Exact factorization of the time-dependent electron-nuclear wave-function: A mixed quantum-classical study

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Contents

Decomposition of electronic and nuclear motion

$$\Psi(r,R,t) = \Phi_R(r,t)\chi(R,t)$$

$$\begin{aligned}
\text{el:} \quad & \left[\hat{H}_{BO}(r,R) + \hat{U}_{en}^{coup} - \epsilon(R,t)\right]\Phi_R(r,t) &=& \; i\hbar\partial_t\Phi_R(r,t) \\
\text{nucl:} \quad & \left[\frac{1}{2M}\left(\hat{P} + A(R,t)\right)^2 + \epsilon(R,t)\right]\chi(R,t) &=& \; i\hbar\partial_t\chi(R,t)
\end{aligned}$$

$$\hat{U}_{en}^{coup} = \frac{(-i\hbar\nabla_R - A(R,t))^2}{2M} + \left(\frac{-i\hbar\nabla_R\chi}{\chi} + A(R,t)\right)\frac{-i\hbar\nabla_R - A(R,t)}{M}$$

$$\epsilon(R,t) = \langle\Phi_R(t)|\,\hat{H}_{BO}\,|\Phi_R(t)\rangle + \frac{\hbar^2}{2M}\langle\nabla_R\Phi_R(t)|\,\nabla_R\Phi_R(t)\rangle - \frac{A^2(R,t)}{2M}$$

$$A(R,t) = \langle\Phi_R(t)|\,-i\hbar\nabla_R\Phi_R(t)\rangle$$

$\mu\Phi$ (Abedi, Maitra and Gross, PRL 2010)

The adiabatic basis

- electronic wave-function $\Phi_R(r,t)$ on BO states

$$\Phi_R(r,t) = \sum_k c_k(R,t)\varphi_R^{(k)}(r)$$

- electronic equation (still exact!)

$$\dot{c}_k(R,t) = f\left(c_j(R,t), c_j'(R,t), c_j''(R,t)\right) \quad \forall\, j$$

- non-adiabatic couplings

$$d_{jk}^{(1)}(R) = \left\langle \varphi_R^{(j)} \middle| \nabla_R \varphi_R^{(k)} \right\rangle, d_{jk}^{(2)}(R) = \left\langle \nabla_R \varphi_R^{(j)} \middle| \nabla_R \varphi_R^{(k)} \right\rangle$$

In the adiabatic basis...

$$\epsilon(R,t) = \frac{\hbar^2}{2M}\left[\sum_k |c_k'|^2 + \sum_{k,l} c_k^* c_l d_{kl}^{(2)} + \sum_{k,l} c_k^* c_l' d_{lk}^{(1)} + c_k^{*\prime} c_l d_{kl}^{(1)}\right] + \sum_k |c_k|^2\, \epsilon_{BO}^{(k)} - \frac{A^2}{2M}$$

$$A(R,t) = -i\hbar \sum_k c_k^* c_k' - i\hbar \sum_{k,l} c_k^* c_l d_{kl}^{(1)}$$

The classical approximation

what does it mean?

- limit $\hbar \to 0$ of quantum mechanics?
- infinitely localized density?
- small mass ratio $\frac{m_q}{M_{cl}} \ll 1$?
- or ...

HERE:

1. $|\chi(R,t)|^2 = \delta\left(R - R_c(t)\right)$: BUT careful!!! $R, t \to R_c(t)$
2. $\frac{-i\hbar\nabla_R\chi}{\chi} = ?$

first semi-classics (Van Vleck, PNAS 1928)

$$\chi(R,t) = \exp\left[\frac{i}{\hbar}\mathcal{S}(R,t)\right] \simeq G(R,t)\exp\left[\frac{i}{\hbar}S_0(R,t)\right]$$

with $\mathcal{S} = S_0 + \hbar S_1 + \mathcal{O}(\hbar^2)$ and $G(R,t) = \exp\left[iS_1(R,t)\right]$

$$\frac{-i\hbar\nabla_R\chi(R,t)}{\chi(R,t)} = \nabla_R S_0(R,t) - i\hbar\frac{\nabla_R G(R,t)}{G(R,t)}$$

then classical limit $\hbar \to 0$ (S_0 is the classical action)

$$\nabla_R S_0 = P$$

proof: derive HJE at the zero-th order in $\hbar$ from TDSE
(Goldstein, *Classical mechanics*)

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HERE:

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2. $\frac{-i\hbar\nabla_R\chi}{\chi} = P$
3. $c_j'(R,t), c_j''(R,t) = 0 \quad \forall\, j$

Mixed quantum-classical evolution

electronic equation

$$\dot{c}_k(t) = -\frac{i}{\hbar}\left[\epsilon^{(k)}_{BO}(R) - \left(V^{(R)}_{eff}(R,P) + iV^{(I)}_{eff}(R)\right)\right] c_k(t) - \sum_j c_j(t) D_{kj}(R,P)$$

nuclear Hamiltonian

$$H_N(R,P) = \frac{P^2}{2M} + V^{(R)}_{eff}(R,P)$$

Mixed quantum-classical evolution

- effective potential $V_{\text{eff}}(R,P) = V_{\text{eff}}^{(R)}(R,P) + iV_{\text{eff}}^{(I)}(R)$

$$\sum_j |c_j(t)|^2 \epsilon_{BO}^{(j)}(R) + \frac{1}{M} P \cdot A(R,t) + \frac{\hbar^2}{M} \sum_{j<l} \Re\left(c_j^*(t) c_l(t)\right) d_{jl}^{(2)}(R)$$

$$-\frac{\hbar^2}{M} \sum_{j<l} \Im\left(c_j^*(t) c_l(t)\right) \nabla_R \cdot d_{jl}^{(1)}(R)$$

