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Libra Summer School and Workshop 2024

TSH: Part 1

Alexey Akimov

University at Buffalo, SUNY

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Basic Concepts and Terminology of
Nonadiabatic Dynamics

Born-Oppenheimer Approximation

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$$\hat{H}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{R}}, t) = \hat{T}(\hat{\boldsymbol{R}}) + \hat{H}_{el}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{R}}, t) + \hat{V}_{nn}(\hat{\boldsymbol{R}}, t)$$

Includes el-el and el-nucl interactions

$$\hat{H}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{R}})\Psi_n(\boldsymbol{r}, \boldsymbol{R}) = E_n\Psi_n(\boldsymbol{r}, \boldsymbol{R})$$

This is an **electron-nuclear (vibronic)** Hamiltonian

This is an **electron-nuclear (vibronic)** wavefunction

Born-Oppenheimer approximation: a general **time-scale separation** approximation = there are fast and slow degrees of freedom, in general. **Enables factorization** $\boldsymbol{X(fast, slow) \approx x(slow)y(fast; slow)}$
the adiabatic approximation applied to **electrons and nuclei**

- Nuclei are heavier than electrons, so nuclei are seeing by electrons as static entities
- Electrons move in the field created by immobile nuclei and themselves
- $m_{nucl} \gg m_{elec}$, so treat nuclei classically, and electrons – quantum-mechanically

$$\hat{H}(\hat{\boldsymbol{r}}, \hat{\boldsymbol{R}})\Psi_n(\boldsymbol{r}, \boldsymbol{R}) = E_n\Psi_n(\boldsymbol{r}, \boldsymbol{R}) \quad \Rightarrow \quad \hat{H}(\hat{\boldsymbol{r}}; \boldsymbol{R}(t))\Psi_n(\boldsymbol{r}; \boldsymbol{R}) = E_n(\boldsymbol{R})\Psi_n(\boldsymbol{r}; \boldsymbol{R}(t))$$

BO approximation

Coordinates of nuclei are the dynamical variables
Energy - is a number

Coordinates of nuclei are parameters
Energy – is a function of these parameters: **potential energy surface**

Potential energy surfaces (PES)

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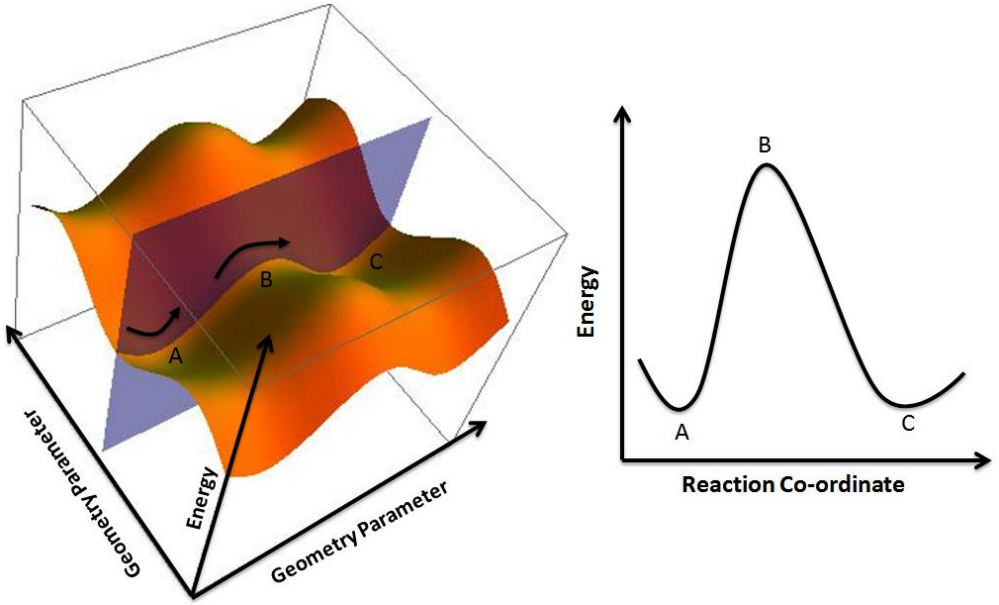
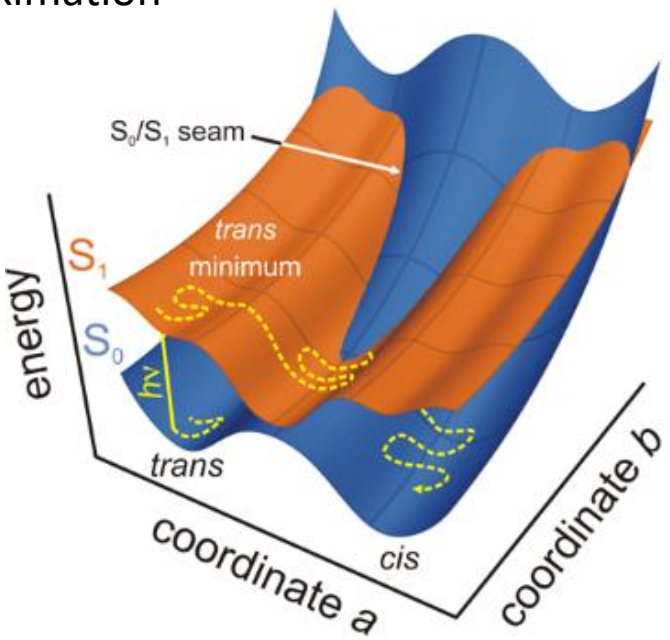
$$E_n(\boldsymbol{R}) = \left\langle \Psi_{\mathrm{n}}(\mathbf{r},\mathbf{R}) \middle| \hat{H}_{el}(\boldsymbol{r},\boldsymbol{R}) \middle| \Psi_{\mathrm{n}}(\mathbf{r},\mathbf{R}) \right\rangle_{\boldsymbol{r}} + V_{nn}(\boldsymbol{R})$$

