# Mixed quantum-classical methods and time correlation functions

S. Bonella
Universita' di Roma
La Sapienza

D. Coker
G. Ciccotti
R. Vuilleuimier

# System of nuclei and electrons
# if necessary beyond Born-Oppenheimer

$$\hat{H} = \frac{\hat{P}^2}{2M} + \hat{h}_{el}(\hat{R}, \hat{p}, \hat{q})$$

$$\hat{h}_{el}(\hat{R}, \hat{p}, \hat{q})$$

electronic kinetic energy
electron-electron interaction
electron-nuclei interaction
nuclei-nuclei interaction
external potential(s)

$$|\Psi\rangle$$

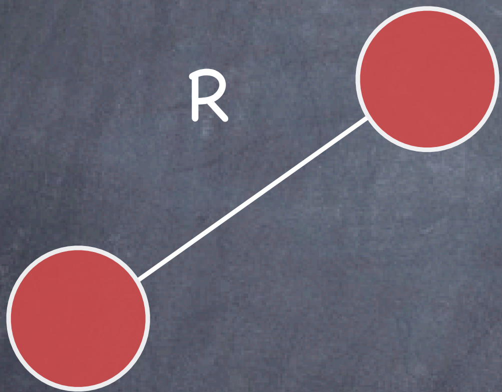
**Adiabatic** $|R\Phi_\lambda(R)\rangle$

$$\langle R|\Psi(t)\rangle = \sum_\lambda \chi^a_\lambda(R,t)|\Phi_\lambda(R)\rangle$$

**Diabatic** $|R\lambda\rangle$

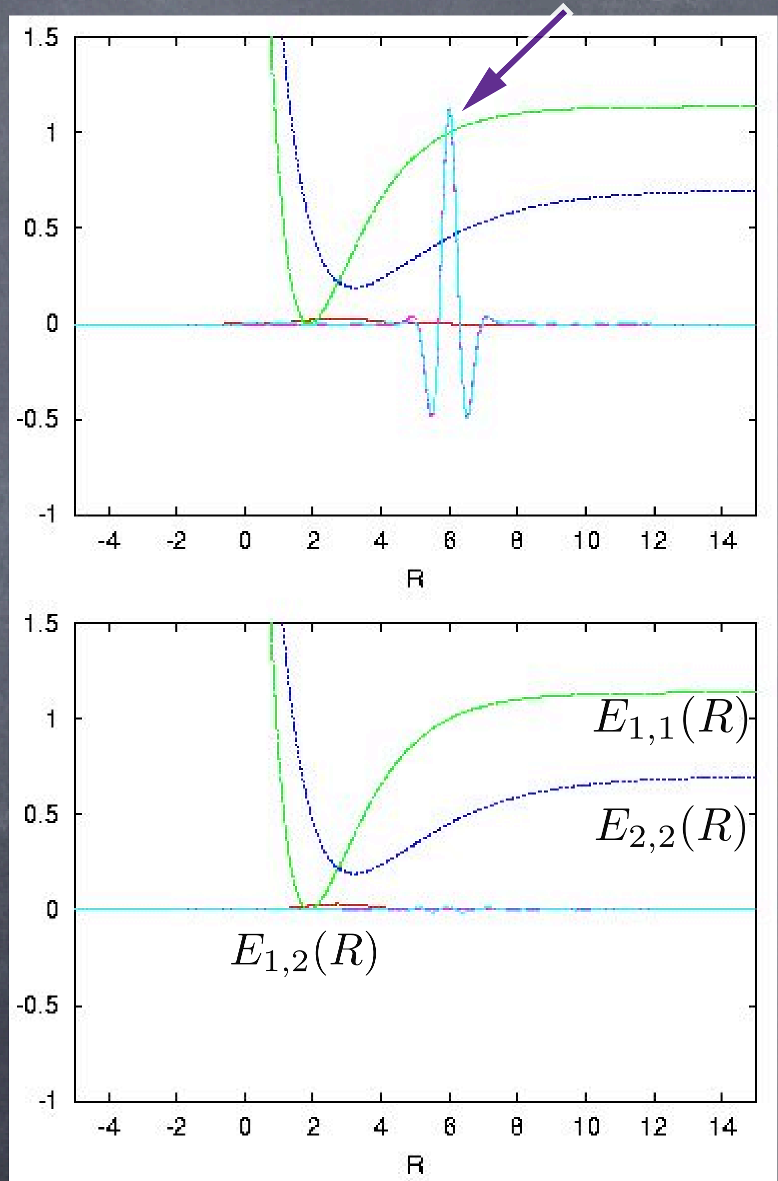
$$\langle R|\Psi(t)\rangle = \sum_\lambda \chi^d_\lambda(R,t)|\lambda\rangle$$

$$i\hbar\frac{\partial \chi_j(R,t)}{\partial t} = \hat{D}_j \chi_j(R,t) + \sum_{k\neq j} \hat{O}_{j,k}\chi_k(R,t)$$

