Exact factorization of the time-dependent electron-nuclear wavefunction

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Coupling between electronic and nuclear motion:

Situations where the electronic and the nuclear motions are strongly coupled and the quantum features of the nuclear motion become substantial:

- molecules in strong laser pulses
- light “nuclei”; muon, positron, ...
- electron-phonon interaction
- branching ratio of the chemical reactions at the conical intersection
System

\( N_e \) electrons, \((r_1 \ldots r_{Ne}) \equiv \mathbf{r} \)

\( N_n \) nuclei, \((R_1 \ldots R_{Nn}) \equiv \mathbf{R} \), masses \( M_1 \ldots M_{Nn} \) and charges \( Z_1 \ldots Z_{Nn} \)

\[
\hat{H} = \hat{H}^{BO}_R + \hat{V}_{ext}(\mathbf{r}, t) + \hat{T}_n(\mathbf{R}) + \hat{V}_{ext}(\mathbf{R}, t)
\]

\( \hat{H}^{BO}_R \) is the traditional Born-Oppenheimer electronic Hamiltonian,

\[
\hat{H}^{BO}_R = \hat{T}_e(\mathbf{r}) + \hat{W}_{ee}(\mathbf{r}) + \hat{V}_{en}(\mathbf{r}, \mathbf{R}) + \hat{W}_{nn}(\mathbf{R})
\]

Time-dependent Schrödinger equation

\[
\hat{H} \Psi(\mathbf{r}, \mathbf{R}) = i \partial_t \Psi(\mathbf{r}, \mathbf{R})
\]
exact numerical solution

- provides the complete information on the system
- only for very small systems like $H_2^+$
- lacks the intuitive picture that potential energy surfaces can provide

approximate methods: nuclear wavepacket dynamics on BO surfaces, Ehrenfest dynamics of nuclei, surface hopping (Tully)

- applicable to larger systems
- based on potential energy surfaces picture or forces acting on nuclei
- approximations are introduced in early stages $\rightarrow$ mean-field or non-correlated $\rightarrow$ don’t work in many situations
Solve

\[ \hat{H}^{BO}_R \Phi^{BO}_R (\mathbf{r}) = \epsilon^{BO}_R (\mathbf{R}) \Phi^{BO}_R (\mathbf{r}) \]

for each fixed nuclear configuration, \( R \).

**Approximate** the full electron-nuclear wave function:

\[ \Psi^{BO}(\mathbf{r}, \mathbf{R}) = \Phi^{BO}_R (\mathbf{r}) \chi^{BO}(\mathbf{R}) \]

**Nuclear equation:**

\[
\left( \sum_{\nu=1}^{N} \frac{1}{2M_\nu} (-i \nabla_\nu + \mathbf{A}_\nu)^2 + \hat{W}_{nn}(\mathbf{R}) + \hat{V}^{\text{ext}}_n(\mathbf{R}) + \epsilon^{BO}(\mathbf{R}) \right) \chi^{BO}(\mathbf{R}) = E \chi^{BO}(\mathbf{R})
\]
Vector potential

\[ A_{\nu}^{BO}(R) = \int \Phi_{R}^{BO^*}(r)(-i\nabla_{\nu})\Phi_{R}^{BO}(r) \, dr \]

denotes geometrical phase

\[ \gamma^{BO}(C) = \oint_{C} A_{\nu}^{BO}(R) \cdot dR \]

**Question**: Is the appearance of Berry phases a consequence of the Born-Oppenheimer approximation or does it survive in the exact treatment?
Vector potential

\[ A_{\nu}^{BO}(R) = \int \Phi_{R}^{BO*}(r)(-i\nabla_{\nu})\Phi_{R}^{BO}(r) \, dr \]

geometrical phase

\[ \gamma^{BO}(C) = \oint_{C} A_{\nu}^{BO}(R) \cdot dR \]

**Question:** Is the appearance of Berry phases a consequence of the Born-Oppenheimer approximation or does it survive in the exact treatment?
Expand full electron-nuclear wave function in complete set of BO states:

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \sum_j \Phi^{BO}_{\mathbf{R}, j}(\mathbf{r}) \chi_j(\mathbf{R}, t)$$

Insert the expansion in the full time-dependent Schrödinger equation→standard non-adiabatic coupling terms from $\hat{T}_n$ acting on $\Phi^{BO}_{\mathbf{R}, j}$.