- Energy of a given state as a function of nuclear coordinates
- Multidimensional, but one is often interested in lower-dimensional cuts (profiles)
- Topology: minima, maxima, barriers, saddle points
- Reaction coordinate – a collective transformation of all atoms
- Present only as a consequence of the BO approximation





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Potential energy surfaces define the reactive dynamics

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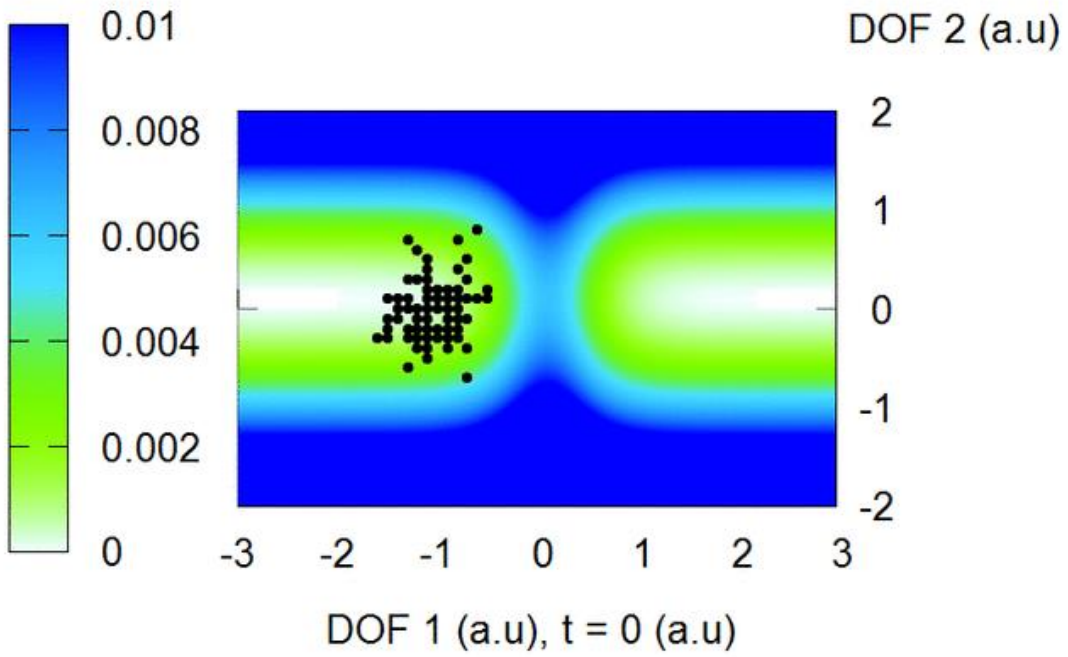
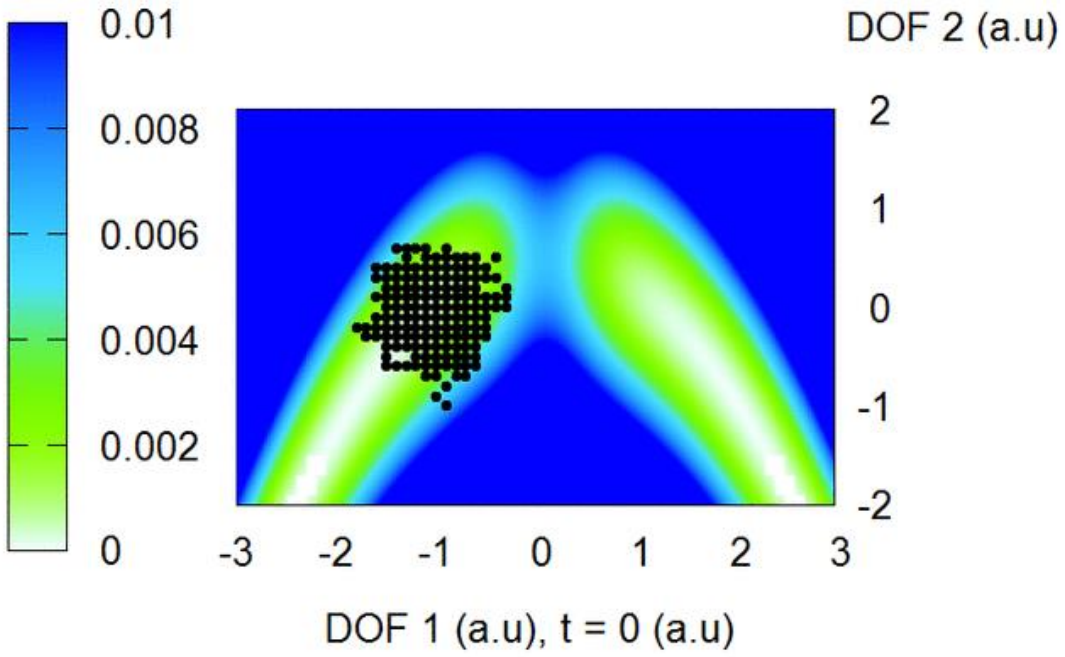
Credit: Brendan Smith





