Coupled motion of electrons and nuclei beyond the Born-Oppenheimer limit: The exact factorization

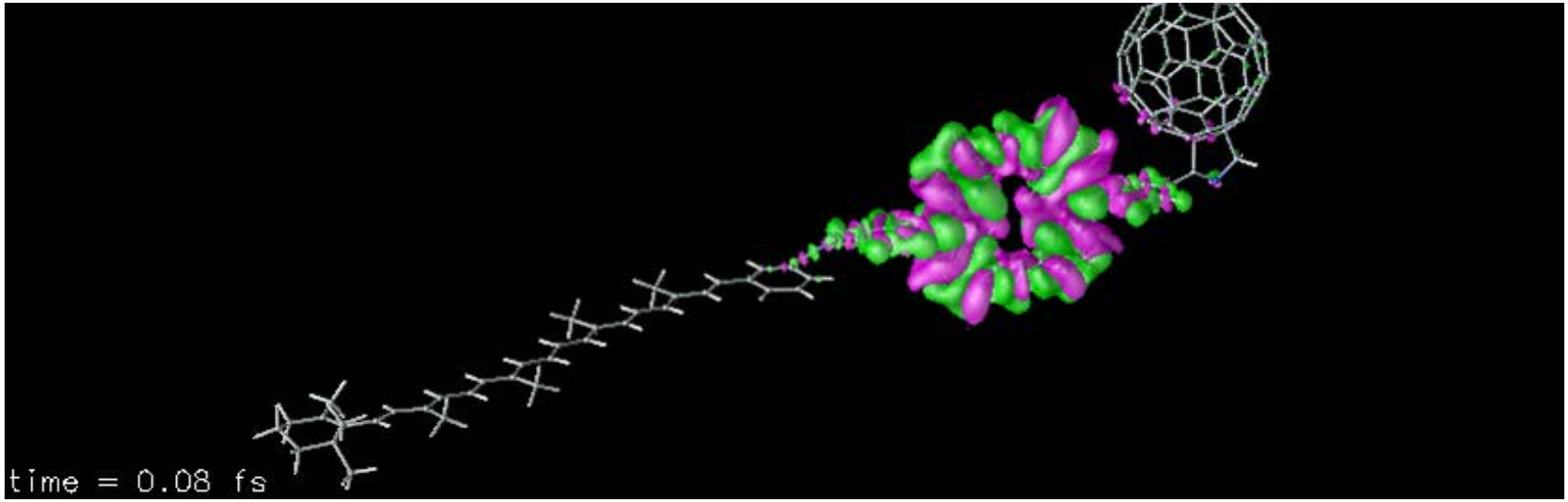
E.K.U. Gross
Fritz Haber Center for Molecular Dynamics

האוניברסיטה העברית בירושלים
THE HEBREW UNIVERSITY OF JERUSALEM

"Triad molecule": Candidate for photovoltaic applications

C.A. Rozzi et al, Nature Communications 4, 1602 (2013)

S.M. Falke et al, Science 344, 1001 (2014)



TDDFT propagation with clamped nuclei

"Triad molecule": Candidate for photovoltaic applications

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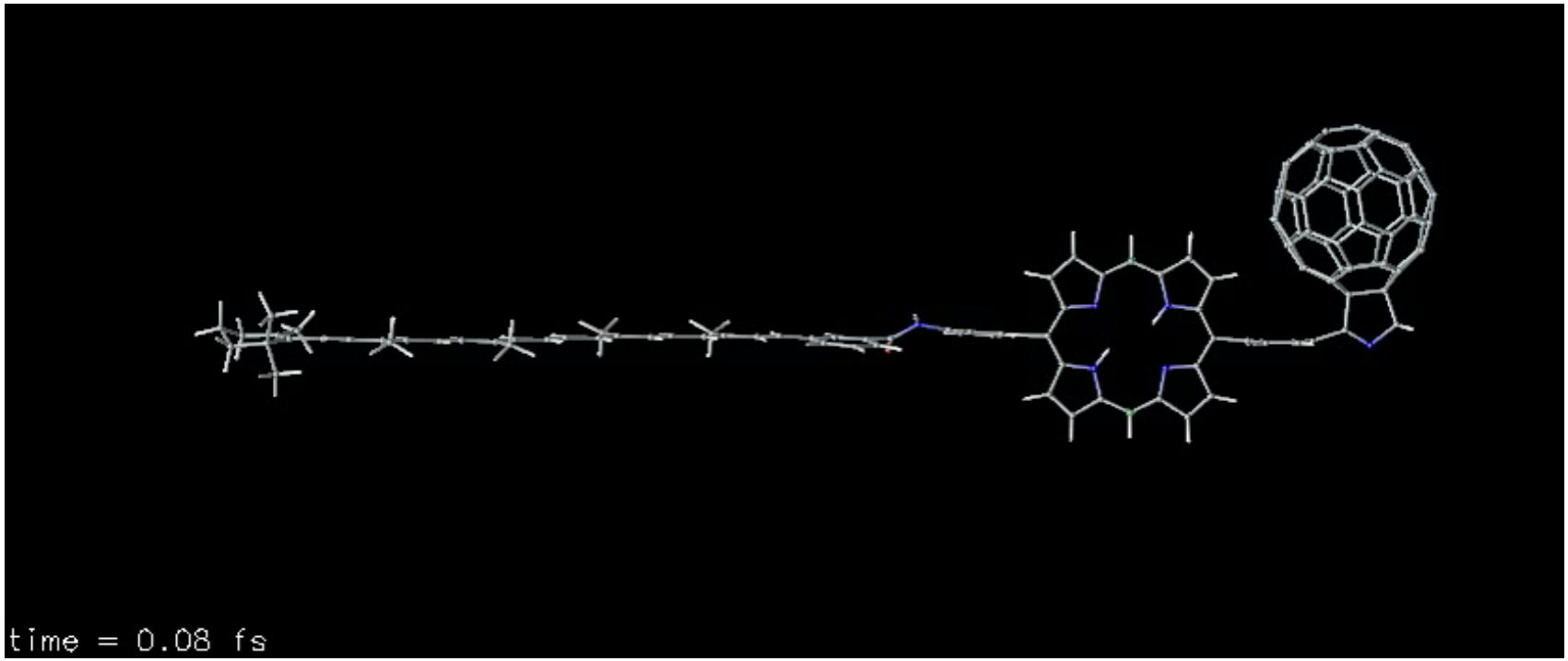


Moving nuclei

Hamiltonian for the complete system of N_e electrons with coordinates $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\underline{\mathbf{r}}}$ and N_n nuclei with coordinates $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{\underline{\mathbf{R}}}}$

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

with

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

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

Stationary Schrödinger equation

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

Hamiltonian for the complete system of N_e electrons with coordinates $(\mathbf{r}_1 \cdots \mathbf{r}_{N_e}) \equiv \underline{\underline{r}}$ and N_n nuclei with coordinates $(\mathbf{R}_1 \cdots \mathbf{R}_{N_n}) \equiv \underline{\underline{R}}$

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

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

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

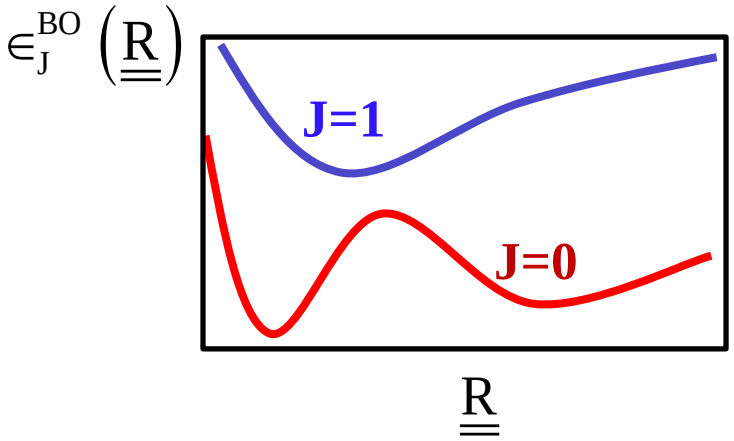
$$V_{laser}(\underline{r}, \underline{\underline{R}}, t) = \left(\sum_{j=1}^{N_e} r_j - \sum_{\nu=1}^{N_n} Z_\nu R_\nu\right) \cdot E \cdot f(t) \cdot \cos\omega t$$

Born-Oppenheimer approximation

solve

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

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



Born-Huang expansion of the full electron-nuclear wave function

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

$$\Psi\left(\underline{\underline{r}},\underline{\underline{R}},t\right)=\sum_{J}\Phi^{BO}_{\underline{\underline{R}},J}\left(\underline{\underline{r}}\right)\cdot\chi_{J}\left(\underline{\underline{R}},t\right)$$

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

Plug Born-Huang expansion in full TDSE:

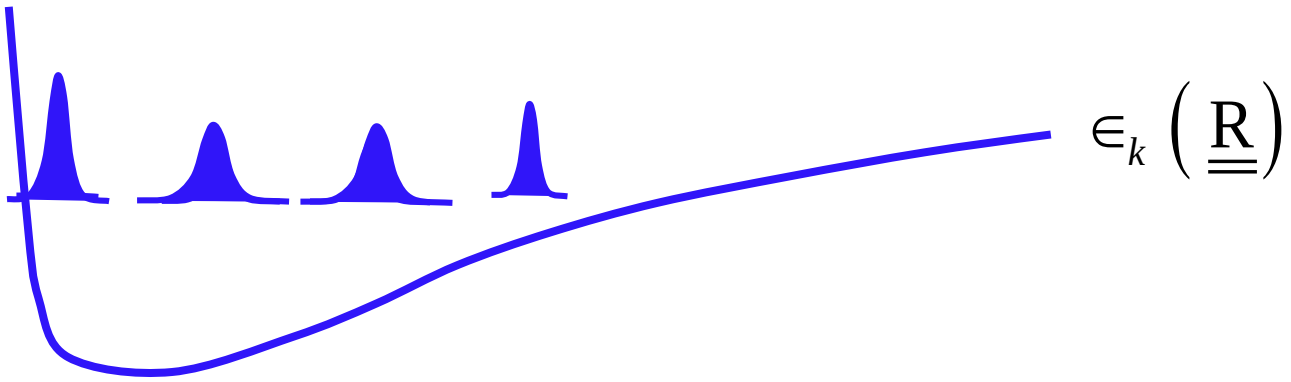
$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \in_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$

$$+\sum_{j\alpha}\left(\frac{\hbar^2}{M_\alpha}\right)\underbrace{\left\langle \phi^{BO}_{\underline{\underline{R}},k}\left|-i\nabla_{\underline{\underline{R}}_\alpha}\right|\phi^{BO}_{\underline{\underline{R}},j}\right\rangle}_{\text{NAC-1}}\left(-i\nabla_{\underline{\underline{R}}_\alpha}\chi_j\left(\underline{\underline{R}},t\right)\right)$$

$$+\sum_{j\alpha}\left(-\frac{\hbar^2}{2M_\alpha}\right)\underbrace{\left\langle \phi^{BO}_{\underline{\underline{R}},k}\left|\nabla^2_{\underline{\underline{R}}_\alpha}\right|\phi^{BO}_{\underline{\underline{R}},j}\right\rangle}_{\text{NAC-2}}\chi_j\left(\underline{\underline{R}},t\right)$$