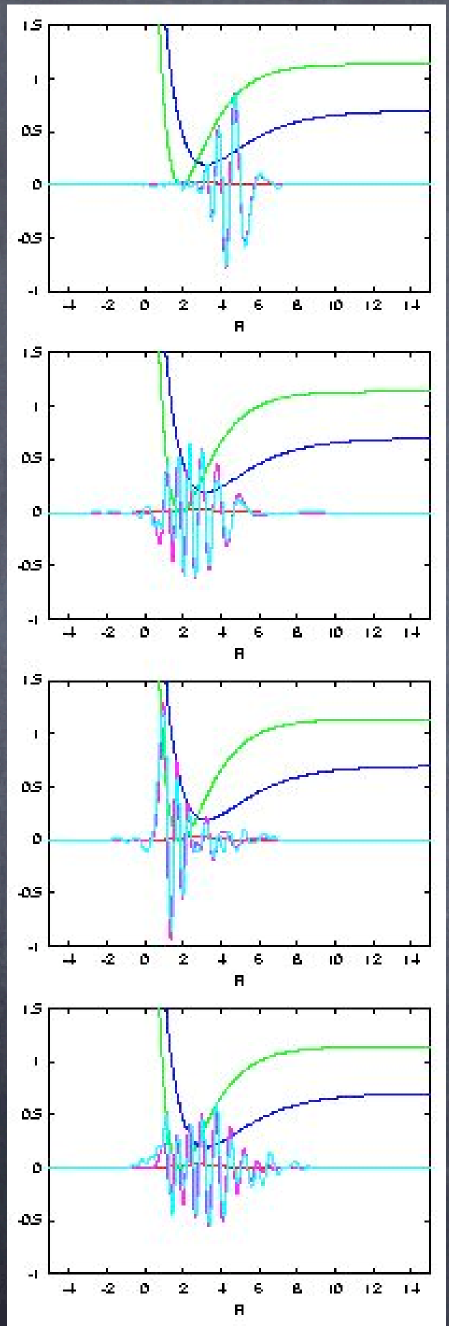



$\mathrm{Re}\{\chi_1(R,0)\}$

$\mathrm{Re}\{\chi_2(R,0)\}$

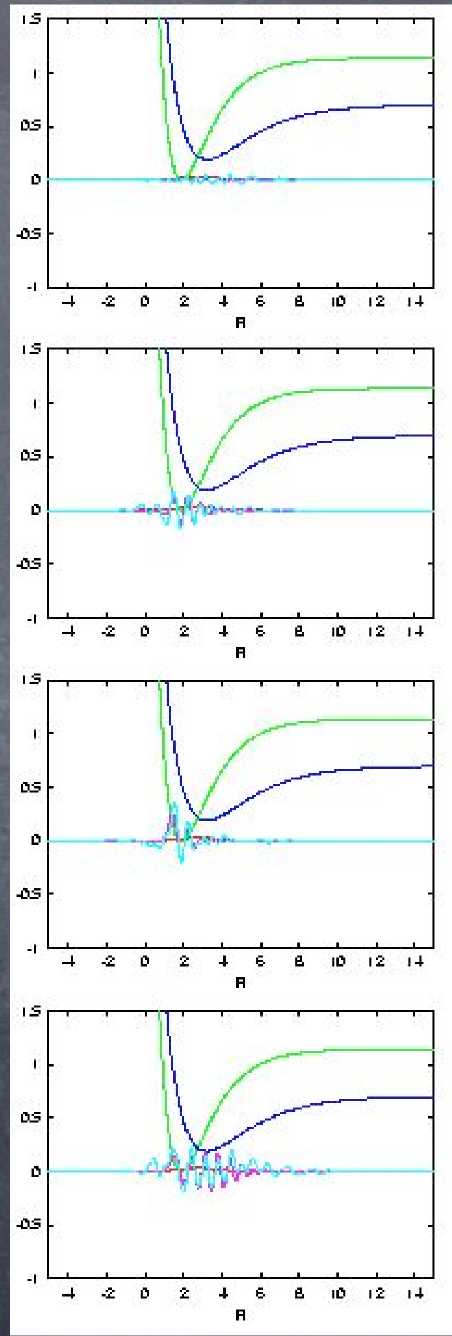


$\mathrm{Re}\{\chi_1(R,t)\}$



$t$

$\mathrm{Re}\{\chi_2(R,t)\}$



## Quantum Mechanics

$$\hat{H} = \frac{\hat{P}^2}{2M} + \hat{V} \qquad |\Psi(t)\rangle$$

$$i\hbar\frac{\partial|\Psi(t)\rangle}{\partial t} = \hat{H}|\Psi(t)\rangle \Longrightarrow |\Psi(t)\rangle = e^{-\frac{i}{\hbar}\hat{H}t}|\Psi(0)\rangle$$

## Classical Mechanics

$$H = \frac{P^2}{2M} + V \qquad (\mathbf{P}_t, \mathbf{Q}_t)$$

$$\frac{d\mathbf{Q}_t}{dt} = \frac{\partial H}{\partial \mathbf{P}_t} \qquad \frac{d\mathbf{P}_t}{dt} = -\frac{\partial H}{\partial \mathbf{Q}_t} \Longrightarrow \mathbf{Q}_t = \mathbf{Q}(\mathbf{P_0}, \mathbf{Q}_0; t) \qquad \mathbf{P}_t = \mathbf{P}(\mathbf{P_0}, \mathbf{Q}_0; t)$$

## Computational complexity

CM: Polynomial n dofs ===> $n^a$ $\quad 256^2 \approx 6.5 \times 10^4$

QM: Exponential n dofs ===> $l^n$ $\quad 3^{256} \approx 1.4 \times 10^{122}$

# Partial classical limit

- Separate "classical" and "quantum" set (mass ratio, environment vs system)
- Collapse "nuclear wavepacket" to a point in phase space (R,P). Determine (or assign) the type of classical evolution.
- Evolve the (small) quantum subset according to quantum mechanics
- Determine (or assign) coupling mechanism

- Partial classical limit

Mean field
Surface hopping
Wigner-Liouville propagation
.......

