15th International Workshop on Computational Physics and Materials Science: Total Energy and Force Methods

13 - 15 January 2011

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

GROSS Eberhard Kurt Ulrich
Max Planck Institute of Microstructure Physics
Weinberg 2
D-06120 Halle
Saale
Germany
Exact factorization of the time-dependent electron-nuclear wave function

E.K.U. Gross
Max-Planck Institute for Microstructure Physics

Co-workers:
Ali Abedi (MPI-Halle)
Neepa Maitra (CUNY)
Nikitas Gidopoulos (Rutherford Lab)
Exact factorization of the time-dependent electron-nuclear wave function: Life beyond the Born-Oppenheimer approximation

E.K.U. Gross
Max-Planck Institute for Microstructure Physics

Co-workers:
Ali Abedi (MPI-Halle)
Neepa Maitra (CUNY)
Nikitas Gidopoulos (Rutherford Lab)
Hamiltonian for the complete system of \( N_e \) electrons with coordinates \((r_1 \ldots r_{N_e}) \equiv \underline{r}\) and \( N_n \) nuclei with coordinates \((R_1 \ldots R_{N_n}) \equiv \underline{R}\), masses \( M_1 \cdots M_{N_n} \) and charges \( Z_1 \cdots Z_{N_n} \).

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

with

\[
\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla^2}{2M_\nu} \quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla^2_i}{2m} \quad \hat{W}_{nn} = \frac{1}{2} \sum_{\mu,\nu}^{N_n} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}
\]

\[
\hat{W}_{ee} = \frac{1}{2} \sum_{j,k}^{N_e} \frac{1}{|r_j - r_k|} \quad \hat{V}_{en} = \sum_{j=1}^{N_e} \sum_{v=1}^{N_n} -\frac{Z_v}{|r_j - R_v|}
\]

**convention:**

Greek indices \( \rightarrow \) nuclei  
Latin indices \( \rightarrow \) electrons

**Full Schrödinger equation:**

\[
\hat{H}\Psi(\underline{r}, \underline{R}) = E\Psi(\underline{r}, \underline{R})
\]
Born-Oppenheimer approximation

solve

\[
\left( \hat{T}_e(r) + \hat{W}_{ee}(r) + \hat{V}_e^{\text{ext}}(r) + \hat{V}_{en}(r, R) \right) \Phi^{\text{BO}}_R(r) = \varepsilon^{\text{BO}}(R) \Phi^{\text{BO}}_R(r)
\]

for each fixed nuclear configuration $R$.

Make adiabatic ansatz for the complete molecular wave function:

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

and find best $\chi^{\text{BO}}$ by minimizing $\langle \Psi^{\text{BO}} | H | \Psi^{\text{BO}} \rangle$ w.r.t. $\chi^{\text{BO}}$.
Nuclear equation

\[ \hat{T}_n(R) + \hat{W}_{nn}(R) + \hat{V}_{\text{ext}}^n(R) + \sum_v \frac{1}{M_v} A_v^{BO}(R) (-i \nabla_v) + \in^{BO}(R) \]

\[ + \int \Phi_R^{BO}(r) \hat{T}_n(R) \Phi_R^{BO}(r) dr \] \[ \chi^{BO}(R) = E \chi^{BO}(R) \]

Berry connection

\[ A_v^{BO}(R) = \int \Phi_R^{BO}(r) (-i \nabla_v) \Phi_R^{BO}(r) dr \]

\[ \gamma^{BO}(C) = \int_C A^{BO}(R) \cdot d\vec{R} \quad \text{is a geometric phase} \]

In this context, potential energy surfaces \( \in^{BO}(R) \) and the Berry potential \( \tilde{A}^{BO}(R) \) 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:

\[ \Psi_K (r, R) = \sum_j \Phi_{R,J}^{BO} (r) \cdot \chi_{K,J} (R) \]

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

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

$$\Psi_0 (r, R) \approx \chi_{00} (R) \Phi_{0,R}^B (r) + \chi_{01} (R) \Phi_{1,R}^B (r)$$
**GOAL:** Show that \( \Psi(r, R) = \Phi_R(r) \cdot \chi(R) \) 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

\[ \hat{H}\Psi(r, R) = E\Psi(r, R) \]

can be written in the form

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

where \( \int dr |\Phi_R(r)|^2 = 1 \) for each fixed \( R \).