Tiers of approximation to the molecular Hamiltonian

Disregard the form of the wavefunction for now

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Everything is operators!

Exact TD-SE

$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t}=\left[\hat{T}(\hat{\boldsymbol{R}})+\hat{H}_{el}(\hat{\boldsymbol{r}},\hat{\boldsymbol{R}})+\hat{V}_{nn}(\hat{\boldsymbol{R}})\right]\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

Electronic DOFs are still operators (quantum)

TD-SE with the BO

$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t}=\left[\hat{T}(\hat{\boldsymbol{R}})+\hat{H}_{el}(\hat{\boldsymbol{r}};\boldsymbol{R})+\hat{V}_{nn}(\boldsymbol{R})\right]\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

Nuclear DOFs are variables – could be independent (quantum) or could be time-dependent (classical path)

In general, we still have nuclear kinetic energy operator (for quantum nuclei)

TD-SE with the classical path approximation (CPA)

$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t}=\left[T(\boldsymbol{P})+\hat{H}_{el}(\hat{\boldsymbol{r}};\boldsymbol{R}(t))+\hat{V}_{nn}(\boldsymbol{R}(t))\right]\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

Nuclear DOFs are time-dependent variables

Kinetic energy is a function of momentum

Adiabatic Approximation. Adiabatic and Nonadiabatic Dynamics

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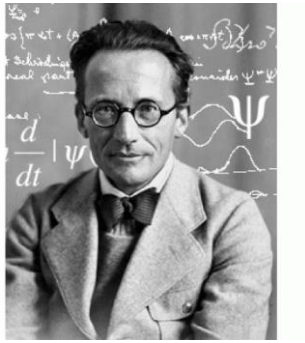
$$i\hbar \frac{\partial \Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = H(t,\hat{\boldsymbol{r}},\hat{\boldsymbol{R}})\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_i(\mathbf{r};\mathbf{R}(t))$$

Except for in the exact factorization ansatz!



