What’s the correct classical force on the nuclei

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What’s the correct classical force on the nuclei or: How to make the Born-Oppenheimer approximation exact

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Hamiltonian for the complete system of $N_e$ electrons and $N_n$ nuclei

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

with \( (r_1 \cdots r_{N_e}) \equiv \underline{r} \) \quad \( (R_1 \cdots R_{N_n}) \equiv \underline{R} \)

\[ \hat{T}_n = \sum_{v=1}^{N_n} \frac{\nabla_v^2}{2M_v} \quad \hat{T}_e = \sum_{i=1}^{N_e} \frac{\nabla_i^2}{2m} \quad \hat{W}_{nn} = \frac{1}{2} \sum_{\mu, v}^{N_n} \frac{Z_\mu Z_v}{|R_\mu - R_v|} \]

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

**Full Schrödinger equation:** \( \hat{H}\Psi(r, R) = E\Psi(r, R) \)
Born-Oppenheimer approximation

solve

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

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 \( \langle \Psi^{\text{BO}} \mid H \mid \Psi^{\text{BO}} \rangle \) w.r.t. \( \chi^{\text{BO}} \):
Nuclear equation

\[ \hat{T}_n (\mathbf{R}) + \hat{W}_{nn} (\mathbf{R}) + \hat{V}_n^{\text{ext}} (\mathbf{R}) + \sum_{\nu} \frac{1}{M_{\nu}} A_{\nu}^{BO}(\mathbf{R})(-i\nabla_{\nu}) + \epsilon^{BO}(\mathbf{R}) \]

\[ + \int \Phi_{\mathbf{R}}^{BO} \ast (\mathbf{r}) \hat{T}_n (\mathbf{R}) \Phi_{\mathbf{R}}^{BO}(\mathbf{r})d\mathbf{r} \right] \chi^{BO}(\mathbf{R}) = E\chi^{BO}(\mathbf{R}) \]

Berry connection

\[ A_{\nu}^{BO}(\mathbf{R}) = \int \Phi_{\mathbf{R}}^{BO} \ast (\mathbf{r})(-i\nabla_{\nu}) \Phi_{\mathbf{R}}^{BO}(\mathbf{r})d\mathbf{r} \]

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

In this context, potential energy surfaces \( \epsilon^{BO}(\mathbf{R}) \) and the Berry potential \( \mathbf{A}^{BO}(\mathbf{R}) \) follow from an APPROXIMATION (the BO approximation).
In this context, potential energy surfaces \( \varepsilon^{\text{BO}}(\mathbf{R}) \) and the Berry potential \( \mathbf{A}^{\text{BO}}(\mathbf{R}) \) follow from an APPROXIMATION (the BO approximation).

“Berry phases arise when the world is approximately separated into a system and its environment.”
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, many BO-PES can be coupled.
Potential energy surfaces are absolutely essential in our understanding of a molecule and can be measured by femto-second pump-probe spectroscopy: 

Example: NaI femtochemistry
Example: NaI femtochemistry

\[ \text{Na}^+ + \text{I}^- \]

\[ \text{Na} + \text{I} \]

emitted neutral Na atoms
Effect of tuning pump wavelength (exciting to different points on excited surface)

Different periods indicative of anharmonic potential

But what’s the classical force when the nuclear wave packet splits??
• Show that the factorisation
  \[ \Psi(r, R) = \Phi_R(r) \cdot \chi(R) \]
  can be made exact

• Concept of exact PES and exact Berry phase

• Concept of time-dependent PES for nuclear motion

• Concept of time-dependent PES for electronic motion

• Mixed quantum-classical treatment
• Show that the factorisation
\[ \Psi(r, R) = \Phi_R(r) \cdot \chi(R) \]
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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”

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

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

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

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

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

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

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

**Eq. 1**

\[
\begin{align*}
\hat{H}_{BO} &= \left( T_e + \hat{W}_{ee} + \hat{V}_e^{\text{ext}} + \hat{V}_{en} \right) + \sum_{n} \frac{1}{2M_v} \left( -i\nabla_v - A_v \right)^2 \\
&+ \sum_{v} \frac{1}{M_v} \left( \frac{-i\nabla_v \chi}{\chi} + A_v \right) \left( -i\nabla_v - A_v \right) \Phi_R(r) = \epsilon(R) \Phi_R(r)
\end{align*}
\]

