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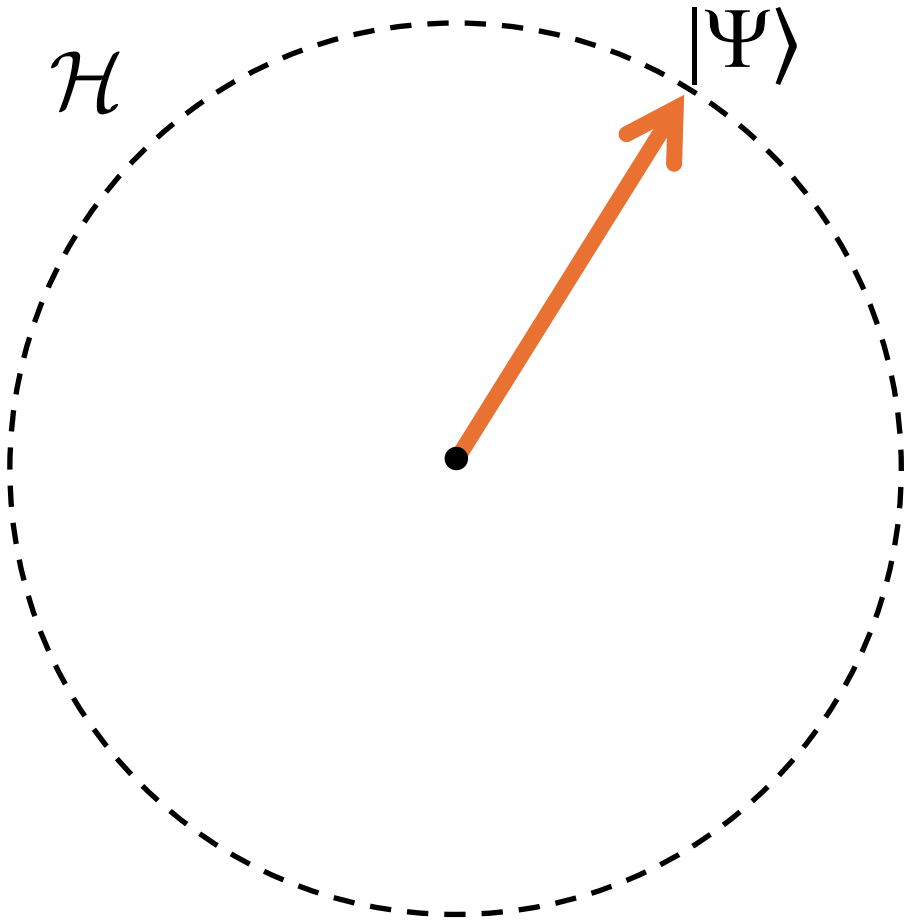
Nonadiabatic Molecular Dynamics: Concepts, Methods, and Emerging Tools