Immediate consequences of Theorem I:

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

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

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

2. $\Phi_R (r)$ and $\chi(R)$ are unique up to within the “gauge transformation”

   $\tilde{\Phi}_R (r) := e^{i\theta(R)} \Phi_R (r) \quad \tilde{\chi}(R) := e^{-i\theta(R)} \chi(R)$
proof: Let $\phi \cdot \chi$ and $\tilde{\phi} \cdot \tilde{\chi}$ be two different representations of an exact eigenfunction $\Psi$ i.e.

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

$$
\Rightarrow \frac{\tilde{\Phi}_R(r)}{\Phi_R(r)} = \frac{\chi(R)}{\tilde{\chi}(R)} \equiv G(R) \quad \Rightarrow \quad \tilde{\Phi}_R(r) = G(R) \Phi_R(r)
$$

$$
\Rightarrow \int dr \left| \tilde{\Phi}_R(r) \right|^2 = \left| G(R) \right|^2 \int dr \left| \Phi_R(r) \right|^2
$$

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

$$
\Rightarrow \quad \tilde{\Phi}_R(r) = e^{i\theta(R)} \Phi_R(r) \quad \tilde{\chi}(R) = e^{-i\theta(R)} \chi(R)
$$
Theorem II: $\Phi_R(x)$ and $\chi(R)$ satisfy the following equations:

\[
\begin{align*}
\text{Eq. 1} & \quad \left( \hat{T}_c + \hat{W}_{cc} + \hat{V}_{\text{ext}}^{\text{ext}} + \hat{V}_{\text{ext}}^{\text{external}} + \sum_{v} \frac{1}{2M_v} (-i\nabla_v - A_v)^2 \right) \hat{H}_{\text{BO}} + \sum_{v} \frac{1}{M_v} \left( -i\nabla_v \chi + A_v \right) \left( -i\nabla_v - A_v \right) \Phi_R(x) = \epsilon(R) \Phi_R(x) \\
\text{Eq. 2} & \quad \left( \sum_{v} \frac{1}{2M_v} (-i\nabla_v + A_v)^2 + \hat{W}_{\text{nn}} + \hat{V}_{\text{ext}}^{\text{ext}} + \epsilon(R) \chi(R) \right) \chi(R) = E \chi(R)
\end{align*}
\]

where

$$A_v(R) = -i \int \Phi_R^*(r) \nabla_v \Phi_R(r) \, dr$$

OBSERVATIONS:

- Eq. 1 is a nonlinear equation in $\Phi_R(r)$
- Eq. 2 contains $\chi(R) \Rightarrow$ selfconsistent solution of 1 and 2 required

- Neglecting the $1/M_v$ terms in 1, BO is recovered
- There is an alternative, equally exact, representation $\Psi = \Phi_R(R)\chi(r)$ (electrons move on the nuclear energy surface)

- Eq. 1 and 2 are form-invariant under the “gauge” transformation

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

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

$$A_v \rightarrow A_v = A_v + \nabla_v \theta(R)$$

$$\varepsilon(R) \rightarrow \tilde{\varepsilon}(R) = \varepsilon(R) \quad \text{Exact potential energy surface is gauge invariant.}$$

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

  the exact geometric phase
Proof of Theorem I:

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

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

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

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

Then, by construction, \( \int d\mathbf{r} |\Phi_{\mathbf{R}}(\mathbf{r})|^2 = 1 \)
Proof of theorem II (basic idea)

first step:
Find the variationally best \( \Phi_R (r) \) and \( \chi (R) \) by minimizing the total energy under the subsidiary condition that \( \int d_\varepsilon |\Phi_R (\varepsilon)|^2 = 1 \). This gives two Euler equations:

**Eq. 1**
\[
\frac{\delta}{\delta \Phi^*_R (r)} \left( \frac{\langle \Phi \chi | \hat{H} | \Phi \chi \rangle}{\langle \Phi \chi | \Phi \chi \rangle} - \int dR \Lambda (R) \int dr |\Phi_R (r)|^2 \right) = 0
\]

**Eq. 2**
\[
\frac{\delta}{\delta \chi (R)} \left( \frac{\langle \Phi \chi | \hat{H} | \Phi \chi \rangle}{\langle \Phi \chi | \Phi \chi \rangle} \right) = 0
\]

second step:
prove the implication

\( \Phi, \chi \) satisfy Eqs. 1, 2 \implies \Psi := \Phi \chi \) satisfies \( H \Psi = E \Psi \)
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
**Exact Berry connection**

\[ A_v (R) = \int dr \; \Phi^*_R (r) \left( -i \nabla_v \right) \Phi_R (r) \]

**Insert:**

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

\[ \chi (R) := e^{i\theta (R)} |\chi (R)| \]

\[ A_v (R) = \text{Im} \left\{ \int dr \; \Psi^* (r, R) \nabla_v \Psi (r, R) \right\} / |\chi (R)|^2 - \nabla_v \theta \]

\[ A_v (R) = J_v (R) / |\chi (R)|^2 - \nabla_v \theta (R) \]

with the exact nuclear current density \( J_v \)
Consider special cases where \( \Phi_R(r) \) is real-valued (e.g. non-degenerate ground state \( \rightarrow \) DFT formulation)

\[
\Rightarrow \quad A_v \left( \frac{R}{\infty} \right) = -i \int \text{d}r \Phi_R^* \left( \frac{r}{\infty} \right) \nabla_v \Phi_R \left( \frac{r}{\infty} \right) = -i \int \text{d}r \frac{1}{2} \nabla_v \Phi_R^2 \left( \frac{r}{\infty} \right) \\
= -\frac{i}{2} \nabla_v \int \text{d}r \Phi_R^2 \left( \frac{r}{\infty} \right) = 0
\]

Eqs. 1, 2 simplify:

\[
\begin{align*}
1 \quad \left( \hat{H}_{BO} + \sum_v -\frac{\nabla_v^2}{2M_v} - \sum_v \frac{1}{2M_v} \left( \frac{\nabla_v \chi}{\chi} \right) \cdot \nabla_v \right) \Phi_R \left( \frac{r}{\infty} \right) = & \epsilon \left( \frac{R}{\infty} \right) \Phi_R \left( \frac{r}{\infty} \right) \\
2 \quad (\hat{T}_n + \hat{W}_{nn} + \hat{V}_{n}^{\text{ext}} + \epsilon \left( \frac{R}{\infty} \right)) \chi \left( \frac{R}{\infty} \right) = & E \chi \left( \frac{R}{\infty} \right)
\end{align*}
\]
Density functional theory beyond BO

What are the “right” densities?

**first attempt**

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

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

A HK theorem \( (V_n^{\text{ext}}, V_e^{\text{ext}}) \leftrightarrow (N, n) \) is easily demonstrated (Parr et al).