Plug Born-Huang expansion in full TDSE:

$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \in_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$

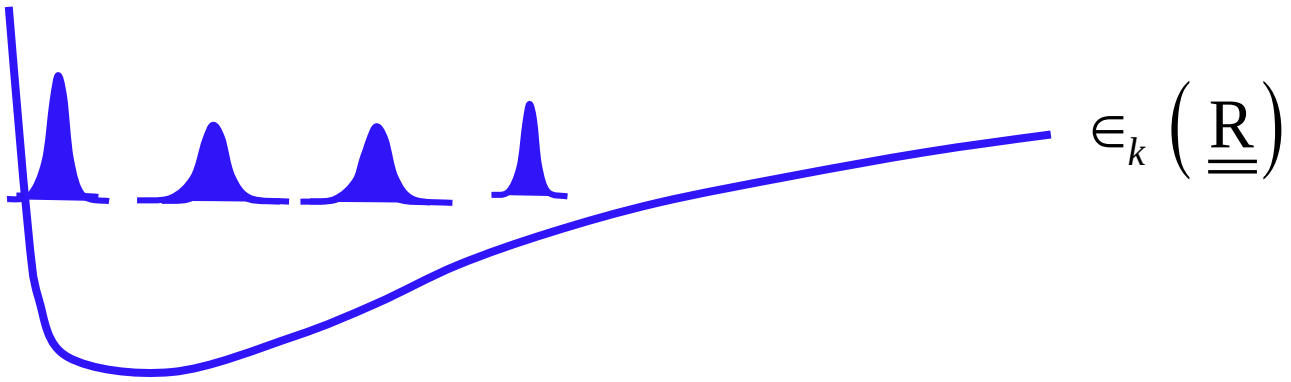


$$\Psi^{adiab}\left(\mathbf{R},\mathbf{r},t\right) \approx \chi_k\left(\mathbf{R},t\right)\Phi_k^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)$$

Adiabatic approximation

Plug Born-Huang expansion in full TDSE:

$$i\partial_t \chi_k\left(\underline{\underline{R}},t\right) = T_n \chi_k\left(\underline{\underline{R}},t\right) + \in_k\left(\underline{\underline{R}}\right)\chi_k\left(\underline{\underline{R}},t\right)$$

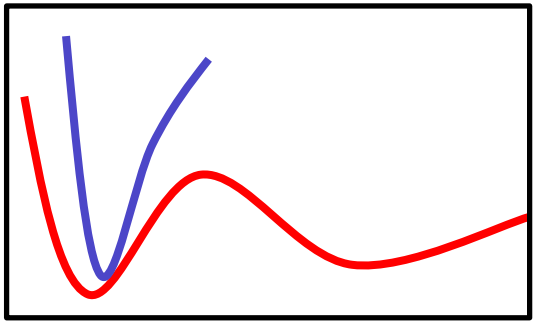


$$\Psi^{adiab}\left(\mathbf{R},\mathbf{r},t\right) \approx \chi_k\left(\mathbf{R},t\right)\Phi_k^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)$$ **Adiabatic approximation**

In calculations of vibrational spectra one usually makes two approximations:

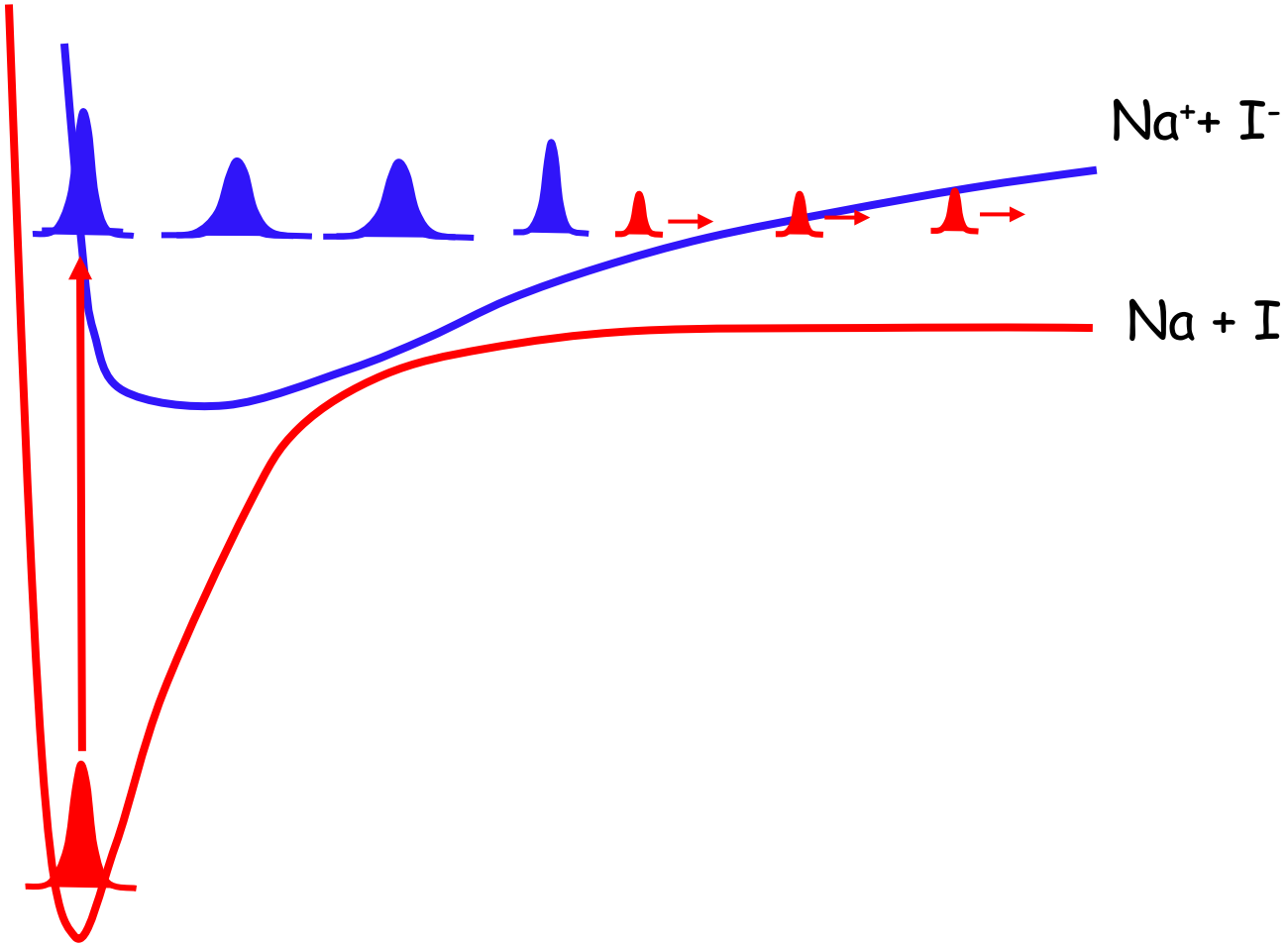
- **Adiabatic approximation**
- **Harmonic approximation**

Vibrational spectra are usually very well described within the adiabatic approach, but not always! (Hammes-Schiffer)



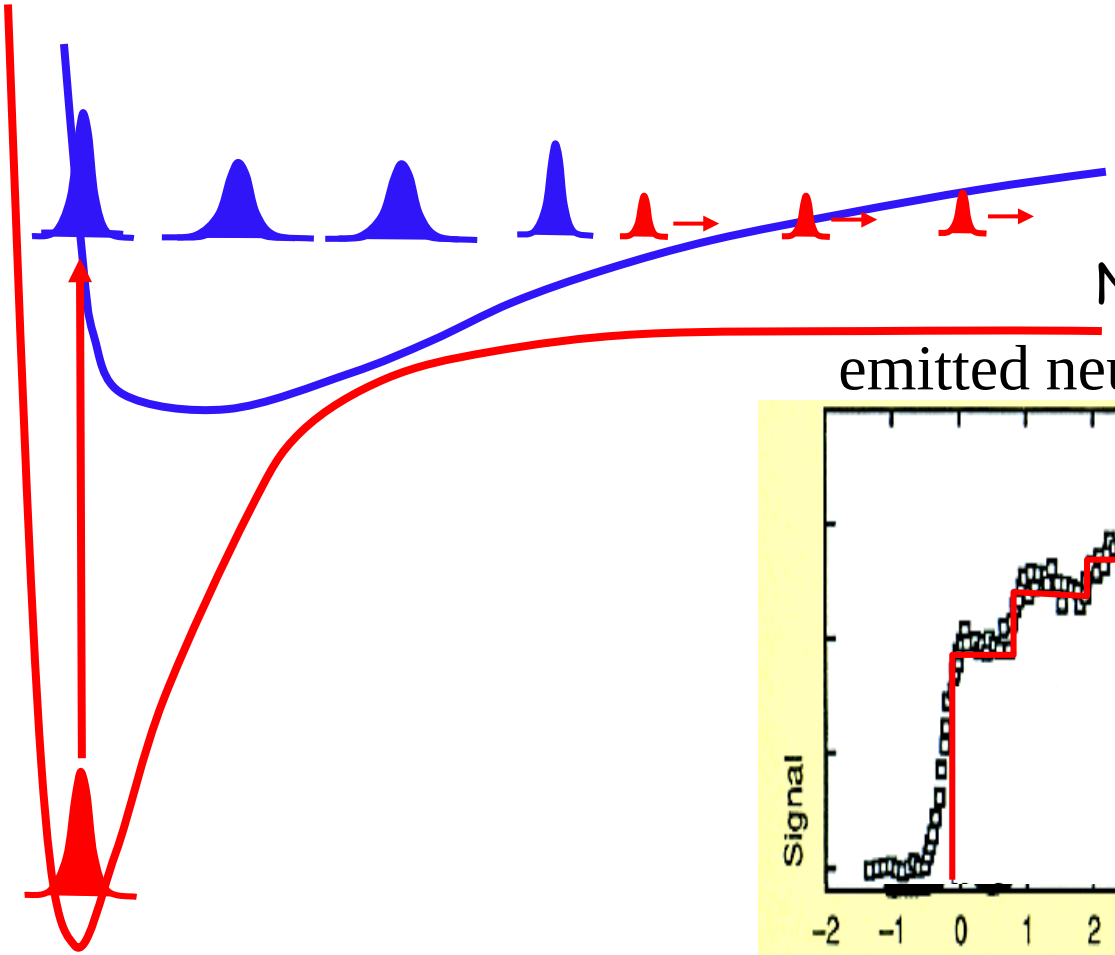
Dramatic failures of the adiabatic approximation:

- **Zewail experiments**
- **Calculation of electronic currents associated with nuclear motion**

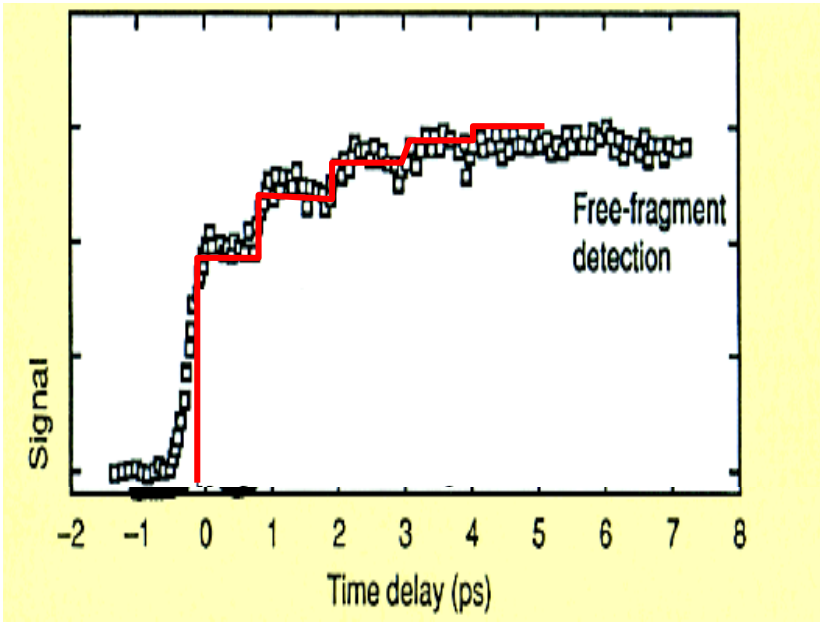


$$\Psi_0\left(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}},t\right) \approx \chi_{00}\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{0,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right) + \chi_{01}\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{1,\underline{\underline{\mathbf{R}}}}\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

When only few BO-PES are important, the BO expansion gives a perfectly clear picture of the dynamics



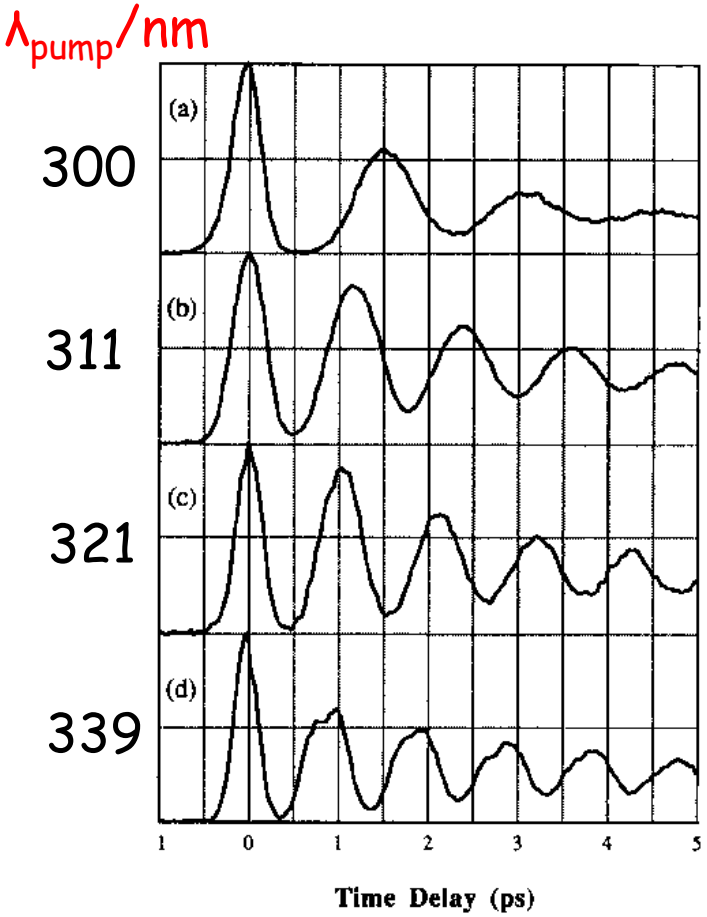
emitted neutral Na atoms

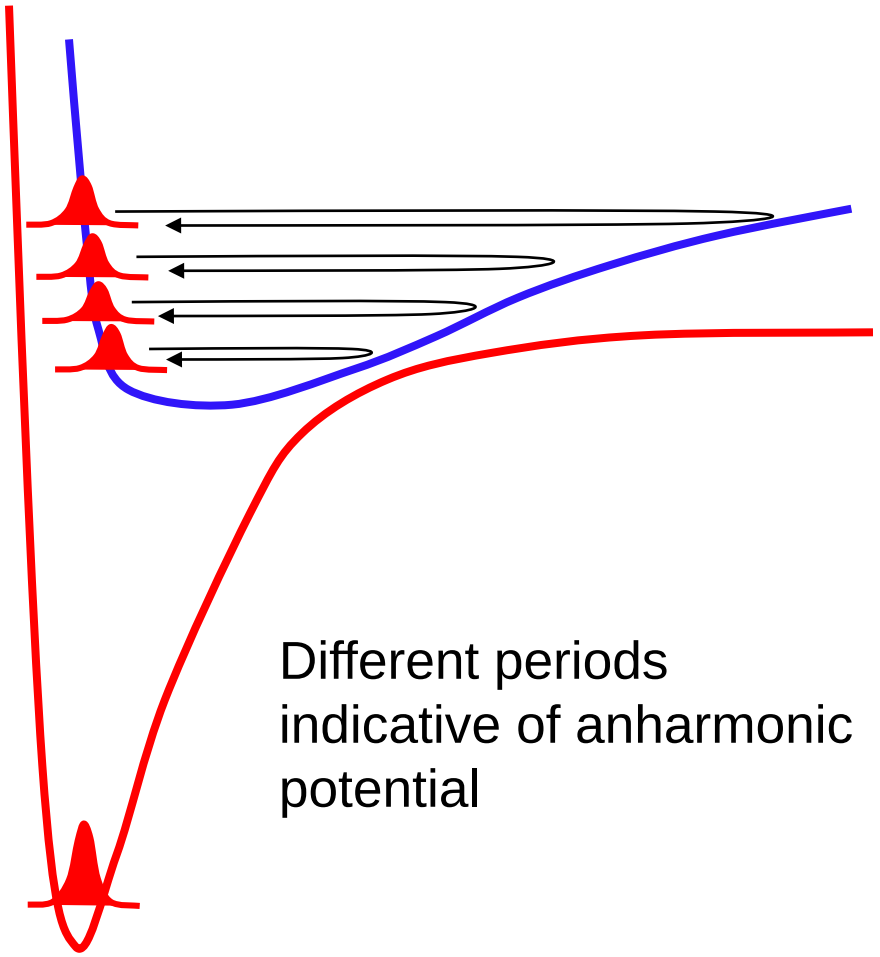


$$\Psi_0\left(\underline{\underline{\mathbf{r}}},\underline{\underline{\mathbf{R}}},t\right) \approx \chi_{00}\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{0,\underline{\underline{\mathbf{R}}}}\left(\underline{\underline{\mathbf{r}}}\right) + \chi_{01}\left(\underline{\underline{\mathbf{R}}},t\right)\Phi^{BO}_{1,\underline{\underline{\mathbf{R}}}}\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

When only few BO-PES are important, the BO expansion gives a perfectly clear picture of the dynamics

Effect of tuning pump wavelength (exciting to different points on excited surface)





Different periods indicative of anharmonic potential

T.S. Rose, M.J. Rosker, A. Zewail, JCP **91**, 7415 (1989)

Most dramatic failure of the adiabatic approximation: Calculation of electronic flux density associated with nuclear motion

Adiabatic approximation (dynamics on a single BO-PES)

$$\Psi\left(\mathbf{R},\mathbf{r},t\right)\approx\chi^{BO}\left(\mathbf{R},t\right)\Phi^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)$$

with non-degenerate, real-valued BO state $\Phi^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)$

Time-dependent electronic (N-body, or one-body) density:

$$\rho^{BO}\left(\mathbf{r},t\right)=\int\left|\chi^{BO}\left(\mathbf{R},t\right)\right|^{2}\left|\Phi^{BO}\left(\mathbf{r}\middle|\mathbf{R}\right)\right|^{2}d\mathbf{R}$$

very close to true TD density

$$\mathbf{j}^{BO}\left(\mathbf{r},t\right)=\int\mathrm{Im}\left(\Psi^{*}\partial_{\mathbf{r}}\Psi\right)d\mathbf{R}=\int\left|\chi^{BO}\left(\mathbf{R},t\right)\right|^{2}\mathrm{Im}\left(\Phi^{BO*}\partial_{\mathbf{r}}\Phi^{BO}\right)d\mathbf{R}=0$$

completely wrong!! Dramatic failure of adiabatic approximation

Problem: Born-Huang expansion not feasible for larger molecules and solids

The exact factorisation

The exact factorisation

"Exactification" $\Psi^{\text{exact}}\left(\underline{\underline{r}},\underline{\underline{R}},t\right)=\Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}},t\right)\cdot\chi\left(\underline{\underline{R}},t\right)$

of the adiabatic approximation

$$\Psi^{\text{adiab}}\left(\underline{\underline{r}},\underline{\underline{R}},t\right)=\Phi^{\text{BO}}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)\cdot\chi\left(\underline{\underline{R}},t\right)$$

Outline

- **Show that the factorisation**

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

  is an exact representation of the electron-nuclear wave function

- **Concept of exact geometric phase**

- **Concept of exact and unique time-dependent PES and the exact classical force on the nuclei**

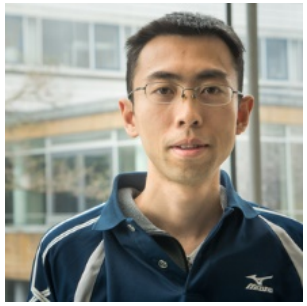
- **Nuclear-velocity perturbation theory**
  -- electronic currents associated with nuclear motion
  -- vibrational circular dichroism

THANKS!