I – Quantum Mechanics

The quantum state

Quantum State in the Hilbert Space



The number of dimensions is the number of possible outputs.*

* If the energy levels are not degenerate

tinyurl.com/hilbertspace

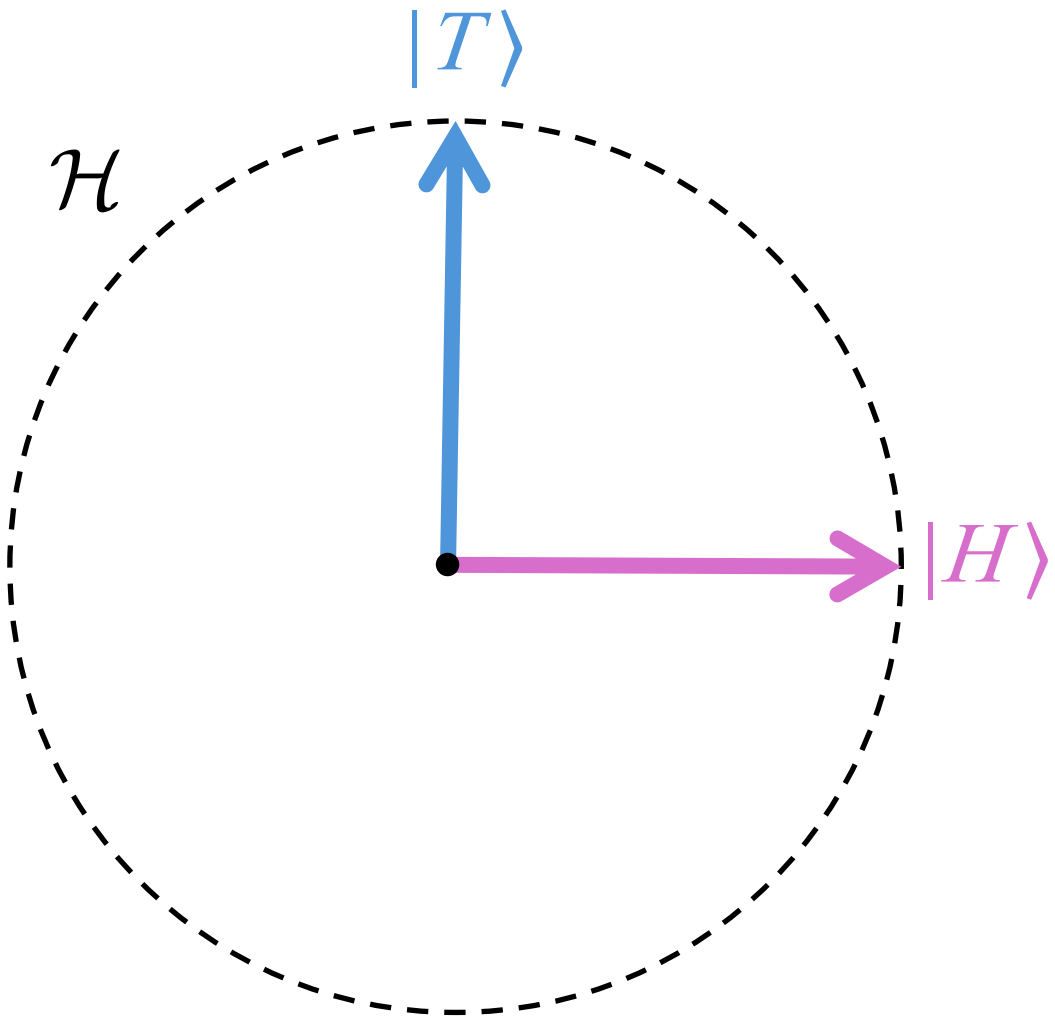
1 Coin

Head

Tail

2 outputs

Observables



Any observable is represented as a self-adjoint operator in $\mathcal{H}$

Example: Observable "Side"

$$\hat{S} = \hat{S}^\dagger$$

$$\hat{S}|H\rangle = h|H\rangle$$

$$\hat{S}|T\rangle = t|T\rangle$$

$$t \in \mathbb{R}$$

$$\langle H|T\rangle = 0$$

$$\langle H|H\rangle = \langle T|T\rangle = 1$$

$$|H\rangle\langle H| + |T\rangle\langle T| = \hat{\mathrm{I}}$$

Commutation relations

$$\hat{S}\hat{R}|\Psi\rangle = \hat{R}\hat{S}|\Psi\rangle$$

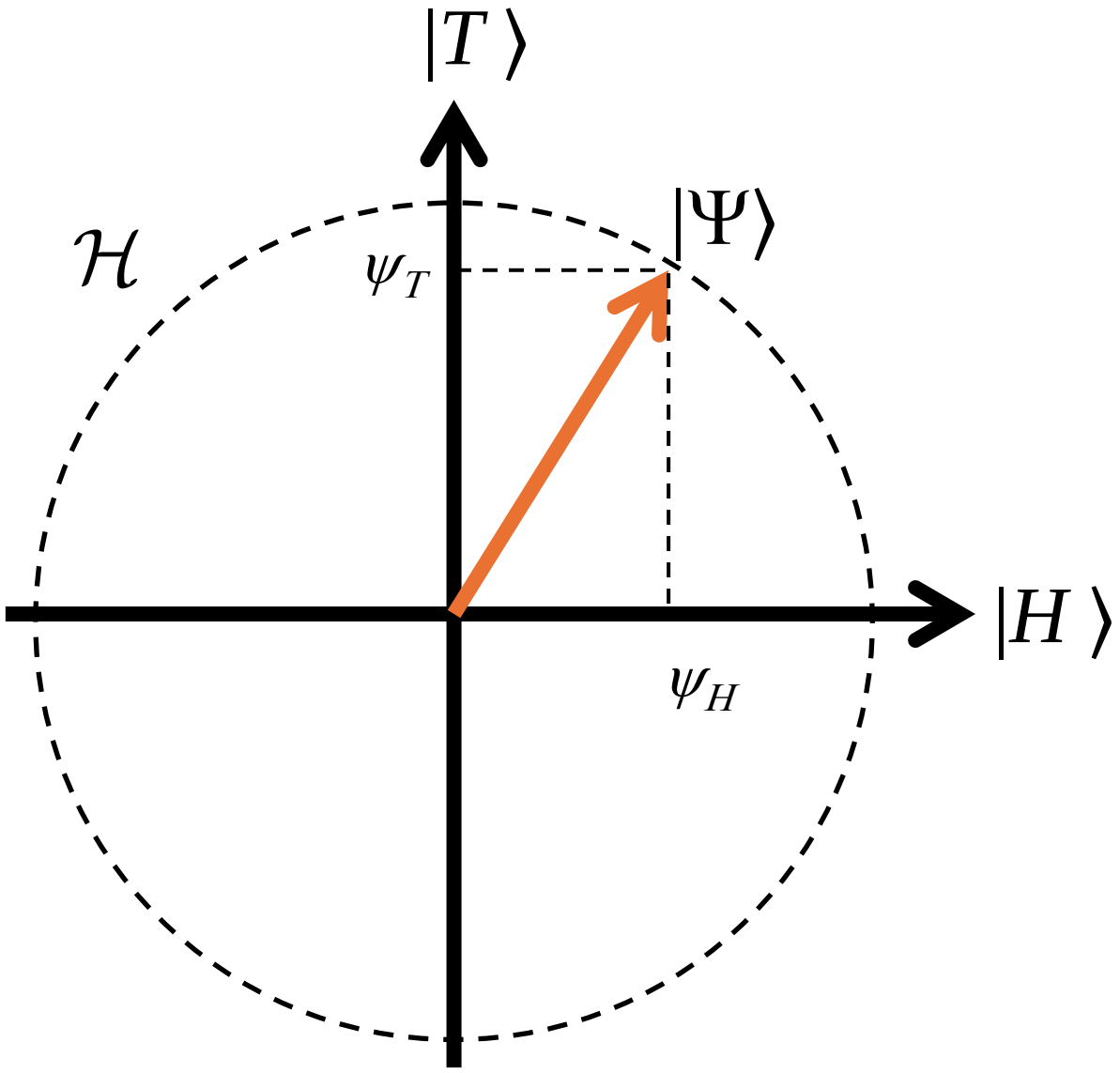
The system **can** have well-defined values for the observables R and S at same time