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

- \( n = \text{constant} \)
- \( N = \text{constant} \)

\[ \left\{ \text{easily verified using } \Psi = e^{-iK_{CM}} \psi \right\} \]
next attempt \( \tilde{n}(r - R_{CM}) \) \( \tilde{N}(R - R_{CM}) \)

NO GOOD, because spherical for ALL systems

Useful densities are:

\[
\Gamma(R) := \int dr |\Psi(r, R)|^2 \quad \text{(diagonal of nuclear DM)}
\]

\[
n_R(r) := \frac{N_e \cdot \int d^{N_e-1}r |\Psi(r, R)|^2}{\Gamma(R)} \quad \text{is a conditional probability density}
\]

\textbf{Note:} \( n_R(r) \) is the density that has always been used in the DFT within BO
now use decomposition $\Psi(r, R) = \Phi_R(r) \chi(R)$

then $\Gamma(R) = \int dr\left|\Phi_R(r)\right|^2 \left|\chi(R)\right|^2 = \left|\chi(R)\right|^2$

$n_R(r) = \frac{N_e \cdot \int d^{N_e-1}r\left|\Phi_R(r)\right|^2 \left|\chi(R)\right|^2}{\left|\chi(R)\right|^2} = N_e \cdot \int d^{N_e-1}r\left|\Phi_R(r)\right|^2$ (like in B.O.)

HK theorem $\left(n^g_{R}(r), \Gamma^g_{R}(R)\right) \leftrightarrow^{1-1} \left(v^e_{R}(r, R), v^e_{n}(R)\right)$

Eq. 1 $\left(\hat{T}_e + \hat{V}_e + \hat{W}_{int}\right) \Phi_R(r) = \varepsilon(R) \Phi_R(r)$

Eq. 2 $\left(\hat{T}_n + \hat{V}_n\right) \chi(R) = E \chi(R)$

where $V_e(r, R) = \sum_j V_e(r_j, R) = \sum_j V_{en}(r_j, R) + V_{ext}(r_j)$

$V_n(R) = W_{nn}(R) + V_{n}^{ext}(R) + \varepsilon(R)$
KS equations

nuclear equation stays the same

\[ (\hat{T}_n + \hat{W}_{nn}(\underline{R}) + \hat{V}_{\text{ext}}^{\text{ext}}(\underline{R}) + \epsilon(\underline{R}))\chi(\underline{R}) = E\chi(\underline{R}) \]

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

\[ (\hat{T}_e + \hat{V}_e(\underline{r},\underline{R}) + W_{\text{int}}[\chi](\underline{r},\underline{R}) + \epsilon(\underline{R}))\Phi_{\underline{R}}(\underline{r}) = \epsilon(\underline{R})\Phi_{\underline{R}}(\underline{r}) \]
KS equations

nuclear equation stays the same

\[ \left( \hat{T}_n + \hat{W}_{nn} \left( R \right) + \hat{V}^\text{ext}_{n} \left( R \right) + \epsilon \left( R \right) \right) \chi \left( R \right) = E \chi \left( R \right) \]

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 \( V^\lambda_e \) for each \( \lambda \) such that \( n_R \left( r \right) \) does not change

\[ V^\lambda_e \left( r, R \right) = \text{KS potential} \quad V_{KS} \left( r, R \right) \]
Electronic equation:

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

\[ v_{KS}(r, R) = v_{en}(r, R) + v_{e}^{ext}(r) + v_{Hxc}[\chi, n_R](r, R) \]

\[ v_{KS}(r, R) = \text{local (multiplicative) one-body potential that contains all non-adiabatic couplings} \]

\[ v_{KS} \text{ depends on } \chi \text{ and } n_R(r) \]

\[ \rightarrow \text{self-consistency with } n_R(r) = \sum_{j=1}^{N_e} |\varphi_{R,j}(r)|^2 \]

and with nuclear equation \( \mathbb{Q} \) required:

\[ \varepsilon(R) = \sum_{j=1}^{N_e} \eta_j(R) - \int n_R(r) v_{Hxc}(r, R) d^3r + E_{Hxc}[\chi, n_R] \]
Time-dependent case
Hamiltonian for the complete system of $N_e$ electrons with coordinates $(r_1 \cdots r_{N_e}) = \mathbf{r}$ and $N_n$ nuclei with coordinates $(R_1 \cdots R_{N_n}) = \mathbf{R}$, masses $M_1 \cdots M_{N_n}$ and charges $Z_1 \cdots Z_{N_n}$.