Axel Schild

Ali Abedi

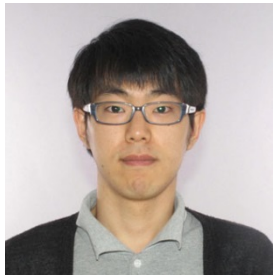
Federica Agostini



Chen Li

Basile Curchod

Ivano Tavernelli



Seung Kyu Min

Neepa Maitra

Rodolphe Vuilleumier

Ryan Requist

Nikitas Gidopoulos

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** $\underline{\underline{R}}$**.**

The factors χ and Φ are unique (up to within an R-dependent gauge transformation).

N.I. Gidopoulos, E.K.U. Gross, Phil. Trans. R. Soc. 372, 20130059 (2014)

Proof of Theorem I:

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

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

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

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

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

Note: If we want χ(R) to be smooth, S(R) may be discontinuous

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

Eq. ❶

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

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

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

N.I. Gidopoulos, E.K.U. Gross, Phil. Trans. R. Soc. 372, 20130059 (2014)

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

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

Exact PES

where

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

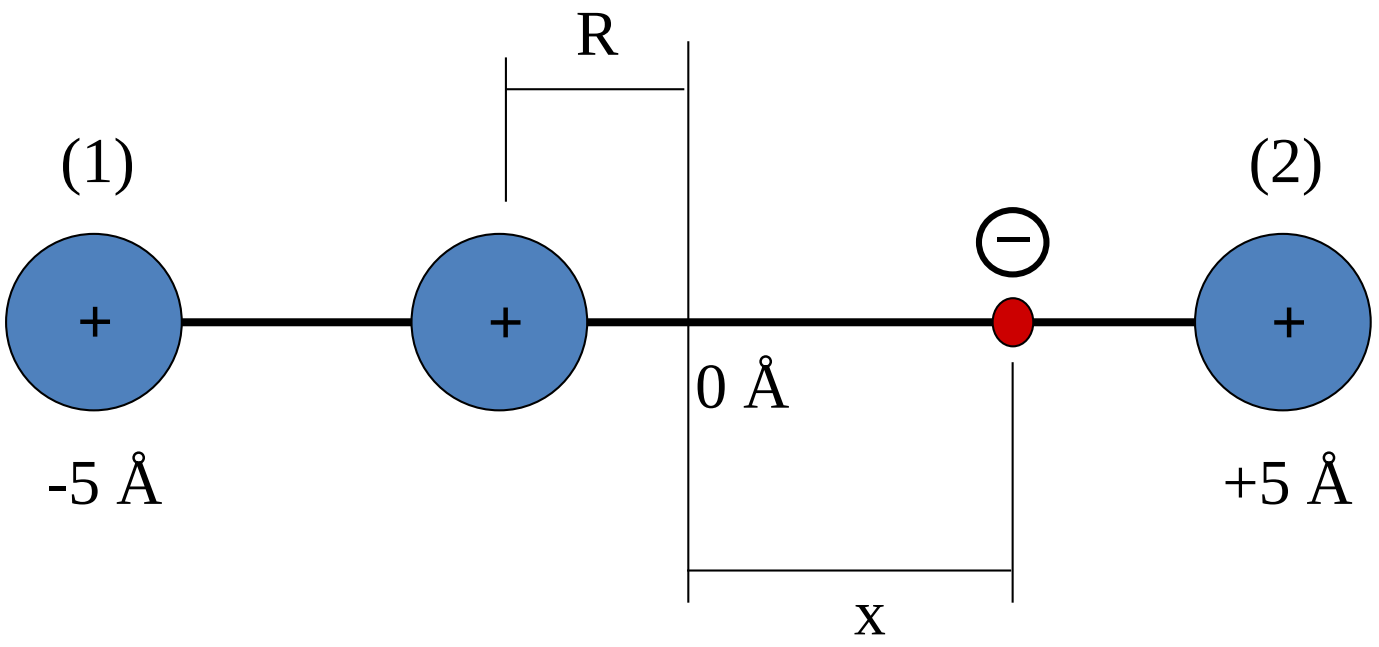
Exact Berry connection

N.I. Gidopoulos, E.K.U. Gross, Phil. Trans. R. Soc. 372, 20130059 (2014)

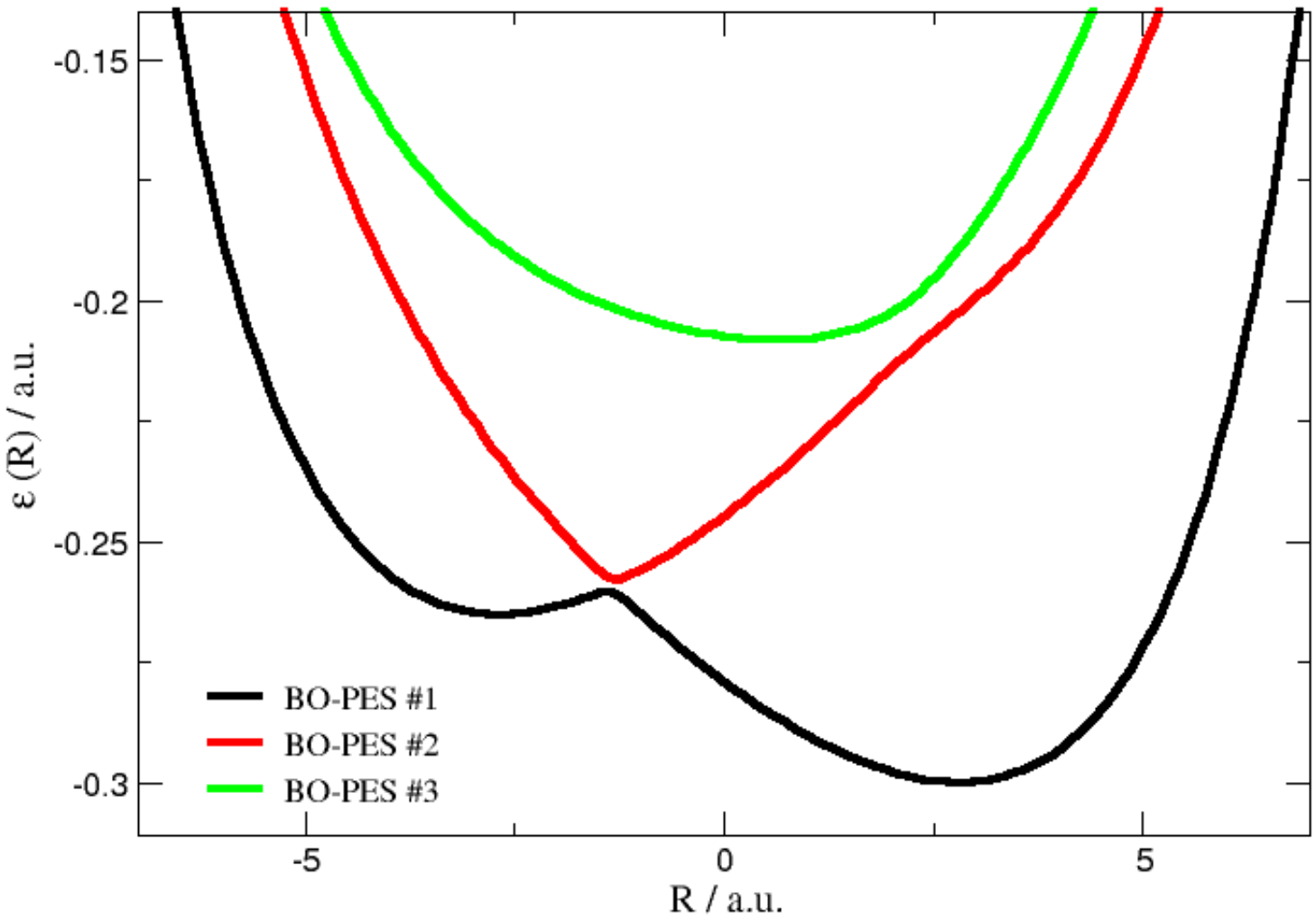
How do the exact PES look like?