**Eq. 2**

\[
\begin{align*}
\sum_{n} \frac{1}{2M_v} \left( -i\nabla_v + A_v \right)^2 + \hat{W}_{nn} + \hat{V}_n^{\text{ext}} + \epsilon(R) \chi(R) = E\chi(R)
\end{align*}
\]

where

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

**Theorem II:** $\Phi_R(r)$ and $\chi(R)$ satisfy the following equations:

**Eq. 1**

$$
\begin{align*}
& \left( \hat{T}_c + \hat{W}_{ce} + \hat{V}_{en}^\text{ext} + \hat{V}_{en} \right) + \sum_{\nu} \frac{1}{2M_\nu} \left( -i \nabla_\nu - A_\nu \right)^2 \\
& + \sum_{\nu} \frac{1}{M_\nu} \left( \frac{-i \nabla_\nu \chi}{\chi} + A_\nu \right) \left( -i \nabla_\nu - A_\nu \right) \Phi_R(r) = \epsilon(R) \Phi_R(r)
\end{align*}
$$

**Eq. 2**

$$
\begin{align*}
& \sum_{\nu} \frac{1}{2M_\nu} \left( -i \nabla_\nu + A_\nu \right)^2 + \hat{W}_{nn} + \hat{V}_{n}^\text{ext} + \epsilon(R) \chi(R) = E\chi(R)
\end{align*}
$$

where

$$
A_\nu(R) = -i \int \Phi_R^*(r) \nabla_\nu \Phi_R(r) dr
$$

**Exact PES**

**Exact Berry connection**

OBSERVATIONS:

- Eq. 1 is a nonlinear equation in $\Phi_R(r)$
- Eq. 1 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

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

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

\[
A_v \rightarrow \tilde{A}_v = A_v + \nabla_v \theta(R)
\]

\[
\epsilon(R) \rightarrow \tilde{\epsilon}(R) = \epsilon(R) \quad \text{Exact potential energy surface is gauge invariant.}
\]

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

the exact geometric phase
How do the exact PES look like?
Nuclei (1) and (2) are heavy: Their positions are fixed

MODEL
Exact Berry connection

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

Insert:

\[ \Phi_R \left( r \right) = \frac{\Psi \left( r, R \right)}{\chi \left( R \right)} \]

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

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

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

with the exact nuclear current density \( J_v \).
Conclusion: The nuclear Schrödinger equation yields both the exact nuclear N-body density and the exact nuclear N-body current density.
Question: Can the true vector potential be gauged away, i.e. is the true Berry phase zero?
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Look at Shin-Metiu model in 2D:
BO-PES of 2D Shin-Metiu model
BO-PES of 2D Shin-Metiu model

conical intersection with Berry phase
• Non-vanishing Berry phase results from a non-analyticity in the electronic wave function $\Phi_{R}^{BO}(r)$ as function of $R$.

• Such non-analyticity is found (for the 2D Shin-Metiu model) in the BO approximation.
• Non-vanishing Berry phase results from a non-analyticity in the electronic wave function $\Phi^\text{BO}_R (r)$ as function of $R$.

• Such non-analyticity is found (for the 2D Shin-Metiu model) in the BO approximation.

Does the exact electronic wave function show such non-analyticity as well (in 2D Shin-Metiu model)?

Look at $D(R) = \int r \Phi_R (r) \, dr$

as function of nuclear mass $M$. 
QUESTION: Can one prove **in general** that the exact molecular Berry phase vanishes? Are there systems where the exact Berry phase does not vanish?
Time-dependent case
Hamiltonian for the complete system of $N_e$ electrons with coordinates $(r_1 \cdots r_{N_e}) \equiv \mathbf{r}$ and $N_n$ nuclei with coordinates $(R_1 \cdots R_{N_n}) \equiv \mathbf{R}$, 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
\[
\hat{T}_n = \sum_{\nu=1}^{N_n} -\frac{\nabla^2 \nu}{2M_\nu}
\]
\[
\hat{T}_e = \sum_{i=1}^{N_e} -\frac{\nabla^2 i}{2m}
\]
\[
\hat{W}_{nn} = \frac{1}{2} \sum_{\mu, \nu \neq \nu} \frac{Z_\mu Z_\nu}{|R_\mu - R_\nu|}
\]
\[
\hat{W}_{ee} = \frac{1}{2} \sum_{j, k, j \neq k} \frac{1}{|r_j - r_k|}
\]
\[
\hat{V}_{en} = \sum_{j=1}^{N_e} \sum_{\nu=1}^{N_n} -\frac{Z_\nu}{|r_j - R_\nu|}
\]