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

with $$\hat{T}_n = \sum_{v=1}^{N_n} -\frac{\nabla^2_v}{2M_v} \quad \hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla^2_i}{2m} \quad \hat{W}_{nn} = \frac{1}{2} \sum_{\mu,\nu \neq \mu} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}$$

$$\hat{W}_{ee} = \frac{1}{2} \sum_{j,k}^{N_e} \frac{1}{|r_j - r_k|} \quad \hat{V}_{en} = \sum_{j=1}^{N_e} \sum_{v=1}^{N_n} -\frac{Z_v}{|r_j - R_v|}$$

Time-dependent Schrödinger equation

$$i \frac{\partial}{\partial t} \Psi(\mathbf{r}, \mathbf{R}, t) = (\hat{H}(\mathbf{r}, \mathbf{R}) + V_{\text{laser}}(\mathbf{r}, \mathbf{R}, t) ) \psi(\mathbf{r}, \mathbf{R}, t)$$

$$V_{\text{laser}}(\mathbf{r}, \mathbf{R}, t) = \left( \sum_{j=1}^{N_e} r_j - \sum_{v=1}^{N_n} Z_v R_v \right) \cdot E \cdot f(t) \cdot \cos \omega t$$
Theorem T-I

The exact solution of

\[ i \partial_t \Psi \left( r, R, t \right) = H \left( r, R, t \right) \Psi \left( r, R, t \right) \]

can be written in the form

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

where \( \int dr \left| \Phi_R \left( r, t \right) \right|^2 = 1 \) for any fixed \( R, t \).

Theorem T-II

\( \Phi_R(r, t) \) and \( \chi(R, t) \) satisfy the following equations

**Eq. 1**

\[
\begin{align*}
\hat{T}_c + \hat{W}_{\text{ce}} + \hat{V}_{\text{c}}^\text{ext}(r, t) + \hat{V}_{\text{en}}(r, R) + \sum_{v}^{N_v} \frac{1}{2M_v} \left( -i\nabla_v - A_v(R, t) \right)^2 \\
\hat{H}_{\text{BO}}(t) \\
+ \sum_{v}^{N_v} \frac{1}{M_v} \left( -i\nabla_v \frac{\chi(R, t)}{\chi(R, t)} + A_v(R, t) \right) \left( -i\nabla_v - A_v \right) \in (R, t) \left( R, t \right) \Phi_R(r) = i\partial_t \Phi_R(r, t)
\end{align*}
\]

**Eq. 2**

\[
\begin{align*}
\sum_{v}^{N_v} \frac{1}{2M_v} \left( -i\nabla_v + A_v(R, t) \right)^2 + \hat{W}_{\text{nn}}(R) + \hat{V}_{\text{n}}^\text{ext}(R, t) + \in (R, t) \chi(R, t) = i\partial_t \chi(R, t)
\end{align*}
\]

\[ \mathcal{E}(R, t) = \int dr \Phi_R^*(r, t) \left( H_{BO}(t) + \sum_{\nu} \frac{1}{2M_{\nu}} (-i\nabla_{\nu} - A_{\nu}(R, t))^2 - i\partial_t \right) \Phi_R(r, t) \]

EXACT time-dependent potential energy surface

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

EXACT time-dependent Berry connection
**Example:** \( \text{H}_2^+ \) 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 $I_1 = 10^{14}\text{W/cm}^2$ (left) and $I_2 = 2.5 \times 10^{13}\text{W/cm}^2$ (right)
Dashed: $I_1 = 10^{14}\text{W/cm}^2$; solid: $I_2 = 2.5 \times 10^{13}\text{W/cm}^2$
Summary:

- $\Psi(r, R) = \Phi_R(r) \cdot \chi(R)$ is an exact representation of the complete electron-nuclear wavefunction if $\chi$ and $\Phi$ satisfy the right equations (namely Eqs. ①, ②).

- Eqs. ①, ② 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 mechanisms
Thanks!