L2 - Quantum Mechanics 2

Quantum mechanics of molecules

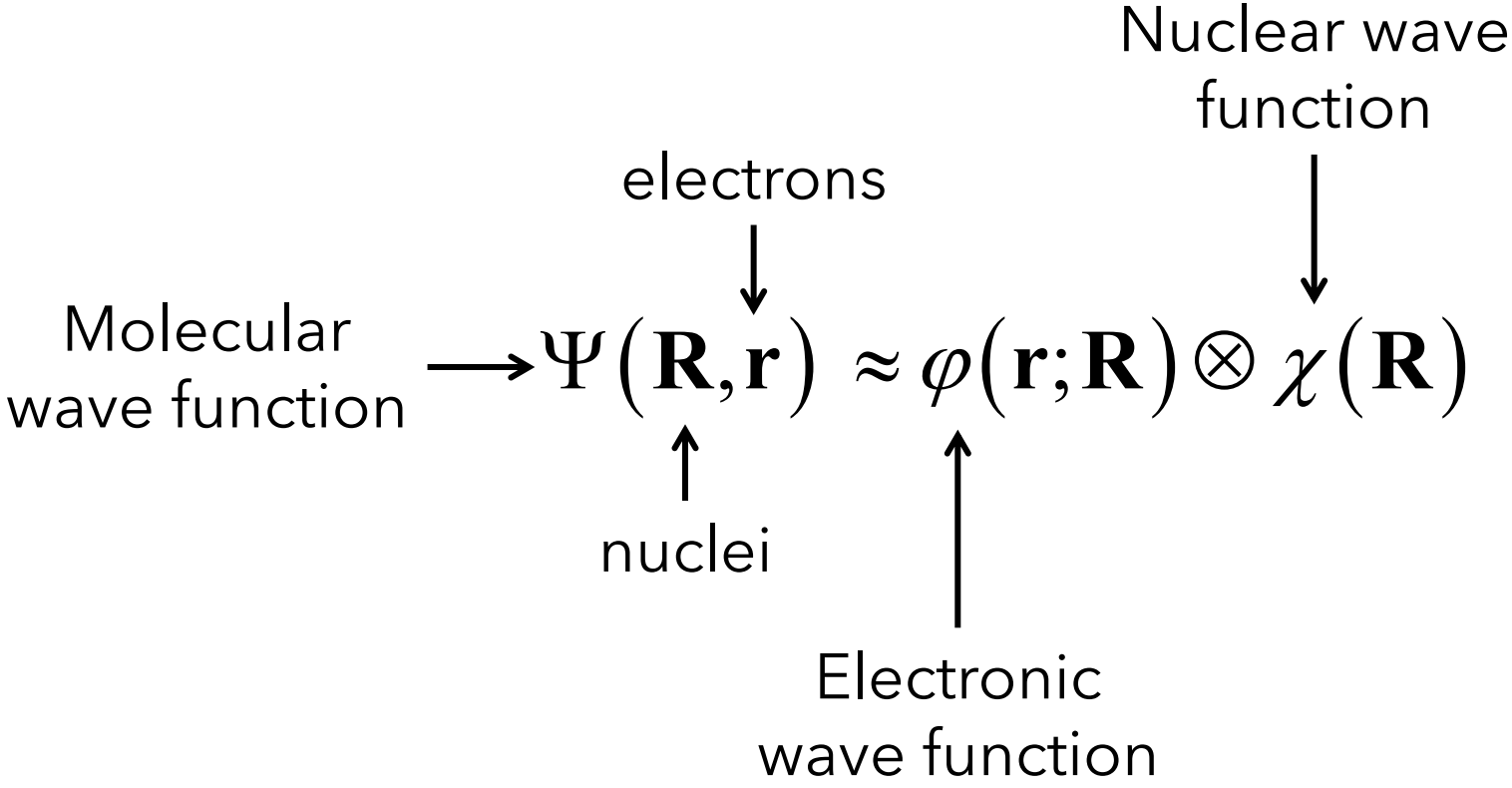
The Born-Oppenheimer approximation

"The **Born-Oppenheimer** idea is one of those wonderful approximations that **even in failure** forms the basis for discussion and systematic corrections.

"Without the Born-Oppenheimer approximation as a foundation, there would be **no molecular structure**, solid-state crystal structure, molecular vibrations, phonons, electronic band structure, and so on.

"Why? Because it is the Born-Oppenheimer approximation that allows **separation of electronic from nuclear motion**. Without it, we appear to be lost in a soggy many-body 'pea soup' or plasma of electrons and nuclei, where there is seemingly no structure at all, save the kind of structure one finds in a two-component liquid."

- Eric J Heller, *The semiclassical way*, 2018


Nuclear wave function
electrons
Molecular wave function
$\Psi(\mathbf{R},\mathbf{r}) \approx \varphi(\mathbf{r};\mathbf{R}) \otimes \chi(\mathbf{R})$
nuclei
Electronic wave function

Molecular problem

$$\hat{H}(\mathbf{R},\mathbf{r})\Psi(\mathbf{R},\mathbf{r}) = \varepsilon\,\Psi(\mathbf{R},\mathbf{r})$$

with

$$\hat{H}(\mathbf{R},\mathbf{r}) = \hat{T}_{nuc}(\mathbf{R}) + \hat{T}_{elec}(\mathbf{r}) + V(\mathbf{r},\mathbf{R})$$

✚

Born-Huang wave function

$$\Psi(\mathbf{R},\mathbf{r}) = \sum_n \varphi_n(\mathbf{r};\mathbf{R})\,\chi_n(\mathbf{R})$$

✚

Adiabatic approximation

$$\langle \varphi_m | \nabla^2_{\mathbf{R}} \varphi_n \rangle = \langle \varphi_m | \nabla_{\mathbf{R}} \varphi_n \rangle = 0$$

=

Time-independent adiabatic formulation

Nuclear Schrödinger equation

$$\left(\hat{T}_{nuc}(\mathbf{R}) + E(\mathbf{R})\right)\chi(\mathbf{R}) = \varepsilon\chi(\mathbf{R})$$

Electronic Schrödinger equation

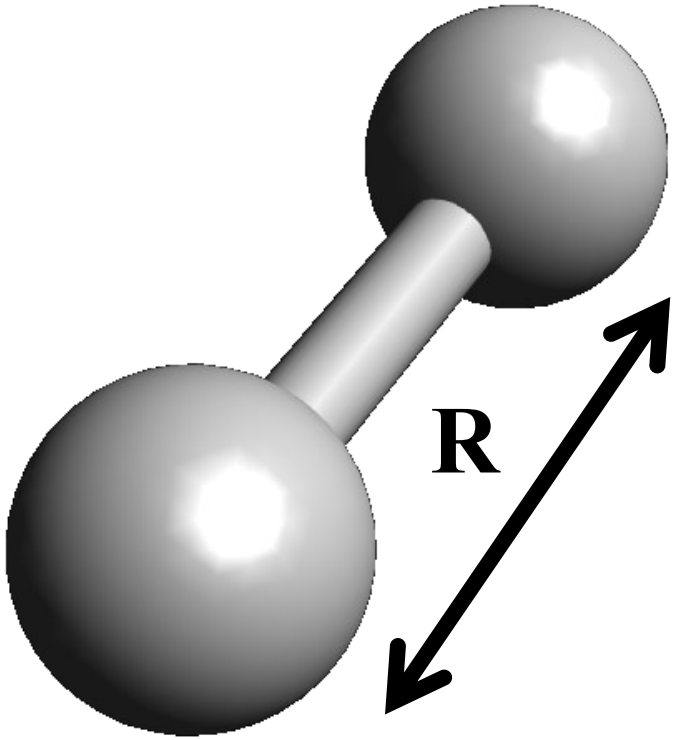
$$\left(\hat{T}_{elec}(\mathbf{r}) + V(\mathbf{r},\mathbf{R})\right)\varphi(\mathbf{r};\mathbf{R}) = E(\mathbf{R})\varphi(\mathbf{r};\mathbf{R})$$

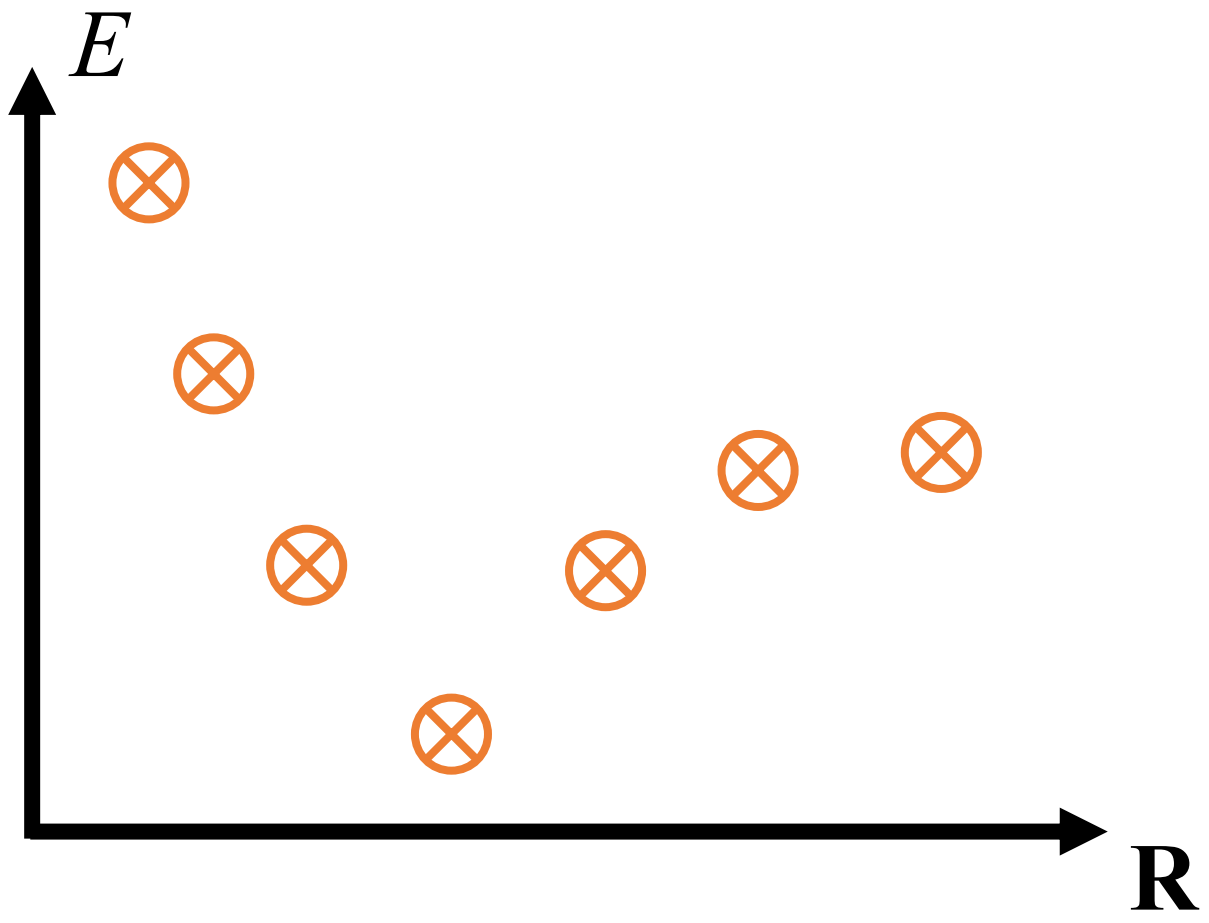
Potential Energy Surface

BO molecular wave function

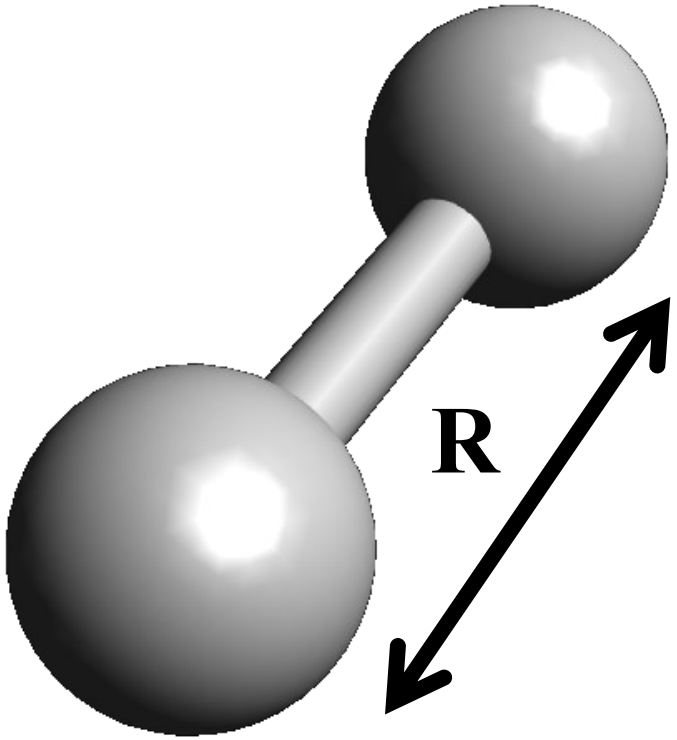
$$\Psi^{BO}(\mathbf{R},\mathbf{r}) = \varphi(\mathbf{r};\mathbf{R})\,\chi(\mathbf{R})$$