$$\hat{S}\hat{R}|\Psi\rangle \neq \hat{R}\hat{S}|\Psi\rangle$$

The system **cannot** have well-defined values for the observables R and S at same time

This property leads to the Heisenberg uncertainty principle for non-commuting observables

Basis projection & Superposition



Inner product

$$\psi_H = \langle H | \cdot | \Psi \rangle = \langle H | \Psi \rangle$$

$$\psi_T = \langle T | \cdot | \Psi \rangle = \langle T | \Psi \rangle$$

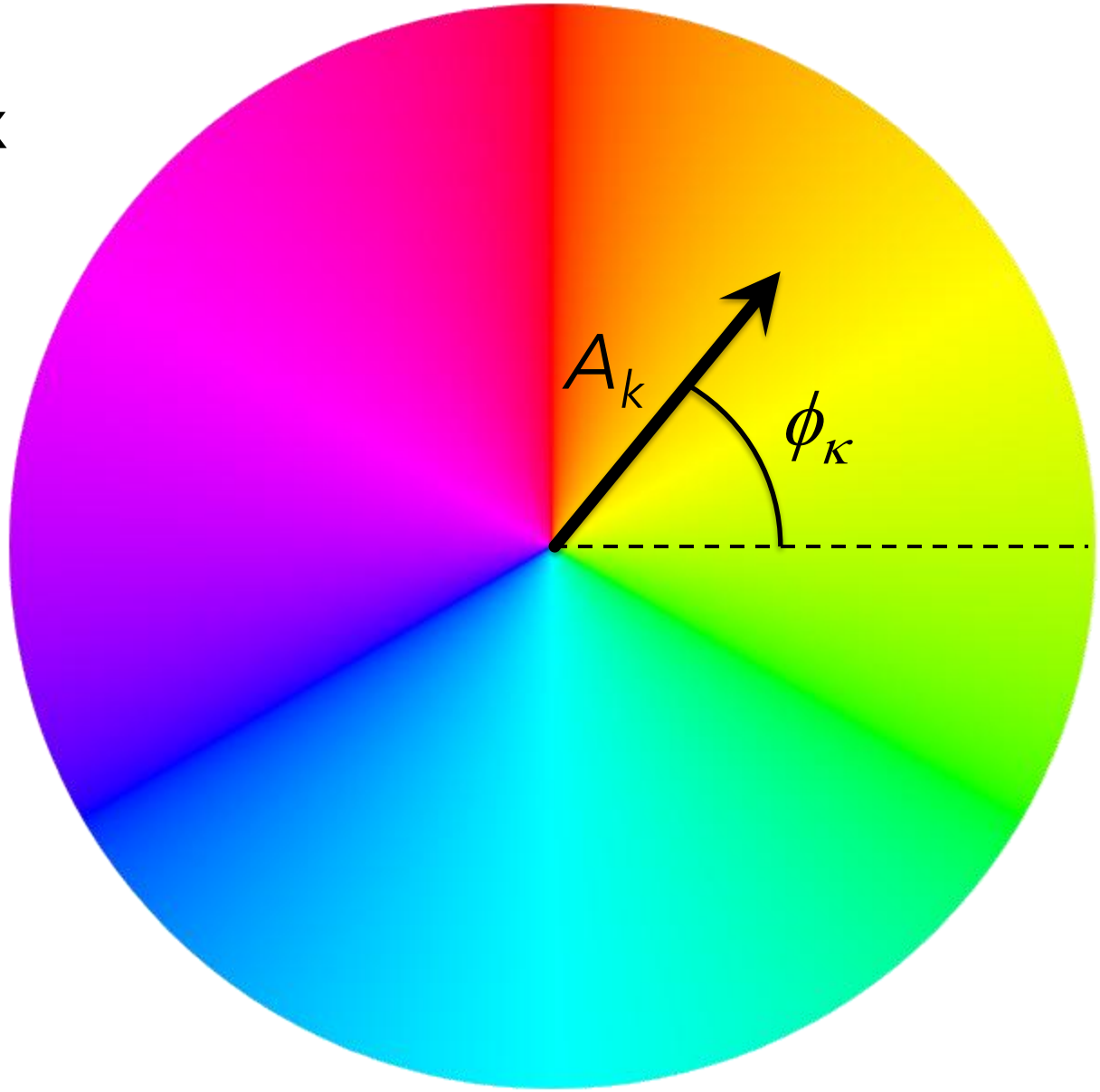
Superposition

$$|\Psi\rangle = \psi_H |H\rangle + \psi_T |T\rangle$$

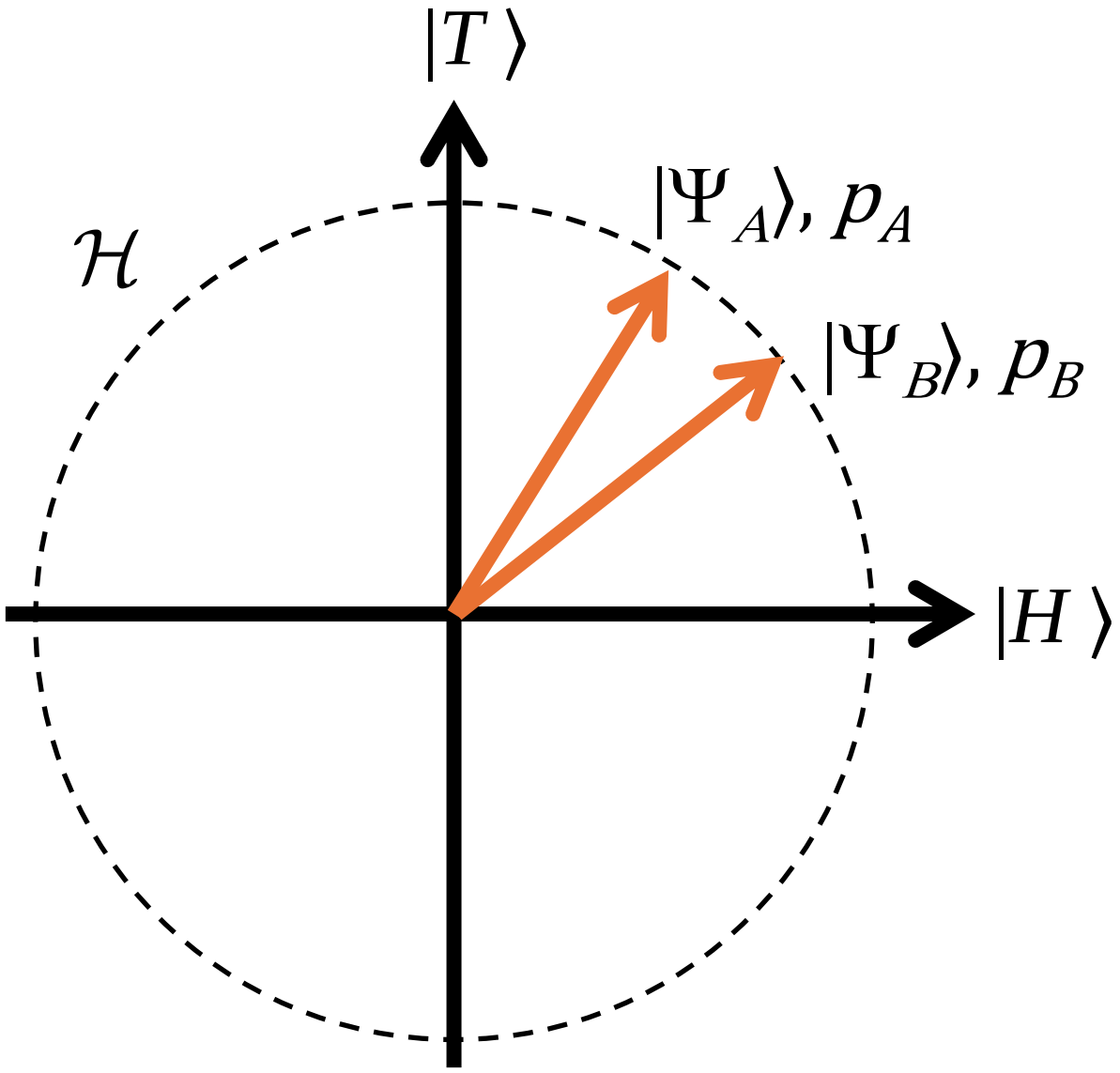
Any unit vector in $\mathcal{H}$ is a possible state