G. Stock M. Thoss
Adv. Chem. Phys. (131) 243

- Linearization methods (TCF)

Q. Shi E.Geva JPC (118) 8173
J. Poulsen G. Nyman P. Rossky JPC (119) 12179
S. Bonella D. Montemayor D. Coker PNAS (102) 6715

# Mean field

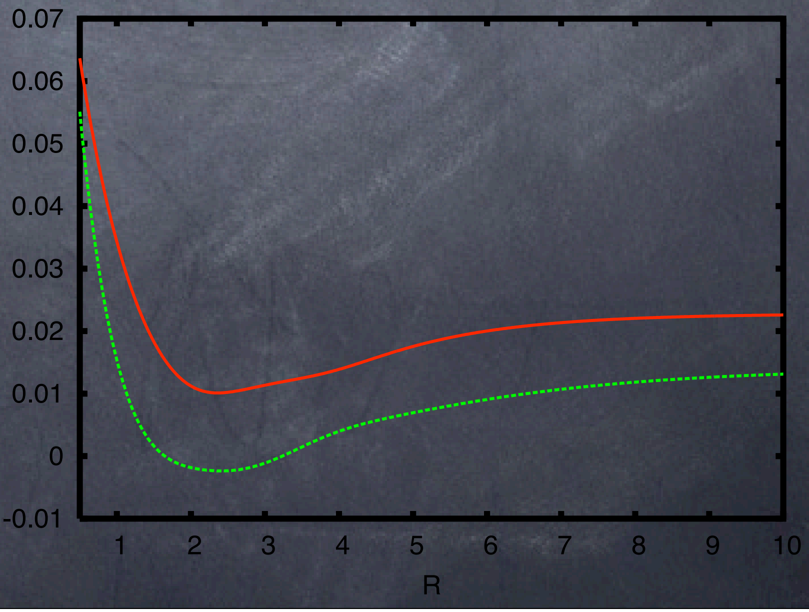
Quantum electronic evolution

Classical nuclear dynamics

$$\frac{dP}{dt} = -\langle\Psi(t)|\frac{\partial H}{\partial R}|\Psi(t)\rangle = -\sum_{k,k'} \chi_k(R,t)\chi^*_{k'}(R,t)\frac{\partial E_{k'k}(R)}{\partial R}$$

Coupled evolution in which nuclei move on an average potential

...Even when they are far from the coupling region



# Surface Hopping

Electronic evolution integrated according to quantum mechanics

Ensemble of trajectories propagated classically on a single adiabatic surface which may change at the crossing

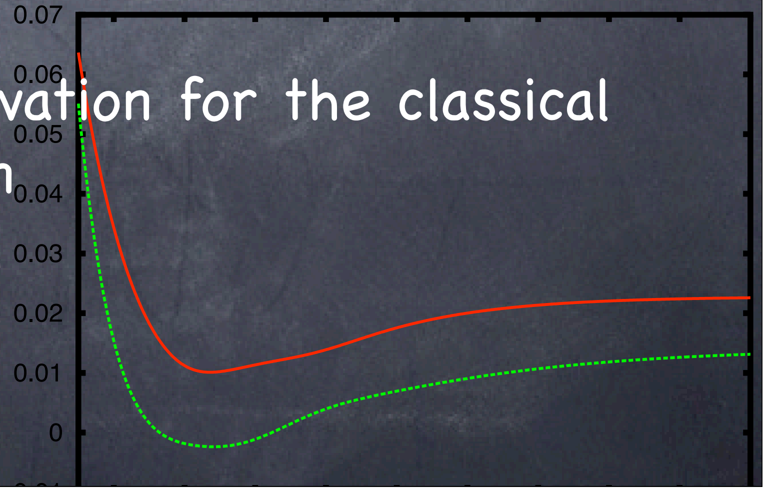
$$\frac{dP}{dt} = -\frac{dE_k(R)}{dR}$$

Transition probability at the crossing region (intuitive but ad hoc)

$$g_{kk'} = 2Re\left\{a_{kk'}\Delta t \rho_{kk'}/\rho_{kk}\right\}$$

Prescription to ensure energy conservation for the classical system during an electronic transition (forbidden hops)

No coherence (electronic or nuclear)



# Time correlation functions

$$\langle \hat{A}\hat{B}(t)\rangle = \mathrm{Tr}\left\{\hat{\rho}\hat{A}e^{\frac{i}{\hbar}\hat{H}t}\hat{B}e^{-\frac{i}{\hbar}\hat{H}t}\right\}$$

## Linear response theory

- Spectroscopy: dipole-dipole
- Transport: velocity-velocity
- Rate Constants: concentration-concentration

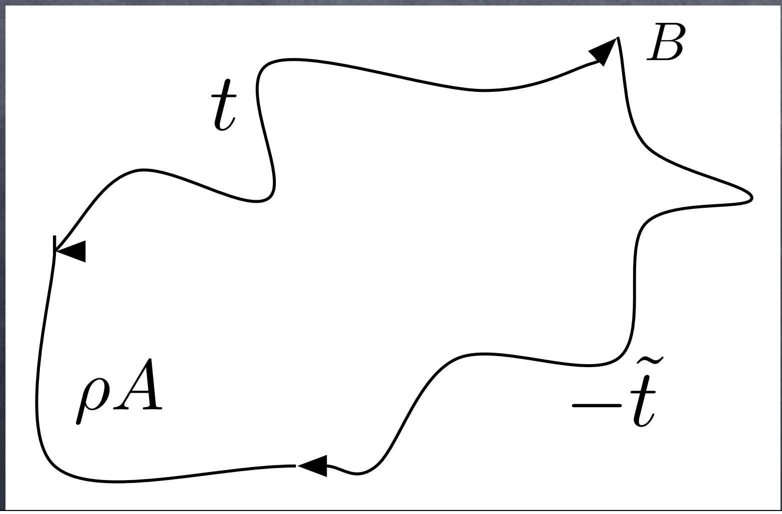
$$\langle \hat{A}\hat{B}(t)\rangle = \mathrm{Tr}\left\{\hat{\rho}\hat{A}e^{\frac{i}{\hbar}\hat{H}t}\hat{B}e^{-\frac{i}{\hbar}\hat{H}t}\right\}$$

Insert resolutions of the identity

$$1 = \sum_{\alpha}\int dR_0 |R_0\alpha\rangle\langle R_0\alpha|$$

$$\sum_{\alpha\beta,\alpha'\beta'}\int dR_0 dR_N d\tilde{R}_0 \ \langle R_0\alpha|\hat{\rho}\hat{A}|\tilde{R}_0\alpha'\rangle \times$$

$$\langle \tilde{R}_0\alpha'|e^{\frac{i}{\hbar}\hat{H}t}|\tilde{R}_N\beta'\rangle\langle\tilde{R}_N\beta'|\hat{B}|R_N\beta\rangle\langle R_N\beta|e^{-\frac{i}{\hbar}\hat{H}t}|R_0\alpha\rangle$$



