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Exact factorization of the time-dependent electron-nuclear wave function

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Exact factorization of the time-dependent electron-nuclear wave function:
Life beyond the Born-Oppenheimer approximation

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Hamiltonian for the complete system of N_e electrons with coordinates $(r_1 \cdots r_{N_e}) \equiv \underline{r}$ and N_n nuclei with coordinates $(R_1 \cdots R_{N_n}) \equiv \underline{\underline{R}}$, masses $M_1 \cdots M_{Nn}$ and charges $Z_1 \cdots Z_{Nn}$.

$$\hat{H} = \hat{T}_n(\underline{\underline{R}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{T}_e(\underline{r}) + \hat{W}_{ee}(\underline{r}) + \hat{V}_{en}(\underline{\underline{R}}, \underline{r})$$

with $\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla_\nu^2}{2M_\nu}$ $\hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m}$ $\hat{W}_{nn} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$

$\hat{W}_{ee} = \frac{1}{2}\sum_{\substack{j,k \\ j\neq k}}^{N_e} \frac{1}{|r_j - r_k|}$ $\hat{V}_{en} = \sum_{j=1}^{N_e}\sum_{\nu=1}^{N_n} -\frac{Z_\nu}{|r_j - R_\nu|}$

convention: **Greek indices → nuclei**
Latin indices → electrons

Full Schrödinger equation: $\hat{H}\Psi(\underline{r}, \underline{\underline{R}}) = E\Psi(\underline{r}, \underline{\underline{R}})$

Born-Oppenheimer approximation

solve

$$\left(\hat{T}_e(\underline{\underline{r}}) + \hat{W}_{ee}(\underline{\underline{r}}) + \hat{V}_e^{ext}(\underline{\underline{r}}) + \hat{V}_{en}(\underline{\underline{r}}, \underline{\underline{R}})\right)\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}}) = \in^{BO}(\underline{\underline{R}})\,\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}})$$

for each fixed nuclear configuration $\underline{\underline{R}}$.

Make adiabatic ansatz for the complete molecular wave function:

$$\Psi^{BO}(\underline{\underline{r}}, \underline{\underline{R}}) = \Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}}) \cdot \chi^{BO}(\underline{\underline{R}})$$

and find best χ^{BO} by minimizing $\langle \Psi^{BO} | H | \Psi^{BO} \rangle$ w.r.t. χ^{BO} :

Nuclear equation

$$\left[\hat{T}_n(\underline{\underline{R}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{V}_n^{ext}(\underline{\underline{R}}) + \sum_\upsilon \frac{1}{M_\upsilon} A_\upsilon^{BO}(\underline{\underline{R}})(-i\nabla_\upsilon) + \in^{BO}(\underline{\underline{R}}) + \int \Phi_{\underline{\underline{R}}}^{BO\,*}(\underline{\underline{r}})\hat{T}_n(\underline{\underline{R}})\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}})d\underline{\underline{r}}\right]\chi^{BO}(\underline{\underline{R}}) = E\chi^{BO}(\underline{\underline{R}})$$

Berry connection

$$A_\upsilon^{BO}(\underline{\underline{R}}) = \int \Phi_{\underline{\underline{R}}}^{BO\,*}(\underline{\underline{r}})(-i\nabla_\upsilon)\Phi_{\underline{\underline{R}}}^{BO}(\underline{\underline{r}})d\underline{\underline{r}}$$

$\gamma^{BO}(C) = \oint_C \vec{A}^{BO}(\underline{\underline{R}})\cdot d\vec{R}$ **is a geometric phase**

In this context, potential energy surfaces $\in^{BO}(\underline{\underline{R}})$ **and the Berry potential** $\vec{A}^{BO}(\underline{\underline{R}})$ **are APPROXIMATE concepts, i.e. they follow from the BO approximation.**

"Berry phases arise when the world is approximately separated into as system and its environment."

GOING BEYOND BORN-OPPENHEIMER

Standard procedure:

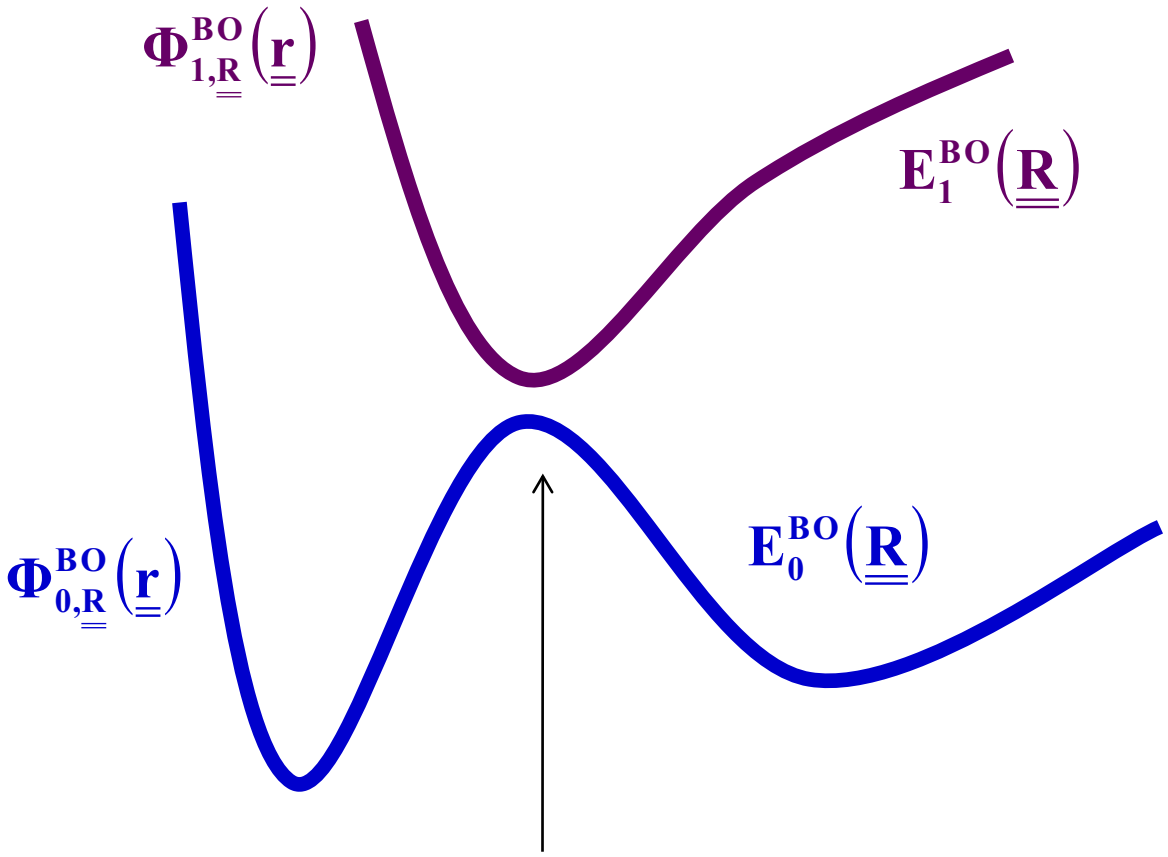
Expand full molecular wave function in complete set of BO states:

$$\Psi_K\left(\underline{r},\underline{\underline{R}}\right) = \sum_J \Phi^{BO}_{\underline{\underline{R}},J}\left(\underline{r}\right)\cdot\chi_{K,J}\left(\underline{\underline{R}}\right)$$

and insert expansion in the full Schrödinger equation → standard non-adiabatic coupling terms from T_n acting on $\Phi^{BO}_{\underline{\underline{R}},J}\left(\underline{r}\right)$.

Drawbacks:

- $\chi_{J,K}$ depends on 2 indices: → looses nice interpretation as "nuclear wave function"
- In systems driven by a strong laser, hundreds of BO-PES can be coupled.



$$\Psi_0\left(\underline{\underline{r}},\underline{\underline{R}}\right) \approx \chi_{00}\left(\underline{\underline{R}}\right)\Phi^{BO}_{0,\underline{\underline{R}}}\left(\underline{\underline{r}}\right) + \chi_{01}\left(\underline{\underline{R}}\right)\Phi^{BO}_{1,\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

Potential energy surfaces are absolutely essential in our understanding of a molecule

<u>GOAL:</u> Show that $\Psi\left(\underline{\underline{r}}, \underline{\underline{R}}\right) = \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) \cdot \chi\left(\underline{\underline{R}}\right)$ **can be made EXACT**

- **Concept of EXACT potential energy surfaces (beyond BO)**
- **Concept of EXACT Berry connection (beyond BO)**
- **Concept of EXACT time-dependent potential energy surfaces for systems exposed to electro-magnetic fields**
- **Concept of ECACT time-dependent Berry connection for systems exposed to electro-magnetic fields**

Theorem I

The exact solutions of

$$\hat{H}\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)=E\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)$$

can be written in the form

$$\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)=\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\cdot\chi\left(\underline{\underline{R}}\right)$$

where $\int d\underline{\underline{r}}\left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\right|^2=1$ **for each fixed** $\underline{\underline{R}}$**.**

First mentioned in: G. Hunter, Int. J.Q.C. 9, 237 (1975)

Immediate consequences of Theorem I:

1. **The diagonal $\Gamma(\underline{\underline{R}})$ of the nuclear N_n-body density matrix is identical with $|\chi(\underline{\underline{R}})|^2$**

   proof: $$\Gamma(\underline{\underline{R}}) = \int d\underline{\underline{r}} |\Psi(\underline{\underline{r}}, \underline{\underline{R}})|^2 = \underbrace{\int d\underline{\underline{r}} |\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})|^2}_{1} |\chi(\mathbf{R})|^2 = |\chi(\underline{\underline{R}})|^2$$

   $\Rightarrow$ in this sense, $\chi(\underline{\underline{R}})$ can be interpreted as a proper nuclear wavefunction.

2. **$\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$ and $\chi(\underline{\underline{R}})$ are <u>unique</u> up to within the "gauge transformation"**

$$\tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}}) := e^{i\theta(\underline{\underline{R}})} \Phi_{\underline{\underline{R}}}(\underline{\underline{r}}) \qquad \tilde{\chi}(\underline{\underline{R}}) := e^{-i\theta(\underline{\underline{R}})} \chi(\underline{\underline{R}})$$

proof: Let $\phi\cdot\chi$ and $\tilde{\phi}\cdot\tilde{\chi}$ be two different representations of an exact eigenfunction Ψ i.e.

$$\Psi(\underline{\underline{r}},\underline{\underline{R}}) = \Phi_{\underline{\underline{R}}}(\underline{\underline{r}})\chi(\underline{\underline{R}}) = \tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}})\tilde{\chi}(\underline{\underline{R}})$$

$$\Rightarrow \quad \frac{\tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}})}{\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})} = \frac{\chi(\underline{\underline{R}})}{\tilde{\chi}(\underline{\underline{R}})} \equiv G(\underline{\underline{R}}) \qquad \Rightarrow \quad \tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}}) = G(\underline{\underline{R}})\,\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$$

$$\Rightarrow \quad \underbrace{\int d\underline{\underline{r}}\left|\tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2}_{1} = \left|G(\underline{\underline{R}})\right|^2 \underbrace{\int d\underline{\underline{r}}\left|\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2}_{1}$$

$$\Rightarrow \quad \left|G(\underline{\underline{R}})\right| = 1 \qquad \Rightarrow G(\underline{\underline{R}}) = e^{i\theta(\underline{\underline{R}})}$$

$$\Rightarrow \quad \tilde{\Phi}_{\underline{\underline{R}}}(\underline{\underline{r}}) = e^{i\theta(\underline{\underline{R}})}\,\Phi_{\underline{\underline{R}}}(\underline{\underline{r}}) \qquad \tilde{\chi}(\underline{\underline{R}}) = e^{-i\theta(\underline{\underline{R}})}\,\chi(\underline{\underline{R}})$$

Theorem II: $\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$ and $\chi\left(\underline{\underline{R}}\right)$ **satisfy the following equations:**

Eq. ❶

$$\left(\underbrace{\hat{T}_e + \hat{W}_{ee} + \hat{V}_e^{ext} + \hat{V}_{en}}_{\hat{H}_{BO}} + \sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu\right)^2 + \sum_{\nu}^{N_n} \frac{1}{M_\nu}\left(\frac{-i\nabla_\nu \chi}{\chi} + A_\nu\right)\left(-i\nabla_\nu - A_\nu\right)\right)\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) = \in\left(\underline{\underline{R}}\right)\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$$

Eq. ❷

$$\left(\sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu + A_\nu\right)^2 + \hat{W}_{nn} + \hat{V}_n^{ext} + \in\left(\underline{\underline{R}}\right)\right)\chi\left(\underline{\underline{R}}\right) = E\chi\left(\underline{\underline{R}}\right)$$

where

$$A_\nu\left(\underline{\underline{R}}\right) = -i\int \Phi^*_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\nabla_\nu \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) d\underline{\underline{r}}$$