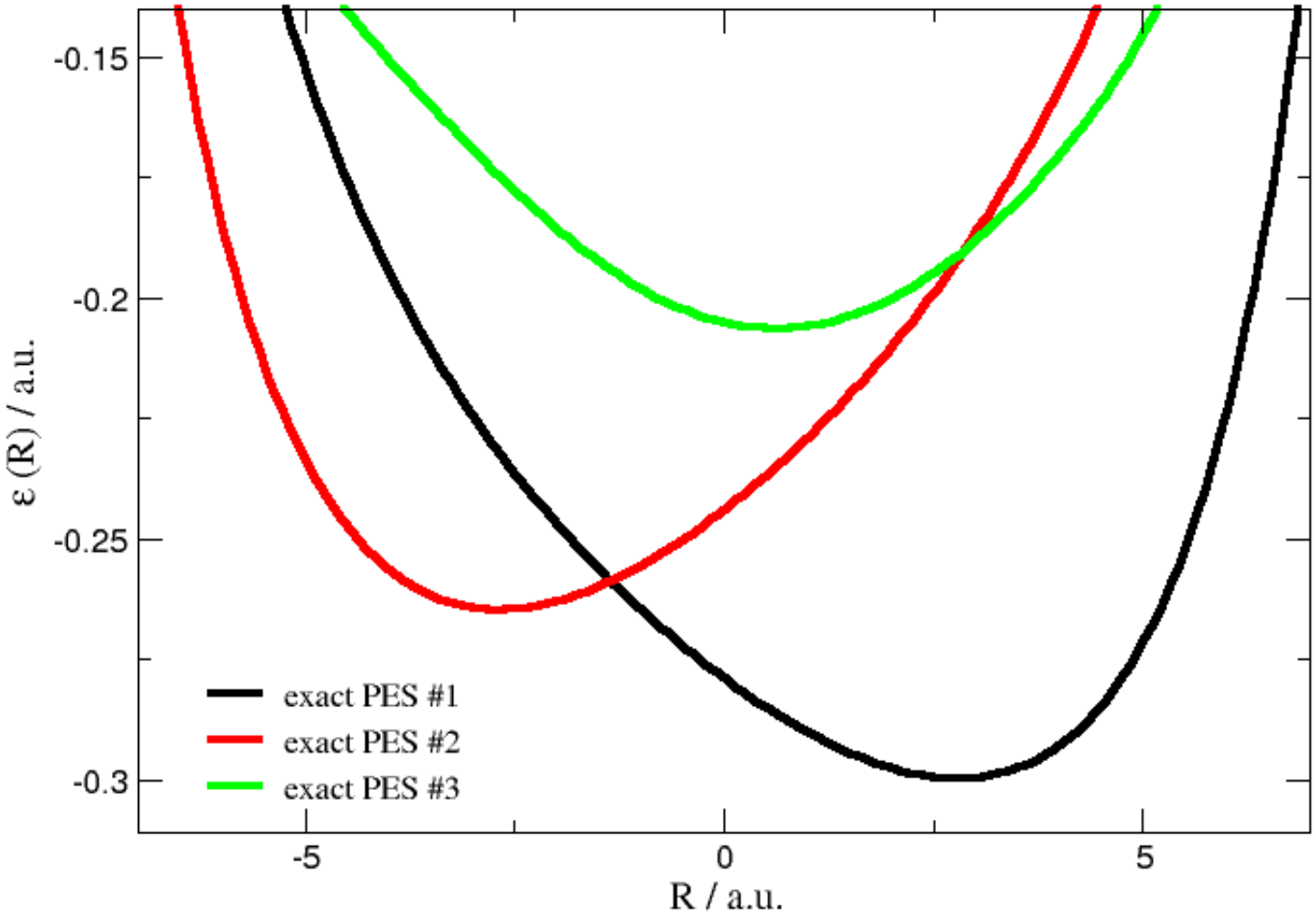
MODEL

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

Exact Berry connection

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

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

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

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

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

with the exact nuclear current density J_ν

Another way of reading this equation:

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

Conclusion: The nuclear Schrödinger equation

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

yields both the exact nuclear N-body density and the exact nucler N-body current density

A. Abedi, N.T. Maitra, E.K.U. Gross, JCP 137, 22A530 (2012)

The exact vector potential defines an "exact geometric phase"

$$\gamma^{\text{exact}} = \oint \vec{\mathbf{A}}^{\text{exact}}\left(\underline{\underline{\mathbf{R}}}\right)\cdot d\vec{\mathbf{R}}$$

<u>Question</u>: How does this exact geometric phase compare to the usual Born-Oppenheimer (Longuet-Higgins) phase

$$\gamma^{\text{BO}} = \oint \vec{\mathbf{A}}^{\text{BO}}\left(\underline{\underline{\mathbf{R}}}\right)\cdot d\vec{\mathbf{R}}$$

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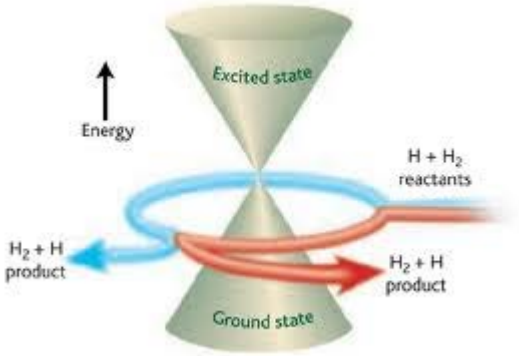
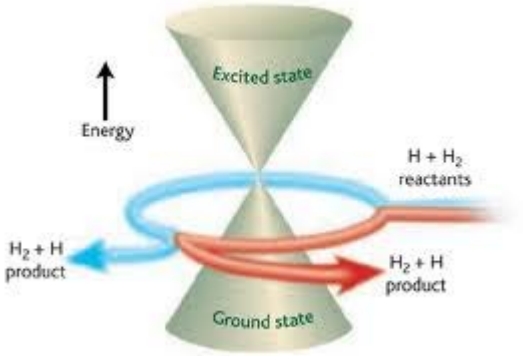


The exact vector potential defines an "exact geometric phase"

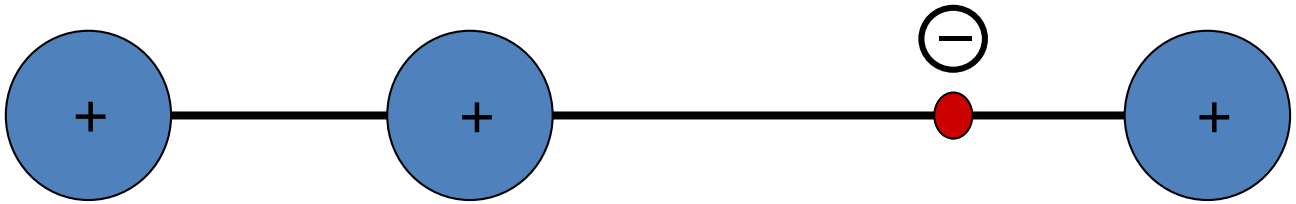
$$\gamma^{\text{exact}} = \oint \vec{\mathbf{A}}^{\text{exact}}\left(\underline{\underline{\mathbf{R}}}\right)\cdot d\vec{\mathbf{R}}$$

<u>Question</u>: How does this exact geometric phase compare to the usual Born-Oppenheimer (Longuet-Higgins) phase

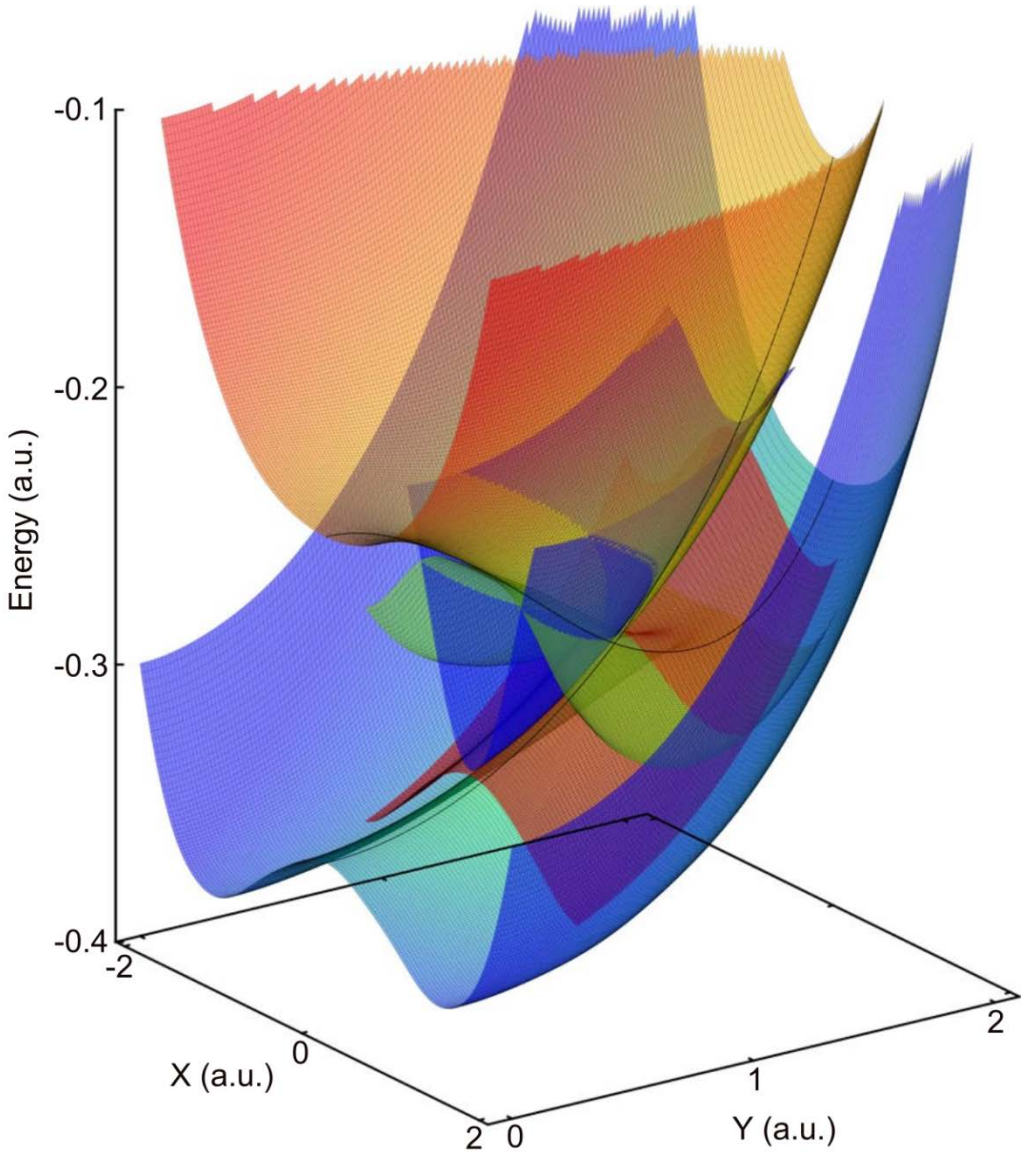
$$\gamma^{\text{BO}} = \oint \vec{\mathbf{A}}^{\text{BO}}\left(\underline{\underline{\mathbf{R}}}\right)\cdot d\vec{\mathbf{R}}$$