Time-dependent Schrödinger equation

\[
i \frac{\partial}{\partial t} \psi (\mathbf{r}, \mathbf{R}, t) = \left( \hat{H} (\mathbf{r}, \mathbf{R}) + V_{laser} (\mathbf{r}, \mathbf{R}, t) \right) \psi (\mathbf{r}, \mathbf{R}, t)
\]

\[
V_{laser} (\mathbf{r}, \mathbf{R}, t) = \left( \sum_{j=1}^{N_e} r_j - \sum_{\nu=1}^{N_n} Z_\nu R_\nu \right) \cdot E \cdot f(t) \cdot \cos \omega t
\]
Theorem T-I

The exact solution of

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

can be written in the form

\[ \Psi \left( \frac{r}{\bar{r}}, \frac{R}{\bar{R}}, t \right) = \Phi_{R} \left( \frac{r}{\bar{r}}, t \right) \chi \left( \frac{R}{\bar{R}}, t \right) \]

where \( \int d\bar{r} \left| \Phi_{R} \left( \frac{r}{\bar{r}}, t \right) \right|^2 = 1 \) for any fixed \( \bar{R}, t \).
Theorem T-II

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

Eq. 1

\[
\left( \hat{T}_e + \hat{W}_{ee} + \hat{V}_{en}^{\text{ext}}(r, t) + \hat{V}_{en}(r, R) + \sum_{\nu} \frac{1}{2M_{\nu}} \left( - \imath \nabla_{\nu} - A_{\nu}(R, t) \right)^2 \right) \hat{H}_{BO}(t) \\
+ \sum_{\nu} \frac{1}{M_{\nu}} \left( - \imath \nabla_{\nu} \chi(R, t) \right) \chi(R, t) + A_{\nu}(R, t) \left( - \imath \nabla_{\nu} - A_{\nu} \right) \in \left( R, t \right) \Phi_R(r) = i \partial_t \Phi_R(r, t)
\]

Eq. 2

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

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Theorem T-II

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

**Eq. 1**

\[
\begin{align*}
\left( \hat{T}_e + \hat{W}_{cc} + \hat{V}_e^{\text{ext}}(r, t) + \hat{V}_e(r, R) + \sum_{n} \frac{1}{2M_v} (-i\nabla - A_v(R, t)) \right)^2 \\
\hat{H}_{BO}(t)
\end{align*}
\]

\[ + \sum_{n} \frac{1}{M_v} \left( -i\nabla \frac{\chi(R, t)}{\chi(R, t)} + A_v(R, t) \right) (-i\nabla - A_v) \in (R, t) \Phi_R(r) = i\partial_t \Phi_R(r, t) \]

**Eq. 2**

**Exact TD Berry connection**

\[
\left( \sum_{n} \frac{1}{2M_v} (-i\nabla + A_v(R, t)) \right)^2 + \hat{W}_{nn}(R) + \hat{V}_n^{\text{ext}}(R, t) + \in (R, t) \chi(R, t) = i\partial_t \chi(R, t)
\]


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\[ \epsilon(R, t) = \int dr \Phi_R^*(r, t) \left( H_{BO}(t) + \sum_{v}^{N_n} \frac{1}{2M_v} \left( -i \nabla_v - A_v(R, t) \right)^2 - i \partial_t \right) \Phi_R(r, t) \]

**EXACT time-dependent potential energy surface**

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

**EXACT time-dependent Berry connection**

**N-body version of Runge-Gross theorem guarantees that**
\( \epsilon(R,t) \) and \( A(R,t) \) **are UNIQUE** (up to within a gauge transformation)
How does the exact time-dependent PES look like?

Example: Nuclear WP going through an avoided crossing (Zewail experiment).