G. Hunter, Int. J. Quant. Chem. 9, 237 (1975).
N.I. Gidopoulos, E.K.U.G. arXiv: cond-mat/0502433

OBSERVATIONS:

- **Eq. ❶ is a nonlinear equation in** $\Phi_{\underline{\underline{R}}}\left(\underline{r}\right)$
- **Eq. ❶ contains** $\chi\left(\underline{\underline{R}}\right)$ **⇒ selfconsistent solution of ❶ and ❷ required**

- **Neglecting the** $1/M_\nu$ **terms in ❶, BO is recovered**
- **There is an alternative, equally exact, representation** $\Psi = \Phi_{\underline{r}}\left(\underline{\underline{R}}\right)\chi\left(\underline{r}\right)$ **(electrons move on the nuclear energy surface)**

- **Eq. ❶ and ❷ are form-invariant under the "gauge" transformation**

$$\Phi \rightarrow \tilde{\Phi} = e^{i\theta\left(\underline{\underline{R}}\right)}\Phi$$

$$\chi \rightarrow \tilde{\chi} = e^{-i\theta\left(\underline{\underline{R}}\right)}\chi$$

$$A_\nu \rightarrow \tilde{A}_\nu = A_\nu + \nabla_\nu\theta\left(\underline{\underline{R}}\right)$$

$$\in\left(\underline{\underline{R}}\right) \rightarrow \tilde{\in}\left(\underline{\underline{R}}\right) = \in\left(\underline{\underline{R}}\right)$$ **Exact potential energy surface is gauge invariant.**

- $\gamma(C) := \oint_C \vec{A}\cdot d\vec{R}$ **is a (gauge-invariant) geometric phase**
  the exact geometric phase

Proof of Theorem I:

Given the exact electron-nuclear wavefuncion $\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)$

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

with some real-valued funcion $S\left(\underline{\underline{R}}\right)$

$$\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right) := \Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right) / \chi\left(\underline{\underline{R}}\right)$$

Then, by construction, $\int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\right|^2 = 1$

Proof of theorem II (basic idea)

first step:

Find the variationally best $\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$ and $\chi(\underline{\underline{R}})$ by minimizing the total energy under the subsidiary condition that $\int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2 = 1$. This gives two Euler equations:

Eq. ❶
$$\frac{\delta}{\delta \Phi^*_{\underline{\underline{R}}}(\underline{\underline{r}})}\left(\frac{\langle \Phi\chi | \hat{H} | \Phi\chi \rangle}{\langle \Phi\chi | \Phi\chi \rangle} - \int d\underline{\underline{R}}\, \Lambda(\underline{\underline{R}}) \int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})\right|^2 \right) = 0$$

Eq. ❷
$$\frac{\delta}{\delta \chi(\underline{\underline{R}})}\left(\frac{\langle \Phi\chi | \hat{H} | \Phi\chi \rangle}{\langle \Phi\chi | \Phi\chi \rangle} \right) = 0$$

second step:

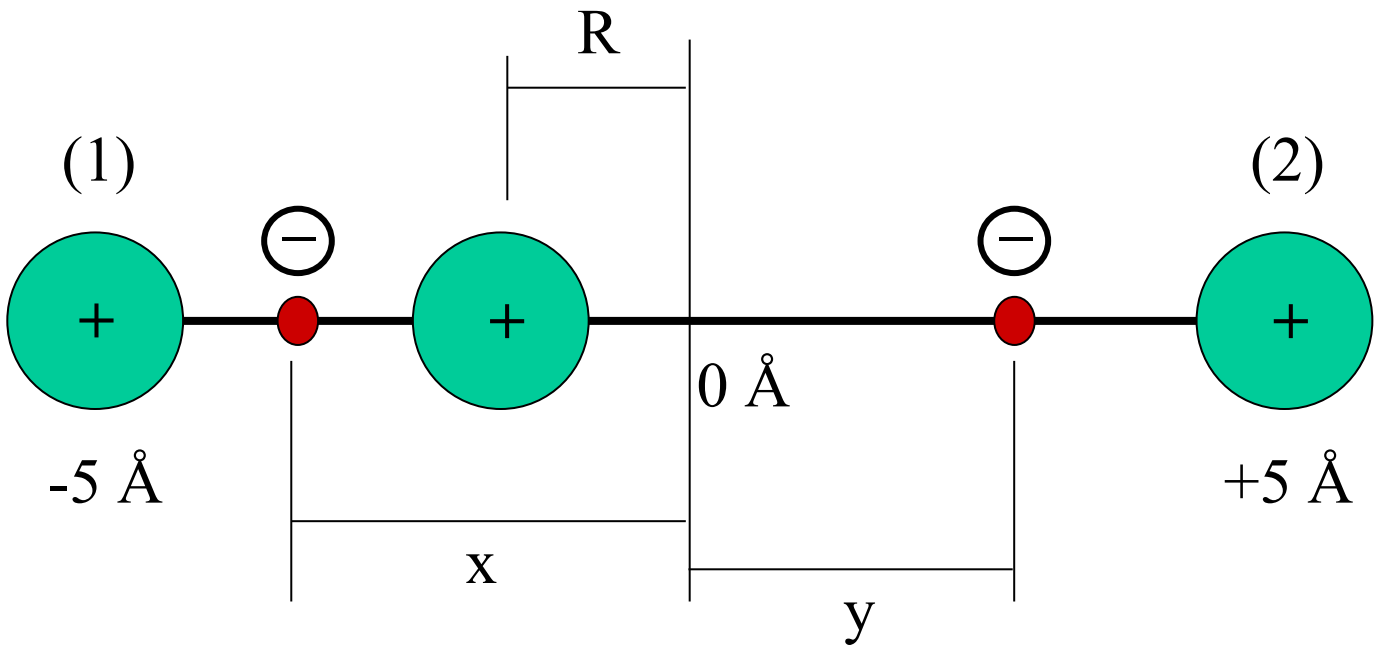
prove the implication

Φ, χ satisfy Eqs. ❶, ❷ $\Rightarrow$ $\Psi := \Phi\chi$ satisfies $H\Psi = E\Psi$

