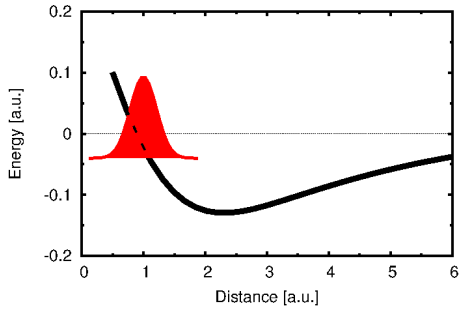
From: Wikipedia

Ehrenfest dynamics (***quantum-classical***)

Von Neumann's equation (***fully quantum***)

Ionic wave function ***very localised***

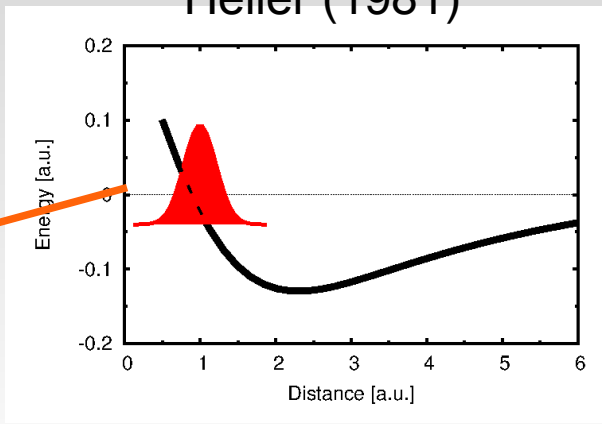
$$\langle x^2 \rangle = \frac{1}{2}\frac{\hbar}{M\omega}$$



Delocalised states (e.g., ***phonons***) not suitable for the classical limit

The frozen Gaussians

Heller (1981)



Ionic WFs: ***time-dependent*** Gaussian packets

$$\Psi(R,t;\bar{R},\sigma)=G(R-\bar{R}(t),\sigma(t))$$

Ionic WFs can have ***nodes*** *(quantum fluctuations)*

Factorise out the ***mean motion*** of the ionic WF

$$\Psi(R,t;\bar{R},\sigma)=G(R-\bar{R}(t),\sigma(t))=\exp\left(\frac{1}{i\hbar}\hat{P}\bar{R}\right)G(R,\sigma(t))$$

Factorise out the mean ***momentum***, too ("kick the WF")

$$\Psi(R,t;\bar{P},\bar{R},\sigma)=\exp\left(-\frac{1}{i\hbar}\hat{R}\bar{P}\right)\exp\left(\frac{1}{i\hbar}\hat{P}\bar{R}\right)G(R,\sigma(t))$$

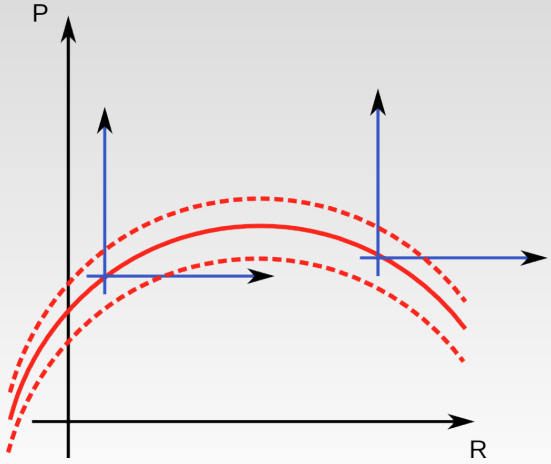
Alternative and equivalent way: ***Wigner transform***
L. Stella *et al. J. Chem. Phys.* **127**, 214104 (2007)

Hydrodynamics analogy

Lagrangian specification of flow:

"...is a way of looking at fluid motion where the observer follows an individual fluid parcel."