Each amplitude ψ_k is a complex number:

$$\psi_k = A_k e^{i\phi_k}$$



Unsure which state we have…



Density

$$\rho = p_A|\Psi_A\rangle\langle\Psi_A| + p_B|\Psi_B\rangle\langle\Psi_B|$$

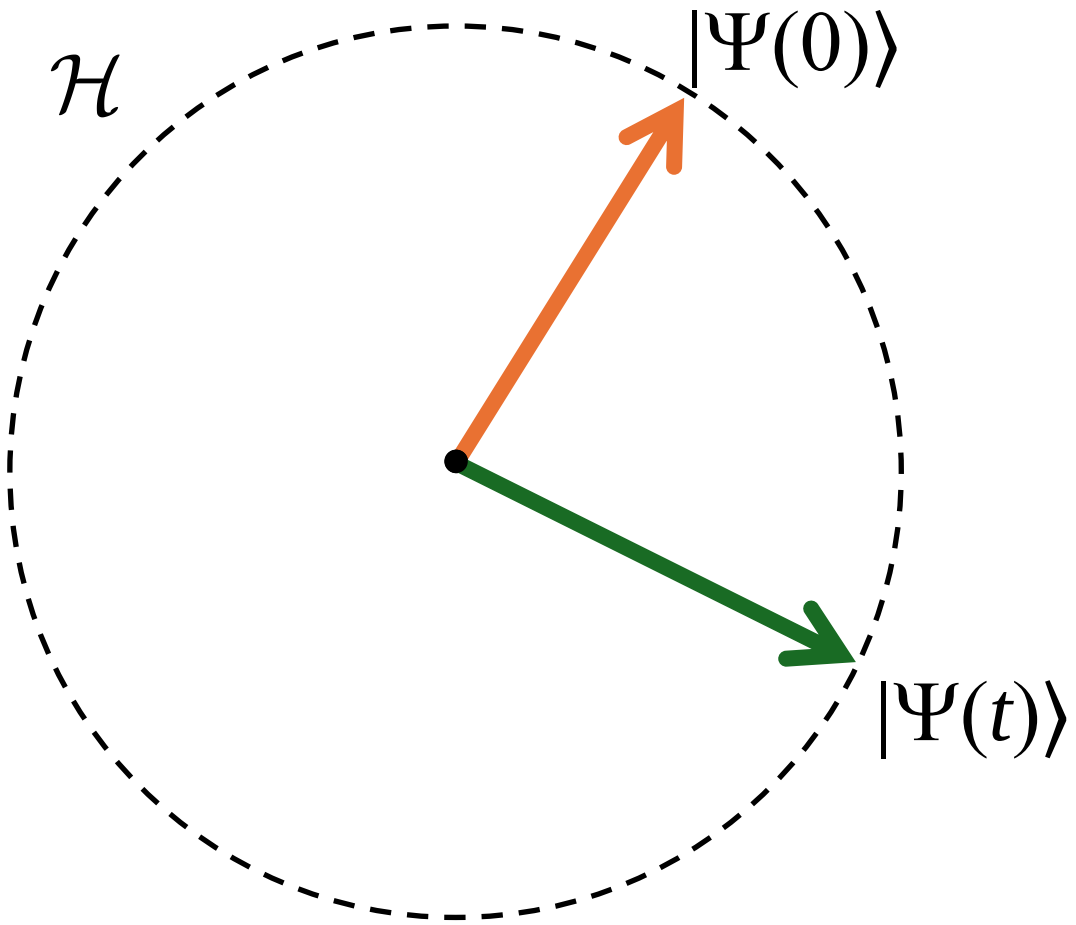
$$p_A + p_B = 1$$

Purity

$$\mathrm{Tr}\left[\rho^2\right] = \sum_i \langle i|\rho^2|i\rangle \begin{cases} = 1 & \text{pure state} \\ < 1 & \text{mixed state} \end{cases}$$

Deterministic evolution of the quantum state

Schrödinger Evolution



$$|\Psi(t)\rangle = U(t)|\Psi(0)\rangle \qquad U^{\dagger}U = 1$$

In the non-relativistic limit, it implies:

Schrödinger Equation

$$i\hbar \frac{d|\Psi\rangle}{dt} = \hat{H}|\Psi\rangle$$

Von Neumann Evolution

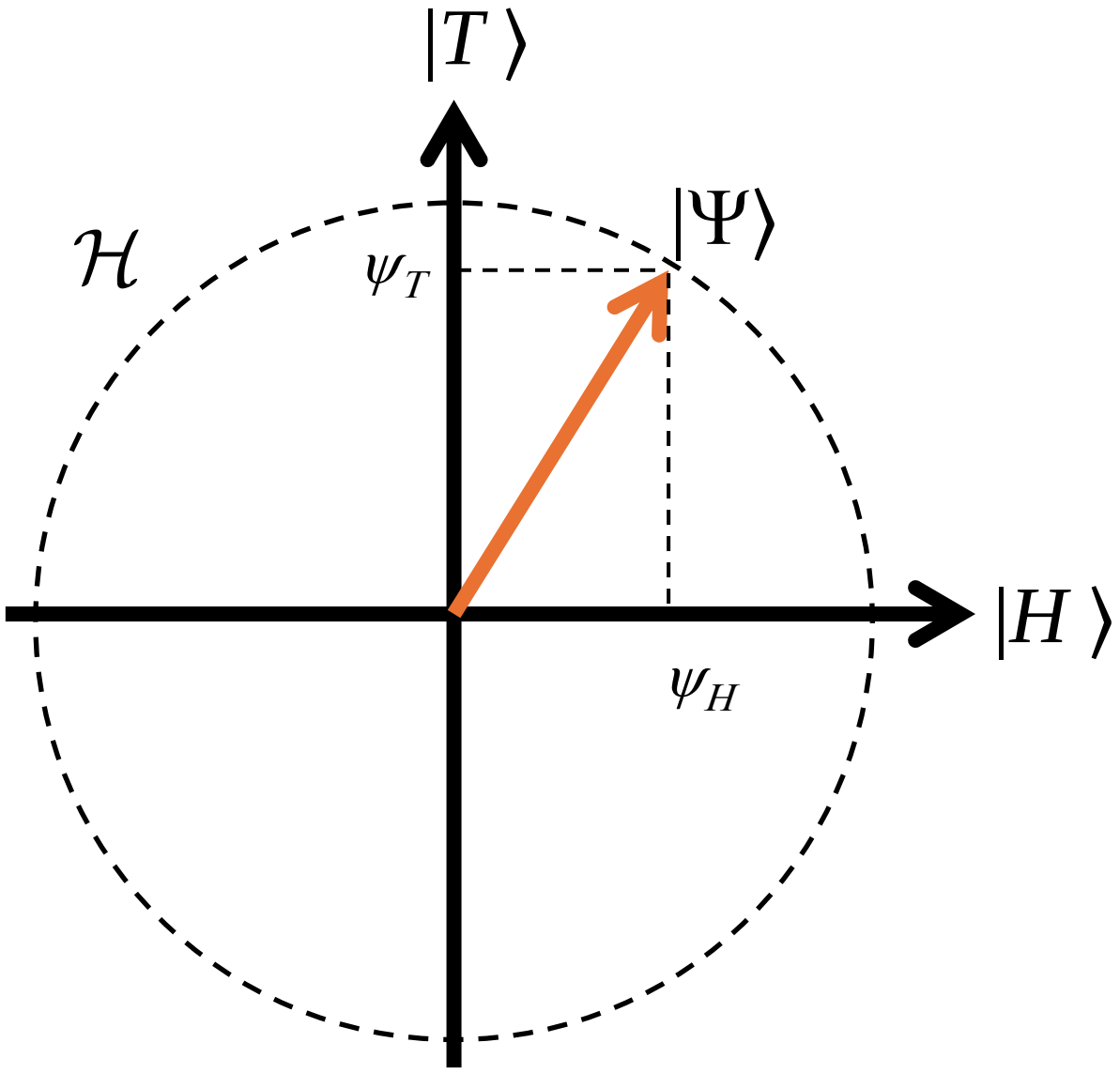
$$\rho = p_A \left|\Psi_A\right\rangle\left\langle\Psi_A\right| + p_B \left|\Psi_B\right\rangle\left\langle\Psi_B\right|$$