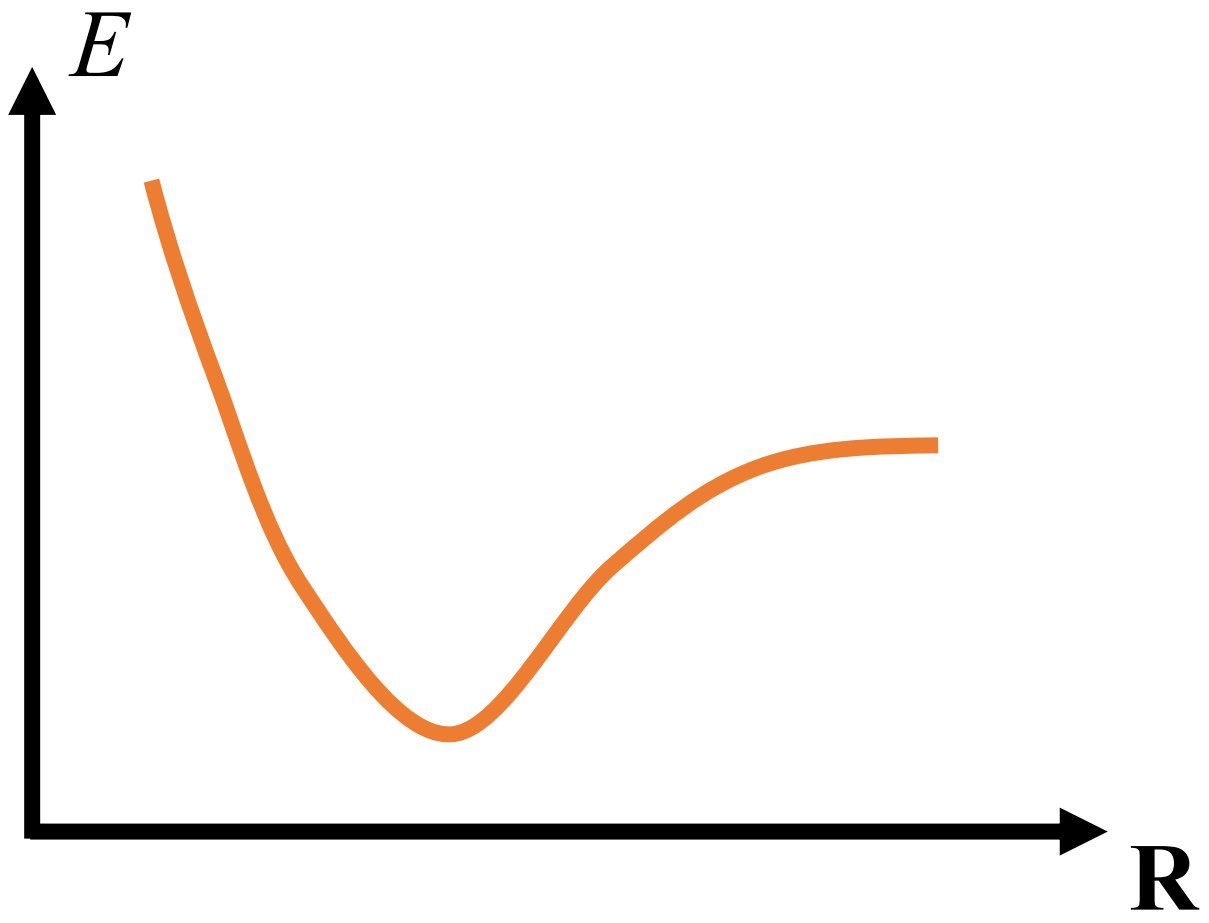
Check the derivation in the appendix





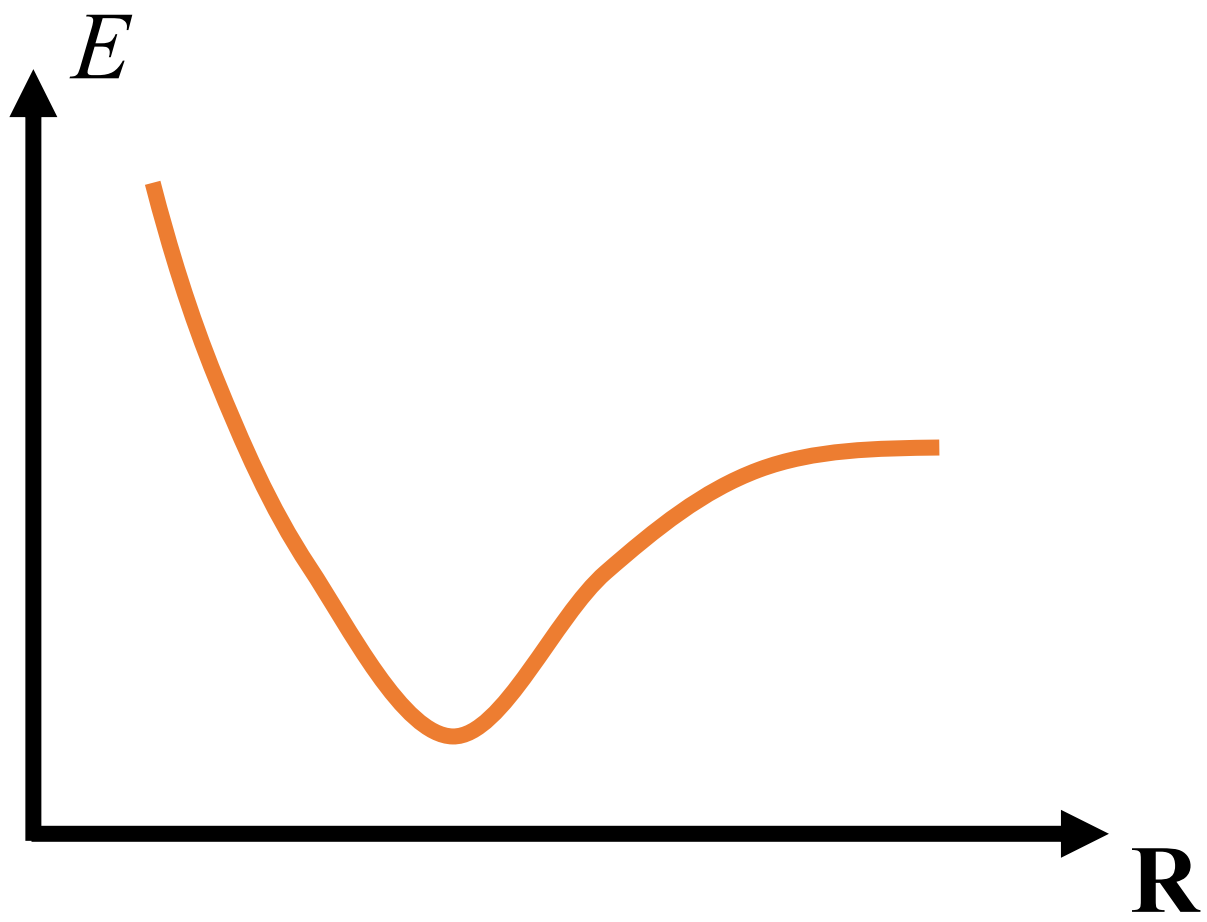
$$\hat{H}_{elec}\varphi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}) = E(\mathbf{R})\varphi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R})$$