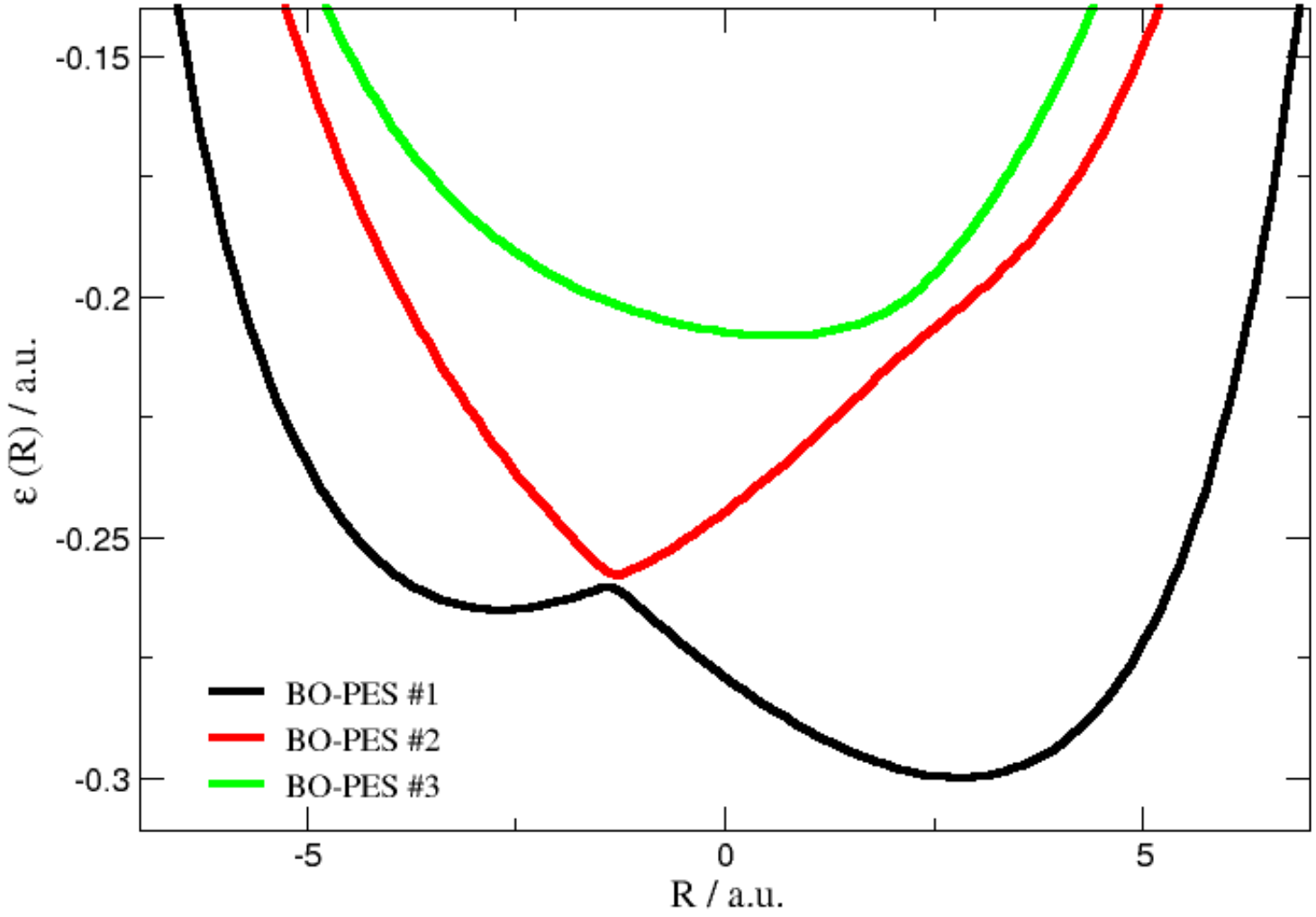
How do the exact PES look like?