- **Numerically very hard:**
  - Need many-electron BO wavefunction
  - Non-adiabatic coupling terms become infinitely large in the vicinity of conical intersections

- $\chi_j(\mathbf{R}, t)$ looses nice interpretation as “nuclear wavefunction”
**Goal:** show that $\Psi(r, R, t) = \Phi_R(r, t) \chi(R, t)$ can be made **Exact**

- Concept of Exact time-dependent potential energy surface
- Concept of Exact time-dependent vector potential

**G. Hunter**, Int. J. Quantum Chem. 9, 237 (1975)

(a) The exact solution of

\[ \hat{H} \Psi(r, R, t) = i \partial_t \Psi(r, R, t) \]

can be written as a single product

\[ \Psi(r, R, t) = \Phi_R(r, t) \chi(R, t) \]

where \( \Phi_R(r, t) \) satisfies the partial normalization condition

\[ \int dr |\Phi_R(r, t)|^2 = 1 \]

for each fixed \( R \), at any time \( t \).

Immediate Consequences:

1— The diagonal $\Gamma(R, t)$ of the nuclear $N_n$-body density matrix is identical with $|\chi(R, t)|^2$

proof: $\Gamma(R, t) = \int dr |\Psi(r, R, t)|^2 = \int dr |\Phi_R(r, t)|^2 |\chi(R, t)|^2 = |\chi(R, t)|^2$

2— $\Phi_R(r, t)$ and $\chi(R, t)$ are unique up to within the gauge transformation:

$$\tilde{\Phi}_R(r, t) := e^{i\theta(R, t)} \Phi_R(r, t)$$

$$\tilde{\chi}(R, t) := e^{-i\theta(R, t)} \chi(r, t)$$
Immediate Consequences:

proof: Let $\Phi_R \cdot \chi$ and $\tilde{\Phi}_R \cdot \tilde{\chi}$ be two different representations of an exact wave function $\Psi(r, R, t)$

$$\Psi(r, R, t) = \Phi_R(r, t) \chi(R, t) = \tilde{\Phi}_R(r, t) \tilde{\chi}(R, t)$$

$$\rightarrow \frac{\chi}{\tilde{\chi}} = \frac{\tilde{\Phi}_R}{\Phi_R} := g(R, t) \rightarrow |\tilde{\Phi}_R(r, t)|^2 = |g(R, t)|^2 |\Phi_R(r, t)|^2$$

$$\int d\mathbf{r} |\tilde{\Phi}_R(r, t)|^2 = |g(R, t)|^2 \int d\mathbf{r} |\Phi_R(r, t)|^2$$

$$\rightarrow |g(R, t)|^2 = 1 \rightarrow g(R, t) = e^{i\theta(R, t)}$$

$$\rightarrow \tilde{\Phi}_R(r, t) = e^{i\theta(R, t)} \Phi_R(r, t) \quad \tilde{\chi}(R, t) = e^{-i\theta(R, t)} \chi(R, t)$$
Proof of part (a):

Given the exact electron-nuclear wavefunction $\Psi(\mathbf{r}, \mathbf{R}, t)$

Choose $\chi(\mathbf{R}, t) := e^{iS(\mathbf{R}, t)} \sqrt{\int d\mathbf{r} |\Psi(\mathbf{r}, \mathbf{R}, t)|^2}$

with some real-valued function $S(\mathbf{R}, t)$

$\Phi_{\mathbf{R}}(\mathbf{r}, t) := \Psi(\mathbf{r}, \mathbf{R}, t)/\chi(\mathbf{R}, t)$

Then, by construction, $\int d\mathbf{r} |\Phi_{\mathbf{R}}(\mathbf{r}, t)|^2 = 1$
(b) The wavefunctions $\Phi_R(r, t)$ and $\chi(R, t)$ satisfy:

**(1) electronic equation**

$$
\left( \hat{H}_R^{BO} + \hat{V}_{ext}(r, t) + \hat{U}_{en}^{coup}[\chi, \Phi_R] - \epsilon(R, t) \right) \Phi_R(r, t) = i \partial_t \Phi_R(r, t)
$$

**(2) nuclear equation**

$$
\left( \sum_{\nu=1}^{N_n} \frac{1}{2M_\nu} (-i \nabla_\nu + A_\nu(R, t))^2 + \hat{V}_{ext}(R, t) + \epsilon(R, t) \right) \chi(R, t) = i \partial_t \chi(R, t)
$$
EXACT time-dependent potential energy surface

\[ \epsilon(\mathbf{R}, t) = \int d\mathbf{r} \Phi^*_R(\mathbf{r}, t) \left[ H^{BO}_R + \hat{V}^e_{\text{ext}}(t) + \sum_{\nu=1}^{N_n} \left( \frac{-i\nabla_\nu - A_\nu}{2M_\nu} \right)^2 - i\partial_t \right] \Phi_R(\mathbf{r}, t) \]

EXACT time-dependent vector potential

\[ A_\nu(\mathbf{R}, t) = \int \Phi^*_R(\mathbf{r}, t) (-i\nabla_\nu) \Phi_R(\mathbf{r}, t) d\mathbf{r} \]

EXACT electron-nuclear correlation operator

\[ \hat{U}_{\text{en}}^{\text{coup}}[\chi, \Phi_R] = \sum_{\nu=1}^{N_n} \frac{1}{M_\nu} \left[ \left( \frac{-i\nabla_\nu - A_\nu}{2} \right)^2 + \left( \frac{-i\nabla_\nu \chi}{\chi} + A_\nu \right) \left( -i\nabla_\nu - A_\nu \right) \right] \]
Observations

- Electronic equation is nonlinear in $\Phi_{\mathbf{R}}(\mathbf{r}, t)$ and contains $\chi(\mathbf{R}, t)$

- There is an alternative, equally exact, representation
  $\Psi = \Phi_{\mathbf{R}}(\mathbf{R}, t)\chi(\mathbf{r}, t)$ (electrons move on the nuclear energy surface)

- Both equations are form-invariant under the gauge transformation

$$\Phi_{\mathbf{R}}(\mathbf{r}, t) \rightarrow \tilde{\Phi}_{\mathbf{R}}(\mathbf{r}, t) = e^{i\theta(\mathbf{R}, t)}\Phi_{\mathbf{R}}(\mathbf{r}, t)$$

$$\chi(\mathbf{R}, t) \rightarrow \tilde{\chi}(\mathbf{R}, t) = e^{-i\theta(\mathbf{R}, t)}\chi(\mathbf{R}, t)$$

$$A_\nu(\mathbf{R}, t) \rightarrow \tilde{A}_\nu(\mathbf{R}, t) = A_\nu(\mathbf{R}, t) + \nabla_\nu \theta(\mathbf{R}, t)$$

$$\epsilon(\mathbf{R}, t) \rightarrow \tilde{\epsilon}(\mathbf{R}, t) = \epsilon(\mathbf{R}, t) + \partial_t \theta(\mathbf{R}, t)$$
Basic idea of the proof part (b)

- **first step:** we apply Frenkel’s stationary action principle, 
  \[ \delta \int_{t_0}^{t_1} dt \langle \Psi | \hat{H} - i \partial_t | \Psi \rangle = 0, \]
  to the product wavefunction and require the action to be stationary with respect to variations in \( \Phi_R(\mathbf{r}, t) \) and \( \chi(\mathbf{R}, t) \), subject to the normalization condition

\[
\frac{\delta}{\delta \Phi_R^*(\mathbf{r})} \left( \frac{\int_{t_0}^{t_1} dt \langle \Psi | \hat{H} - i \partial_t | \Psi \rangle}{\langle \Phi \chi | \Phi \chi \rangle} \right) = 0
\]

\[
\frac{\delta}{\delta \chi^*(\mathbf{R})} \left( \frac{\int_{t_0}^{t_1} dt \langle \Psi | \hat{H} - i \partial_t | \Psi \rangle}{\langle \Phi \chi | \Phi \chi \rangle} \right) = 0
\]