Fluid parcel = ionic wave packet/density matrix



$$\rho_L(t;\bar{P},\bar{R}) = \exp\left(\frac{1}{i\hbar}\hat{R}\,\bar{P}\right)\exp\left(-\frac{1}{i\hbar}\hat{P}\,\bar{R}\right)\rho(t)\exp\left(\frac{1}{i\hbar}\hat{P}\,\bar{R}\right)\exp\left(-\frac{1}{i\hbar}\hat{R}\,\bar{P}\right)$$

It does not depend on the order of the exps. (Baker–Campbell–Hausdorff)

Equation of motion (Lagrangian spec.): $\dot{\rho}_L = \frac{1}{i\hbar}[H_L^{mat}, \rho_L]$

Effective (material) Hamiltonian:

$$H_L^{mat}(\bar{P},\bar{R}) = H_L + \dot{\bar{P}}(R-\bar{R})_L - \dot{\bar{R}}(P-\bar{P})_L$$

Analogy with the ***material derivative*** of hydrodynamics

Summary I

From: Wikipedia

$$\dot{\rho}_e = \frac{1}{i\hbar}[H_e(R), \rho_e]$$

$$\dot{P} = -\langle \rho_e \frac{\partial H_e}{\partial R} \rangle$$

$$\dot{R} = P/M$$

$$\dot{\rho}_L = \frac{1}{i\hbar}[H_L^{mat}(\bar{P}, \bar{R}), \rho_L]$$

$$\dot{\bar{P}} = -\langle \rho_L \frac{\partial H_L}{\partial \bar{R}} \rangle$$

$$\dot{\bar{R}} = \bar{P}/M$$

From: Wikipedia

- Ehrenfest dynamics (***quantum-classical***)
- Von Neumann equation, ***redux*** (***fully quantum, still exact!***)
- Now the "***interpolation***" between the two limits is easier!

$$\rho_L = \rho_e \times \delta(P - \bar{P}, R - \bar{R}) \Rightarrow ED$$

- The variant of CEID provides a ***convergent approximation scheme*** from Ehrenfest's to Von Neumann's

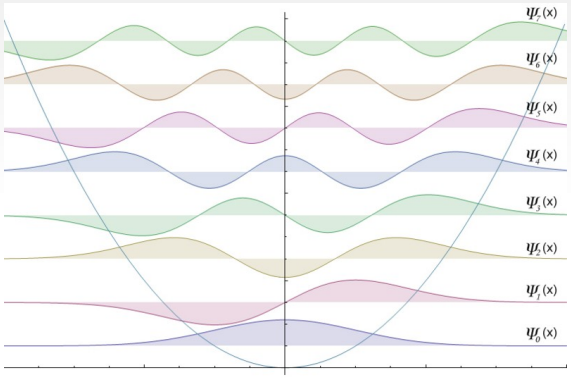
CEID expansion

Expand by using the ***quantum harmonic oscillator*** eigenfunctions

3N quantised modes (phonons/vibrons)

$$\rho_L = \sum_{\boldsymbol{n},\boldsymbol{m}}^{N_{ceid}} |\boldsymbol{n}\rangle \rho_{\boldsymbol{n},\boldsymbol{m}} \langle \boldsymbol{m}|$$

$$\boldsymbol{n} = (n_1, n_2, \ldots), \quad |\boldsymbol{n}| = \sum_i n_i \leqslant N_{ceid}$$
$$\boldsymbol{m} = (m_1, m_2, \ldots), \quad |\boldsymbol{m}| = \sum_i m_i \leqslant N_{ceid}$$



From: Wikipedia

🎓***Partial expansion***: The "coefficients" ρ_{nm} are not scalars, but ***operators*** *(matrices)* ***acting on the electronic states!***

CEID equations

$$\dot{\rho}_{n,m} = -\frac{1}{4M_0\imath\hbar}\sum_\alpha b_\alpha^2\Big[\sqrt{(n_\alpha+2)(n_\alpha+1)}\rho_{n+2_\alpha,m} - (2n_\alpha+1)\rho_{n,m} + \sqrt{n_\alpha(n_\alpha-1)}\rho_{n-2_\alpha,m}$$

$$-\sqrt{m_\alpha(m_\alpha-1)}\rho_{n,m-2_\alpha} + (2m_\alpha+1)\rho_{n,m} - \sqrt{(m_\alpha+2)(m_\alpha+1)}\rho_{n,m+2_\alpha}\Big] + \frac{1}{\imath\hbar}[H_e(\bar{\zeta}),\,\rho_{n,m}]$$