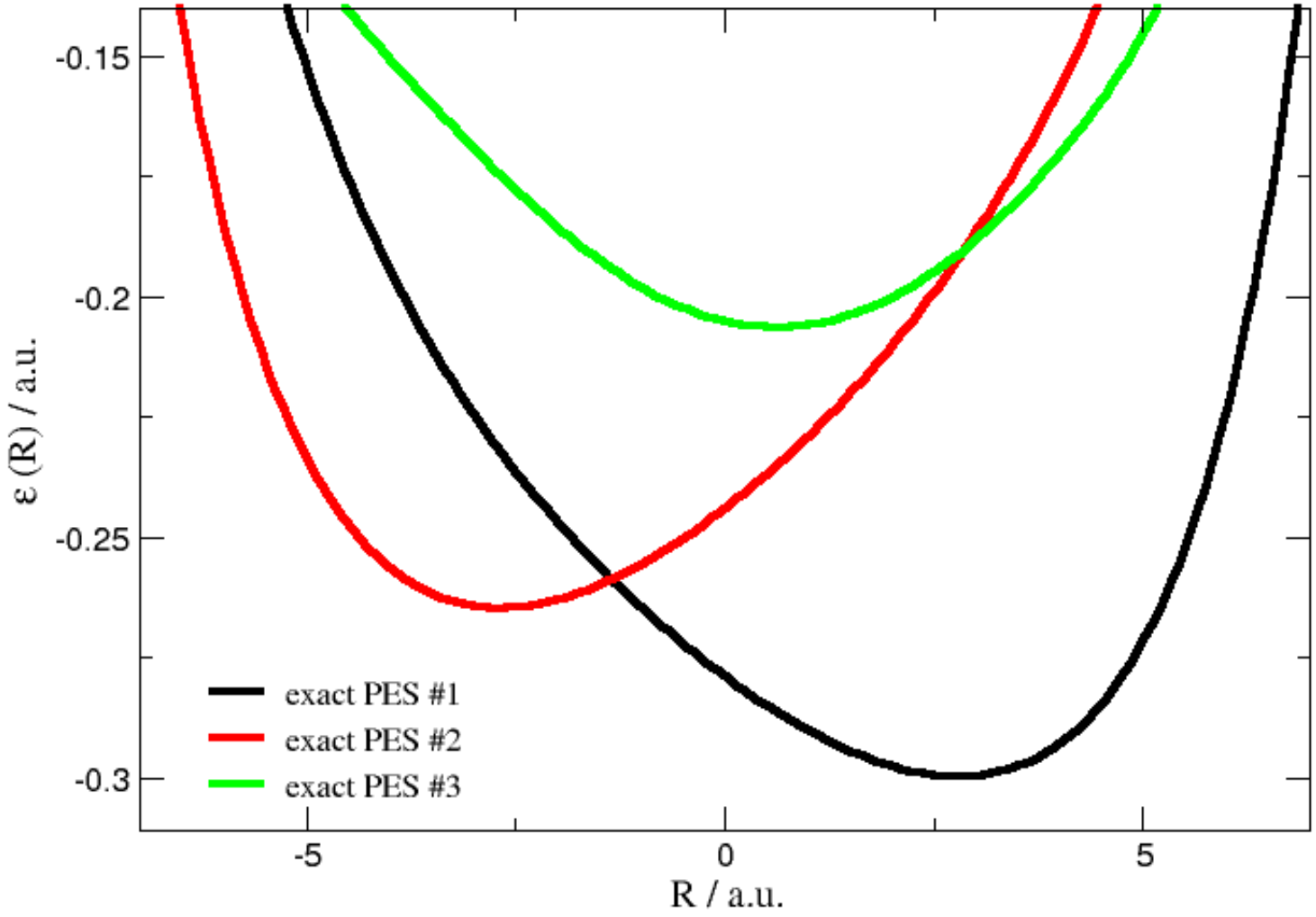
MODEL

(S. Shin, H. Metiu, JCP 102, 9285 (1995), JPC 100, 7867 (1996))



Nuclei (1) and (2) are heavy: Their positions are fixed


-0.15
-0.2
-0.25
-0.3
ε (R) / a.u.
-5
0
5
R / a.u.
BO-PES #1
BO-PES #2
BO-PES #3


-0.15
-0.2
-0.25
-0.3
ε (R) / a.u.
-5
0
5
R / a.u.
exact PES #1
exact PES #2
exact PES #3

Exact Berry connection

$$A_\nu(\underline{\underline{R}}) = \int d\underline{\underline{r}}\ \Phi^*_{\underline{\underline{R}}}(\underline{\underline{r}})\ (-i\nabla_\nu)\ \Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$$

Insert: $\Phi_{\underline{\underline{R}}}(\underline{\underline{r}}) = \Psi(\underline{\underline{r}},\underline{\underline{R}}) / \chi(\underline{\underline{R}})$

$$\chi(\underline{\underline{R}}) := e^{i\theta(\underline{\underline{R}})} \left|\chi(\underline{\underline{R}})\right|$$

$$A_\nu(\underline{\underline{R}}) = \mathrm{Im}\left\{\int d\underline{\underline{r}}\ \Psi^*(\underline{\underline{r}},\underline{\underline{R}})\ \nabla_\nu \Psi(\underline{\underline{r}},\underline{\underline{R}})\right\} / \left|\chi(\underline{\underline{R}})\right|^2 - \nabla_\nu\theta$$

$$\boxed{A_\nu(\underline{\underline{R}}) = J_\nu(\underline{\underline{R}}) / \left|\chi(\underline{\underline{R}})\right|^2 - \nabla_\nu\theta(\underline{\underline{R}})}$$

with the exact nuclear current density J_ν

Consider special cases where $\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$ is real-valued (e.g. non-degenerate ground state → DFT formulation)

$$\Rightarrow \quad A_\nu(\underline{\underline{R}}) = -i\int d\underline{\underline{r}}\, \Phi^*_{\underline{\underline{R}}}(\underline{\underline{r}})\, \nabla_\nu \Phi_{\underline{\underline{R}}}(\underline{\underline{r}}) = -i\int d\underline{\underline{r}} \frac{1}{2}\nabla_\nu \Phi^2_{\underline{\underline{R}}}(\underline{\underline{r}})$$

$$= -\frac{i}{2}\nabla_\nu \int d\underline{\underline{r}}\, \Phi^2_{\underline{\underline{R}}}(\underline{\underline{r}}) = 0$$

Eqs. ❶, ❷ simplify:

❶
$$\left(\hat{H}_{BO} + \sum_\nu \frac{-\nabla^2_\nu}{2M_\nu} - \sum_\nu \frac{1}{2M_\nu}\left(\frac{\nabla_\nu \chi}{\chi}\right)\cdot\nabla_\nu\right)\Phi_{\underline{\underline{R}}}(\underline{\underline{r}}) = \in(\underline{\underline{R}})\,\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})$$

❷
$$\left(\hat{T}_n + \hat{W}_{nn} + \hat{V}^{ext}_n + \in(\underline{\underline{R}})\right)\chi(\underline{\underline{R}}) = E\chi(\underline{\underline{R}})$$

Density functional theory beyond BO

What are the "right" densities?

first attempt

$$n(r) = N_e \int d^{N_e - 1} \underline{r} \int d^{N_n} \underline{\underline{R}} \left| \Psi\left(\underline{r}, \underline{\underline{R}} \right) \right|^2$$

$$N(R) = N_n \int d^{N_e} \underline{r} \int d^{N_n - 1} \underline{\underline{R}} \left| \Psi\left(\underline{r}, \underline{\underline{R}} \right) \right|^2$$

A HK theorem $\left(V_n^{ext}, V_e^{ext}\right) \xleftrightarrow{1\text{–}1} (N, n)$ **is easily demonstrated (Parr et al).**

This, however, is NOT useful (though correct) because, for $V_n^{ext} \equiv 0 \equiv V_e^{ext}$ **, one has:**

n = constant
N = constant !

(**easily verified using** $\Psi = e^{-ik \cdot R_{CM}} \psi$)

next attempt $\tilde{n}(r - R_{CM})$ $\tilde{N}(R - R_{CM})$

NO GOOD, because spherical for ALL systems

Useful densities are:

$$\Gamma(\underline{\underline{R}}) := \int d\underline{\underline{r}} \left|\Psi(\underline{\underline{r}}, \underline{\underline{R}})\right|^2$$ **(diagonal of nuclear DM)**

$$n_{\underline{\underline{R}}}(r) := \frac{N_e \cdot \int d^{N_e-1}\underline{\underline{r}} \left|\Psi(\underline{\underline{r}}, \underline{\underline{R}})\right|^2}{\Gamma(\underline{\underline{R}})}$$ **is a conditional probability density**

Note: $n_{\underline{\underline{R}}}(r)$ **is the density that has always been used in the DFT within BO**

now use decomposition $\Psi\left(\underline{\underline{r}},\underline{\underline{R}}\right)=\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\chi\left(\underline{\underline{R}}\right)$

then $\Gamma\left(\underline{\underline{R}}\right)=\int \underbrace{d\underline{\underline{r}}\left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\right|^2}_{1}\left|\chi(R)\right|^2=\left|\chi(R)\right|^2$

$$n_{\underline{\underline{R}}}\left(r\right)=\frac{N_e\cdot\int d^{N_e-1}\underline{\underline{r}}\left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\right|^2\cancel{\left|\chi(R)\right|^2}}{\cancel{\left|\chi(R)\right|^2}}=N_e\cdot\int d^{N_e-1}\underline{\underline{r}}\left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\right|^2$$ **(like in B.O.)!**