Adiabatic approximation: keep only one term

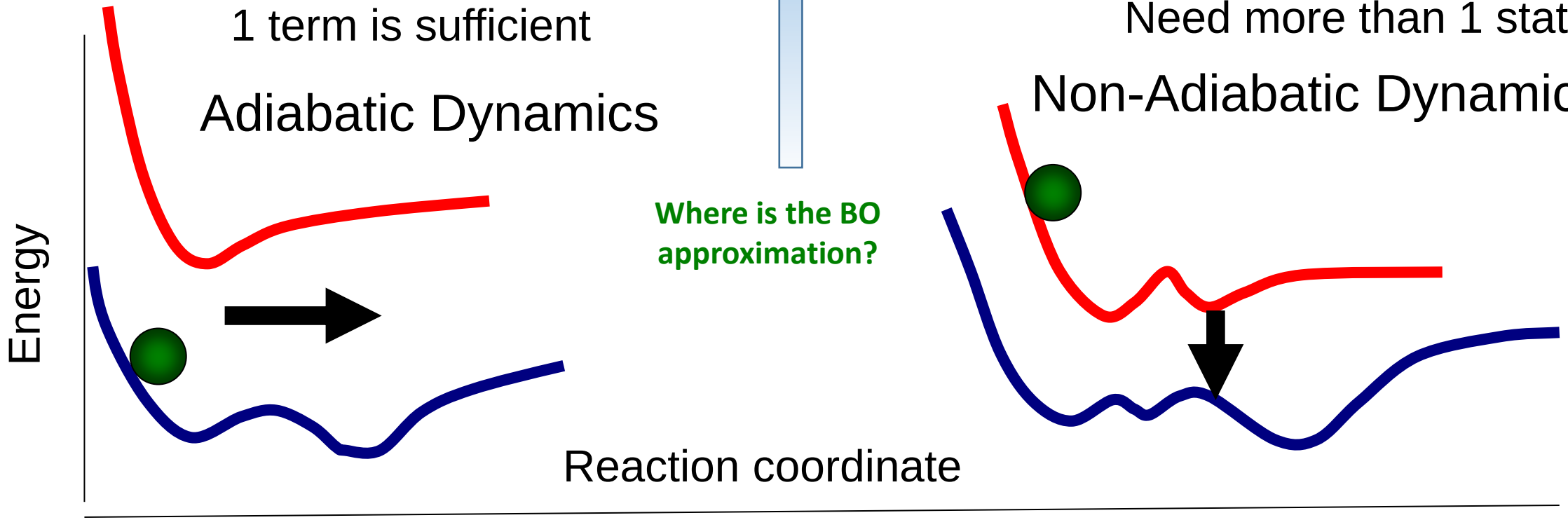
1 term is sufficient

Adiabatic Dynamics

Need more than 1 state

Non-Adiabatic Dynamics

Where is the BO approximation?



When NA dynamics is needed: Failure of the Born-Oppenheimer Approximation

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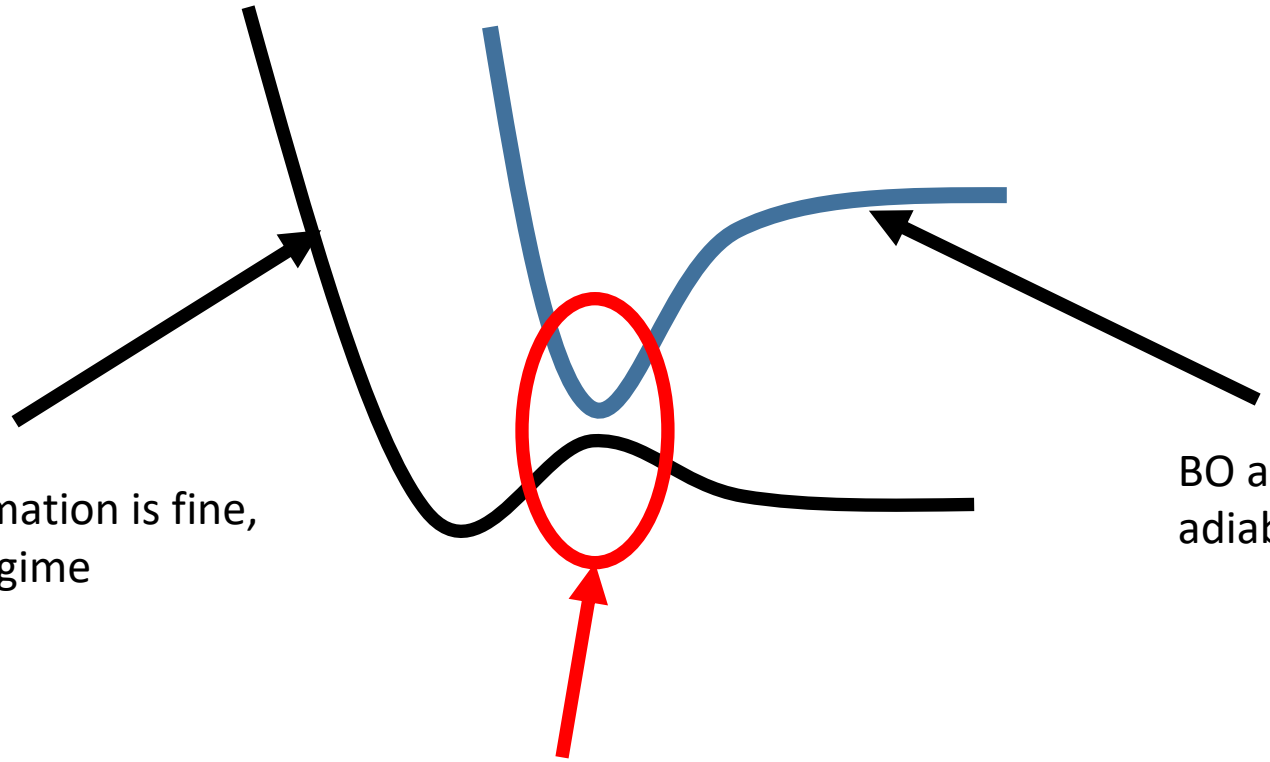
$$E_{kin} \gg |E_i - E_j|$$

$$v = \frac{p}{m}$$

- light atoms (e.g. H – quantum nuclear effects)
- high-energy (momentum) – e.g. colliding particles
- degeneracies of quantum states (bond-breaking, plasmas, metals)