$$-\frac{1}{\sqrt{2}\imath\hbar}\sum_\alpha a_\alpha[\Delta\tilde{F}_\alpha(\bar{\zeta})(\sqrt{n_\alpha+1}\rho_{n+1_\alpha,m} + \sqrt{n_\alpha}\rho_{n-1_\alpha,m}) - (\sqrt{m_\alpha}\rho_{n,m-1_\alpha} + \sqrt{m_\alpha+1}\rho_{n,m+1_\alpha})\Delta\tilde{F}_\alpha(\bar{\zeta})]$$

$$+\frac{1}{4\imath\hbar}\sum_\alpha a_\alpha^2\Big[\tilde{K}_{\alpha,\alpha}(\bar{\zeta})(\sqrt{(n_\alpha+2)(n_\alpha+1)}\rho_{n+2_\alpha,m} + (2n_\alpha+1)\rho_{n,m} + \sqrt{n_\alpha(n_\alpha-1)}\rho_{n-2_\alpha,m})$$

$$-(\sqrt{m_\alpha(m_\alpha-1)}\rho_{n,m-2_\alpha} + (2m_\alpha+1)\rho_{n,m} + \sqrt{(m_\alpha+2)(m_\alpha+1)}\rho_{n,m+2\alpha})\tilde{K}_{\alpha,\alpha}(\bar{\zeta})\Big]$$

$$+\frac{1}{2\imath\hbar}\sum_{\alpha<\beta} a_\alpha a_\beta[\tilde{K}_{\alpha,\beta}(\bar{\zeta})(\sqrt{(n_\alpha+1)(n_\beta+1)}\rho_{n+1_\alpha+1_\beta,m} + \sqrt{(n_\alpha+1)n_\beta}\rho_{n+1_\alpha-1_\beta,m}$$

$$+\sqrt{n_\alpha(n_\beta+1)}\rho_{n-1_\alpha+1_\beta,m} + \sqrt{n_\alpha n_\beta}\rho_{n-1_\alpha-1_\beta,m}) - (\sqrt{m_\alpha m_\beta}\rho_{n,m-1_\alpha-1_\beta} + \sqrt{m_\alpha(m_\beta+1)}\rho_{n,m-1_\alpha+1_\beta}$$

$$+\sqrt{(m_\alpha+1)m_\beta}\rho_{n,m+1_\alpha-1_\beta} + \sqrt{(m_\alpha+1)(m_\beta+1)}\rho_{n,m+1_\alpha+1_\beta})\tilde{K}_{\alpha,\beta}(\bar{\zeta})],$$