HK theorem $\left(n^{gs}_{\underline{\underline{R}}}\left(r\right),\Gamma^{gs}\left(\underline{\underline{R}}\right)\right)\overset{1\text{–}1}{\longleftrightarrow}\left(v_e\left(r,\underline{\underline{R}}\right),v_n\left(\underline{\underline{R}}\right)\right)$

Eq. ❶ $\left(\hat{T}_e+\hat{V}_e+\hat{W}_{int}\right)\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)=\in\left(\underline{\underline{R}}\right)\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$

Eq. ❷ $\left(\hat{T}_n+\hat{V}_n\right)\chi\left(\underline{\underline{R}}\right)=E\,\chi\left(\underline{\underline{R}}\right)$

where $V_e\left(\underline{\underline{r}},\underline{\underline{R}}\right)=\sum_j v_e\left(r_j,\underline{\underline{R}}\right)=\sum_j v_{en}\left(r_j,\underline{\underline{R}}\right)+v_e^{ext}\left(r_j\right)$

$$V_n\left(\underline{\underline{R}}\right)=W_{nn}\left(\underline{\underline{R}}\right)+v_n^{ext}\left(\underline{\underline{R}}\right)+\in\left(\underline{\underline{R}}\right)$$

KS equations

nuclear equation stays the same

❷ $$\left(\hat{T}_n + \hat{W}_{nn}\left(\underline{\underline{R}}\right) + \hat{V}_n^{ext}\left(\underline{\underline{R}}\right) + \in\left(\underline{\underline{R}}\right)\right)\chi\left(\underline{\underline{R}}\right) = E\chi\left(\underline{\underline{R}}\right)$$

❶ $$\left(\hat{T}_e + \hat{V}_e\left(\underline{r},\underline{\underline{R}}\right) + \quad W_{int}\left[\chi\right]\left(\underline{r},\underline{\underline{R}}\right) + \in\left(\underline{\underline{R}}\right)\right)\Phi_{\underline{\underline{R}}}\left(\underline{r}\right) = \in\ \left(\underline{\underline{R}}\right)\Phi_{\underline{\underline{R}}}\left(\underline{r}\right)$$

is replaced by a standard (i.e. 1-body) KS scheme

KS equations

nuclear equation stays the same

❷ $\left(\hat{T}_n + \hat{W}_{nn}\left(\underline{\underline{R}}\right) + \hat{V}_n^{ext}\left(\underline{\underline{R}}\right) + \in\left(\underline{\underline{R}}\right)\right)\chi\left(\underline{\underline{R}}\right) = E\chi\left(\underline{\underline{R}}\right)$

❶ $\left(\hat{T}_e + \hat{V}_e^{\lambda}\left(\underline{r}, \underline{\underline{R}}\right) + \lambda \cdot W_{int}\left[\chi\right]\left(\underline{r}, \underline{\underline{R}}\right) + \in\left(\underline{\underline{R}}\right)\right)\Phi_{\underline{\underline{R}}}\left(\underline{r}\right) = \in^{\lambda}\left(\underline{\underline{R}}\right)\Phi_{\underline{\underline{R}}}\left(\underline{r}\right)$

is replaced by a standard (i.e. 1-body) KS scheme

constructed by adiabatic connection, switching from

$\lambda = 1$ (fully interacting system) to $\lambda = 0$ (non-interacting system)

and adjusting V_e^{λ} for each λ such that $n_{\underline{\underline{R}}}(r)$ does not change

$V_e^{\lambda=0}\left(\underline{r}, \underline{\underline{R}}\right) =$ KS potential $V_{KS}\left(\underline{r}, \underline{\underline{R}}\right)$

Electronic equation:

$$\left(-\frac{\nabla^2}{2m} + v_{KS}\left(r, \underline{\underline{R}}\right)\right)\varphi_{\underline{\underline{R}},j}(r) = \eta_j\left(\underline{\underline{R}}\right)\varphi_{\underline{\underline{R}},j}(r)$$

$$v_{KS}\left(r, \underline{\underline{R}}\right) = v_{en}\left(r, \underline{\underline{R}}\right) + v_e^{ext}(r) + v_{Hxc}\left[\chi, n_{\underline{\underline{R}}}\right]\left(r, \underline{\underline{R}}\right)$$

$v_{KS}\left(\underline{\underline{r}}, \underline{\underline{R}}\right)$ = **local (multiplicative) one-body potential that contains all non-adiabatic couplings**

v_{KS} depends on χ and $n_{\underline{\underline{R}}}(r)$

→ self-consistency with $n_{\underline{\underline{R}}}(r) = \sum_{j=1}^{N_e}\left|\varphi_{\underline{\underline{R}},j}(r)\right|^2$

and with nuclear equation ❷ required:

$$\in\left(\underline{\underline{R}}\right) = \sum_{j=1}^{N_e}\eta_j\left(\underline{\underline{R}}\right) - \int n_{\underline{\underline{R}}}(r)\, v_{Hxc}\left(r, \underline{\underline{R}}\right) d^3r + E_{Hxc}\left[\chi, n_{\underline{\underline{R}}}\right]$$

Time-dependent case

Hamiltonian for the complete system of N_e electrons with coordinates $(r_1 \cdots r_{N_e}) \equiv \underline{r}$ and N_n nuclei with coordinates $(R_1 \cdots R_{N_n}) \equiv \underline{\underline{R}}$, masses $M_1 \cdots M_{Nn}$ and charges $Z_1 \cdots Z_{Nn}$.

$$\hat{H} = \hat{T}_n(\underline{\underline{R}}) + \hat{W}_{nn}(\underline{\underline{R}}) + \hat{T}_e(\underline{r}) + \hat{W}_{ee}(\underline{r}) + \hat{V}_{en}(\underline{\underline{R}}, \underline{r})$$

with

$$\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla_\nu^2}{2M_\nu} \qquad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla_i^2}{2m} \qquad \hat{W}_{nn} = \frac{1}{2}\sum_{\substack{\mu,\nu \\ \mu\neq\nu}}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$$

$$\hat{W}_{ee} = \frac{1}{2}\sum_{\substack{j,k \\ j\neq k}}^{N_e} \frac{1}{|r_j - r_k|} \qquad \hat{V}_{en} = \sum_{j=1}^{N_e}\sum_{\nu=1}^{N_n} -\frac{Z_\nu}{|r_j - R_\nu|}$$