## Two steps:

- Obtain a convenient representation of the individual propagators (exact)

- Recast the electronic problem in a suitable form (Mapping Hamiltonian method)

- Introduce a path integral expression for the propagator (nuclear variables)

- Combine the forward and backwards propagators to obtain a computable (trajectory based) approximate expression for the correlation function

- LINEARIZATION in the nuclear variables

## The electronic problem

$$\hat{H} = \frac{\hat{P}^2}{2M} + \hat{h}_{el}(\hat{R}, \hat{p}, \hat{q})$$

$$\langle R_N \beta | e^{-\frac{i}{\hbar}\hat{H}t} | R_0 \alpha \rangle$$

## Mapping

(1) States $\quad |\alpha\rangle \rightarrow |m_\alpha\rangle = |0_1, ..., 1_\alpha, ..0_n\rangle$

(2) Electronic Hamiltonian

$$\hat{h}_{el} \rightarrow h_m(\hat{R}) = \frac{1}{2}\sum_{\lambda} h_{\lambda,\lambda}(\hat{R})(\hat{q}_\lambda^2 + \hat{p}_\lambda^2 - \hbar) + \frac{1}{2}\sum_{\lambda \neq \lambda'} h_{\lambda,\lambda'}(\hat{R})(\hat{q}_{\lambda'}\hat{q}_\lambda + \hat{p}_{\lambda'}\hat{p}_\lambda)$$

$$\langle R_N m_\beta | e^{-\frac{i}{\hbar}\hat{H}_m t} | R_0 m_\alpha \rangle$$

$$\boxed{\langle R_N \beta | e^{-\frac{i}{\hbar}\hat{H}t} | R_0 \alpha \rangle = \langle R_N m_\beta | e^{-\frac{i}{\hbar}\hat{H}_m t} | R_0 m_\alpha \rangle}$$

# Path integral expression of the propagator

$$\langle R_N m_\beta | e^{-\frac{i}{\hbar}\hat{H}_m t} | R_0 m_\alpha \rangle$$

Insert resolutions of the identity in nuclear position and momentum

$$\int \prod_{k=1}^{N-1} dR_k \frac{dP_k}{2\pi\hbar} e^{\frac{i}{\hbar}S} \langle m_\beta | e^{-\frac{i}{\hbar}\epsilon \hat{h}_m(R_N)} \ldots . e^{-\frac{i}{\hbar}\epsilon \hat{h}_m(R_1)} | m_\alpha \rangle$$

with

$$S = \epsilon \sum_{k=1}^{N} \left[ P_k \frac{(R_k - R_{k-1})}{\epsilon} - \frac{P_k^2}{2M} \right]$$

and

$$h_m(R) = \frac{1}{2} \sum_\lambda h_{\lambda,\lambda}(R)(\hat{q}_\lambda^2 + \hat{p}_\lambda^2 - \hbar) + \frac{1}{2} \sum_{\lambda \neq \lambda'} h_{\lambda,\lambda'}(R)(\hat{q}_{\lambda'}\hat{q}_\lambda + \hat{p}_{\lambda'}\hat{p}_\lambda)$$

Hamiltonian is quadratic in mapping operators

# Exact rewriting of the mapping transition amplitude

$$\langle m_\beta | e^{-\frac{i}{\hbar}\epsilon \hat{h}_m(R_N)} \ldots . e^{-\frac{i}{\hbar}\epsilon \hat{h}_m(R_1)} | m_\alpha \rangle = \int dq_0 dp_0 r_{t,\beta}(\{R_k\}) e^{-i\theta_{t\beta}(\{R_k\})} r_{0\alpha} e^{i\theta_{0,\alpha}} G_0$$

with

$$\theta_{t,\beta}(\{R_k\}) = \tan^{-1}\left(\frac{p_{0,\beta}}{q_{0,\beta}}\right) + \int_0^t d\tau h_{\beta,\beta}(R_\tau) + \int_0^t d\tau \sum_{\lambda \neq \beta} \left[ h_{\beta,\lambda}(R_\tau) \frac{(p_{\tau\beta} p_{\tau\lambda} + q_{\tau\beta} q_{\tau\lambda})}{(p_{\tau\beta}^2 + q_{\tau\beta}^2)} \right] \; ;$$

$$r_{t,\beta}(\{R_k\}) = \sqrt{q_{t,\beta}^2(\{R_k\}) + p_{t,\beta}^2(\{R_k\})}$$ and $$G_0 = e^{-\frac{1}{2}\sum_\lambda (q_{0\lambda}^2 + p_{0\lambda}^2)}$$

All quantities can be computed, once a nuclear path has been specified, by solving

$$\frac{dp_\beta}{dt} = -h_{\beta,\beta}(R) q_\beta - \sum_{\lambda \neq \beta} h_{\beta,\lambda}(R) q_\lambda$$

$$\frac{dq_\beta}{dt} = h_{\beta,\beta}(R) p_\beta + \sum_{\lambda \neq \beta} h_{\beta,\lambda}(R) p_\lambda$$

# Path integral expression for the correlation function

$$\sum_{m_\alpha m_\beta, m_{\alpha'} m_{\beta'}} \int dR_0 dR_N d\tilde{R}_0 \int \prod_{k=1}^{N-1} dR_k \frac{dP_k}{2\pi\hbar}\frac{dP_N}{2\pi\hbar} \int \prod_{k=1}^{N-1} d\tilde{R}_k \frac{d\tilde{P}_k}{2\pi\hbar}\frac{d\tilde{P}_N}{2\pi\hbar} \int dq_0 dp_0 d\tilde{q}_0 d\tilde{p}_0$$