L. Stella *et al. J. Chem. Phys.* **134**, 194105 (2011)


Equations of motion of the matrix coefficients

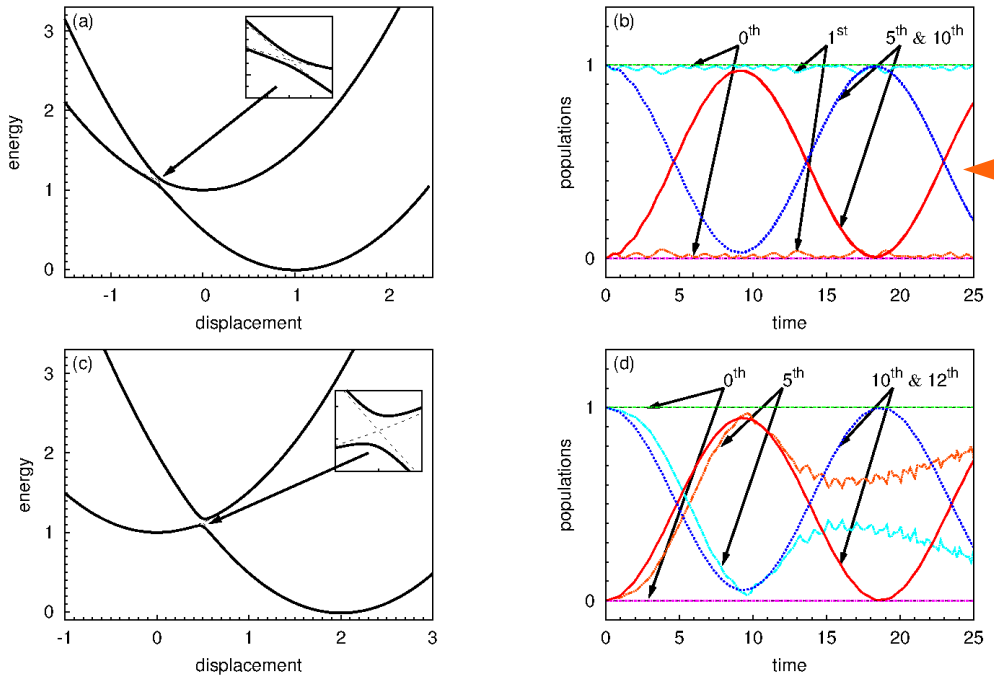

Implemented in the code: ***PolyCEID*** https://bitbucket.org/lstella/polyceid

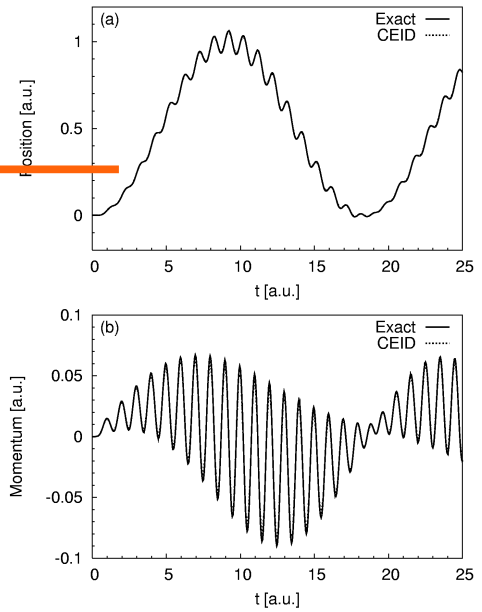
Resonant two-level systems

L. Stella *et al. J. Chem. Phys.* **127**, 214104 (2007)

$$\hat{H}_e(R) = \begin{pmatrix} \frac{1}{2}K(R-R_0)^2 & -f_c R \\ -f_c R & \frac{1}{2}KR^2 + \Delta\varepsilon \end{pmatrix},$$

Resonance: $\Delta\epsilon \simeq \hbar\omega$





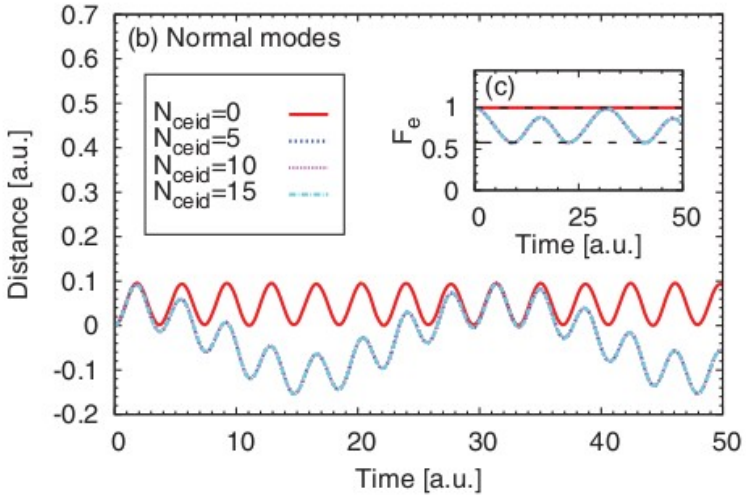
CEID 0 ~ ED: No transition! (No spontaneous emission)