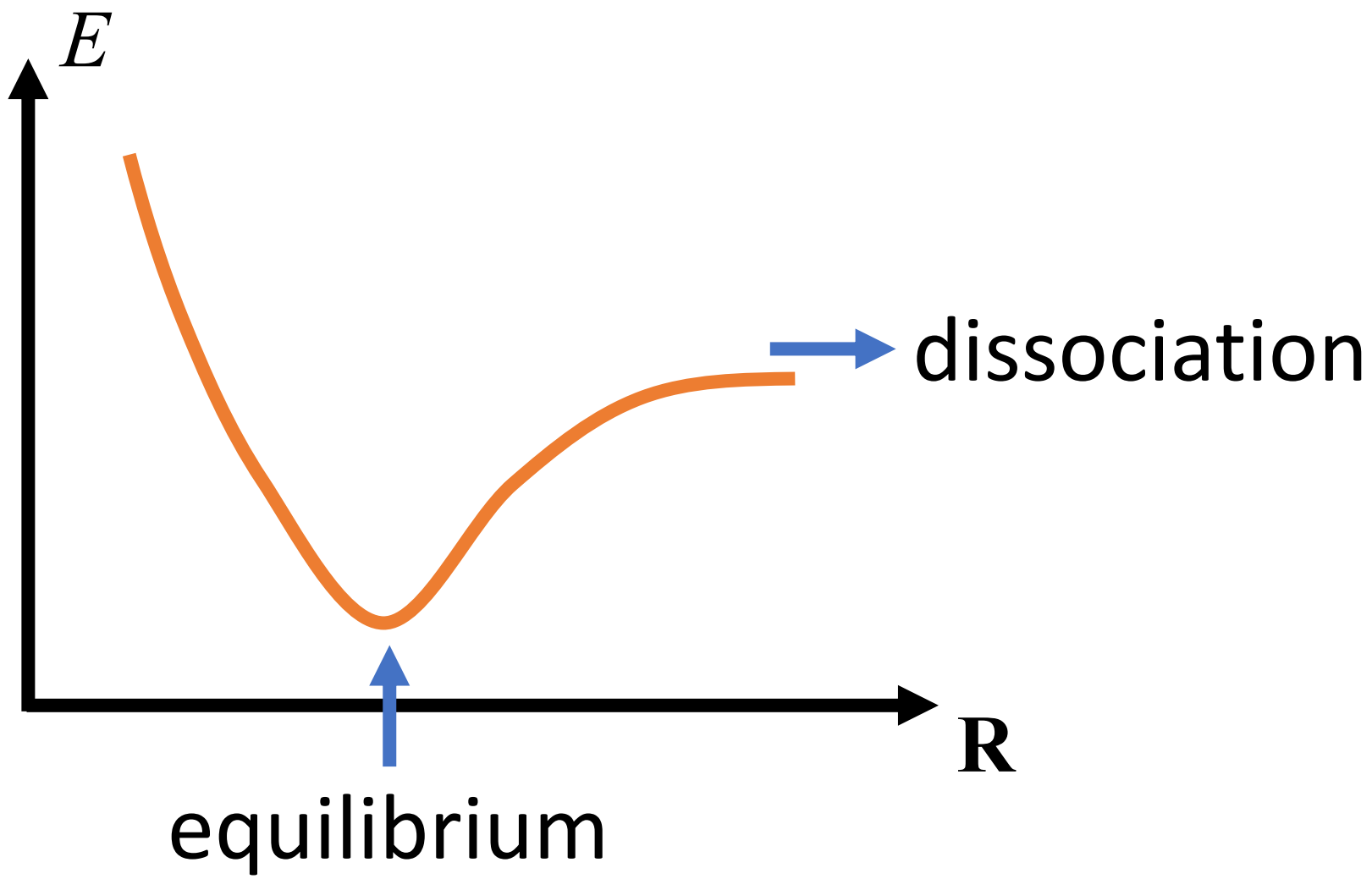


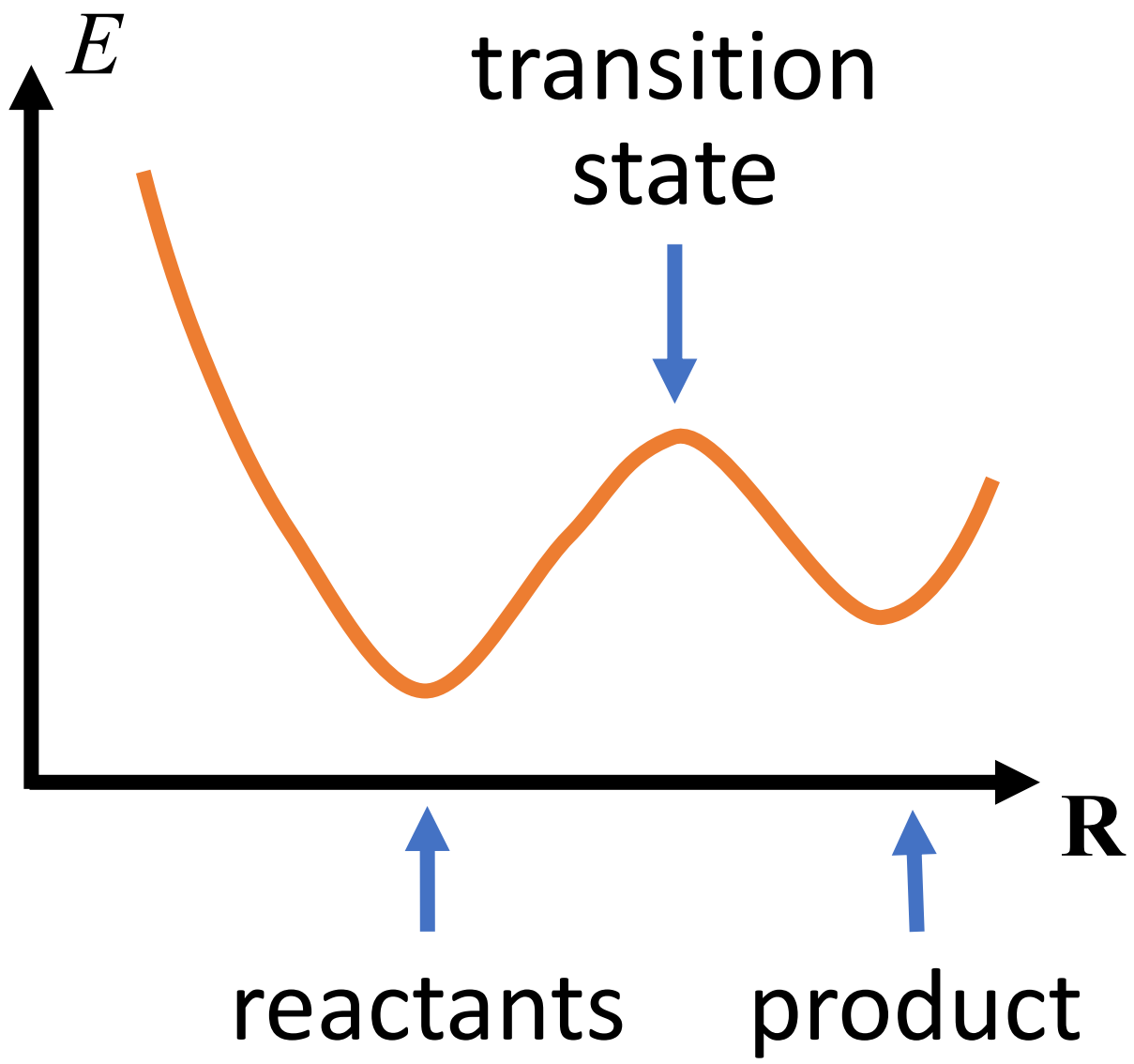


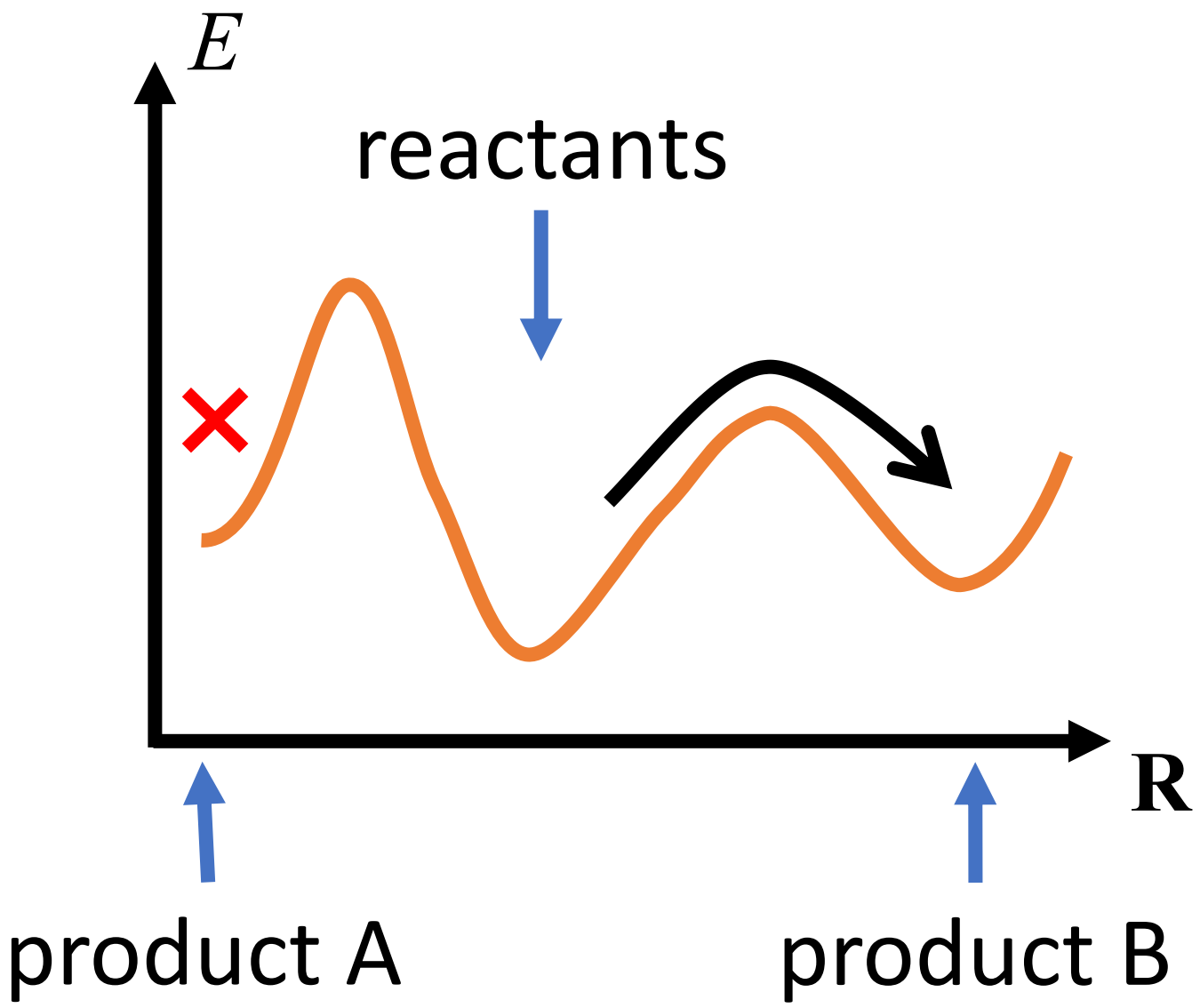
$$\hat{H}_{elec}\varphi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}) = E(\mathbf{R})\varphi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R})$$

Potential energy surface

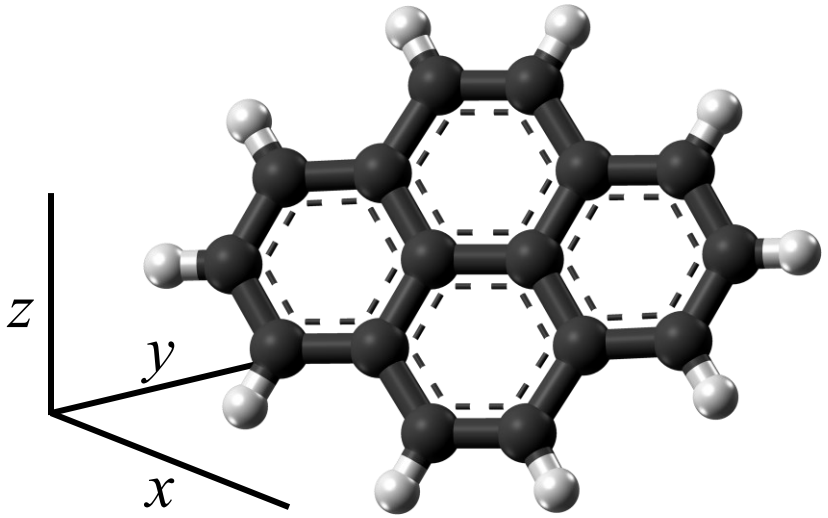


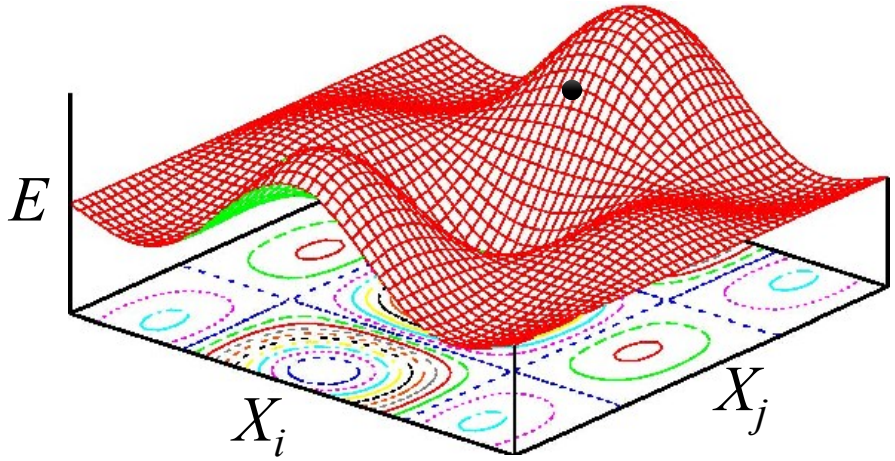

E
dissociation
R
equilibrium


E
transition
state
R
reactants
product

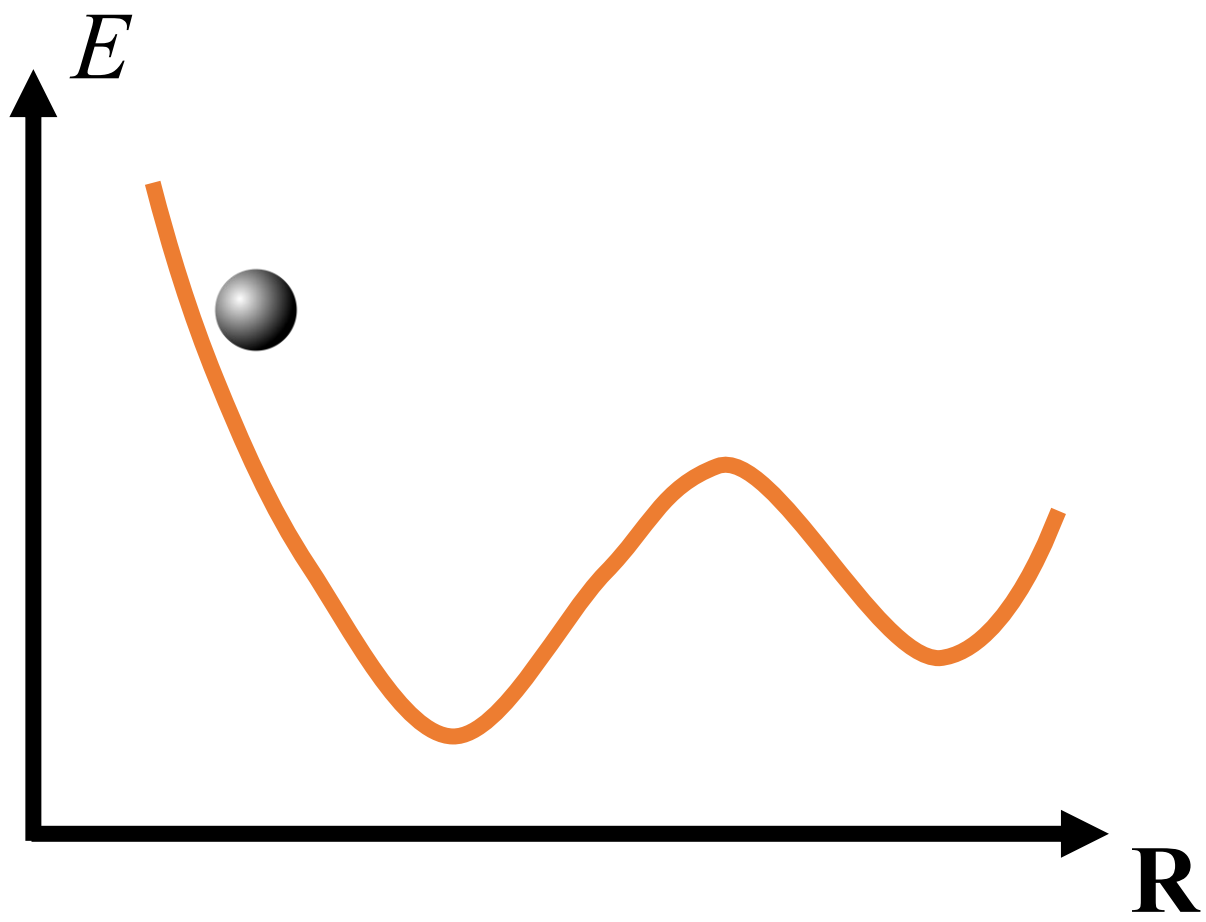

E
reactants
R
product A
product B

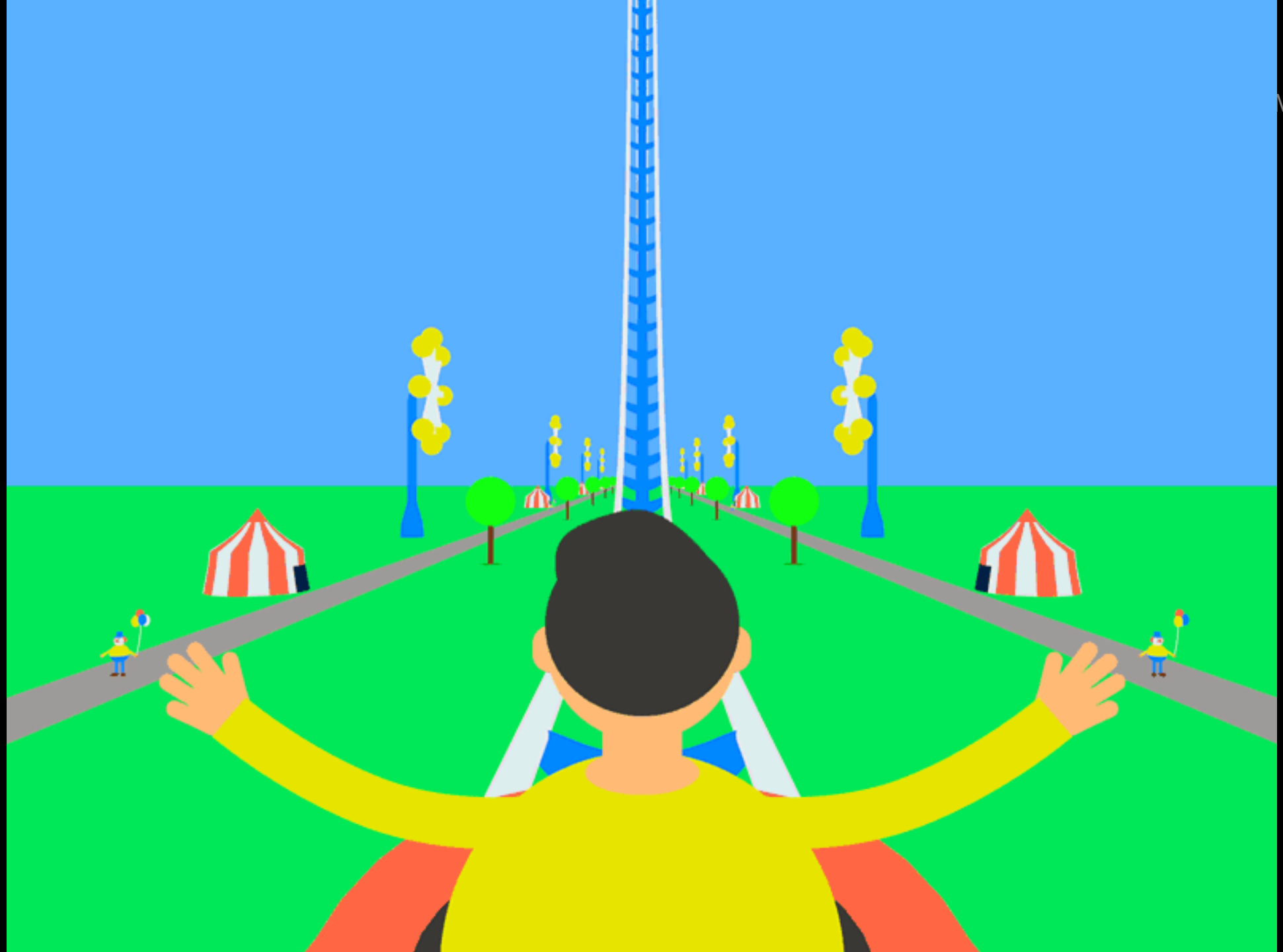
$$E(\mathbf{R}) \equiv E(X_1, Y_1, Z_1, \cdots, X_N, Y_N, Z_N)$$