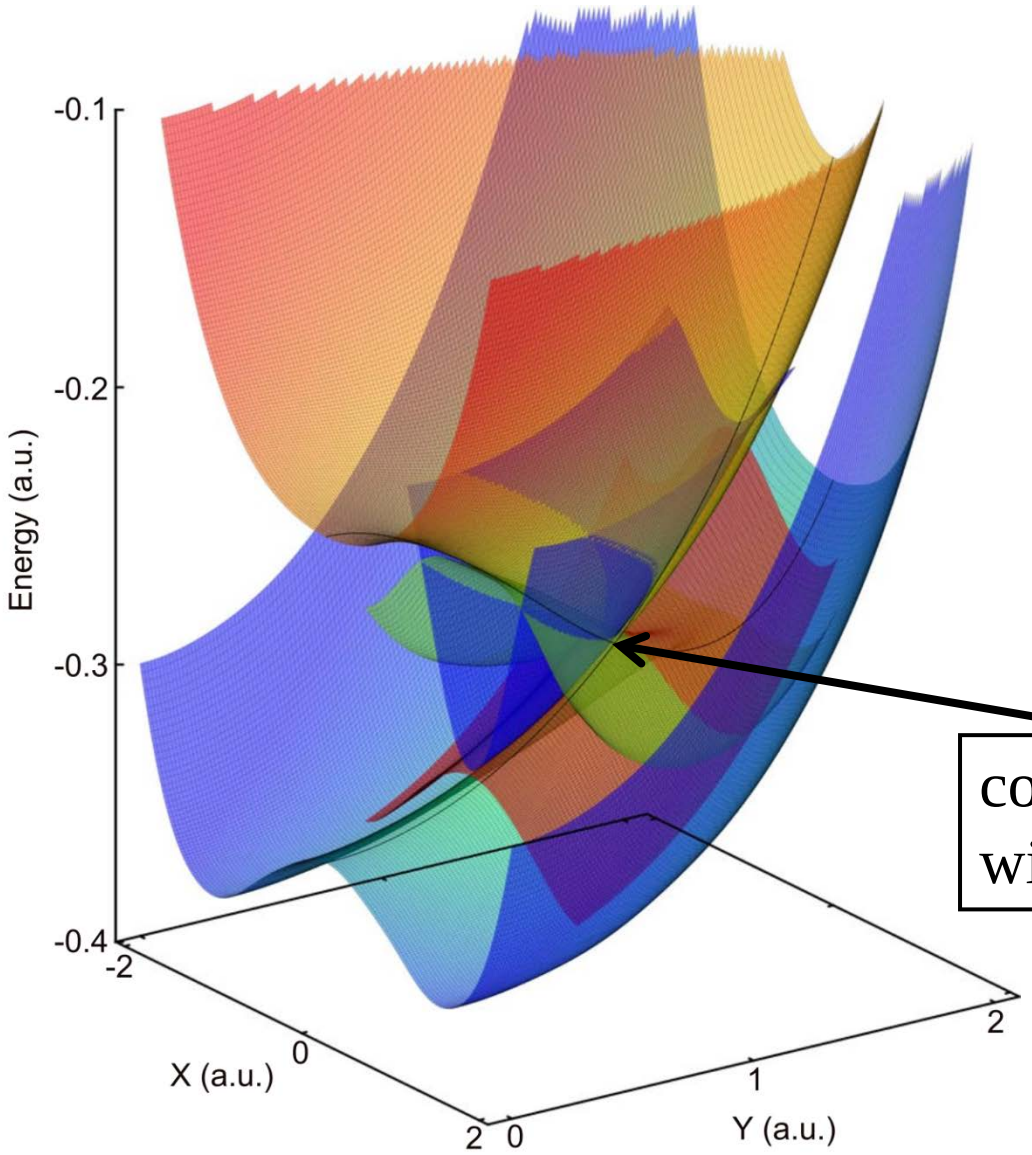
<u>Look at Shin-Metiu model in 2D:</u>



BO-PES of 2D Shin-Metiu model



BO-PES of 2D Shin-Metiu model



conical intersection with Berry phase π

In this system, the geometric phase associated with the exact vector potential is zero!!
(although there is a proper geometric phase of π in BO)

In this system, the geometric phase associated with the exact vector potential is zero!!
(although there is a proper geometric phase of π in BO)

How can this be true,
in view of BO being the M→ϖ limit of the exact treatment?

- Non-vanishing geometric phase results from a non-analyticity in the electronic wave function $\Phi^{BO}_{\underline{\underline{R}}}\left(\underline{\underline{r}}\right)$ as function of R.

- Such non-analyticity is found in BO approximation.

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- Such non-analyticity is found in BO approximation.

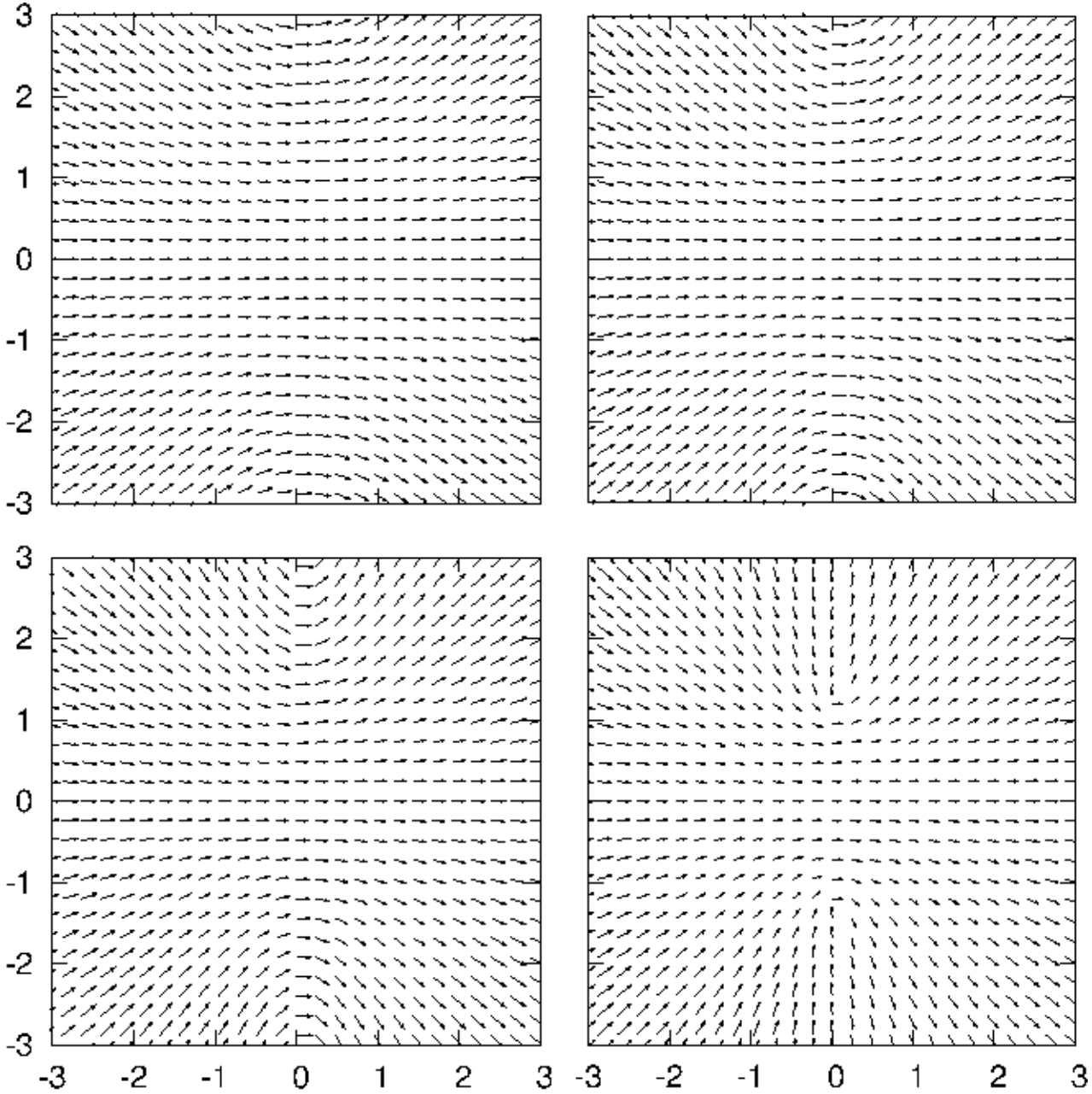
Does the exact electronic wave function show such non-analyticity as well (in 2D Shin-Metiu model)?

Look at $$D(\mathbf{R}) = \int \mathbf{r}\,\Phi_{\mathbf{R}}(\mathbf{r})\,d\mathbf{r}$$

as function of nuclear mass M.

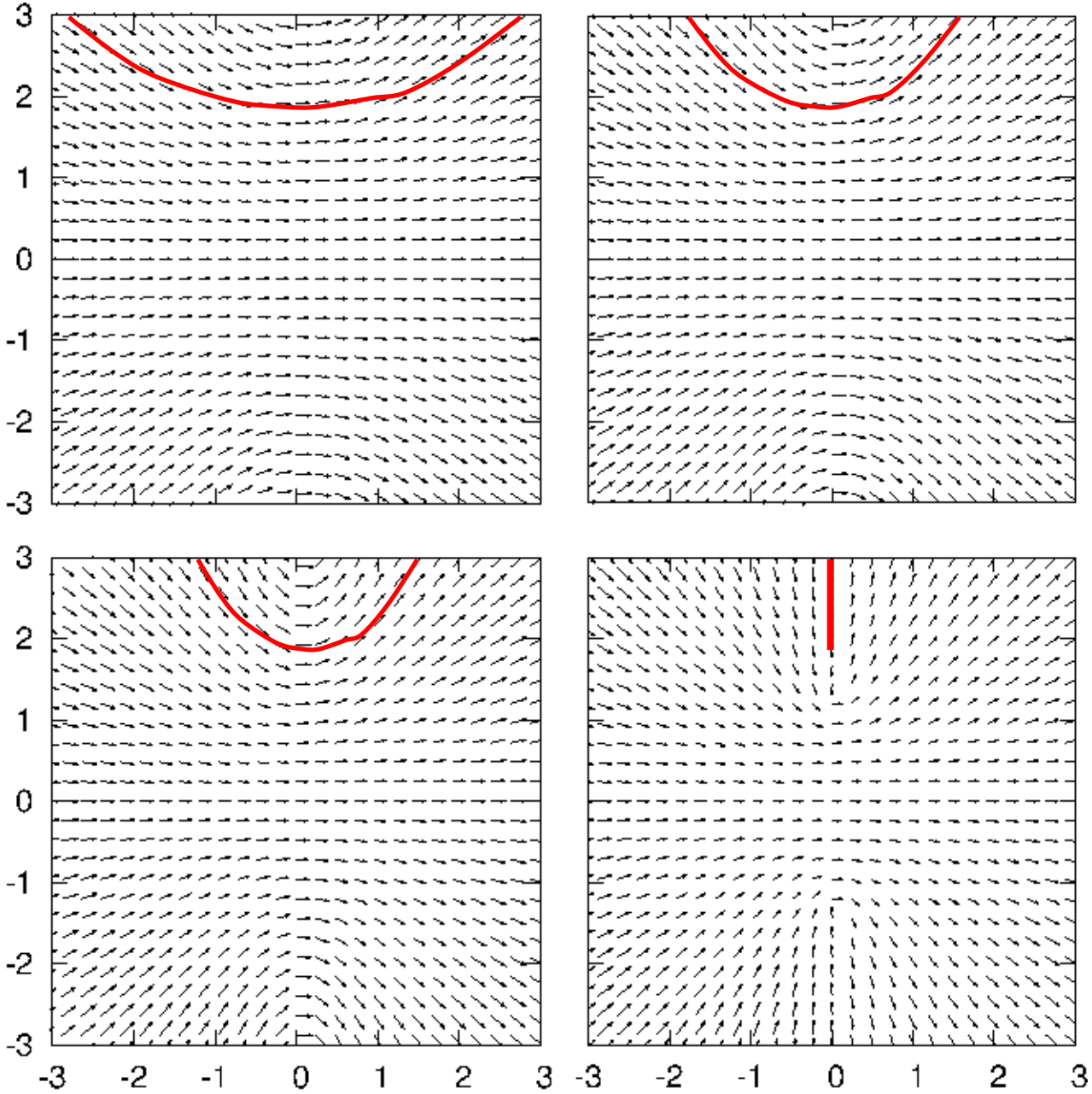
S.K. Min, A. Abedi, K.S. Kim, E.K.U. Gross, PRL 113, 263004 (2014)