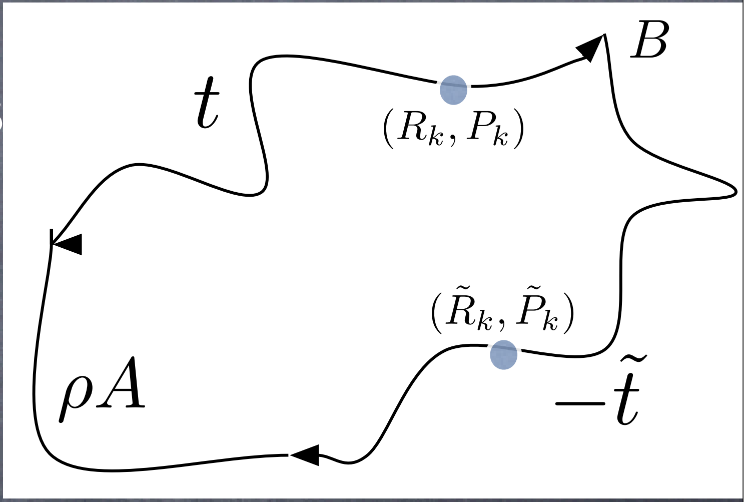
$$\langle R_0\alpha|\hat{\rho}\hat{A}|\tilde{R}_0\alpha'\rangle \langle \tilde{R}_N\beta'|\hat{B}|R_N\beta\rangle\, e^{i(S-\tilde{S})}$$

$$r_{t,\beta}(\{R_k\})e^{-i\theta_{t\beta}(\{R_k\})} r_{0\alpha} e^{i\theta_{0,\alpha}} G_0 \tilde{r}_{t,\beta'}(\{\tilde{R}_k\}) e^{i\tilde{\theta}_{t\beta'}(\{\tilde{R}_k\})} \tilde{r}_{0\alpha'} e^{-i\tilde{\theta}_{0,\alpha'}} \tilde{G}_0$$

Introduce mean and difference paths

$$\Delta R_k = R_k - \tilde{R}_k \qquad \Delta P_k = P_k - \tilde{P}_k$$

$$\bar{R}_k = \frac{R_k + \tilde{R}_k}{2} \qquad \bar{P}_k = \frac{P_k + \tilde{P}_k}{2}$$




Expand phase to linear order in the difference path

Perform integrals on difference variables analytically

Integrals over "end points" generate Wigner transforms of operators

Integrals over "intermediate" points generate delta functions (time-stepping prescription for evolution of nuclear variables)

## Linearized correlation function

$$\langle \hat{A}\hat{B}(t)\rangle = \sum_{\alpha\beta,\alpha'\beta'} \int d\bar{R}_0 dq_0 dp_0 d\tilde{q}_0 d\tilde{p}_0 \int \prod_{k=1}^{N} d\bar{R}_k \frac{d\bar{P}_k}{2\pi\hbar} B^W_{\beta'\beta}(\bar{R}_N \bar{P}_N)$$

$$\left[\hat{\rho}\hat{A}\right]^W_{\alpha,\alpha'} (\bar{R}_0, \bar{P}_1) G_0 \tilde{G}_0 r_{0\alpha} e^{i\theta_{0,\alpha}} \tilde{r}_{0\alpha'} e^{-i\tilde{\theta}_{0,\alpha'}}$$

$$r_{t,\beta}(\{\bar{R}_k\})\tilde{r}_{t,\beta'}(\{\bar{R}_k\}) e^{-i\epsilon \sum_{k=1}^{N} (\theta_\beta(\bar{R}_k) - \tilde{\theta}_{\beta'}(\bar{R}_k))}$$

$$\prod_{k=1}^{N-1} \delta\left(\frac{\bar{P}_{k+1} - \bar{P}_k}{\epsilon} - F_k^{\beta,\beta'}\right) \prod_{k=1}^{N} \delta\left(\frac{\bar{P}_k}{M} - \frac{\bar{R}_k - \bar{R}_{k-1}}{\epsilon}\right)$$

- Initial conditions sampled from quantum densities

$$\left[\hat{\rho}\hat{A}\right]^{W}_{\alpha,\alpha'}(\bar{R}_0,\bar{P}_1)=\int \Delta R_0 e^{-\frac{i}{\hbar}\bar{P}_1\Delta R_0}\langle \bar{R}_0+\frac{\Delta R}{2}|\hat{\rho}\hat{A}|\bar{R}_0-\frac{\Delta R}{2}\rangle$$

- Nuclear dynamics classical. Forces determined by final states

throughout $\quad F_k^{\beta,\beta'}=-\frac{1}{2}\left\{\nabla_{\bar{R}_k}h_{\beta,\beta}(\bar{R}_k)+\nabla_{\bar{R}_k}h_{\beta',\beta'}(\bar{R}_k)\right\}$

$$-\frac{1}{2}\sum_{\lambda\neq\beta}\nabla_{\bar{R}_k}h_{\beta,\lambda}(\bar{R}_k)\left\{\frac{(p_{\beta k}p_{\lambda k}+q_{\beta k}q_{\lambda k})}{(p^2_{\beta k}+q^2_{\beta k})}\right\}-\frac{1}{2}\sum_{\lambda\neq\beta'}\nabla_{\bar{R}_k}h_{\beta',\lambda}(\bar{R}_k)\left\{\frac{(\tilde{p}_{\beta' k}\tilde{p}_{\lambda k}+\tilde{q}_{\beta' k}\tilde{q}_{\lambda k})}{(\tilde{p}^2_{\beta' k}+\tilde{q}^2_{\beta' k})}\right\}$$

- Electronic transitions accounted for exactly (but with

"classical" dynamics)