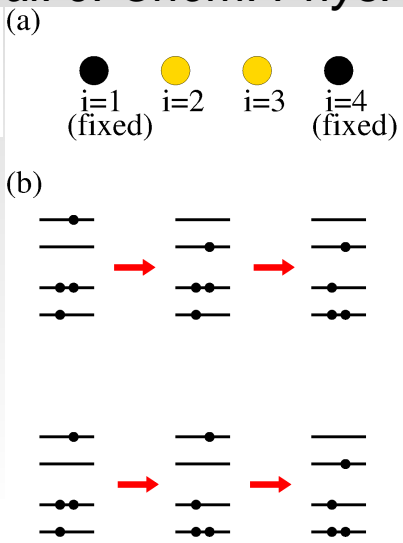
Fast convergence to the exact solution

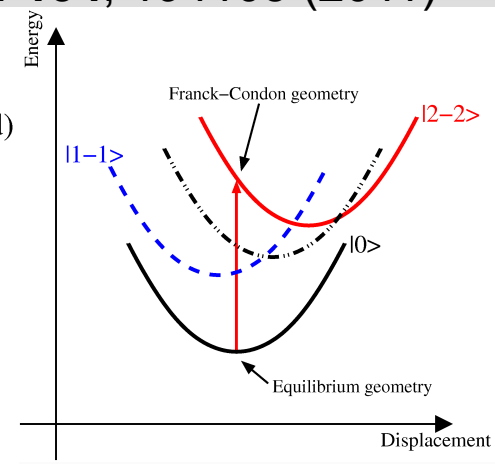
Analog of Rabi oscillations

L. Stella *et al. J. Chem. Phys.* **134**, 194105 (2011)

$$H_{ssh} = \frac{1}{2}\sum_i \hat{P}_i^2 - \sum_{\langle i,j\rangle}\left(1-\alpha|\hat{R}_i-\hat{R}_j|\right)\left(c_i^\dagger c_j + c_j^\dagger c_i\right) + \frac{1}{2}\sum_{\langle i,j\rangle}(\hat{R}_i-\hat{R}_j)^2$$

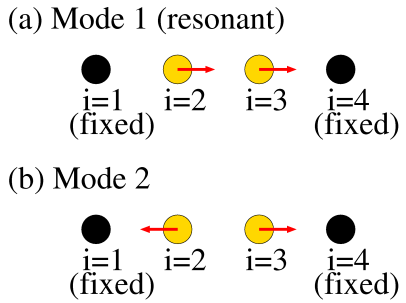


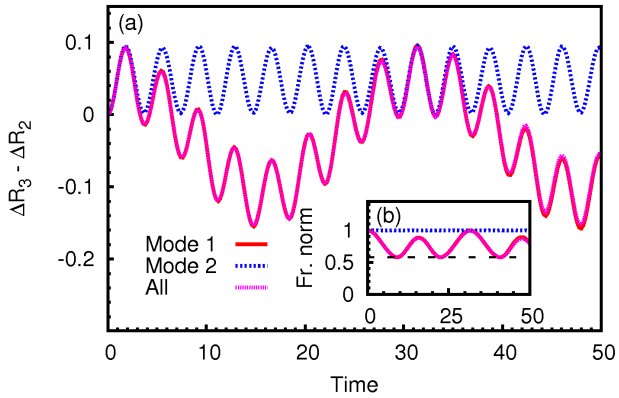




CEID 0 ~ ED: Only “Franck-Condon” oscillations

Just one relevant (resonant) **_ionic mode_**: Neglect the other!



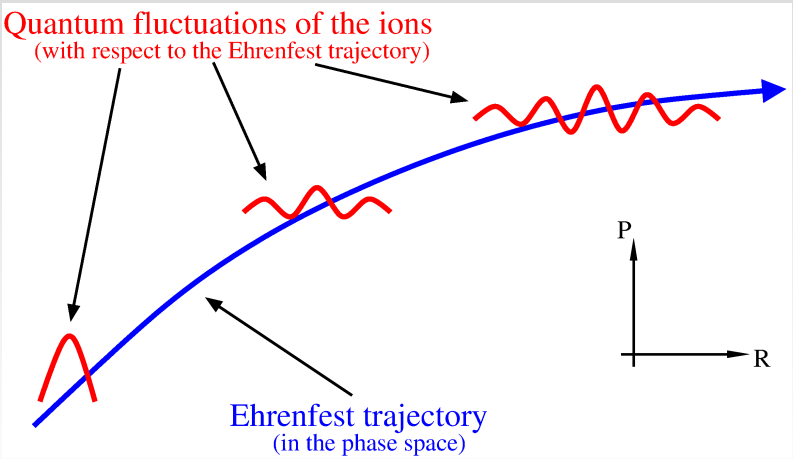


CEID Scaling

$$\dot{\rho}_L = \frac{1}{i\hbar}[H_L^{mat}(\bar{P},\bar{R}),\rho_L]$$

$$\dot{\bar{P}} = -\langle \rho_L \frac{\partial H_L}{\partial \bar{R}} \rangle$$

$$\dot{\bar{R}} = \bar{P}/M$$



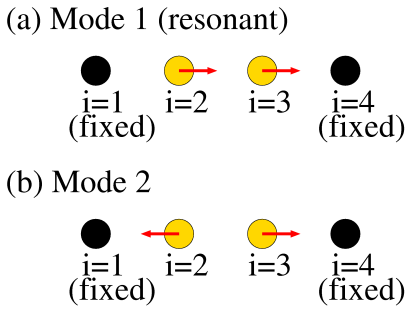
Molecular dynamics for ***all*** 6N classical variables: $\bar{P}, \bar{R}$