$t = 1000$ Exact TDPES
BOPES (ground state)
BOPES (1st excited state)

$t = 1000$ Nuclear Wavepacket on exact TDPES
$t = 1000$ Exact
$t = 4000$ Exact TDPES
BOPES (ground state)
BOPES (1st excited state)

$t = 4000$ Nuclear Wavepacket on exact TDPES
$t = 4000$ Exact
$t = 5000$ Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
$t = 5000$ Nuclear Wavepacket on exact TDPES
$t = 5000$ Exact
t = "9000" Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
t = "9000" Nuclear Wavepacket on exact TDPES
$\begin{array}{l}
\text{Exact TDPES (a.u.)} \\
\text{R (a.u.)}
\end{array}$
$t = "10000"$ Exact TDPES
BOPES (ground state)
BOPES (1st excited state)
$t = "10000"$ Nuclear Wavepacket on exact TDPES
$t = "10000"$ Exact
$t = 17000$ Exact TDPES
BOPES (ground state)
BOPES (1st excited state)

$t = 17000$ Nuclear Wavepacket on exact TDPES
$t = 17000$ Exact
New MD scheme:
Perform classical limit of the nuclear equation, but retain the quantum treatment of the electronic degrees of freedom.
Nuclear wavefunction

\[ \chi(R, t) = e^{\frac{i}{\hbar} S(R,t)} |\chi(R, t)| \]

Classical limit

\[
\begin{cases}
|\chi(R, t)|^2 \rightarrow \delta(R - R_c(t)) \\
\nabla_R S(R, t) \rightarrow P_c(t)
\end{cases}
\]

Hence

\[ -i\hbar \nabla_R \chi \quad \xrightarrow{\hbar \rightarrow 0} \quad P_c(t) \]
Expand the exact electronic wave function in the adiabatic basis:

$$\Phi_R(r, t) = \sum_j c_j(R, t) \varphi_{R,j}^{BO}(r)$$

Insert this in the (exact) electronic equation of motion:

$$\dot{c}_j(R, t) = f_j\left(\{c_k(R, t)\}, \{\nabla_R c_k(R, t)\}, \{\nabla_R^2 c_k(R, t)\}\right)$$

in the classical limit:

$$\nabla_R c_k(R, t), \nabla_R^2 c_k(R, t) \to 0$$

i.e. in this limit the $c_k(R,t)$ become independent of $R$. 
In practice we solve the following equations:

\[
\dot{c}_j(t) = -\frac{i}{\hbar} \left[ \epsilon^{(j)}_{BO} - (V^{(I)}_{\text{eff}} + iV^{(R)}_{\text{eff}}) \right] c_j(t) - \sum_k c_k(t) D_{jk}
\]

\[
V^{(1)}_{\text{eff}} = \sum_j |c_j|^2 \epsilon^{BO}_{R,j} + \frac{P \cdot A}{M} + \frac{\hbar^2}{M} \sum_{j<k} \Re \left[ c_j^* c_k \right] d^{(2)}_{jk}
\]

\[
V^{(R)}_{\text{eff}} = -\frac{\hbar^2}{M} \sum_{j<k} \Im \left[ c_j^* c_k \right] \nabla_R \cdot d^{(1)}_{jk}
\]

\[
D_{jk} = \frac{P}{M} \cdot d^{(1)}_{jk} - \frac{i\hbar}{2M} \left( \nabla_R \cdot d^{(1)}_{jk} - d^{(2)}_{jk} \right)
\]

\[
d^{(1)}_{jk}(R) = \left< \phi^{BO}_{R,j} \left| \nabla_R \phi^{BO}_{R,k} \right> \right.
\]

and classical EoM for the nuclear Hamiltonian:

\[
H_N = \frac{P^2}{2M} + V^{(R)}_{\text{eff}}
\]
Shin-Metiu model
populations of the BO states as functions of time
nuclear kinetic energy as a function of time

kinetic energy (a.u.)

0

0.05

0.1

0 500 1000 1500
time (a.u.)

quantum

MQC
Summary:

- \( \Psi(r, R) = \Phi_R(r) \cdot \chi(R) \) is exact

- Eqs. of motion for \( \Phi_R(r) \) and \( \chi(R) \) lead to
  
  --- exact potential energy surface
  --- exact Berry connection

both in the static and the time-dependent case

- Exact Berry phase may vanish when BO Berry phase \( \neq 0 \)

- TD-PES shows jumps resembling surface hopping

- mixed quantum classical algorithm
Thanks!