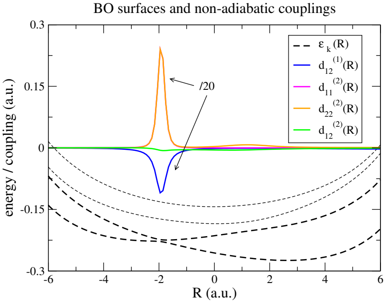
- effective non-adiabatic couplings $D_{kj}(R,P)$

$$\frac{P}{M} \cdot d_{kj}^{(1)}(R) - \frac{i\hbar}{2M}\left(\nabla_R \cdot d_{kj}^{(1)}(R) - d_{kj}^{(2)}(R)\right)$$

Quantum vs MQC evolution

Model Hamiltonian (Shin and Metiu, JCP 1995)

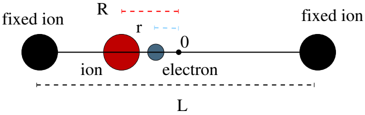
$$\hat{H}(r,R) = -\frac{1}{2}\frac{\partial^2}{\partial r^2} - \frac{1}{2M}\frac{\partial^2}{\partial R^2} + \frac{1}{\left|\frac{L}{2}-R\right|} + \frac{1}{\left|\frac{L}{2}+R\right|} - \frac{\operatorname{erf}\frac{|R-r|}{R_f}}{|R-r|} - \frac{\operatorname{erf}\frac{\left|r-\frac{L}{2}\right|}{R_l}}{\left|r-\frac{L}{2}\right|} - \frac{\operatorname{erf}\frac{\left|r+\frac{L}{2}\right|}{R_r}}{\left|r+\frac{L}{2}\right|}$$



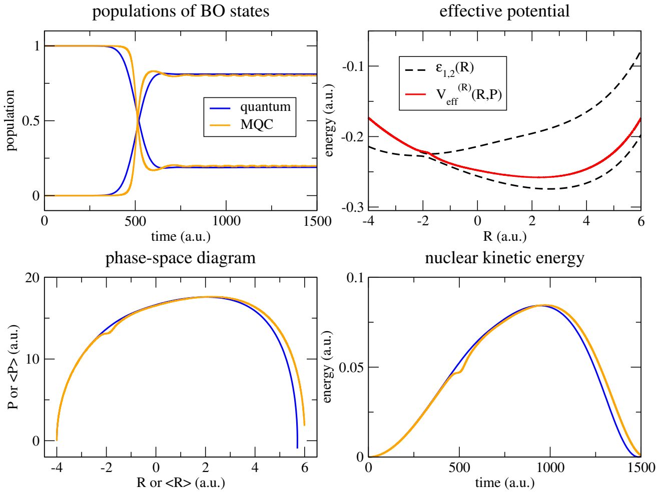
$M = 1836.1528$ a.u.

$L = 19.050$ a.u.

$R_f = 5.0,\ R_l = 3.1,\ R_r = 4.0$ a.u.



Quantum vs MQC evolution



Some observations

- no *ad-hoc* reaction of the classical system to quantum transitions
- effective non-adiabatic coupling $D_{kj}(R,P)$ approximates the exact electron-nuclear coupling
- velocity-dependent term in the classical nuclear Hamiltonian coupled to the vector potential
- electronic evolution is norm-conserving
- nuclear potential $V_{eff}^{(R)}(R,P)$ is known!
- only one trajectory is needed

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- César Proetto
- Kieron Burke
- The Organizers

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THANK YOU FOR YOUR ATTENTION!

Populations of adiabatic states

$$\Psi(r,R,t) = \sum_k F_k(R,t)\varphi_R^{(k)}(r) \quad \text{with} \quad F_k(R,t) = c_k(R,t)\chi(R,t)$$

remember: $|\chi(R,t)|^2 = \delta\left(R - R_c(t)\right)$

therefore

$$\left|c_k^{\text{exact}}(t)\right|^2 = \int dR\ |F_k(R,t)|^2 = \int dR\ |c_k(R,t)|^2\,\delta\left(R - R_c(t)\right)$$

$$= |c_k(R_c(t))|^2 = |c_k(t)|^2$$

Vector potential

EXACT!

$$A(R,t) = -i\hbar \sum_k c_k^*(R,t)c_k'(R,t) - i\hbar \sum_{k,l} c_k^*(R,t)c_l(R,t)d_{kl}^{(1)}(R)$$

APPROXIMATED?

$$A(R,t) = -i\hbar \sum_{k,l} c_k^*(R,t)c_l(R,t)d_{kl}^{(1)}(R)$$

NO, STILL EXACT! because of the choice of the gauge

$$\langle \Phi_R(t) | \partial_t \Phi_R(t) \rangle = 0 = \dot{R} \sum_k c_k^*(R,t)c_k'(R,t)$$

Scalar potential

EXACT!

$$\langle \nabla_R \Phi_R(t) | \nabla_R \Phi_R(t) \rangle = \sum_k \left| c_k'(R,t) \right|^2 + \sum_{k,l} c_k^*(R,t) c_l(R,t) d_{kl}^{(2)}(R)$$
$$+ \sum_{k,l} c_k^*(R,t) c_l'(R,t) d_{lk}^{(1)}(R) + c_k^{*\prime}(R,t) c_l(R,t) d_{kl}^{(1)}(R)$$

APPROXIMATED?

$$\langle \nabla_R \Phi_R(t) | \nabla_R \Phi_R(t) \rangle = \sum_{k,l} c_k^*(R,t) c_l(R,t) d_{kl}^{(2)}(R)$$

YES!