N points × 3 dimensions → 1 point × 3*N* dimensions


E
R



Molecular problem

$$\hat{H}(\mathbf{R},\mathbf{r})\Psi(\mathbf{R},\mathbf{r}) = \varepsilon\Psi(\mathbf{R},\mathbf{r})$$

with

$$\hat{H}(\mathbf{R},\mathbf{r}) = \hat{T}_{nuc}(\mathbf{R}) + \hat{T}_{elec}(\mathbf{r}) + V(\mathbf{r},\mathbf{R})$$

✚

Born-Huang wave function

$$\Psi(\mathbf{R},\mathbf{r}) = \sum_n \varphi_n(\mathbf{r};\mathbf{R})\chi_n(\mathbf{R})$$

✚

Adiabatic approximation

$$\left\langle \varphi_{n'} \middle| \nabla^2_{\mathbf{R}} \varphi_n \right\rangle = \left\langle \varphi_{n'} \middle| \nabla_{\mathbf{R}} \varphi_n \right\rangle = 0$$

〓

Time-independent adiabatic formulation

Nuclear Schrödinger equation

$$\left(\hat{T}_{nuc}(\mathbf{R}) + E(\mathbf{R})\right)\chi(\mathbf{R}) = \varepsilon\chi(\mathbf{R})$$

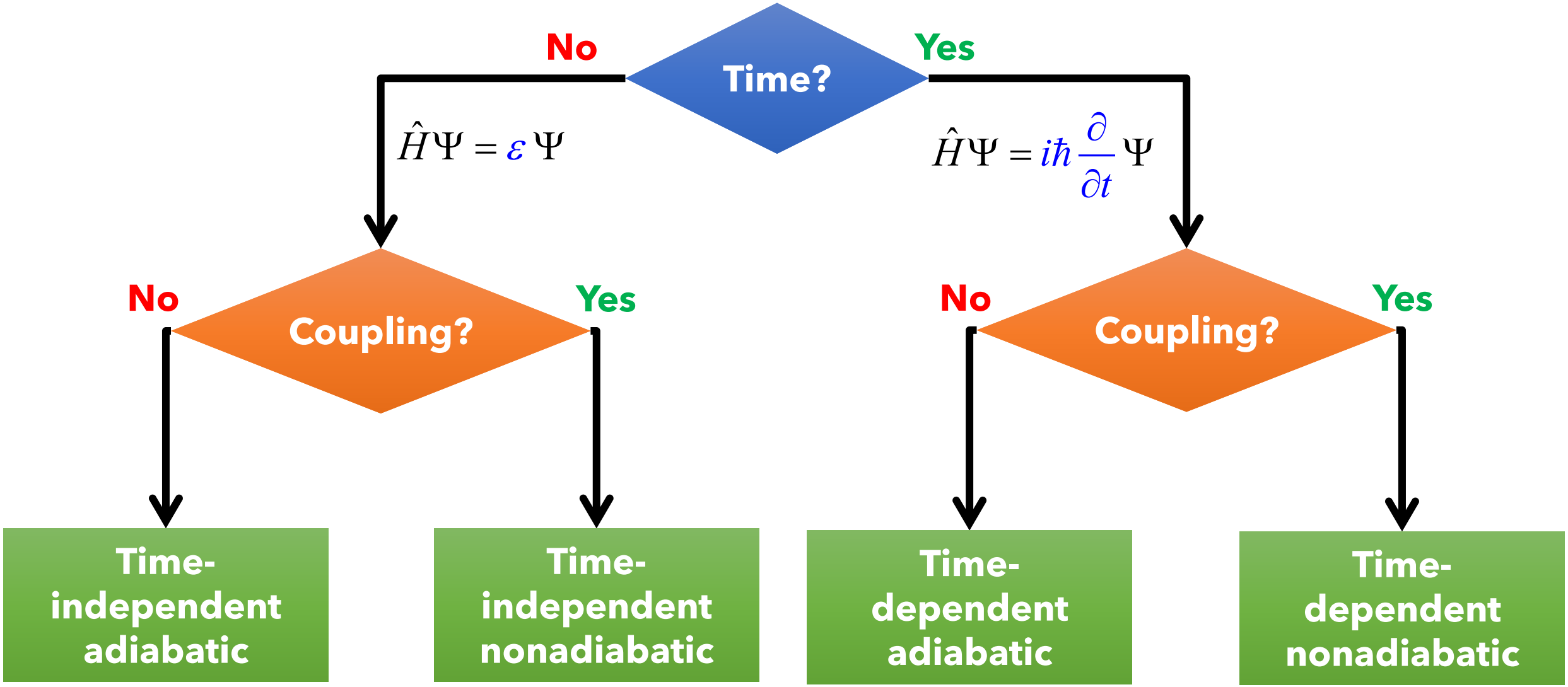
Electronic Schrödinger equation

$$\left(\hat{T}_{elec}(\mathbf{r}) + V(\mathbf{r},\mathbf{R})\right)\varphi(\mathbf{r};\mathbf{R}) = E(\mathbf{R})\varphi(\mathbf{r};\mathbf{R})$$

BO molecular wave function

$$\Psi^{BO}(\mathbf{R},\mathbf{r}) = \varphi(\mathbf{r};\mathbf{R})\chi(\mathbf{R})$$

Born-Oppenheimer-Huang formulation



Born-Oppenheimer-Huang formulation

Electronic Schrödinger equation

$$\left(\hat{T}_{elec} + V\right)\varphi_n = E_n\varphi_n$$

Nuclear Schrödinger equation

Adiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n = 0$$

Nonadiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Molecular wave function

$$\Psi = \varphi_n\chi_n$$

$$\Psi = \sum_m \varphi_n\chi_n$$

Adiabatic approximation

Born-Oppenheimer-Huang formulation

Electronic Schrödinger equation

$$\left(\hat{T}_{elec} + V\right)\varphi_n = E_n\varphi_n$$

Coupling terms

$$\hat{N}_{nm} = -\sum_{\alpha}\frac{\hbar^2}{2M_\alpha}\left[2\mathbf{F}_{mn}^{(\alpha)}\cdot\nabla_\alpha + G_{mn}^{(\alpha)}\right]$$

Nuclear Schrödinger equation

Adiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n = 0$$

Nonadiabatic

Time-independent

$$\left(\hat{T}_{nuc} + E_n - \varepsilon\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Time-dependent

$$\left(\hat{T}_{nuc} + E_n - i\hbar\partial_t\right)\chi_n + \sum_m \hat{N}_{nm}\chi_m = 0$$

Molecular wave function

$$\Psi = \varphi_n\chi_n$$

$$\Psi = \sum_m \varphi_n\chi_n$$

First-order nonadiabatic coupling vector

$$\mathbf{F}_{nm} = \begin{bmatrix} F_{nm,1,X} & F_{nm,1,Y} & F_{nm,1,Z} \\ F_{nm,2,X} & F_{nm,2,Y} & F_{nm,2,Z} \\ \vdots & \vdots & \vdots \\ F_{nm,N_{at},X} & F_{nm,N_{at},Y} & F_{nm,N_{at},Z} \end{bmatrix}$$

$$F_{nm,\alpha,X} = \left\langle \varphi_n \left| \frac{\partial \varphi_m}{\partial X_\alpha} \right\rangle \right.$$

$$= \int d\mathbf{r} \varphi_n^* \left(\mathbf{r};\mathbf{R}_\alpha\right) \frac{\partial \varphi_m \left(\mathbf{r};\mathbf{R}_\alpha\right)}{\partial X_\alpha}$$

$$\mathbf{F}_{mn}\left(\mathbf{R}\right) = \left\langle \varphi_m \left(\mathbf{r};\mathbf{R}\right) \middle| \nabla_{\mathbf{R}} \varphi_n \left(\mathbf{r};\mathbf{R}\right) \right\rangle_{\mathbf{r}}$$

For the more info, see the appendix to this presentation.

Second-order scalar coupling

$$G_{mn} = \begin{bmatrix} G_{mn,1} \\ G_{mn,2} \\ \vdots \\ G_{mn,N_{at}} \end{bmatrix} \qquad G_{mn,\alpha} = \left\langle \varphi_m \left| \frac{\partial^2 \varphi_n}{\partial X_\alpha^2} \right\rangle + \left\langle \varphi_m \left| \frac{\partial^2 \varphi_n}{\partial Y_\alpha^2} \right\rangle + \left\langle \varphi_m \left| \frac{\partial^2 \varphi_n}{\partial Z_\alpha^2} \right\rangle \right. \right. \right.$$

$$\begin{aligned} G_{mn}(\mathbf{R}) &= \left\langle \varphi_m(\mathbf{r};\mathbf{R}) \middle| \nabla_{\mathbf{R}}^2 \varphi_n(\mathbf{r};\mathbf{R}) \right\rangle_{\mathbf{r}} \\ &= \nabla \cdot \mathbf{F}_{mn}(\mathbf{R}) + \mathbf{F}_{mn}(\mathbf{R}) \cdot \mathbf{F}_{mn}(\mathbf{R}) \end{aligned}$$

Usually, G = 0 is assumed in trajectory-based nonadiabatic dynamics.

Adiabatic approximation

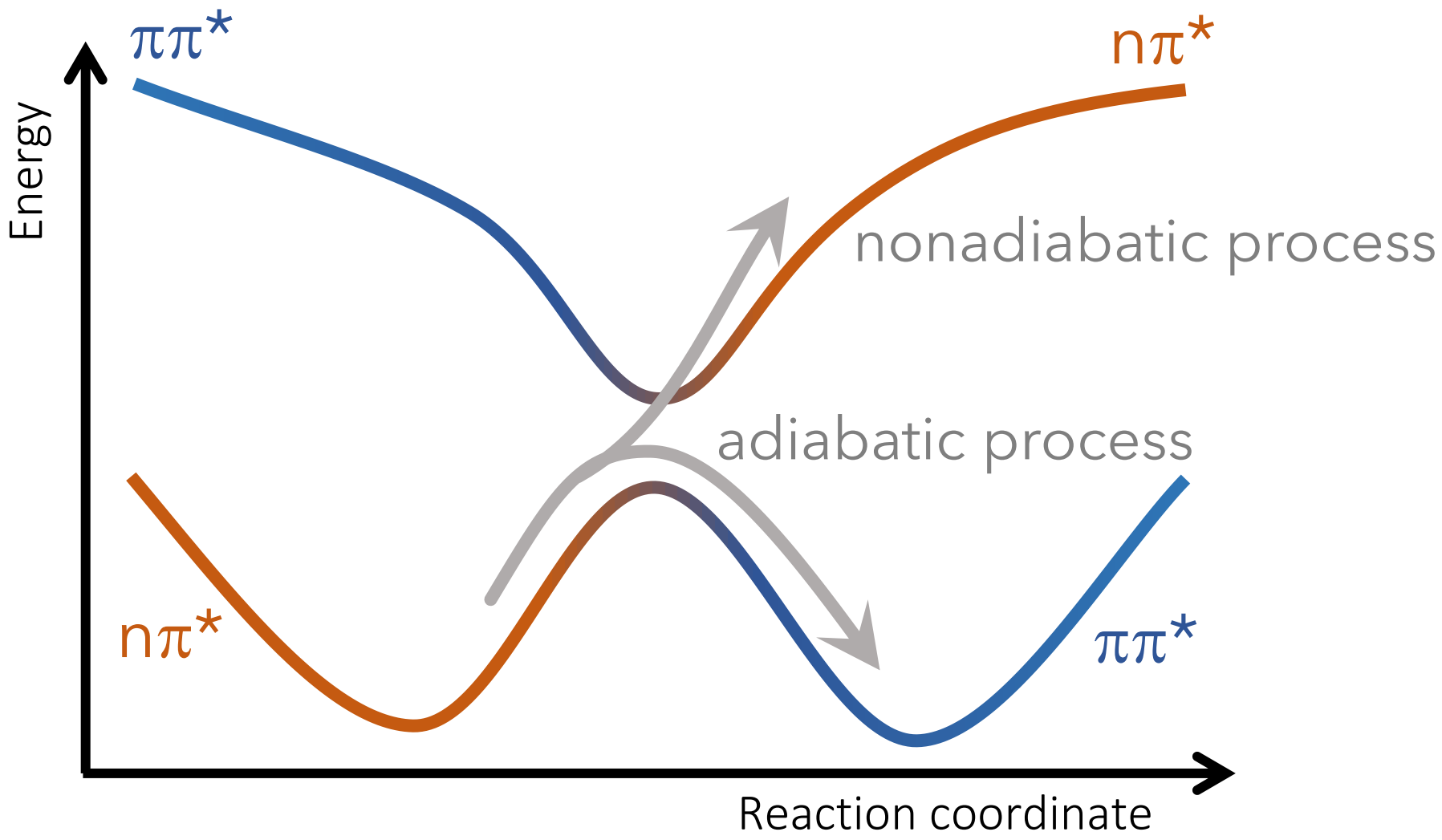
All coupling terms between electronic states are null.