- **second step:** prove the implication:
  \( \Phi, \chi \) satisfy Eqs. 1, 2 \( \implies \) \( \Psi := \Phi \chi \) satisfies \( \hat{H} \Psi = i \partial_t \Psi \).
\[ \epsilon(R, t), \ A_\nu(R, t) \text{ and } \hat{U}_{en}^{coup}[\chi, \Phi_R] \] mediate the coupling between the nuclear and the electronic degrees of freedom in a formally \textit{exact} way.

- Vector potential appears in the exact treatment.

Does it produce a real effect or can it be made disappear by a suitable gauge transformation?
\[ \epsilon(R, t), \ A_\nu(R, t) \text{ and } \hat{U}_{en}^{coup}[\chi, \Phi_R] \text{ mediate the coupling} \]
between the nuclear and the electronic degrees of freedom in a formally exact way.

- Vector potential appears in the exact treatment.

Does it produce a real effect or can it be made disappear by a suitable gauge transformation?
Vector potential as the difference of paramagnetic nuclear velocity fields derived from the full and nuclear wavefunctions:

\[
A_\nu(R, t) = \frac{Im \langle \Psi(t) | \nabla_\nu \Psi(t) \rangle}{|\chi(R, t)|^2} - \frac{Im(\chi^* \nabla_\nu \chi)}{|\chi(R, t)|^2}
\]

\[Im(\chi^* \nabla_\nu \chi) + |\chi|^2 A_\nu \rightarrow \text{reproduce the exact nuclear current density.}\]

\[\chi(R, t) \rightarrow \text{proper nuclear many-body wavefunction:}\]

- Its absolute-value squared gives the exact nuclear (\(N\)-body) density
- Its phase yields the correct nuclear (\(N\)-body) current density.
Time-Dependent Potential Energy Surfaces
**Example: 1D – $H_2^+$ in strong laser field**

**1D-model (soft Coulomb potentials)**

$H_2^+$ molecular ion exposed to $\lambda = 228$ nm laser field

$E(t) = E_0 f(t) \sin(\omega t)$, for two peak intensities, $I_1 = |E_0|^2 = 10^{14}$ W/cm$^2$ (dashed) and $I_2 = |E_0|^2 = 2.5 \times 10^{13}$ W/cm$^2$ (solid)

$f(t)$ is chosen such that the field is linearly ramped from zero to its maximum strength at $t = 7.6$ fs and thereafter held constant

$\hat{H}(t) = -\frac{1}{M} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_e} \frac{\partial^2}{\partial z^2} - \frac{1}{\sqrt{1 + (z - R/2)^2}} + \sqrt{1 + (z + R/2)^2} + \frac{1}{\sqrt{0.03 + R^2}} + \hat{V}_{laser}(z, t)$

**Graph:**

- Plot of $E(t)$ vs. Optical Cycle
- Plot of $\varepsilon(R,t)$ vs. $R(a.u.)$ at $t = 0$ fs
Example: $1D - H_2^+$ in strong laser field

exact solution of $i\partial_t \Psi(r, R, t) = \hat{H} \Psi(r, R, t)$

**Compared with:**

- Hartree approximation (TDSCF): $\Psi_H(r, R, t) = \chi(R, t)\phi(r, t)$
- Standard Ehrenfest dynamics
- “Exact Ehrenfest dynamics” where the forces on nuclei are calculated from the exact TDPES
Results: $I_1 = 10^{14} \text{W/cm}^2$

Snapshots of the TDPES (blue lines) and nuclear density (black) at times indicated. The circles indicate the position and energy of the classical particle in the exact-Ehrenfest calculation. For reference, the ground-state BO surface is shown as the thin red line.
Results: \( I_1 = 10^{14} \text{W/cm}^2 \)

The internuclear separation \( \langle R \rangle(t) \)
Results: $I_2 = 2.5 \times 10^{13}$