- Complex weights........Interference

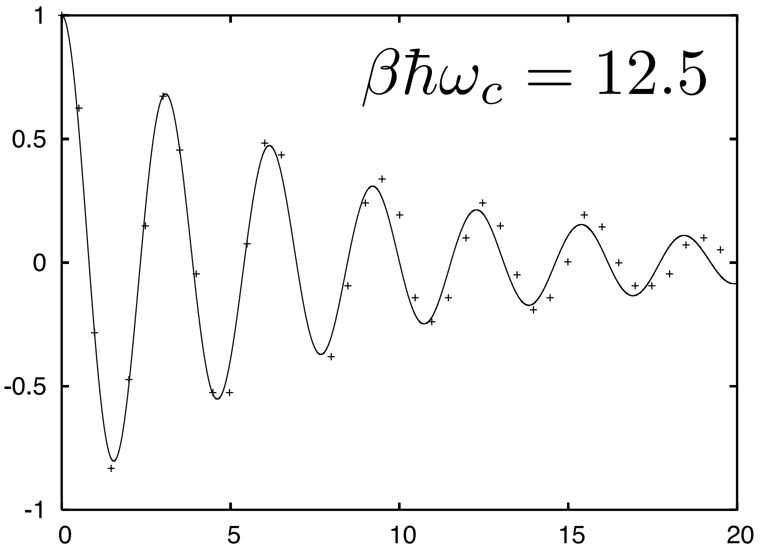
# Spin-Boson system

$$\hat{H} = -\Omega\hat{\sigma}_x + \sum_{j=1}^{N}\left[\frac{P_j^2}{2} + \frac{1}{2}\omega_j'^2 R_j^2 - c_j R_j \hat{\sigma}_z\right]$$

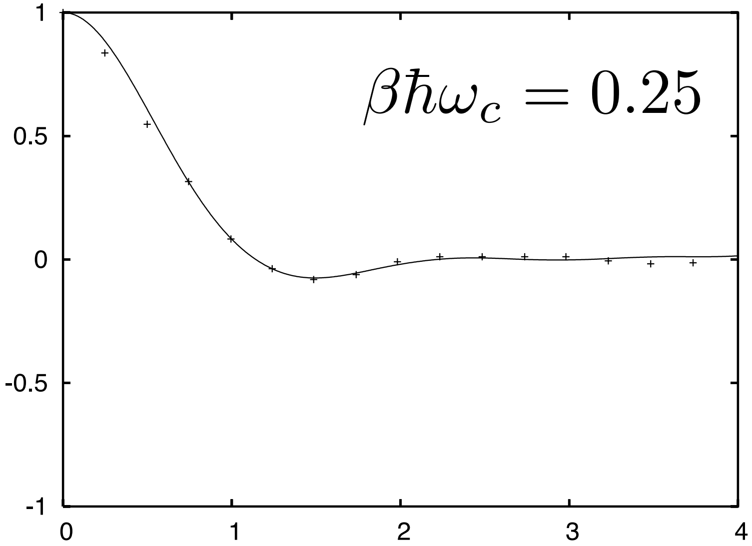
$$J(\omega) = \xi\omega e^{-\omega/\omega_c}$$