$$\hat{N}_{nm}(\mathbf{R})\chi_n(\mathbf{R}) = 0$$

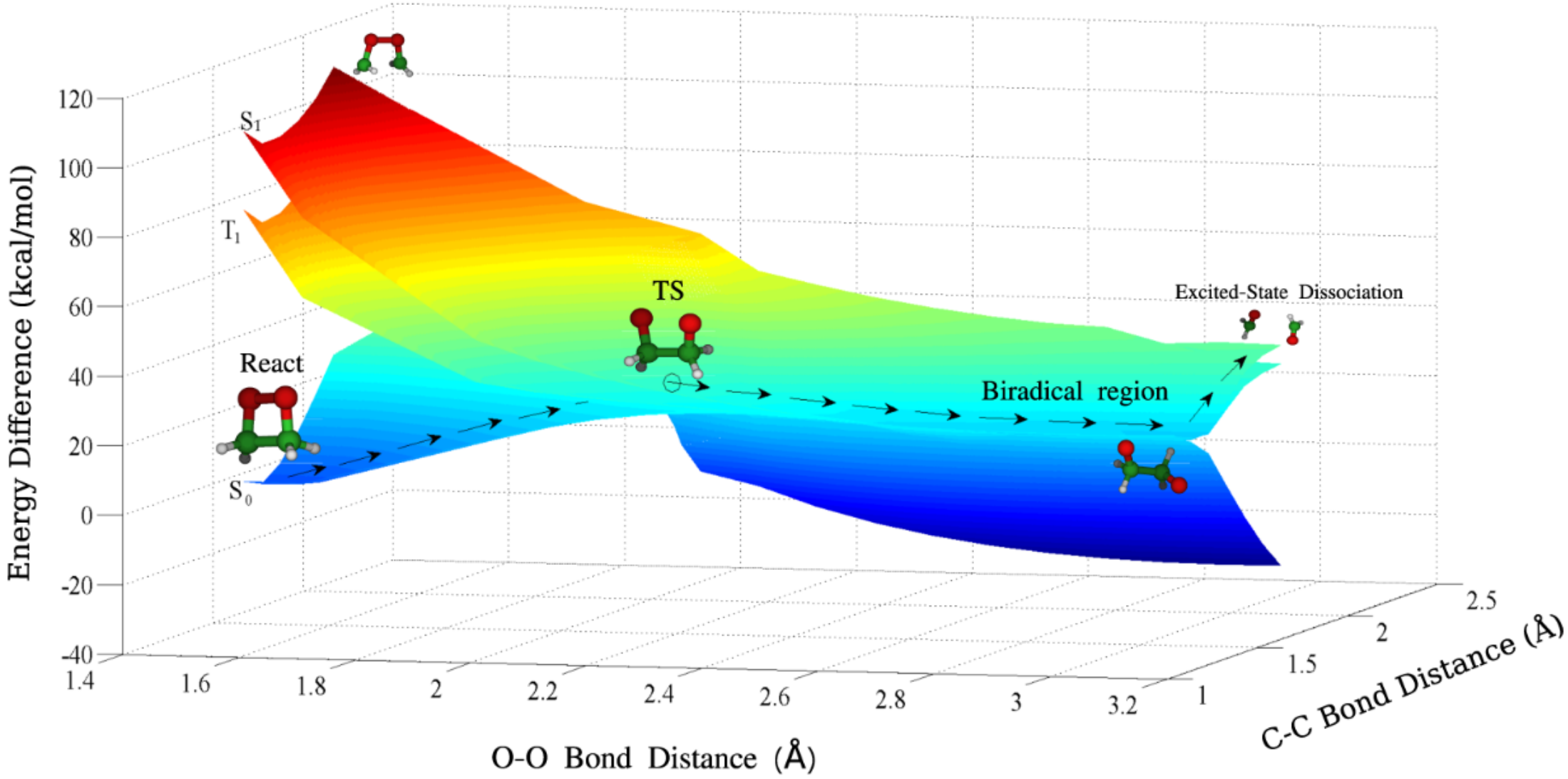
In practical terms, it means:

$$\left\langle \varphi_m \middle| \nabla^2_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} = 0$$

$$\left\langle \varphi_m \middle| \nabla_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} = 0$$


ππ*
nπ*
Energy
nonadiabatic process
adiabatic process
nπ*
ππ*
Reaction coordinate

1,2-Dioxetane decomposition (bioluminescence)



Farahani *et al*. *JCTC* **2013**, *9*, 5404

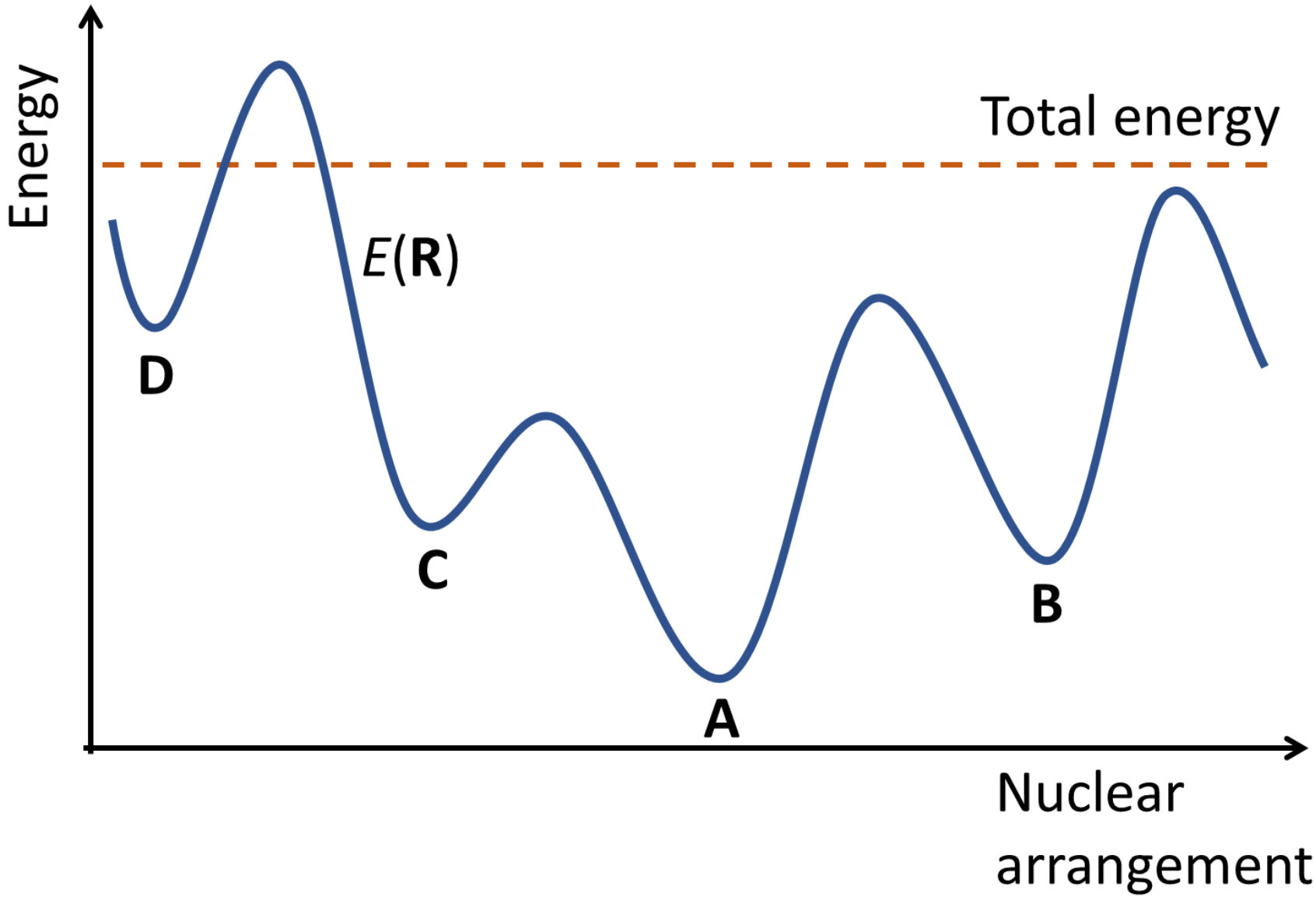
Riding the molecular roller coaster

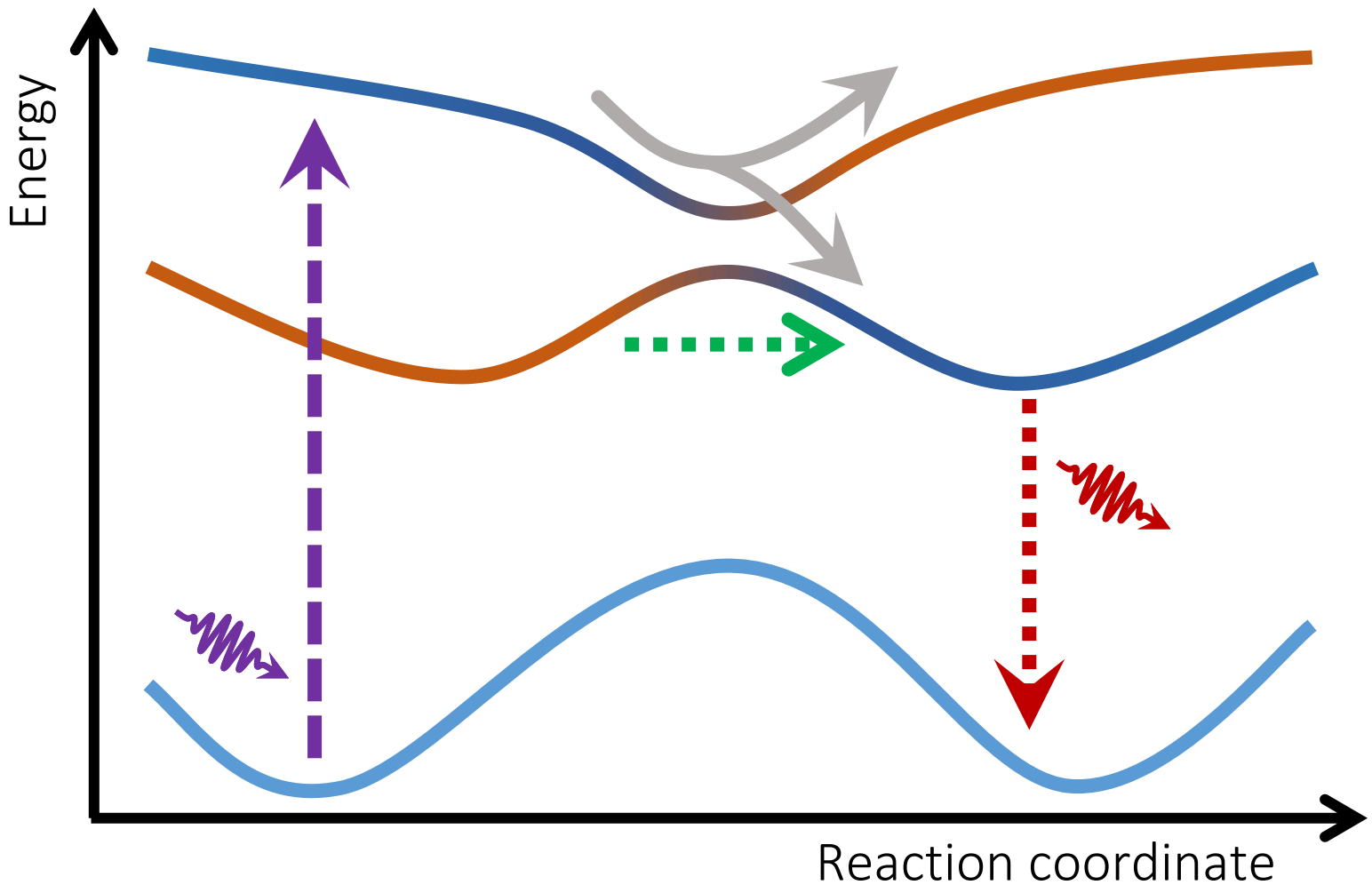
Laying down the ground rules

1. Each valley corresponds to a different set of molecules.

2. We can only move between two valleys by rearranging the nuclear positions. We cannot add or remove nuclei after the ride starts.