D(R)



M = ∞

D(R)



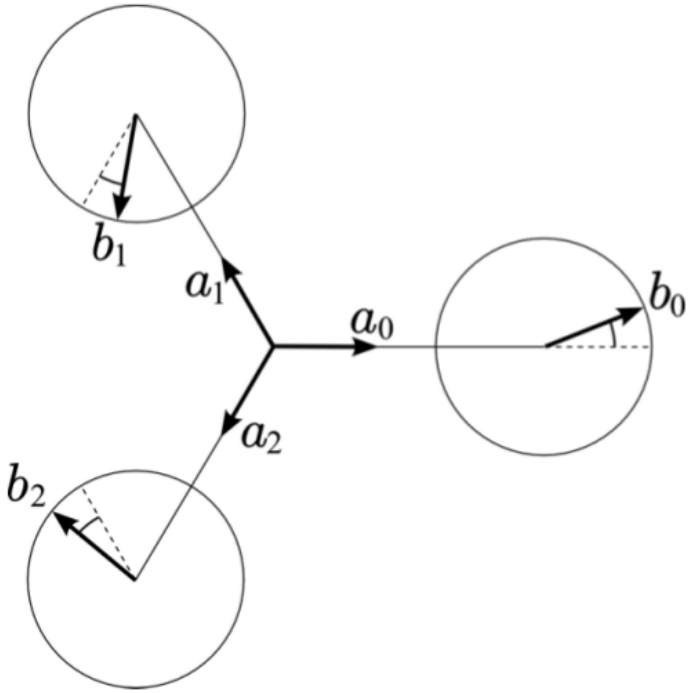
M = ∞

Question: Can one prove in general that the exact molecular geometric phase vanishes?

Question: Can one prove in general that the exact molecular geometric phase vanishes?

Answer: No! There are cases where a nontrivial Berry phase appears in the exact treatment.

R. Requist, F. Tandetzky, EKU Gross, Phys. Rev. A 93, 042108 (2016).



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

<u>Note</u>: When the vector potential cannot be gauged away, this can have two distinct reasons.

<u>Either</u>

- **The curl of nuclear velocity field does not vanish**

<u>Or</u>

- **The phase θ(R) has a discontinuity/non-analyticity**

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- **The phase θ(R) has a discontinuity/non-analyticity**
  → <u>topological</u> phase with quantized value nπ

Time-dependent case

Theorem T-I

The exact solution of

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

can be written in the form

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

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

A. Abedi, N.T. Maitra, E.K.U.G., PRL 105, 123002 (2010)
JCP 137, 22A530 (2012)

Theorem T-II

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

Eq. ❶

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

Eq. ❷

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

A. Abedi, N.T. Maitra, E.K.U.G., PRL 105, 123002 (2010)
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Exact TD vector potential

Exact TDPES

Eq. ❷

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

A. Abedi, N.T. Maitra, E.K.U.G., PRL 105, 123002 (2010)

JCP 137, 22A530 (2012)

Theorem T-III

The nuclear equation of motion yields the true nuclear N-body density and the true nuclear N-body current density that one would also obtain from the full electron-nuclear wave function Ψ.

Note: Theorem T-III similar to TDKS theorem!!

Consequence:

The gradient of the TDPES appearing in this Schrödinger equation is the only correct classical force on the nuclei, unique up to within an R-dependent gauge transformation.

Properties of the exact electronic EoM:

- Non-linear equation in $\phi_R(r)$ because of $A[\phi]$
- Non-adiabatic terms are not operators in the electronic Hilbert space
- in BO-basis: non-Hermitian matrix, still the time-propagation conserves norm
- Electronic EoM depends on $\chi(R)$

Properties of the exact nuclear EoM:

- Standard TDSE
- Scalar potential is time-dependent N_n-body interaction
- Vector potential is N_n-body operator, i.e. 3D vector field depending on $\left(\vec{R}_1 \ldots \vec{R}_{N_n}\right)$

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On the exact level, the two EoMs are equivalent to the full TDSE

Crucial advantage:

Nuclei and electrons satisfy separate equations

$\Longrightarrow$ **Useful starting point to make approximations**

Use electronic EoM of exact factorization and treat the non-adiabatic terms in 1st-order perturbation theory

$$\left(\underbrace{\hat{T}_e + \hat{W}_{ee} + \hat{V}_{en}\left(\underline{\underline{r}}, \underline{\underline{R}}\right)}_{H_{BO}} + \sum_{\nu}^{N_n} \frac{1}{2M_\nu}\left(-i\nabla_\nu - A_\nu\left(\underline{\underline{R}}, t\right)\right)^2\right.$$

$$\left. + \sum_{\nu}^{N_n} \frac{1}{M_\nu}\left(\frac{-i\nabla_\nu \chi\left(\underline{\underline{R}}, t\right)}{\chi\left(\underline{\underline{R}}, t\right)} + A_\nu\left(\underline{\underline{R}}, t\right)\right)\left(-i\nabla_\nu - A_\nu\right)\right) \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right) = i\partial_t \Phi_{\underline{\underline{R}}}\left(\underline{\underline{r}}, t\right)$$

Allows the calculation of electronic flux densities very efficiently

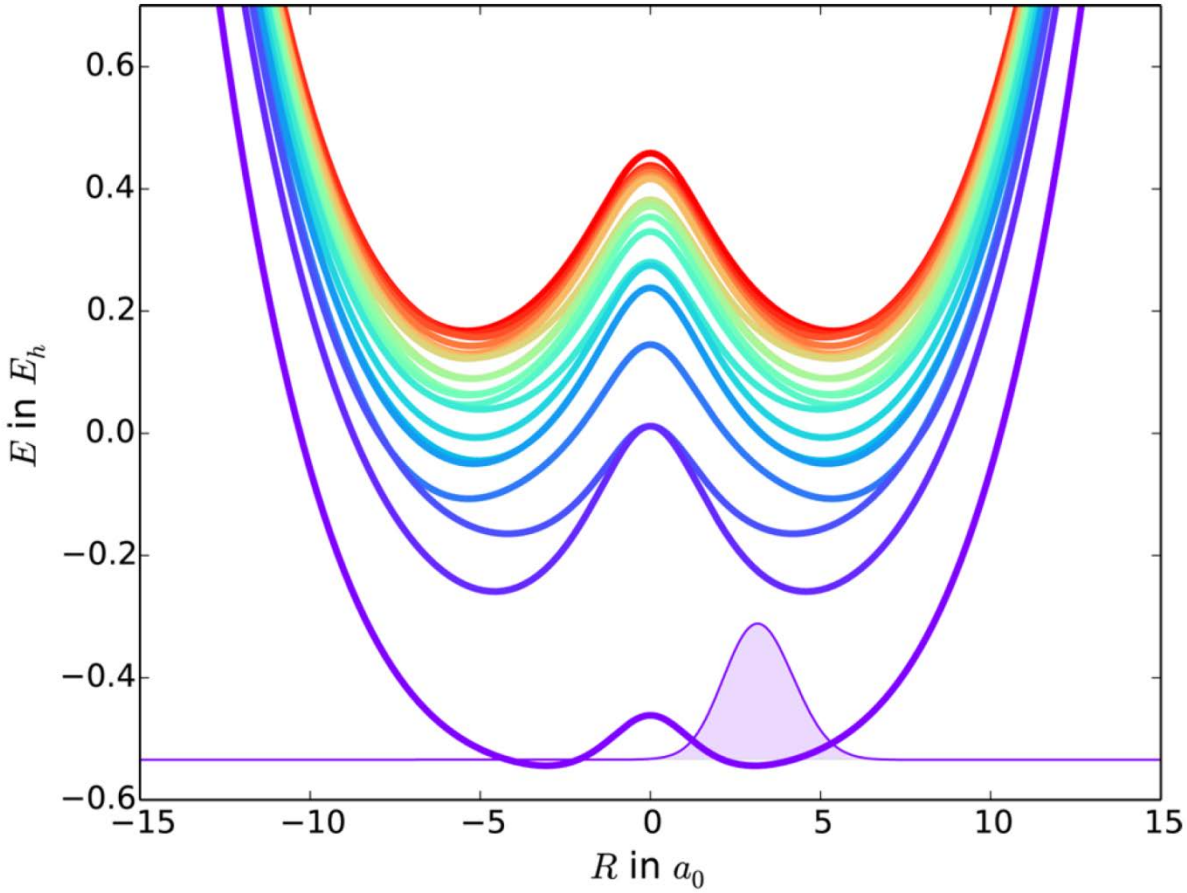
A. Schild, F. Agostini, EKUG., J. Phys. Chem. A 120, 3316 (2016)