Snapshots of the TDPES (blue lines) and nuclear density (black) at times indicated. The circles indicate the position and energy of the classical particle in the exact-Ehrenfest calculation. For reference, the ground-state BO surface is shown as the thin red line.
Results: \( I_2 = 2.5 \times 10^{13} \)

The internuclear separation \( \langle R \rangle(t) \)
Model (S. Shin and H. Metiu, JCP 102 1995)

\[ \hat{H}(x, R) = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2M} \frac{\partial^2}{\partial R^2} + \frac{1}{|L/2-R|} + \frac{1}{|L/2+R|} - \frac{\text{erf}(|R-x|/R_f)}{|R-x|} - \frac{\text{erf}(|x-L/2|/R_{c1})}{|x-L/2|} - \frac{\text{erf}(|x+L/2|/R_{c2})}{|x+L/2|} \]
Time-Dependent potential energy surfaces

$\varepsilon(R)(\text{a.u.})$

$t = 0 \text{ fs}$

$\text{R(a.u.)}$
Time-Dependent potential energy surfaces

t = 10.89 fs

\[ \epsilon(R)(\text{a.u.}) \]

\[ \text{R(a.u.)} \]
Time-Dependent potential energy surfaces

$t = 18.15$ fs
Time-Dependent potential energy surfaces

$t = 38.72 \text{ fs}$

$\varepsilon(R) (\text{a.u.})$

$R (\text{a.u.})$

Exact factorization of the time-dependent electron-nuclear wavefunction
Analysis of the step

\[ \Psi(r, R, t) = \chi_1(R, t)\phi_R^{(1)}(r) + \chi_2(R, t)\phi_R^{(2)}(r) \]

\[ \Phi_R(r, t) = F_1(R, t)\phi_R^{(1)}(r) + F_2(R, t)\phi_R^{(2)}(r) \]

where \( F_k(R, t) = \frac{e^{i\theta}\chi_k(R,t)}{\sqrt{|\chi_1(R,t)|^2 + |\chi_2(R,t)|^2}} \)

\[ \epsilon(R, t) = |F_1|^2 \left( \epsilon_{BO}^{(1)} + \dot{\gamma}_1 \right) + |F_2|^2 \left( \epsilon_{BO}^{(2)} + \dot{\gamma}_2 \right) \]

at \( R_0 \), the cross-over of \( |\chi_1| \) and \( |\chi_2| \), where \( |\chi_1(R_0, t)| = |\chi_2(R_0, t)| = |X(t)| \), regardless of \( |X(t)|'s \) value, \( |F_1|^2 \) and \( |F_2|^2 \) are always \( |F_1(R_0, t)|^2 = |F_2(R_0, t)|^2 = 1/2 \), \( R_0 \) being the center of the region where steps form

\[ \Delta R = \frac{2}{\alpha} \]

\[ \alpha(t) = \frac{(\nabla_R |\chi_1(R, t)|)|_R_0 - (\nabla_R |\chi_2(R, t)|)|_R_0}{|X(t)|} \]
Analysis of the step

Exact factorization of the time-dependent electron-nuclear wavefunction

$t = 38.72 \text{ fs}$

$\varepsilon (R) \text{ (a.u.)}$

$\chi (R) \text{ (a.u.)}$

$|\chi_k|^2 \text{ solid line, } |F_k|^2 \text{ dashed line}$

$R \text{ (a.u.)}$
We have shown that \( \Psi(\mathbf{r}, \mathbf{R}, t) = \Phi_R(\mathbf{r}, t) \cdot \chi(\mathbf{R}, t) \) is an exact representation of the complete electron-nuclear wavefunction if \( \Phi_R(\mathbf{r}, t) \) and \( \chi(\mathbf{R}, t) \) satisfy the right equations.