3. We can only move between valleys if the $E(\mathbf{R})$ remains smaller than the total energy.

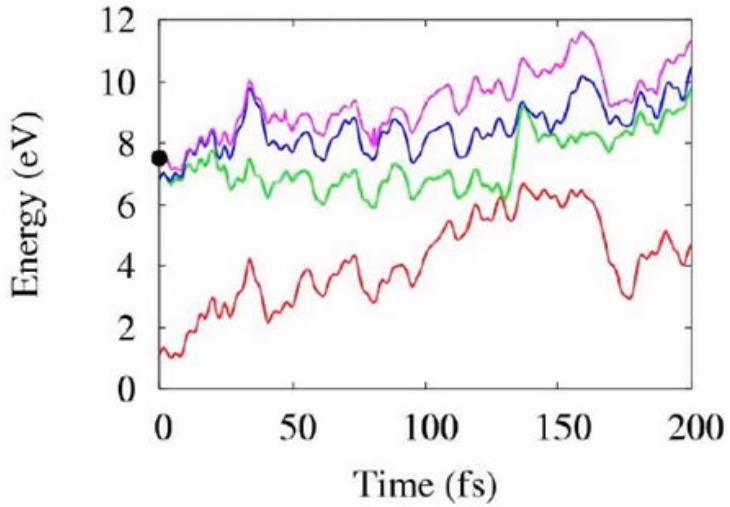

Energy
Total energy
E(R)
D
C
A
B
Nuclear
arrangement

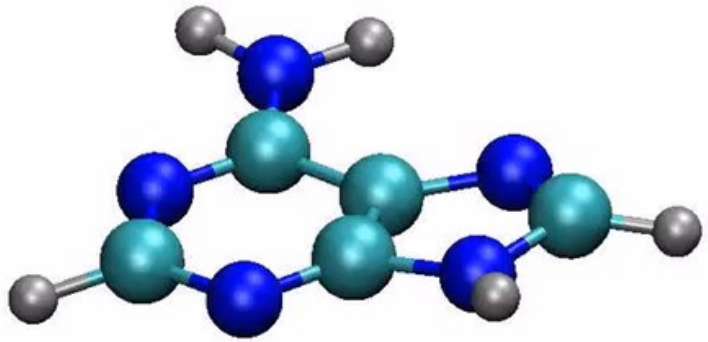


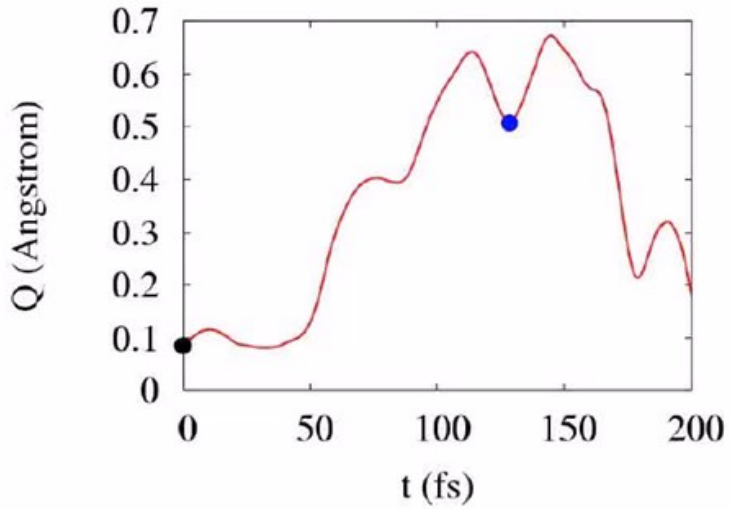
- Nuclear quantum delocalization (Tunneling)
- EM fields (photoabsorption, stimulated emission)
- Diabatic mixing (internal conversion, intersystem crossing)
- Vacuum fluctuations (fluorescence, phosphorescence)

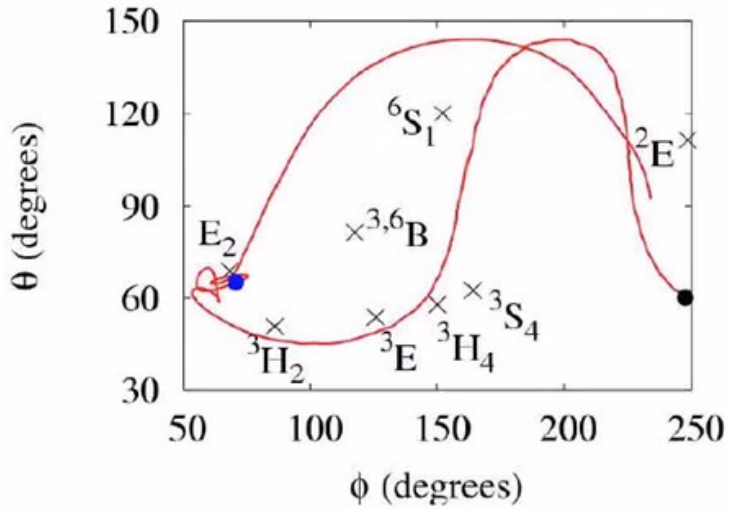
Setting the quantum patches

4. A proton can tunnel to the other valley even if the total energy is slightly lower than the barrier maximum. We know the tunneling probability.
5. If the track bifurcates during the reaction, the molecule can follow either, releasing or absorbing heat, with known probabilities.
6. If the molecule is in a lower track, it can be promoted to an upper track by absorbing light. We know the probability of populating each higher track.
7. If the molecule is in an upper track, it can spontaneously go to the lower track by emitting light. We know the probability of this emission happening.









youtube.com/user/mbarbatti

Quantum Chemistry

Time-independent BO adiabatic formulation

Nuclear Schrödinger equation

$$\left(\hat{T}_{nuc}\left(\mathbf{R}\right)+E_n\left(\mathbf{R}\right)\right)\chi_n\left(\mathbf{R}\right)=\varepsilon_n\chi_n\left(\mathbf{R}\right)$$

Electronic Schrödinger equation

$$\left(\hat{T}_{elec}\left(\mathbf{r}\right)+\hat{V}\left(\mathbf{r},\mathbf{R}\right)\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)=E_n\left(\mathbf{R}\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)$$

BO molecular wave function

$$\Psi_n^{BO}\left(\mathbf{R},\mathbf{r}\right)=\varphi_n\left(\mathbf{r};\mathbf{R}\right)\chi_n\left(\mathbf{R}\right)$$

Quantum chemistry's primary goal

Given a nuclear geometry **R**, solve the electronic Schrödinger equation in the adiabatic approximation

$$\left(\hat{T}_{elec}\left(\mathbf{r}\right)+\hat{V}\left(\mathbf{r},\mathbf{R}\right)\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)=E_n\left(\mathbf{R}\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)$$

to get electronic energies E_n and electronic wave function φ_n for state n.

Quantum chemistry's methods

Wave-function based

$$|\varphi_n\rangle$$

- Hartree-Fock
- MP
- CC
- CASSCF
- CASPT2
- CI
- ADC
- …

Density based

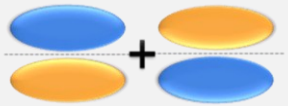
$$\rho_n = |\varphi_n\rangle\langle\varphi_n|$$

- DFT
- DFTB
- TDDFT
- TDA
- DFT-CI
- REKS
- BSE
- …

Quantum chemistry's bottom-up approach

4. Use WF to get the final electronic WF or density

3. Use MOs to build electronic wave function (WF) guess

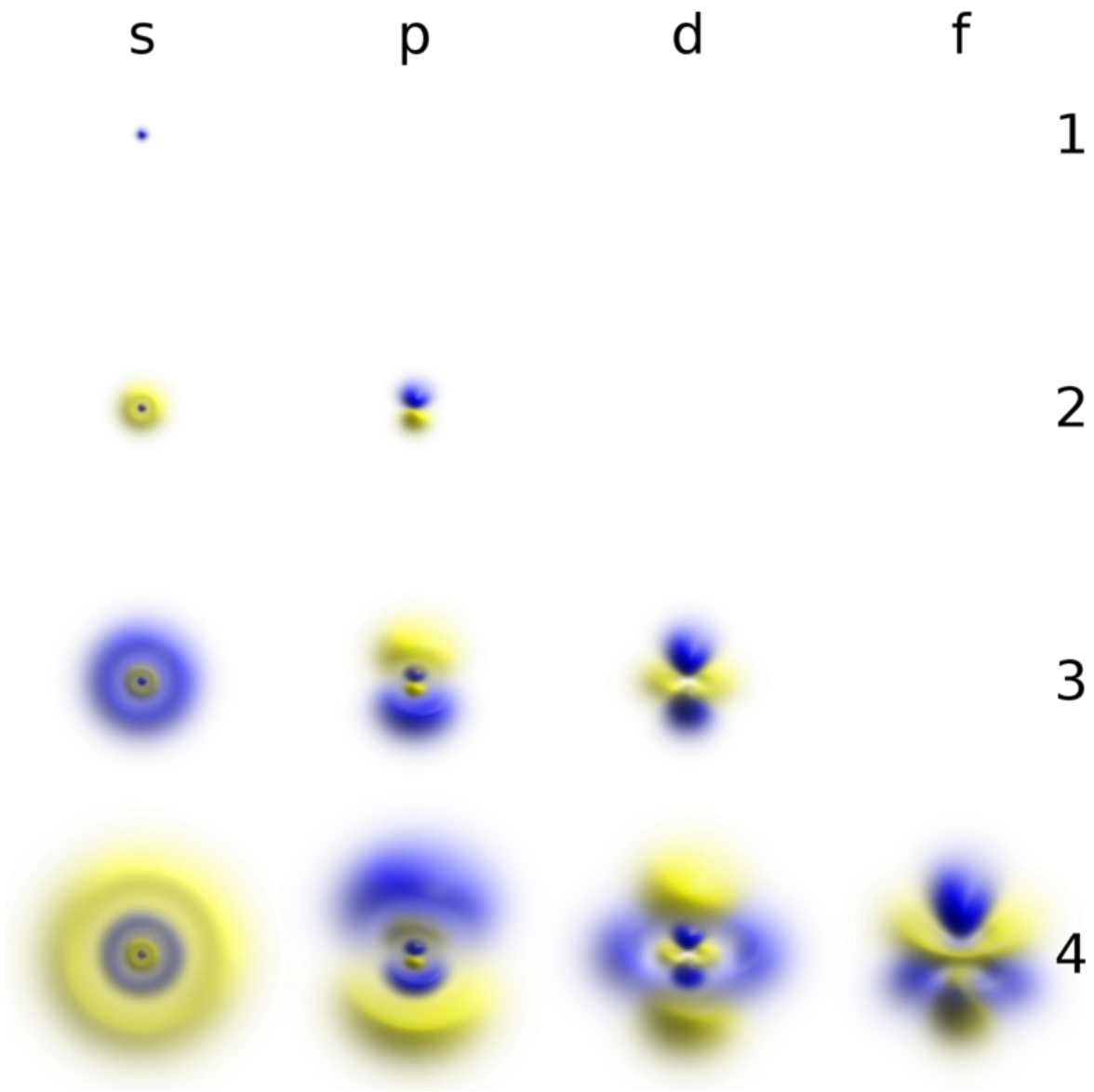


2. Use AOs to build molecular orbitals (MO)

1. Define atomic orbital (AO) basis

1. Define AO basis

AOs are hydrogen-like orbitals



Gaussian basis sets

$$G_{nlm}(r,\theta,\psi) = N_n \underbrace{r^{n-1}e^{-\alpha r^2}}_{\text{radial part}} \underbrace{Y_l^m(\theta,\psi)}_{\text{angular part}}$$

Example: 1s AO for hydrogen using STO-3G basis set:

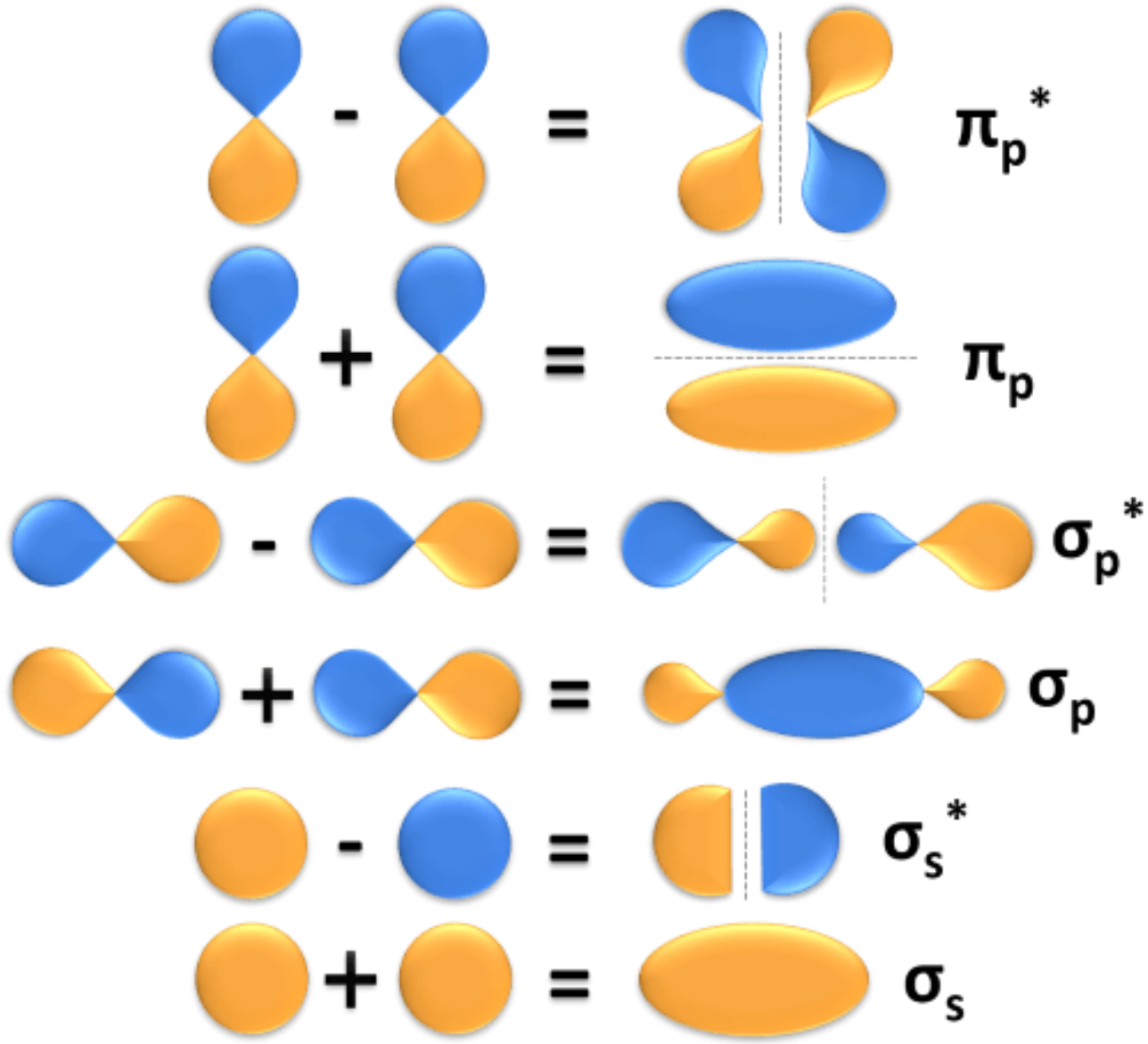
$$\phi_{1s}(r) = \sum_{j=1}^{3} d_j G_{100}(r;\alpha_j)$$

j	α_j	d_j
1	0.1688	0.4
2	0.6239	0.7
3	3.425	1.3

- STO-3G
- 6-31G(d,p)
- cc-pVDZ
- SVP
- ...