A. Scherrer, F Agostini, D. Sebastiani, EKUG., R. Vuilleumier, JCP 143, 074106 (2015) , and PRX 7, 031035 (2017).

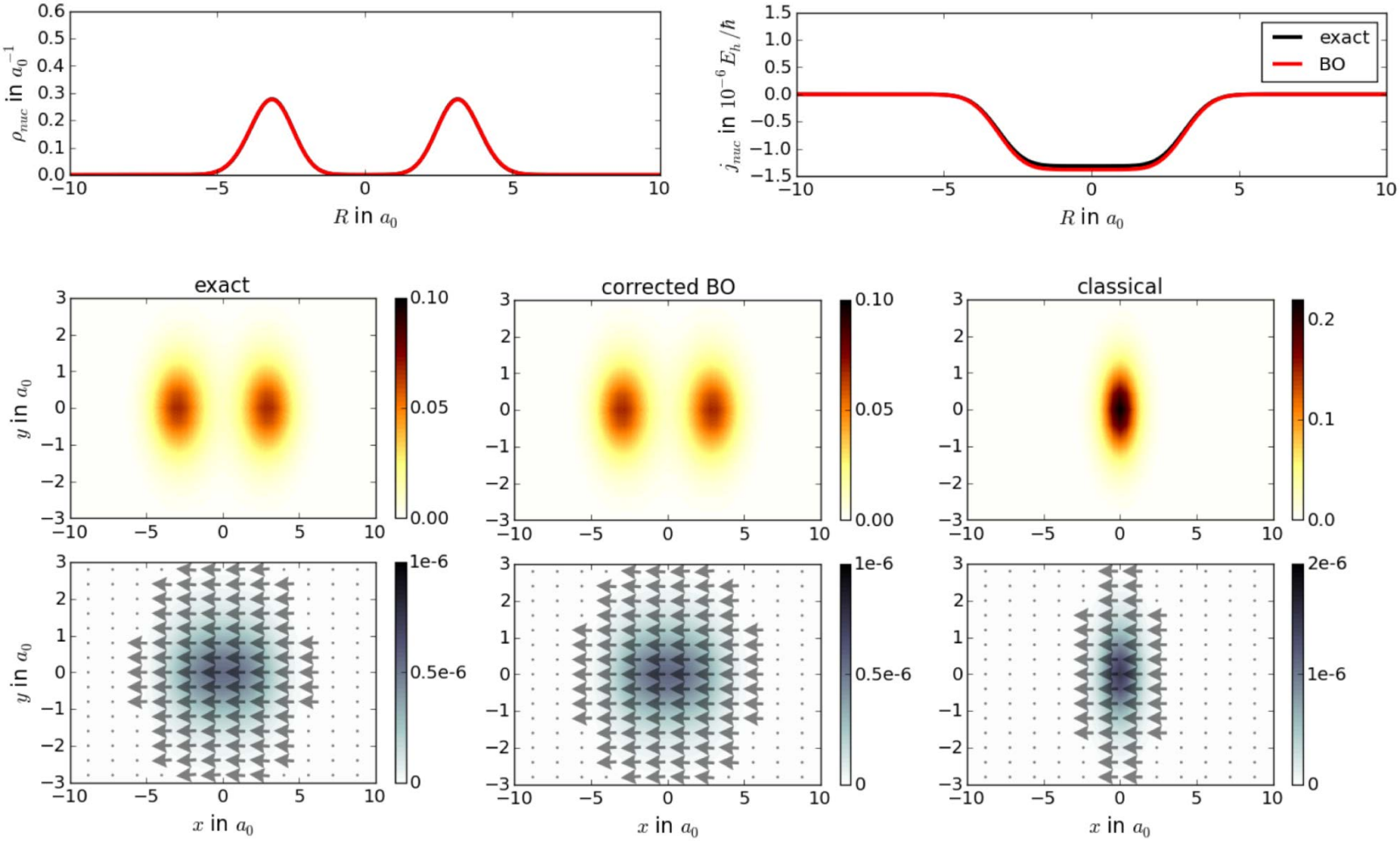
Model Study:

One electron in 2D (x,y), one nucleus in 1D (R), and another very heavy nucleus clamped at the origin, all interacting with soft Coulomb potentials

$$V = -\frac{1}{\sqrt{x^2 + y^2 + \alpha_2}} + \left(\frac{R}{R_0}\right)^4 + \frac{1}{\sqrt{R^2 + \beta}} - \frac{1}{\sqrt{(R - x)^2 + y^2 + \alpha_1}}$$



Lowest 20 Born−Oppenheimer potential energy surfaces and initial BO wave function.



Top: nuclear density (left) and flux density (right) for the exact nuclear wave function χ and for the Born−Oppenheimer (BO) nuclear wave function χ^{BO}, after one-quarter of the tunneling time, for a nucleus with mass 50 m_e. Below: electron density (top) and flux density (below, with contours indicating the magnitude and arrows indicating the direction, for points where the flux is more than 1% of its maximum value) at that time for the exact wave function (left), for the BO electronic wave function corrected by nuclear velocity perturbation theory (NVPT, center), and for the NVPT electronic wave function at the expectation value of nuclear position and momentum (right).

Vibrational circular dichroism

Absorption difference between lefthanded and righthanded circularly polarized light:

$$\Delta \in (\omega) = 4 \frac{8\pi^3}{3Vhcn(\omega)} \sum_k R_k \omega \delta(\omega - \omega_k)$$

with harmonic vibrational frequencies ω_k and refractive index n(ω) and

Rotational strength: $$R_k = \frac{\partial \langle \hat{\boldsymbol{m}} \rangle}{\partial \dot{q}_k} \cdot \frac{\partial \langle \hat{\dot{\boldsymbol{\mu}}} \rangle}{\partial \dot{q}_k} \langle \dot{q}_k \rangle^2$$

$$\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\mu}}^e + \hat{\boldsymbol{\mu}}^n = -\sum_{i=1}^{N_e} \frac{e}{m} \hat{\mathbf{p}}_i + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{M_\upsilon} \hat{\mathbf{P}}_\upsilon$$

$$\hat{\mathbf{m}} = \hat{\mathbf{m}}^e + \hat{\mathbf{m}}^n = -\sum_{i=1}^{N_e} \frac{e}{2mc} \hat{\mathbf{r}}_i \times \hat{\mathbf{p}}_i + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{2M_\upsilon c} \hat{\mathbf{R}}_\upsilon \times \hat{\mathbf{P}}_\upsilon$$

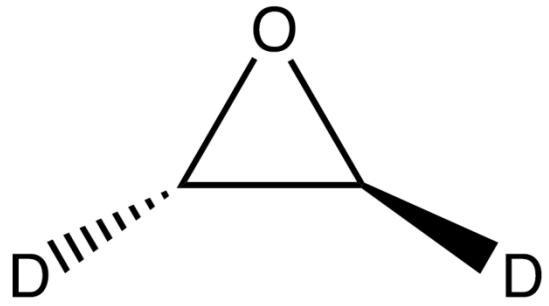
Electronic contributions to the linear current and to the magnetic dipole moment vanish identically in the adiabatic approximation.

Employ the exact factorization:

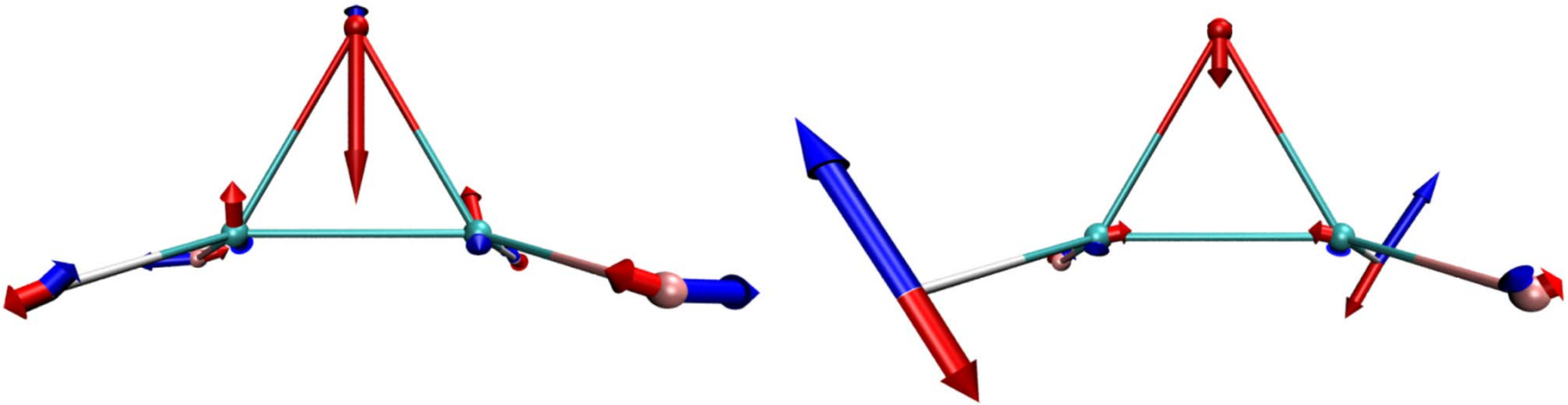
$$\left\langle \hat{\boldsymbol{\mu}} \right\rangle_\Psi = \int d\mathbf{R} \chi^* (\mathbf{R},t) \left[\left\langle \Phi_{\mathbf{R}}(t) \middle| \hat{\boldsymbol{\mu}}^e \middle| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}} + \hat{\boldsymbol{\mu}}^n + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{M_\upsilon} \mathbf{A}_\upsilon (\mathbf{R},t) \right] \chi(\mathbf{R},t)$$

$$\left\langle \hat{\mathbf{m}} \right\rangle_\Psi = \int d\mathbf{R} \chi^* (\mathbf{R},t) \left[\left\langle \Phi_{\mathbf{R}}(t) \middle| \hat{\mathbf{m}}^e \middle| \Phi_{\mathbf{R}}(t) \right\rangle_{\mathbf{r}} + \hat{\mathbf{m}}^n + \sum_{\upsilon=1}^{N_n} \frac{Z_\upsilon e}{2M_\upsilon c} \hat{\mathbf{R}}_\upsilon \times \hat{\mathbf{A}}_\upsilon (\mathbf{R},t) \right] \chi(\mathbf{R},t)$$

and evaluate $\Phi_{\mathbf{R}}$ within first-order nuclear-velocity PT, employing DFT-PT



(S)-d2-oxirane



Vibrational modes at 896 cm^{-1} (left) and at 1089 cm^{-1} (right) for (S)-d_2-oxirane, with nuclear velocities indicated as blue arrows. The corresponding vector potential is shown as red arrows.

Normal modes, dipole and rotational strengths, for (S)-d_2-oxirane..

	D_{MFP}	D_{NVP}	R_{MFP}	R_{NVP}
$\tilde{\upsilon}(cm^{-1})$	$(10^{-44}\ esu^2\ cm^2)$		$(10^{-44}\ esu^2\ cm^2)$	
647.50	0.55	0.85	−0.35	−0.45
733.42	123.35	124.88	8.73	10.54
769.76	53.44	51.77	3.17	3.29
856.38	145.31	145.55	4.31	2.70
894.67	9.78	10.24	−3.37	−3.89
936.33	39.73	39.24	−19.14	−20.26
1088.21	3.79	4.44	6.95	8.34
1093.95	1.41	1.71	−3.98	−4.97
1210.44	26.26	26.09	9.56	10.45
1326.86	0.34	0.37	−0.91	−0.76
1377.38	11.65	10.78	−7.50	−8.17
2235.16	49.17	50.88	−22.60	−22.90
2244.19	12.63	12.81	16.80	16.78
3047.68	11.43	11.66	−32.80	−32.59
3054.15	58.64	60.16	46.63	47.04

A. Scherrer, F Agostini, D. Sebastiani, EKUG., R. Vuilleumier, JCP 143, 074106 (2015)