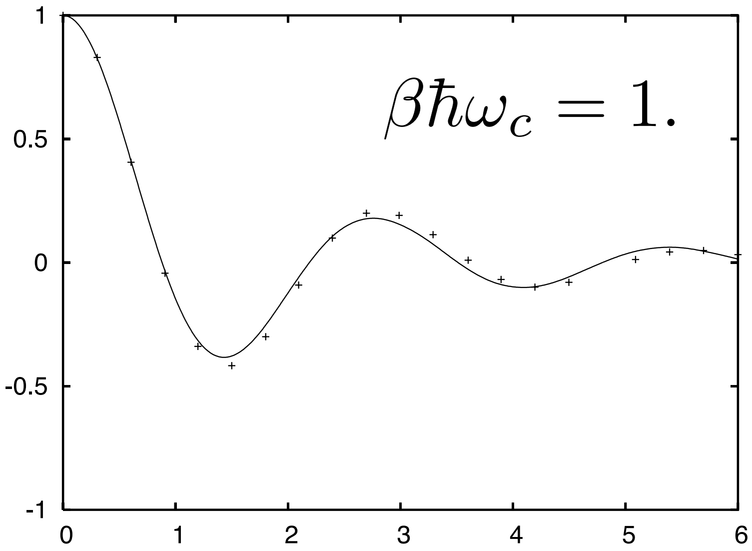
$$\langle\hat{\sigma}_z(t)\rangle$$

$$\hat{\rho}_{sb} = \rho(\mathbf{R}_0, \mathbf{P}_0)|1\rangle\langle 1|$$




$\Omega/\omega_c = 0.4 \qquad \xi \approx 0.1$



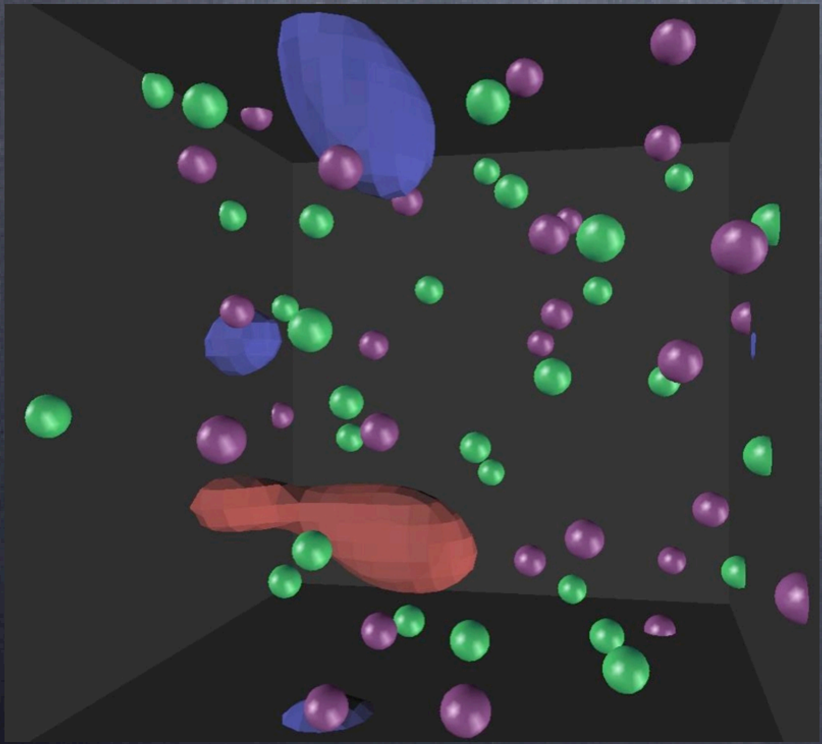



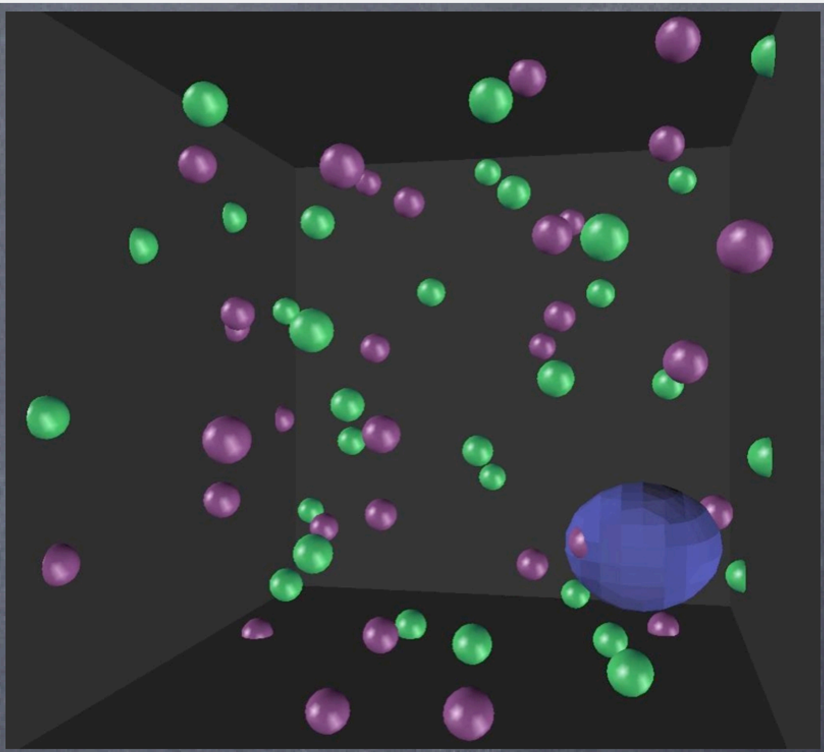
# Diffusion properties of an excess electron in a metal molten salt solution