www.basissetexchange.org

2. Use AOs to build MOs

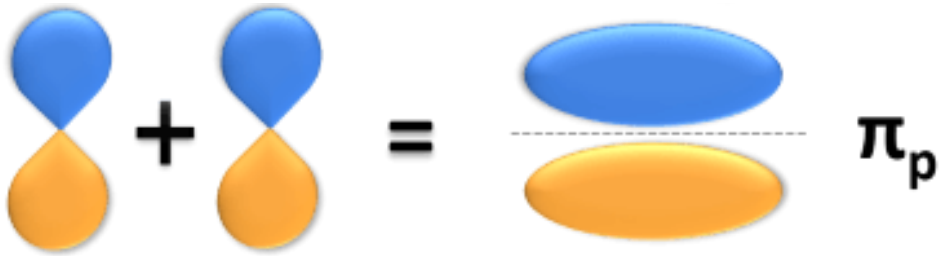


LCAO: linear combination of atomic orbitals

Given a basis of AOs $\{\phi_\mu\}$, the MOs ψ_i are written as

$$\psi_i(\mathbf{r}) = \sum_\mu c_{\mu i}\phi_\mu(\mathbf{r})$$

For example



To take the electron spin into account, we define spin orbitals

$$\eta_i(\mathbf{x}) = \psi_i(\mathbf{r})\sigma_i(\omega) \quad \mathbf{x} = (r, \omega)$$

ω is spin up or down.

$\psi_i(\mathbf{r})$ can hold **two** electrons (up and down)

$\eta_i(\mathbf{x})$ can hold **one** electron (up or down)

known

$$\eta_i(\mathbf{x}) = \left(\sum_{\mu} c_{\mu i} \phi_{\mu}(\mathbf{r}) \right) \sigma_i(\omega)$$

unknown

just for bookkeeping

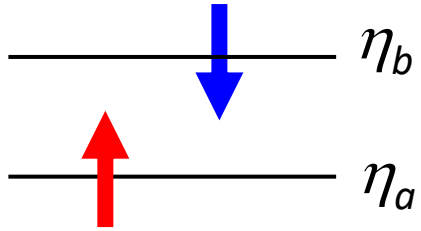
3. Use MOs to build WF guess

Pauli Exclusion Principle

$$\varphi\left(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_k, \mathbf{x}_l, \cdots, \mathbf{x}_{N_{el}}\right) = -\varphi\left(\mathbf{x}_1, \mathbf{x}_2, \cdots, \mathbf{x}_l, \mathbf{x}_k, \cdots, \mathbf{x}_{N_{el}}\right)$$

Wave function guess for two electrons

Consider two electrons, one up in spin-orbital η_a and one down in η_b



First wave function guess:

$$\varphi_{guess1}(\mathbf{x}_1, \mathbf{x}_2) = \eta_a(\mathbf{x}_1)\eta_b(\mathbf{x}_2)$$

Switch the electrons:

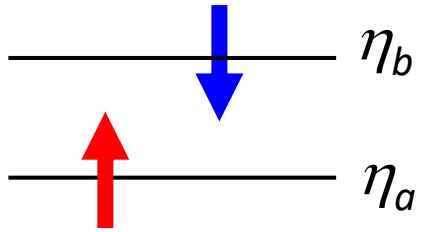
$$\varphi_{guess1}(\mathbf{x}_2, \mathbf{x}_1) = \eta_a(\mathbf{x}_2)\eta_b(\mathbf{x}_1)$$

φ_{guess1} **does not satisfy** Pauli exclusion principle:

$$\varphi_{guess1}(\mathbf{x}_1, \mathbf{x}_2) = \varphi_{guess1}(\mathbf{x}_2, \mathbf{x}_1)$$

Wave function guess for two electrons

Consider two electrons, one up in spin-orbital η_a and one down in η_b



Second wave function guess:

$$\varphi_{guess2}(\mathbf{x}_1,\mathbf{x}_2)=\frac{1}{\sqrt{2}}\left[\eta_a(\mathbf{x}_1)\eta_b(\mathbf{x}_2)-\eta_b(\mathbf{x}_1)\eta_a(\mathbf{x}_2)\right]$$

Switch the electrons:

$$\varphi_{guess2}(\mathbf{x}_2,\mathbf{x}_1)=\frac{1}{\sqrt{2}}\left[\eta_a(\mathbf{x}_2)\eta_b(\mathbf{x}_1)-\eta_b(\mathbf{x}_2)\eta_a(\mathbf{x}_1)\right]$$

φ_{guess2} **satisfies** Pauli exclusion principle:

$$\varphi_{guess2}(\mathbf{x}_1,\mathbf{x}_2)=-\varphi_{guess2}(\mathbf{x}_2,\mathbf{x}_1)$$

$$\varphi_{guess\,2}\left(\mathbf{x}_1,\mathbf{x}_2\right)=\frac{1}{\sqrt{2}}\left[\eta_a\left(\mathbf{x}_1\right)\eta_b\left(\mathbf{x}_2\right)-\eta_b\left(\mathbf{x}_1\right)\eta_a\left(\mathbf{x}_2\right)\right]$$

can be written as the determinant of the matrix

$$\varphi_{guess\,2}\left(\mathbf{x}_1,\mathbf{x}_2\right)=\frac{1}{\sqrt{2}}\det\begin{bmatrix}\eta_a\left(\mathbf{x}_1\right) & \eta_b\left(\mathbf{x}_1\right)\\ \eta_a\left(\mathbf{x}_2\right) & \eta_b\left(\mathbf{x}_2\right)\end{bmatrix}$$

Such an antisymmetric wave function guess is called a **Slater determinant**.

Multiple electron Slater determinant

$$\Phi\left(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N\right)=\left(N!\right)^{-1/2}\det\begin{bmatrix}\eta_a\left(\mathbf{x}_1\right) & \eta_b\left(\mathbf{x}_1\right) & \cdots & \eta_K\left(\mathbf{x}_1\right)\\ \eta_a\left(\mathbf{x}_2\right) & \eta_b\left(\mathbf{x}_2\right) & \cdots & \eta_K\left(\mathbf{x}_2\right)\\ \vdots & \vdots & \cdots & \vdots\\ \eta_a\left(\mathbf{x}_N\right) & \eta_b\left(\mathbf{x}_N\right) & \cdots & \eta_K\left(\mathbf{x}_N\right)\end{bmatrix}$$

Factorial:

$4!=4\times3\times2\times1=24$

$0!=1$

Methods like HF and DFT use a single Slater determinant to guess the electronic wave function.

$$\varphi_{guess}\left(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N\right)=\Phi\left(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N\right)$$

The unknowns are $c_{\mu i}$ from MOs.

Methods like CASSCF and CI use multiple Slater determinants to guess the electronic wave function.

$$\varphi_{guess}\left(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N\right)=\sum_L C_L\Phi_L\left(\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_N\right)$$

The unknowns are $c_{\mu i}$ and C_L.

4. Use WF guess to get final WF or density

Solving the time-independent Schrödinger eq.

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

expand $$|\psi\rangle = \sum_i C_i |\phi_i\rangle$$ ← known

unknown

replace $$\hat{H}\sum_i C_i |\phi_i\rangle = E\sum_i C_i |\phi_i\rangle$$

project & integrate $$\sum_i C_i \langle\phi_j|\hat{H}|\phi_i\rangle = EC_j$$

$$\sum_{i=1}^{N} C_i H_{ji} = EC_j \qquad \text{where } H_{ji} = \langle \phi_j | H | \phi_i \rangle$$

Suppose $N = 2$:

$$C_1 H_{11} + C_2 H_{12} = EC_1$$
$$C_1 H_{21} + C_2 H_{22} = EC_2$$

Rewrite as a matrix multiplication:

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E \begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

Rewrite as a matrix equation:

$$\mathbf{HC} = E\mathbf{C}$$

Most quantum chemical methods can be rewritten as

$$\mathbf{HC} = E\mathbf{C}$$

Usually, **H** depends on E and **C**

$$\mathbf{H}\left(E,\mathbf{C}\right)\mathbf{C} = E\mathbf{C}$$

everything is unknown!

Such a problem is solved with a self-consistent field approach (SCF):

1. Guess an approximated $E^{(0)}$ and $\mathbf{C}^{(0)}$ and solve

$$\mathbf{H}\left(E^{(0)},\mathbf{C}^{(0)}\right)\mathbf{C}^{(1)} = E^{(1)}\mathbf{C}^{(1)}$$

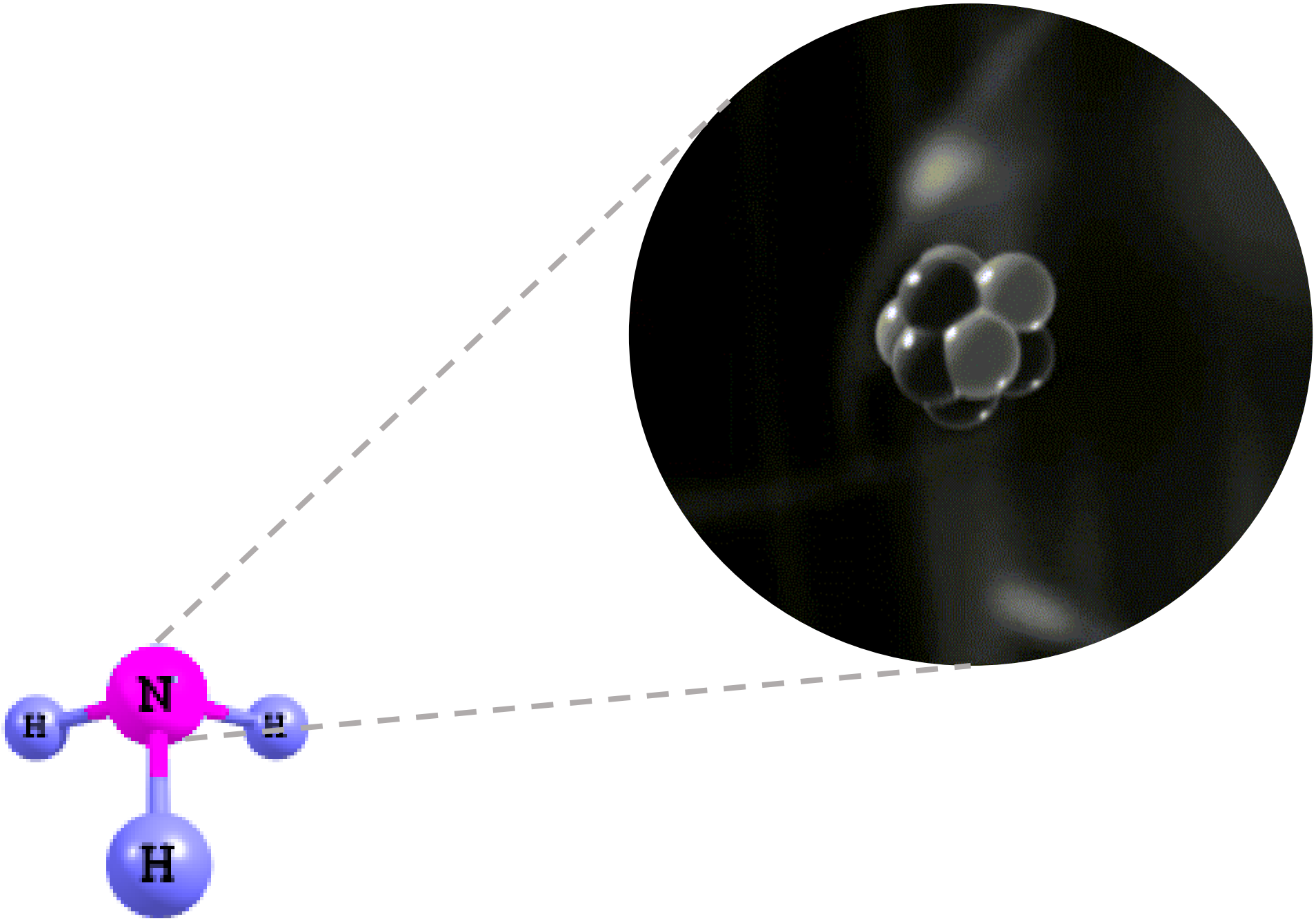
2. Use $E^{(1)}$ and $\mathbf{C}^{(1)}$ to solve

$$\mathbf{H}\left(E^{(1)},\mathbf{C}^{(1)}\right)\mathbf{C}^{(2)} = E^{(2)}\mathbf{C}^{(2)}$$

3. Continue the iterations until

$$E^{(N)} = E^{(N-1)}$$

A note about molecular time


N
H
H
H

There's no time dependency.