- Proper definition of the of Exact time-dependent potential energy surfaces
- Proper definition of the of Exact time-dependent vector potential
- We have shown that the TDPES is a useful tool to interpret different dissociation mechanisms
- We have investigated the structure of the TDPES in the presence of strong non-adiabatic coupling (avoided-crossing)
THANKS!
**Equations**

**Electronic equation**

\[
\left( \hat{H}_{BO}^{R} + \hat{V}_{ext}^e (\mathbf{r}, t) + \hat{U}_{en}^{coup} - \epsilon (\mathbf{R}, t) \right) \Phi_{R} (\mathbf{r}, t) = i \partial_t \Phi_{R} (\mathbf{r}, t)
\]

**Nuclear equation**

\[
\left( \sum_{\nu=1}^{N_n} \frac{1}{2M_{\nu}} (-i \nabla_{\nu} + A_{\nu})^2 + \hat{V}_{ext}^n (\mathbf{R}, t) + \epsilon (\mathbf{R}, t) \right) \chi(R, t) = i \partial_t \chi(R, t)
\]

**Gauge transformation**

\[
\Phi_{R} (\mathbf{r}, t) \rightarrow \tilde{\Phi}_{R} (\mathbf{r}, t) = e^{i \theta (\mathbf{R}, t)} \Phi_{R} (\mathbf{r}, t)
\]

\[
\chi(R, t) \rightarrow \tilde{\chi}(R, t) = e^{-i \theta (\mathbf{R}, t)} \chi(R, t)
\]

\[
A_{\nu} (\mathbf{R}, t) \rightarrow \tilde{A}_{\nu} (\mathbf{R}, t) = A_{\nu} (\mathbf{R}, t) + \nabla_{\nu} \theta (\mathbf{R}, t)
\]

\[
\epsilon (\mathbf{R}, t) \rightarrow \tilde{\epsilon}(\mathbf{R}, t) = \epsilon (\mathbf{R}, t) + \partial_t \theta (\mathbf{R}, t)
\]
\[ \Psi(\mathbf{r}, \mathbf{R}, t) = e^{-iEt} \Phi(\mathbf{r}) \chi(\mathbf{R}) = \left[ e^{-i\epsilon(\mathbf{R})t} \Phi(\mathbf{r}) \right] \left[ e^{-i(E-\epsilon(\mathbf{R}))t} \chi(\mathbf{R}) \right] \]

**Electronic equation:**

\[
\left( \hat{H}^{BO}_\mathbf{R} + \hat{U}_{en}^{coup} \right) \Phi(\mathbf{r}) = \epsilon(\mathbf{R}) \Phi(\mathbf{r})
\]

**Nuclear equation:**

\[
\left( \sum_{\nu=1}^{N_n} \frac{1}{2M_\nu} (-i \nabla_\nu + A_\nu)^2 + \hat{V}^\text{ext}_\mathbf{R} + \epsilon(\mathbf{R}) \right) \chi(\mathbf{R}) = E \chi(\mathbf{R})
\]

- \( \epsilon(\mathbf{R}) = \langle \Phi(\mathbf{r}) | \hat{H}^{BO}_\mathbf{R} + \sum_{\nu=1}^{N_n} \frac{(-i \nabla_\nu - A_\nu)^2}{2M_\nu} | \Phi(\mathbf{r}) \rangle \)  
  exact potential energy surface is gauge invariant

- neglecting the \( 1/M_\nu \) terms in the electronic equation leads to the BO electronic equation and potential energy surfaces

- The static decomposition was shown first by Hunter (G. Hunter, Int. J. Quantum Chem. 9, 237 (1975))
Vector potential

\[ A_\nu(R, t) = \frac{Im \langle \Psi | \nabla_\nu \Psi \rangle}{|\chi(R, t)|^2} - \nabla_\nu S(R) \]

where \( \chi(R) := e^{iS(R)} |\chi(R)| \)

For a non current carrying molecular ground state

\[ A_\nu(R) = -\nabla_\nu S(R) \]
Nuclei (1) and (2) are heavy: their positions are fixed
Adiabatic potential energy surfaces

- BO-PES #1
- BO-PES #2
- BO-PES #3
Exact potential energy surfaces

\[ \epsilon(R) / \text{a.u.} \]

-5 \quad 0 \quad 5

R / \text{a.u.}

exact PES #1
exact PES #2
exact PES #3