$$32K^+, 31Cl^-, 1e$$

$$\rho = 1.52 \times 10^3 \frac{\text{kg}}{\text{m}^3}$$

$$T = 1300\text{K}$$



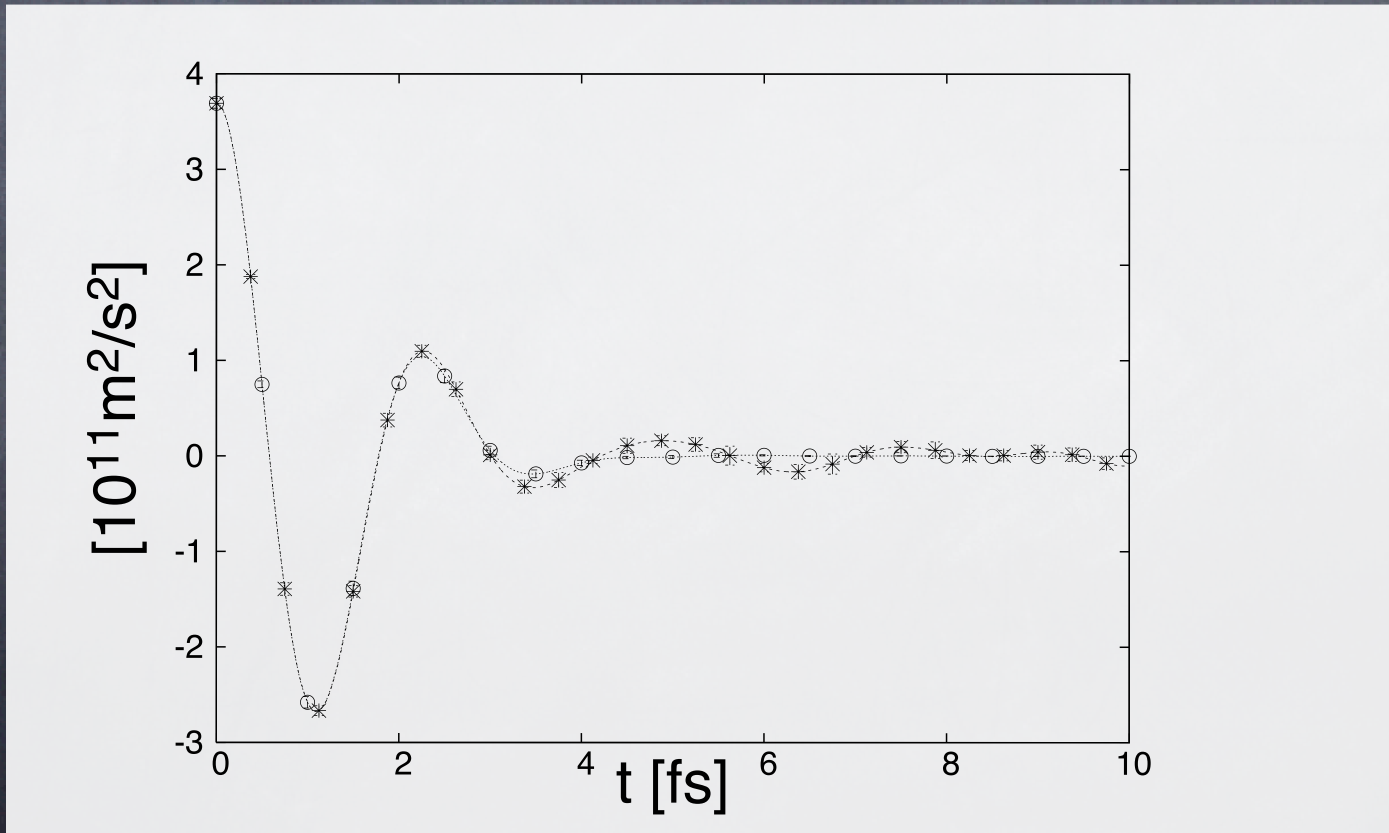


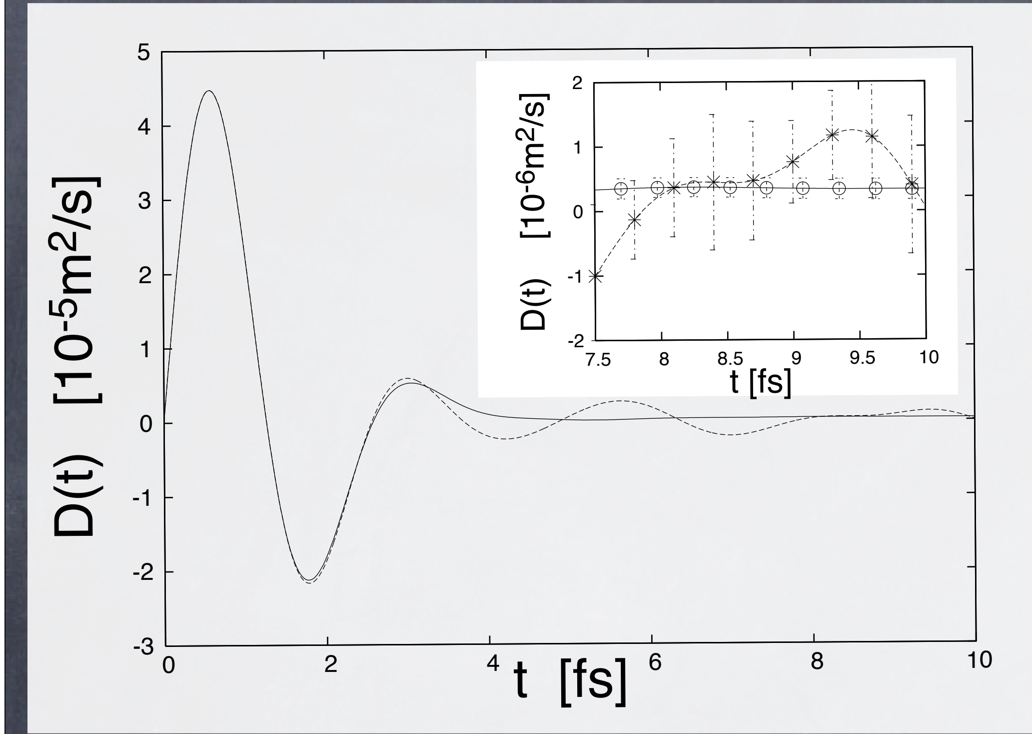
$$D_v = \frac{1}{3} Re \int_0^\infty C_{vv}(t)dt$$

$$C_{vv}(t) = \langle \hat{v} \cdot \hat{v}(t) \rangle = \mathrm{Tr}\{\hat{\rho}\hat{v}\hat{v}(t)\}$$

$$\langle vv(t)\rangle_{ad} = \sum_{\alpha'=2}^{10} \int d\bar{R}_0 \int \prod_{k=1}^{N} d\bar{R}_k \frac{d\bar{P}_k}{2\pi\hbar}\, e^{-\beta\left[\frac{\bar{P}_1^2}{2M} + E_1(\bar{R}_0)\right]}\, v_{1,\alpha'}(\bar{R}_0,\bar{P}_0) v_{\alpha' 1}(\bar{R}_N,\bar{P}_N)$$

$$e^{-i\epsilon \sum_{k=1}^{N}(E_1(\bar{R}_k) - E_{\alpha'}(\bar{R}_k))} \prod_{k=1}^{N-1} \delta\left(\frac{\bar{P}_{k+1}-\bar{P}_k}{\epsilon} - F_k^{1,\alpha'}\right) \delta\left(\frac{\bar{P}_k}{M} - \frac{\bar{R}_k - \bar{R}_{k-1}}{\epsilon}\right)$$






$$D_v = \frac{1}{3} Re \int_0^\infty C_{vv}(t)dt$$

$$D_v \approx 2 \times 10^{-3} \mathrm{cm}^2 \mathrm{s}^{-1}$$
$$D_S \approx 2 \times 10^{-3} \mathrm{cm}^2 s^{-1}$$
$$D_{exp} = 3 \times 10^{-3} \mathrm{cm}^2 \mathrm{s}^{-1}$$

Phase creates noise at longer times

$$e^{-i\epsilon \sum_{k=1}^{N} (E_1(\bar{R}_k) - E_{\alpha'}(\bar{R}_k))}$$

Problem is common to both adiabatic and non-adiabatic LAND-Map (cumulant expansion to mitigate it)

$$D_v = (2 \pm 1) \times 10^{-3} \mathrm{cm}^2 \mathrm{s}^{-1}$$

# Conclusions

- Mixed quantum-classical methods are extremely useful BUT they come in different flavors each with its advantages and disadvantages (formal or numerical)

- The linearized method converges with relatively small ensembles of trajectories and it is as accurate as the other available approaches

- Nuclei are classical but there is still interference for the observables

- Most of the computational effort goes in the calculation of the electronic structure and in controlling the phase factor

- Sampling of initial conditions from Wigner density