A molecule is not rotating or vibrating!
Electrons are not orbiting!

$$\left(\hat{T}_{nuc}\left(\mathbf{R}\right)+E_n\left(\mathbf{R}\right)\right)\chi_n\left(\mathbf{R}\right)=\varepsilon_n\chi_n\left(\mathbf{R}\right)$$

$$\left(\hat{T}_{elec}\left(\mathbf{r}\right)+\hat{V}\left(\mathbf{r},\mathbf{R}\right)\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)=E_n\left(\mathbf{R}\right)\varphi_n\left(\mathbf{r};\mathbf{R}\right)$$

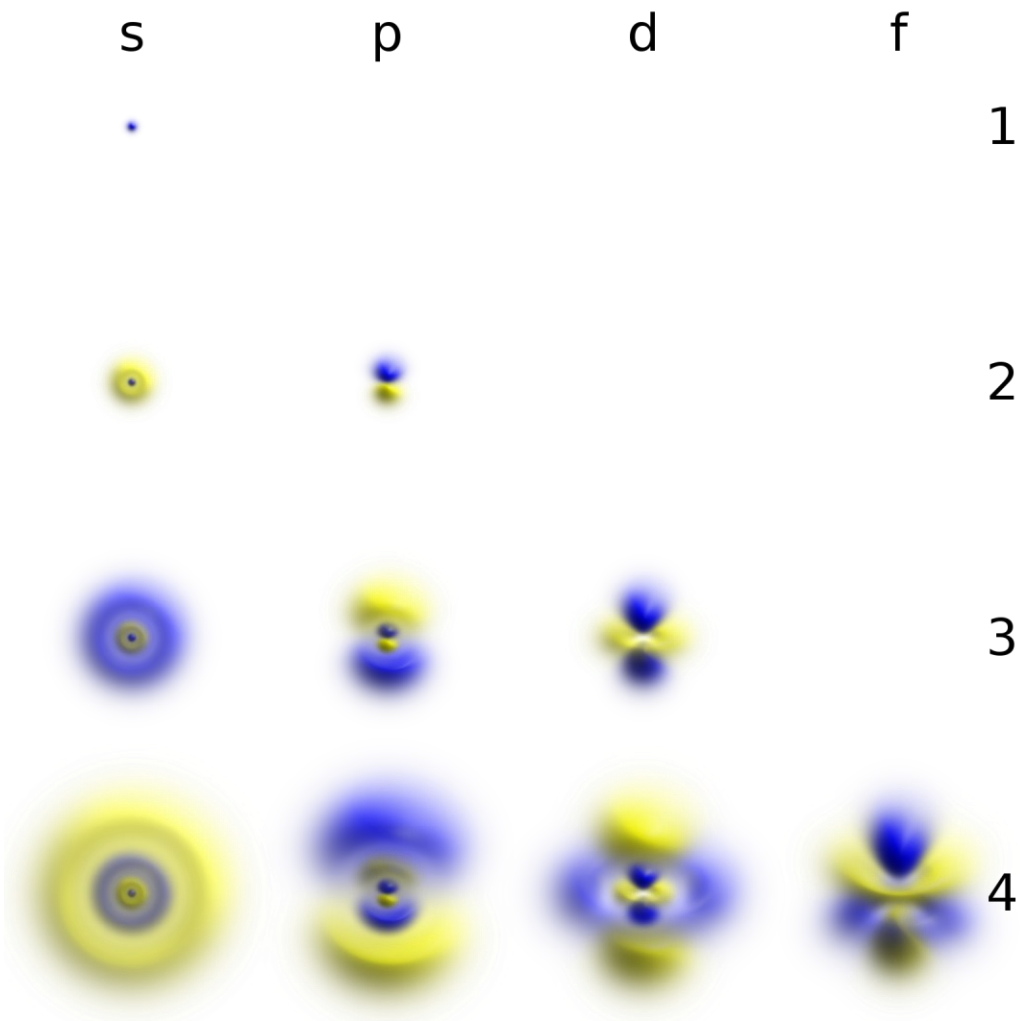
Barbatti, Aeon Magazine **2023**, tinyurl.com/emptyatom

For a stationary state

- Momentum = wave function steepness $\left[-i\hbar\nabla\psi\right]$
- Kinetic energy = field stress (how much the wave function differs from the mean) $\left[-\frac{\hbar^2}{2M}\nabla^2\psi\right]$
- Spin = curl of the electron density * $\left[\frac{\hbar}{4}\nabla\times\left(\tilde{\psi}^{\dagger}\boldsymbol{\sigma}\tilde{\psi}\right)\right]$

* Ohanian. *Am J Phys* **1986,** *54*, 500

- Angular momentum = wave function blobs and nodes



"**Electronic correlation** is the interaction between electrons in the electronic structure of a quantum system. The correlation energy is a measure of how much the **movement** of one electron is influenced by the presence of all other electrons."

- Wikipedia

"**Electron correlation** is the adjustment of electron **motion** to the instantaneous (as opposed to time-averaged) positions of all the electrons in a molecular entity."

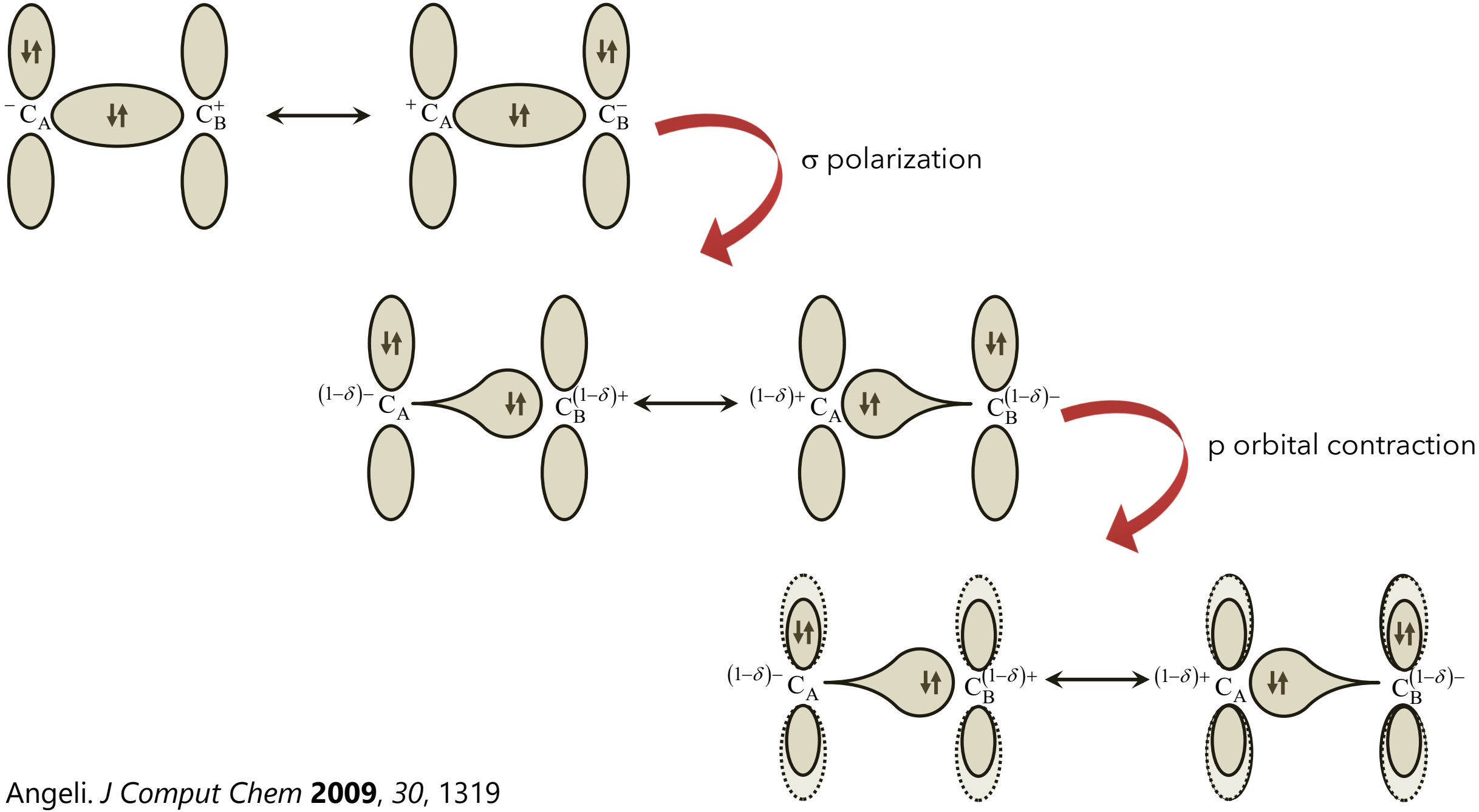
- IUPAC Gold Book

Which motion are they talking about?

Do orbitals exist?

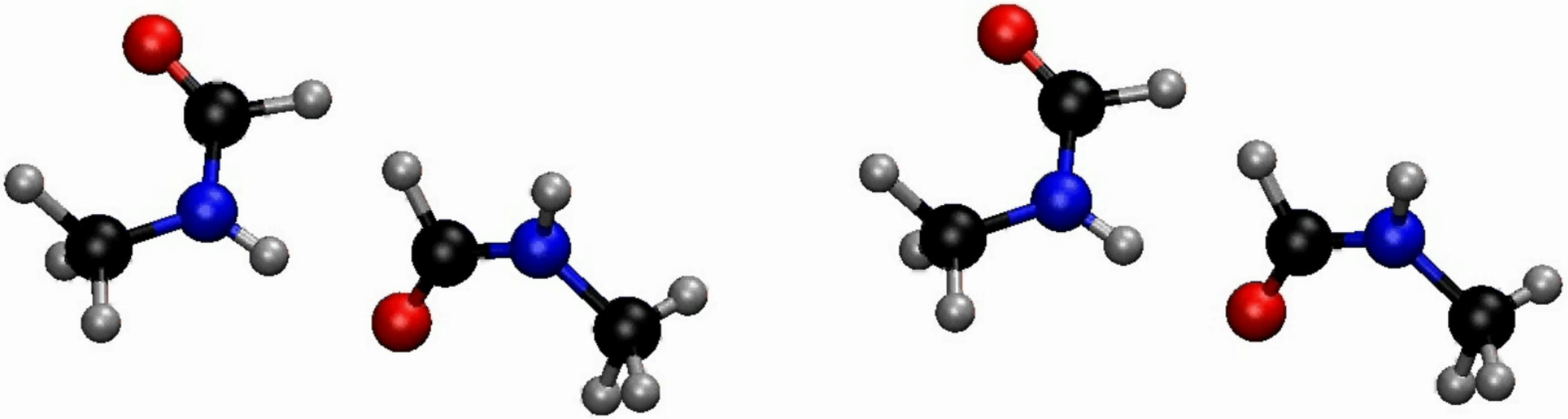
$$\varphi(\mathbf{r};\mathbf{R}) = f\left(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N; \mathbf{R}\right) \quad \mathbf{x}_i = \mathbf{r}_i \omega_i$$

$$\varphi(\mathbf{r};\mathbf{R}) = A\left\{\phi_1(\mathbf{x}_1;\mathbf{R})\phi_2(\mathbf{x}_2;\mathbf{R})\ldots\phi_N(\mathbf{x}_N;\mathbf{R})\right\}$$



Angeli. *J Comput Chem* **2009**, *30*, 1319

Time becomes important again during chemical reactions or field interactions



Crespo-Otero *et al. PCCP* **2014,** *16*, 18877

To know more:

Introduction to quantum chemistry:

- Jensen, *Introduction to Computational Chemistry*. **2017**

About molecular time

- Barbatti, Aeon Magazine **2023**, tinyurl.com/emptyatom
- Minute physics, https://youtu.be/W2Xb2GFK2yc

Appendix:
Gradients and Hessians

Gradients and Hessian matrices

In addition to electronic energies E_n, wave functions φ_n, and densities ρ_n, quantum chemistry also aims to get:

- Electronic energy gradient $\mathbf{g}_n$
- Electronic energy Hessian $\mathbf{H}_n$

Electronic energy gradient

$$\mathbf{g}_n = \nabla E_n = \begin{pmatrix} \frac{\partial E_n}{\partial X_1} & \frac{\partial E_n}{\partial Y_1} & \frac{\partial E_n}{\partial Z_1} \\ \vdots & \vdots & \vdots \\ \frac{\partial E_n}{\partial X_{N_{at}}} & \frac{\partial E_n}{\partial Y_{N_{at}}} & \frac{\partial E_n}{\partial Z_{N_{at}}} \end{pmatrix}$$

Electronic force acting on the nuclei

$$\mathbf{F}_n = -\nabla E_n$$

At a geometry of minimum or maximum energy,

$$\mathbf{F}_n = 0$$

Electronic energy Hessian

$$\mathbf{H}_n = \nabla^2 E_n = \begin{pmatrix} \frac{\partial^2 E_n}{\partial X_1 \partial X_1} & \frac{\partial^2 E_n}{\partial X_1 \partial Y_1} & \cdots & \frac{\partial^2 E_n}{\partial X_1 \partial Z_{N_{at}}} \\ \frac{\partial^2 E_n}{\partial Y_1 \partial X_1} & \frac{\partial^2 E_n}{\partial Y_1 \partial Y_1} & \cdots & \frac{\partial^2 E_n}{\partial Y_1 \partial Z_{Nat}} \\ \vdots & \vdots & \cdots & \vdots \\ \frac{\partial^2 E_n}{\partial Z_{N_{at}} \partial X_1} & \frac{\partial^2 E_n}{\partial Z_{N_{at}} \partial Y_1} & \cdots & \frac{\partial^2 E_n}{\partial Z_{N_{at}} \partial Z_{N_{at}}} \end{pmatrix}$$

Used to find the vibrational normal modes

At a geometry of minimum $\mathbf{H}_n > 0$