Von Neumann Equation

$$i\hbar \frac{d\rho}{dt} = \left[\hat{H}, \rho\right]$$

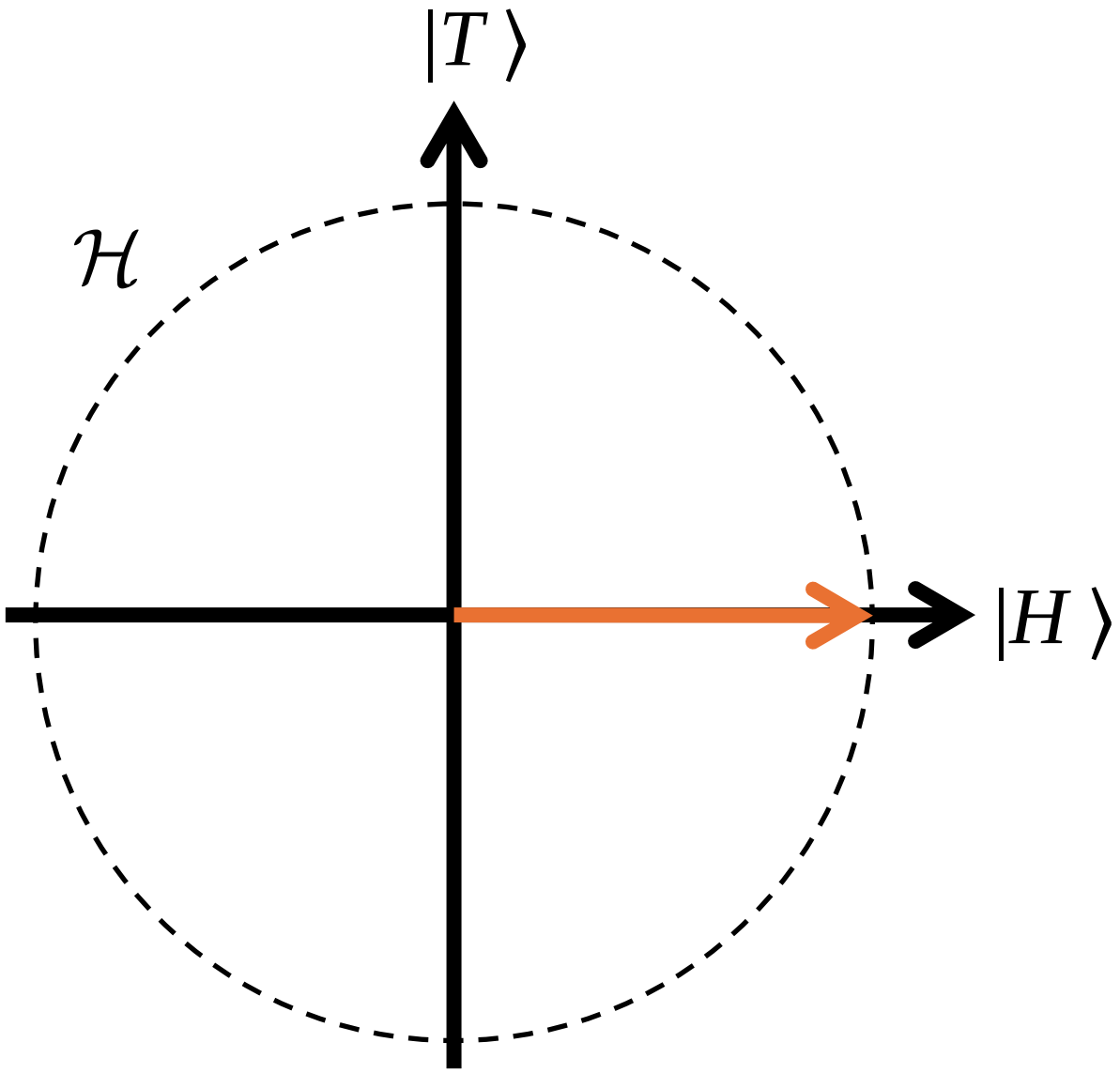
$$\left[\hat{H}, \rho\right] = \hat{H}\rho - \rho\hat{H}$$