BO approximation is fine, adiabatic regime

BO approximation is fine, adiabatic regime

BO approximation breaks down here, non-adiabatic regime

Tiers of approximations to the wavefunction

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The solution largely depends on the approximation we make to represent the total wavefunction $\Psi(t, \boldsymbol{r}, \boldsymbol{R})$

	Nonadiabatic	Adiabatic
	$\Psi(t, \boldsymbol{r}, \boldsymbol{R}) = \chi(t, \boldsymbol{R})\Phi_{\mathbf{R}}(t, \mathbf{r})$ $\int d\boldsymbol{r}\lvert\Phi_{\boldsymbol{R}}(\boldsymbol{r}, t)\rvert = 1, \forall \boldsymbol{R}$	
Exact factorization Agostini, F.; Curchod, B. F. E. *WIREs Computational Molecular Science* **2019**, *9*, e1417.	$\Psi(t, \boldsymbol{r}, \boldsymbol{R}) = \sum_i \chi_i(t, \boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r}; \mathbf{R})$	$\Psi(t, \boldsymbol{r}, \boldsymbol{R}) = \chi(t, \boldsymbol{R})\Phi(\mathbf{r}; \mathbf{R})$
Quantum nuclei, with BO approximation (AIMS, QTAG, etc.) Makhov, D. V.; Glover, W. J.; Martinez, T. J.; Shalashilin, D. V. *J. Chem. Phys.* **2014**, *141*, 054110.		
Wavepacket-dressed trajectories Dutra, M.; Garashchuk, S.; Akimov, A. V. *Int. J. Quantum Chem.* **2023** e27078.	$\Psi(t, \boldsymbol{r}, \boldsymbol{R}) = \sum_i \chi_i(t, \boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r}; \mathbf{R}(t))$	$\Psi(t, \boldsymbol{r}, \boldsymbol{R}) = \chi(t, \boldsymbol{R})\Phi(\mathbf{r}; \mathbf{R}(t))$
Bare trajectories Tully, J. C. *J. Chem. Phys.* **1990**, *93*, 1061–1071.	$\Psi(t, \boldsymbol{r}; \boldsymbol{R}(\boldsymbol{t})) = \sum_i c_i(t)\Phi_{\mathrm{i}}(\mathbf{r}; \mathbf{R}(t))$	$\Psi(t, \boldsymbol{r}; \boldsymbol{R}(\boldsymbol{t})) = c(t)\Phi(\mathbf{r}; \mathbf{R}(t))$

Terminology: Adiabatic and Diabatic States

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Adiabatic

- unique
- eigenstates of molecular Hamiltonian:
- not always chemically-intuitive

Adiabatic (Hamiltonian is diagonal):

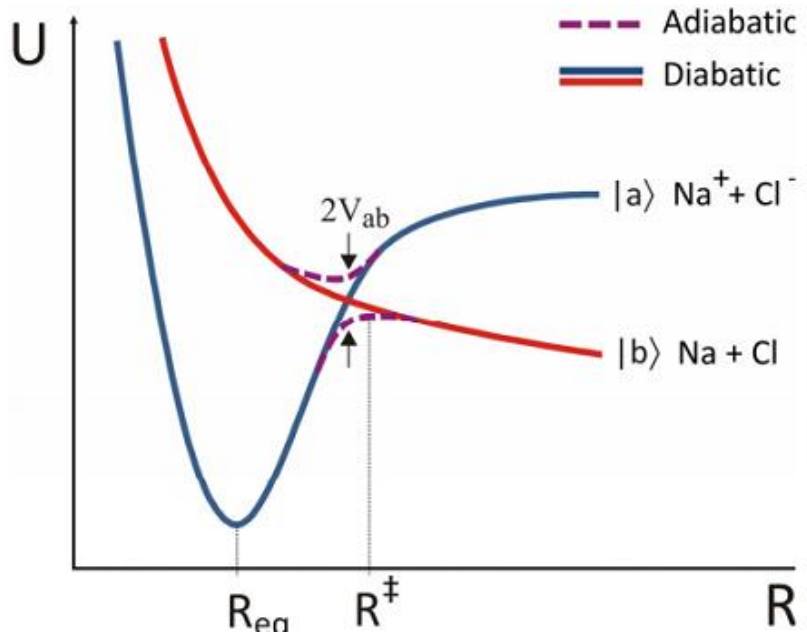
$$\langle \psi_{adi,i} | \hat{H}_{el} | \psi_{adi,j} \rangle = 0, \forall i \neq j$$