Time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\underline{r}, \underline{\underline{R}}, t) = \left(H(\underline{r}, \underline{\underline{R}}) + V_{laser}(\underline{r}, \underline{\underline{R}}, t)\right)\psi(\underline{r}, \underline{\underline{R}}, t)$$

$$V_{laser}(\underline{r}, \underline{\underline{R}}, t) = \left(\sum_{j=1}^{N_e} r_j - \sum_{\nu=1}^{N_n} Z_\nu R_\nu\right) \cdot E \cdot f(t) \cdot \cos\omega t$$

Theorem T-I

The exact solution of

$$i\partial_t \Psi\left(\underline{\underline{r}}, \underline{\underline{R}}, t\right) = H\left(\underline{\underline{r}}, \underline{\underline{R}}, t\right)\ \Psi\left(\underline{\underline{r}}, \underline{\underline{R}}, t\right)$$

can be written in the form

$$\Psi\left(\underline{\underline{r}}, \underline{\underline{R}}, t\right) = \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right)\ \chi\left(\underline{\underline{R}}, t\right)$$

where $\int d\underline{\underline{r}} \left|\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right)\right|^2 = 1$ **for any fixed** $\underline{\underline{R}}, t$.

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Theorem T-II

$\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},t)$ and $\chi(\underline{\underline{R}},t)$ satisfy the following equations

Eq. ❶

$$\Big(\underbrace{\hat{T}_e+\hat{W}_{ee}+\hat{V}_e^{ext}(\underline{\underline{r}},t)+\hat{V}_{en}(\underline{\underline{r}},\underline{\underline{R}})}_{\hat{H}_{BO}(t)}+\sum_\nu \frac{1}{2M_\nu}\left(-i\nabla_\nu-A_\nu(\underline{\underline{R}},t)\right)^2$$
$$+\sum_\nu \frac{1}{M_\nu}\left(\frac{-i\nabla_\nu\chi(\underline{\underline{R}},t)}{\chi(\underline{\underline{R}},t)}+A_\nu(\underline{\underline{R}},t)\right)\left(-i\nabla_\nu-A_\nu\right)-\in(\underline{\underline{R}},t)\Big)\Phi_{\underline{\underline{R}}}(\underline{\underline{r}})=i\partial_t\Phi_{\underline{\underline{R}}}(\underline{\underline{r}},t)$$

Eq. ❷

$$\left(\sum_\nu \frac{1}{2M_\nu}\left(-i\nabla_\nu+A_\nu(\underline{\underline{R}},t)\right)^2+\hat{W}_{nn}(\underline{\underline{R}})+\hat{V}_n^{ext}(\underline{\underline{R}},t)+\in(\underline{\underline{R}},t)\right)\chi(\underline{\underline{R}},t)=i\partial_t\chi(\underline{\underline{R}},t)$$

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$$\in \left(\underline{\underline{R}}, t\right) = \int d\underline{\underline{r}}\, \Phi^{*}_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right)\left(H_{BO}(t) + \sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu\left(\underline{\underline{R}}, t\right)\right)^2 - i\partial_t \right)\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right)$$

EXACT time-dependent potential energy surface

$$A_\nu\left(\underline{\underline{R}}, t\right) = -i\int \Phi^{*}_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right)\nabla_\nu \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right) d\underline{\underline{r}}$$

EXACT time-dependent Berry connection

Example: H_2^+ **in 1D in strong laser field**

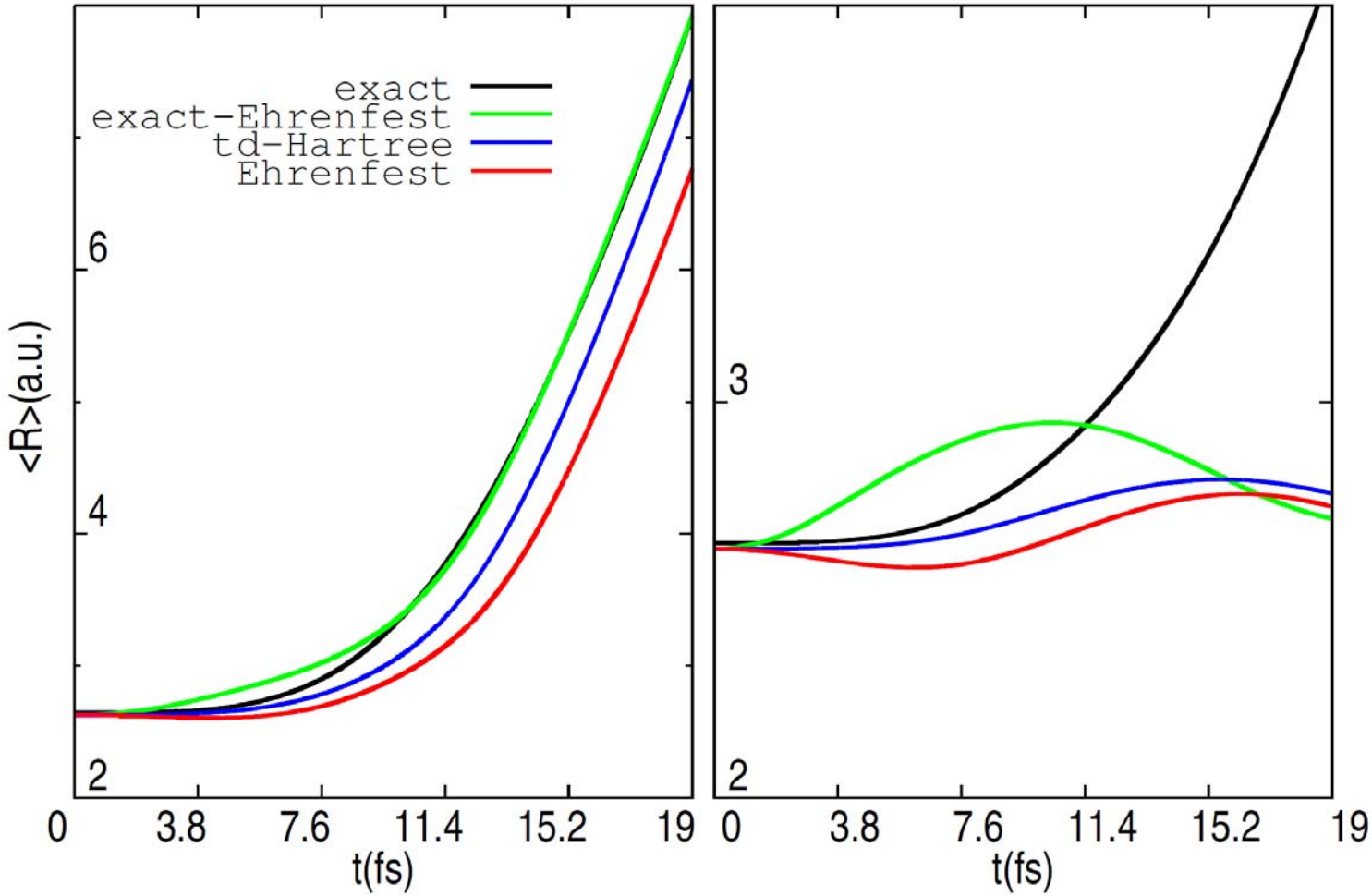
exact solution of $i\partial_t \Psi(r,R,t) = H\,\Psi(r,R,t)$:

Compare with:

- Hartree approximation: $\Psi(r,R,t) = \chi(R,t)\cdot\varphi(r,t)$

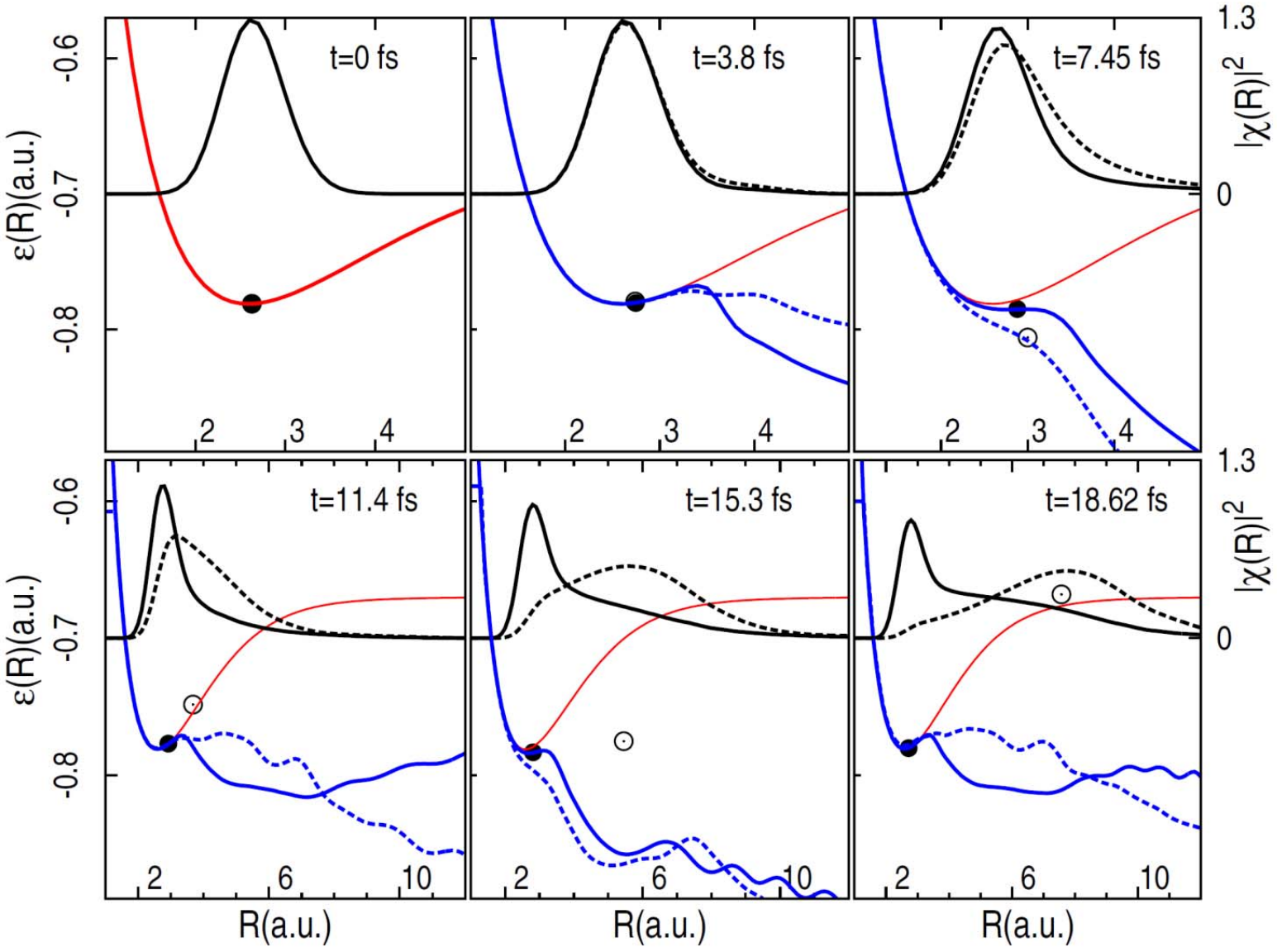
- Standard Ehrenfest dynamics

- "Exact Ehrenfest dynamics" where the forces on the nuclei are calculated from the **exact** TD-PES



The internuclear separation < R>(t) for the intensities
$I_1 = 10^{14}$W/cm^2 (left) and $I_2 = 2.5 \times 10^{13}$W/cm^2 (right)

Exact time-dependent PES



Dashed: $I_1 = 10^{14}$W/cm^2 ; solid: $I_2 = 2.5 \times 10^{13}$W/cm^2

Summary:

- $\Psi\left(\underline{\underline{r}}, \underline{\underline{\underline{R}}}\right) = \Phi_{\underline{\underline{\underline{R}}}}\left(\underline{\underline{r}}\right) \cdot \chi\left(\underline{\underline{\underline{R}}}\right)$ **is an exact representation of the complete electron-nuclear wavefunction if χ and Φ satisfy the right equations (namely Eqs. ❶, ❷)**

- **Eqs. ❶, ❷ provide the proper definition of the**

  --- exact potential energy surface
  --- exact Berry connection

  both in the static and the time-dependent case

- **Multi-component (TD)DFT framework**

- **TD-PES useful to interpret different dissociation meachanisms**


Thanks !