Quantum dynamics for selected (relevant) quantised modes

Two limits:

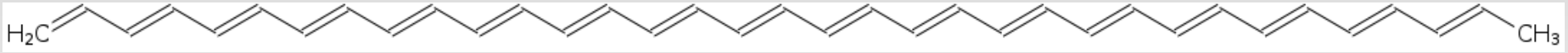
$N_{modes} \ll N_{ceid}$ ***Exponential*** scaling with N_{modes}

$N_{modes} \gg N_{ceid}$ ***Polynomial*** scaling with N_{modes}



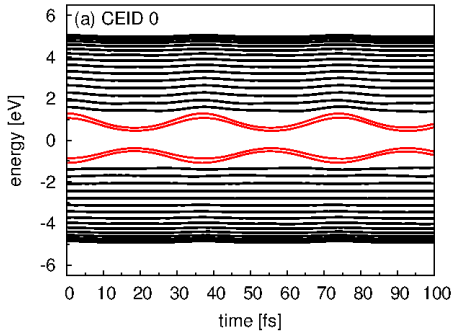
Conjugated polymers

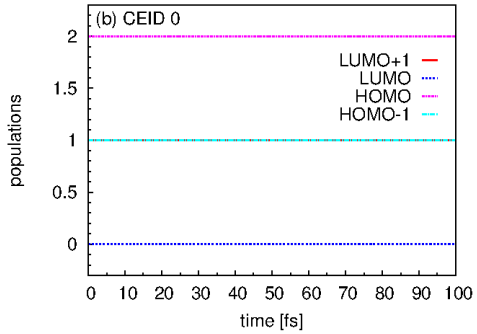
E. McEniry *et al. EPJ B.* **77**, 305 (2010)

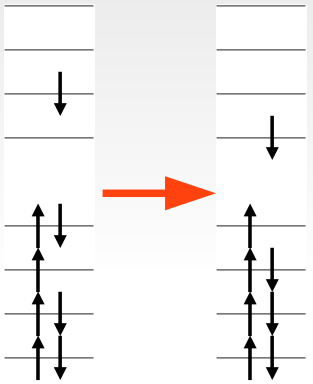


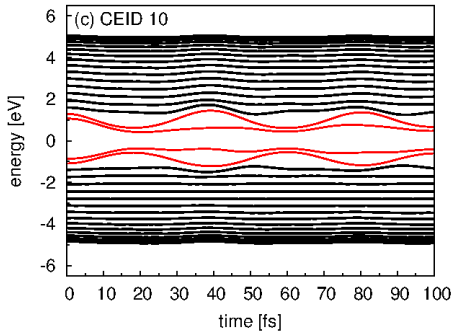
Kasha's rule: Luminescence observed from the ***lowest singlect exciton***