(Quasi-)Diabatic

- non-unique, infinite # of possibilities
- Is not an eigenstate of molecular Hamiltonian
- usually chosen to be chemically-intuitive

Diabatic (NACs are exactly zero):

$$\langle \psi_{dia,i} | \nabla_{\boldsymbol{R}} | \psi_{dia,j} \rangle = 0, \forall \boldsymbol{R}$$



https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Book%3A_Time_Dependent_Quantum_Mechanics_and_Spectroscopy_(Tokmakoff)/06%3A_Adiabatic_Approximation/6.03%3A_Diabatic_and_Adiabatic_States

Examples of Deriving Equations of Motion with Different Approximations

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Example 1: BO with quantum nuclei

$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = H(t,\hat{\boldsymbol{r}},\hat{\boldsymbol{R}})\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R})$$

Example 2: BO with wavepacket-dressed trajectories

$$i\hbar\frac{\partial\Psi(t,\boldsymbol{r},\boldsymbol{R})}{\partial t} = H(t,\hat{\boldsymbol{r}},\hat{\boldsymbol{R}})\Psi(t,\boldsymbol{r},\boldsymbol{R})$$

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R}(\boldsymbol{t}))$$

Case 1: Compute the action of $\hat{T}$ on Ψ

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$$\nabla^2(AB) = \nabla\big(\nabla(AB)\big) = \nabla\big((\nabla \mathrm{A})\mathrm{B} + A\nabla B\big) = (\nabla^2 \mathrm{A})\mathrm{B} + 2(\nabla \mathrm{A})(\nabla \mathrm{B}) + A\nabla^2 B$$

$$\left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\right)\chi_j\Phi_j = \left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\chi_j\right)\Phi_j - \left(2\sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla_\alpha\Phi_j\nabla_\alpha\chi_j\right) + \left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\Phi_j\right)\chi_j$$

$$\hat{T}\chi_j\Phi_j = (\hat{T}\chi_j)\Phi_j - \left(\sum_\alpha \frac{\hbar^2}{M_\alpha}\nabla_\alpha\Phi_j\nabla_\alpha\chi_j\right) + (\hat{T}\Phi_j)\chi_j$$

We keep all terms, because Φ is a function of *R*

Project on an arbitrary state Φ_i:

$$\langle\Phi_i|\hat{T}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \langle\Phi_i|\Phi_j\rangle_{\boldsymbol{r}}\hat{T}\chi_j - \left(\sum_\alpha \frac{\hbar^2}{M_\alpha}\langle\Phi_i|\nabla_\alpha\Phi_j\rangle_{\boldsymbol{r}}\nabla_\alpha\chi_j\right) + \langle\Phi_i|\hat{T}|\Phi_j\rangle_{\boldsymbol{r}}\chi_j$$

$$\langle\Phi_i|\hat{T}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \delta_{ij}\hat{T}\chi_j - \left(\sum_\alpha \frac{\hbar^2}{M_\alpha}\langle\Phi_i|\nabla_\alpha\Phi_j\rangle_{\boldsymbol{r}}\nabla_\alpha\chi_j\right) + \langle\Phi_i|\hat{T}|\Phi_j\rangle_{\boldsymbol{r}}\chi_j$$

$$\langle\Phi_i|\hat{H}_{nucl}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \langle\Phi_i|\hat{H}_{nucl}|\Phi_j\rangle_{\boldsymbol{r}}\chi_j = \langle\Phi_i|E_j(\boldsymbol{R})|\Phi_j\rangle_{\boldsymbol{r}}\chi_j = E_j(\boldsymbol{R})\langle\Phi_i|\Phi_j\rangle_{\boldsymbol{r}}\chi_j = E_j(\boldsymbol{R})\delta_{ij}\chi_j$$

$$\langle\Phi_i|\hat{T}+\hat{H}_{nucl}|\Psi\rangle = \sum_j\langle\Phi_i|\hat{T}+\hat{H}_{nucl}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \sum_j\left[\delta_{ij}\hat{T}\chi_j - \left(\sum_\alpha \frac{\hbar^2}{M_\alpha}\langle\Phi_i|\nabla_\alpha\Phi_j\rangle_{\boldsymbol{r}}\nabla_\alpha\chi_j\right) + \langle\Phi_i|\hat{T}|\Phi_j\rangle_{\boldsymbol{r}}\chi_j + E_j(\boldsymbol{R})\delta_{ij}\right]$$

Compute the LHS: Case 1

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$$\left\langle \Phi_i \left| \frac{\partial}{\partial t} \right| \chi_j \Phi_j \right\rangle_{\boldsymbol{r}} = \langle \Phi_i | \Phi_j \rangle_{\boldsymbol{r}} \frac{\partial}{\partial t} \chi_j + \left\langle \Phi_i \left| \frac{\partial}{\partial t} \right| \Phi_j \right\rangle_{\boldsymbol{r}} \chi_j = \delta_{ij} \frac{\partial}{\partial t} \chi_j$$

$$i\hbar \left\langle \Phi_i \left| \frac{\partial}{\partial t} \right| \Psi \right\rangle_{\boldsymbol{r}} = i\hbar \sum_j \left\langle \Phi_i \left| \frac{\partial}{\partial t} \right| \chi_j \Phi_j \right\rangle_{\boldsymbol{r}} = i\hbar \sum_j \delta_{ij} \frac{\partial}{\partial t} \chi_j = i\hbar \frac{\partial}{\partial t} \chi_i$$

Now, combine the two parts of the equation:

$$i\hbar \frac{\partial \Psi(t, \boldsymbol{r}, \boldsymbol{R})}{\partial t} = H(t, \boldsymbol{r}, \boldsymbol{R}) \Psi(t, \boldsymbol{r}, \boldsymbol{R})$$

$$i\hbar \frac{\partial}{\partial t} \chi_i = \left[\hat{T} + E_i(\boldsymbol{R}) + \langle \Phi_i | \hat{T} | \Phi_i \rangle \right] \chi_i - \sum_{j,\alpha} \frac{\hbar^2}{M_\alpha} \langle \Phi_i | \nabla_\alpha \Phi_j \rangle \nabla_\alpha \chi_j - \sum_{j \neq i, \alpha} \frac{\hbar^2}{2M_\alpha} \langle \Phi_i | \nabla_\alpha^2 \Phi_j \rangle \chi_j$$

$$i\hbar \frac{\partial}{\partial t} \chi_i = \left[\hat{T} + E_i(\boldsymbol{R}) + \langle \Phi_i | \hat{T} | \Phi_i \rangle \right] \chi_i - i\hbar \sum_{j,\alpha} \langle \Phi_i | \nabla_\alpha \Phi_j \rangle \frac{(-i\hbar \nabla_\alpha) \chi_j}{M_\alpha} - \sum_{j \neq i, \alpha} \frac{\hbar^2}{2M_\alpha} \langle \Phi_i | \nabla_\alpha^2 \Phi_j \rangle \chi_j$$

$$i\hbar \frac{\partial}{\partial t} \chi_i = \left[\hat{T} + E_i(\boldsymbol{R}) + \langle \Phi_i | \hat{T} | \Phi_i \rangle \right] \chi_i - i\hbar \sum_{j,\alpha} \langle \Phi_i | \nabla_\alpha \Phi_j \rangle \frac{\hat{p}_\alpha \chi_j}{M_\alpha} - \sum_{j \neq i, \alpha} \frac{\hbar^2}{2M_\alpha} \langle \Phi_i | \nabla_\alpha^2 \Phi_j \rangle \chi_j$$

Nonadiabatic dynamics

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This is what defines the evolution of nuclear component of the wavefunction and populations of all electronic states.

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_i(\mathbf{r},\mathbf{R})$$

Diagonal BO correction to the PES!
(ZPE of electrons)

In the **adiabatic basis**

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}(t)) + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i - i\hbar\sum_{j,\alpha} D^{(1)}_{ij,\alpha}\frac{\hat{p}_\alpha\chi_j}{M_\alpha} - \sum_{j\neq i,\alpha}\frac{\hbar^2}{2M_\alpha}D^{(2)}_{ij,\alpha}\chi_j$$

$D^{(1)}_{ij,\alpha} = \langle\Phi_i|\nabla_\alpha\Phi_j\rangle$ first-order nonadiabatic couplings (NAC) - vector

Describes how a nuclear DOF α couples electronic state i and j
This is what determines the rates of nonadiabatic transitions.