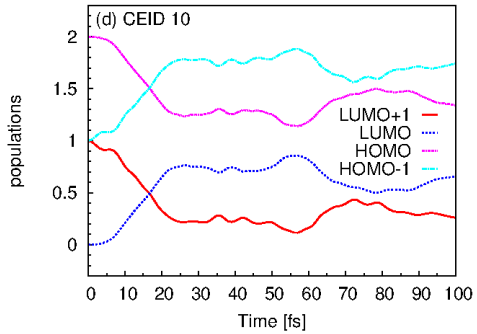
Ultrafast nonradiative exciton decay









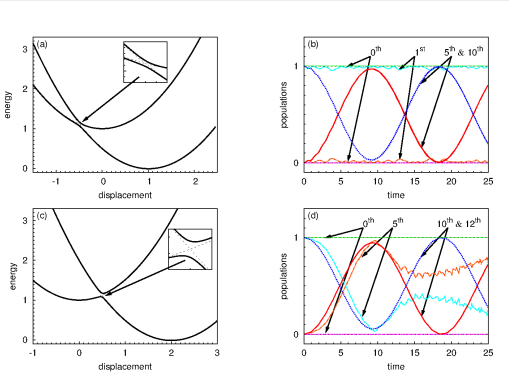


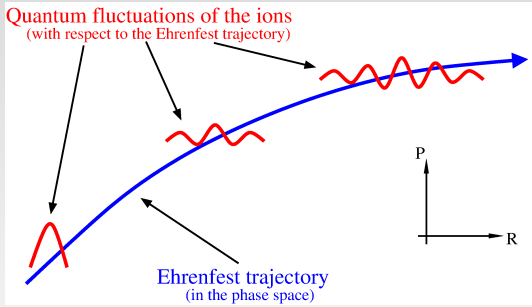
Technical details: 32 atoms, 34 electronic states, 20 Slater determinants, one quantised mode (dimerising mode)

"Surface hopping" without sudden quantum jumps!

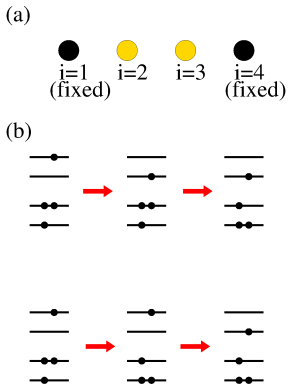
Conclusions

CEID improves on ED, without losing its good properties



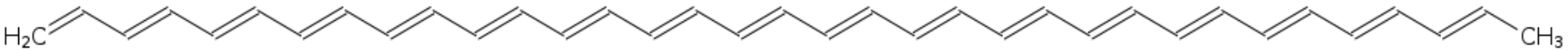


CEID provides a ***systematically convergent expansion*** of the quantum fluctuations of the ions



The ***"spontaneous emission of phonons"*** missed in ED, is correctly described (resonance)

New "decay channels" are open by the quantum fluctuations of the ions (off resonance)



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High order expansion and applications to simple models

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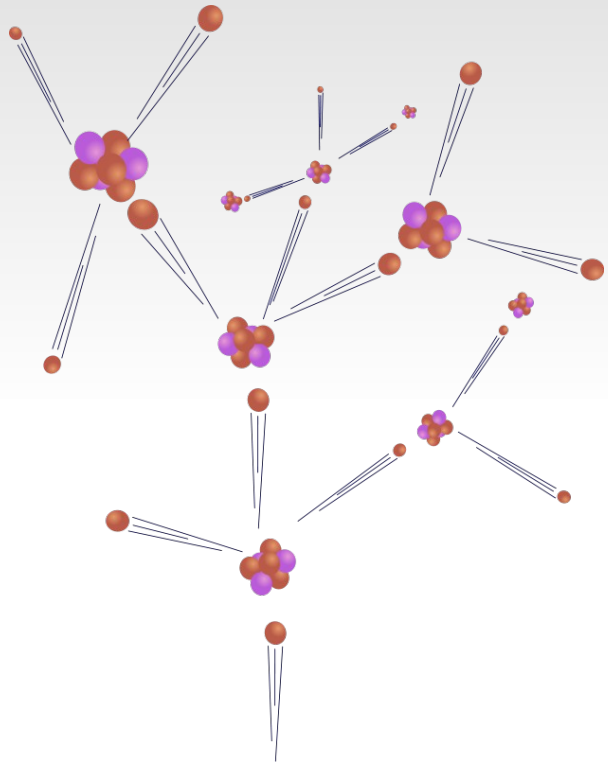
CEID for Radiation Damage?

- (Time-dependent) ***tight-binding*** approximation
- Effective one-electron theory: ***CEID + TDDFT(?)***
- With e-ion interaction, it is ***always many-body***...
- ***Non-resonant limit:*** $N_{modes} \gg N_{ceid}$
- Limited to the end of the cascade (?)



PolyCEID

- “Customisable” ***Su-Schrieffer-Heeger***-like Hamiltonian (so far)
- Possibility to ***fix classical atomic positions***
- **Periodic Boundary conditions** (experimental)
- ***Factorised initial condition*** (Born-Oppenheimer approximation)
- Initially ***relaxed atomic structure***
- ***No temperature*** (so far)
- ***Many-body electronic states*** (Quantum Chemistry)
- Choice of the ***quantised fluctuations of ions*** (efficiency)

Work in progress...