$D^{(2)}_{ij,\alpha} = \langle\Phi_i|\nabla^2_\alpha\Phi_j\rangle$ second-order NAC - scalar

In the **diabatic basis**

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i$$

Nuclear dynamics on state *i* is defined by the probability density: $P_i(t,\boldsymbol{R}) = |\langle\Phi_i|\Psi\rangle_{\boldsymbol{r}}|^2 = |\chi_i(t,\boldsymbol{R})|^2$

Population of a state i: $P_i(t) = \left|\langle\Phi_i|\Psi\rangle_{\boldsymbol{r},\boldsymbol{R}}\right|^2 = |\chi_i(t)|^2$

Case 2: Compute the action of $\hat{T}$ on Ψ

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$$\left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\right)\chi_j\Phi_j = \left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\chi_j\right)\Phi_j - \left(2\sum_\alpha \frac{\hbar^2}{2M_\alpha}\nabla_\alpha\Phi_j\nabla_\alpha\chi_j\right) + \left(\sum_\alpha -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2\Phi_j\right)\chi_j$$

$$\hat{T}(\chi_j\Phi_j) = (\hat{T}\chi_j)\Phi_j$$

because Φ is only a function of time, not $\boldsymbol{R}$

$$\langle\Phi_i|\hat{T}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \delta_{ij}\hat{T}\chi_j$$

$$\langle\Phi_i|\hat{T}+\hat{H}_{nucl}|\Psi\rangle = \sum_j\langle\Phi_i|\hat{T}+\hat{H}_{nucl}|\chi_j\Phi_j\rangle_{\boldsymbol{r}} = \sum_j[\delta_{ij}\hat{T}\chi_j + E_j(\boldsymbol{R})\delta_{ij}]$$

Compute the LHS

$$\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\chi_j\Phi_j\right\rangle = \langle\Phi_i|\Phi_j\rangle_{\boldsymbol{r}}\frac{\partial}{\partial t}\chi_j + \left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle\chi_j = \delta_{ij}\frac{\partial}{\partial t}\chi_j + \left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle\chi_j$$

$$i\hbar\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Psi\right\rangle_{\boldsymbol{r}} = i\hbar\sum_j\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\chi_j\Phi_j\right\rangle_{\boldsymbol{r}} = i\hbar\sum_j\delta_{ij}\frac{\partial}{\partial t}\chi_j + i\hbar\sum_j\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle\chi_j = i\hbar\frac{\partial}{\partial t}\chi_i + i\hbar\sum_j\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle\chi_j$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = [\hat{T} + E_i(\boldsymbol{R}(t))]\chi_i - i\hbar\sum_j\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle\chi_j$$

$$\left\langle\Phi_i\left|\frac{\partial}{\partial t}\right|\Phi_j\right\rangle = \sum_{j,\alpha}\left\langle\Phi_i\left|\frac{\partial}{\partial \boldsymbol{R}_\alpha}\right|\Phi_j\right\rangle\frac{\partial \boldsymbol{R}_\alpha}{\partial t} = \sum_{j,\alpha}D^{(1)}_{ij,\alpha}\frac{\boldsymbol{P}_\alpha}{M_\alpha}$$

This terms appears because Φ is an implicit function of time, via $\boldsymbol{R}(t)$

Summary

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Example 1: BO with quantum nuclei

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R})$$

Nonadiabatic, adiabatic basis

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}(t)) + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i - i\hbar\sum_{j,\alpha} D^{(1)}_{ij,\alpha}\frac{\hat{p}_\alpha\chi_j}{M_\alpha} - \sum_{j\neq i,\alpha}\frac{\hbar^2}{2M_\alpha}D^{(2)}_{ij,\alpha}\chi_j$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi_i$$

Nonadiabatic, diabatic basis

$$i\hbar\frac{\partial}{\partial t}\chi = \left[\hat{T} + E_i(\boldsymbol{R}(t)) + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi$$

Adiabatic, adiabatic basis

$$i\hbar\frac{\partial}{\partial t}\chi = \left[\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle + \langle\Phi_i|\hat{T}|\Phi_i\rangle\right]\chi$$

Adiabatic, diabatic basis

Example 2: BO with wavepacket-dressed trajectories

$$\Psi(t,\boldsymbol{r},\boldsymbol{R}) = \sum_i \chi_i(t,\boldsymbol{R})\Phi_{\mathrm{i}}(\mathbf{r};\mathbf{R}(\boldsymbol{t}))$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + E_i(\boldsymbol{R}(t))\right]\chi_i - i\hbar\sum_{j,\alpha} D^{(1)}_{ij,\alpha}\frac{\boldsymbol{P}_\alpha}{M_\alpha}\chi_j$$

$$i\hbar\frac{\partial}{\partial t}\chi_i = \left[\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle\right]\chi_i$$

$$i\hbar\frac{\partial}{\partial t}\chi = \left[\hat{T} + E_i(\boldsymbol{R}(t))\right]\chi$$

$$i\hbar\frac{\partial}{\partial t}\chi = \left[\hat{T} + \langle\Phi_i|\hat{H}_{el}|\Phi_i\rangle\right]\chi$$