Stochastic evolution of the quantum state



$$|\Psi\rangle = \psi_H |H\rangle + \psi_T |T\rangle$$

Quantum State Measurement



$$|\Psi\rangle = \psi_H |H\rangle + \psi_T |T\rangle$$

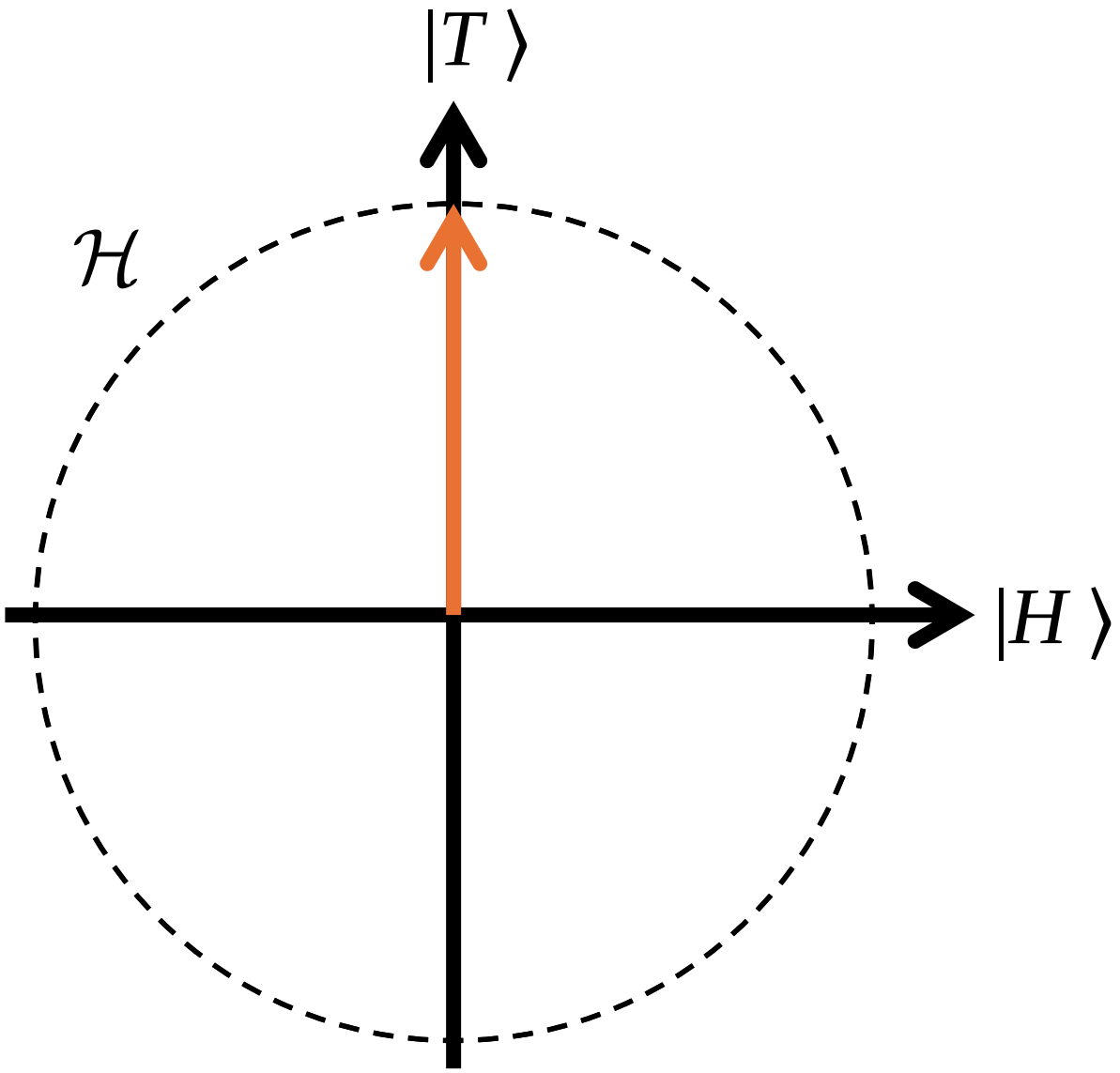
$$|\Psi\rangle = |H\rangle$$

$$P(H) = |\langle H|\Psi\rangle|^2 = |\psi_H|^2$$

or

$$P(H) = \mathrm{Tr}\left[|H\rangle\langle H|\rho\right]$$

Quantum State Measurement



$$|\Psi\rangle = \psi_H |H\rangle + \psi_T |T\rangle$$

$$|\Psi\rangle = |T\rangle$$

$$P(T) = |\langle T|\Psi\rangle|^2 = |\psi_T|^2$$

or

$$P(T) = \mathrm{Tr}\left[|T\rangle\langle T|\rho\right]$$

A quantum state may follow two types of time evolution:

1. On itself, it evolves with the **Schrödinger equation** (unitary and deterministic)

2. During a measurement, it evolves with the **Born rule** (non-unitary and stochastic)

Generalization 1: Multidimensional systems

How many outputs?

36 outputs

uncountable ∞ outputs

$$|\Psi\rangle = \psi_1|1\rangle + \psi_2|2\rangle + \cdots = \sum_k \psi_k |k\rangle$$

countable outputs

State vector

$$|\Psi\rangle = \int \psi(x)|x\rangle dx$$

Wave function

uncountable ∞ outputs

Generalization 2: Composite systems

1 Coin

2 outputs

2 Coins

4 outputs

$\mathcal{H}_A : \{|H\rangle, |T\rangle\}$ 

$\mathcal{H}_B : \{|H\rangle, |T\rangle\}$ 

$\mathcal{H}_T = \mathcal{H}_A \otimes \mathcal{H}_B : \{|H,H\rangle,$ 

$|H,T\rangle,$ 

$|T,H\rangle,$ 

$|T,T\rangle\}$ 

Entanglement

$$|\Psi\rangle = \sum_{i,j} C_{ij} |A_i, B_j\rangle$$ Entangled state

$$|\Psi\rangle = |A_i, B_i\rangle = |A_i\rangle \otimes |B_i\rangle$$ Separable state

Permutation symmetry

Indistinguishable particles A and B

$$|\Psi_1\rangle = \sum_{i,j} C_{ij} |A_i, B_j\rangle$$

$$|\Psi_2\rangle = \sum_{i,j} C_{ji} |A_i, B_j\rangle$$

Fermions

$$|\Psi_1\rangle = -|\Psi_2\rangle$$

Bosons

$$|\Psi_1\rangle = |\Psi_2\rangle$$

This property leads to the Pauli exclusion principle for fermions

Info from a subsystem

ρ_{AB} Density of a composite system AB

$\rho_A = \mathrm{Tr}_B\left[\rho_{AB}\right] = \sum_i \left\langle B_i \middle| \rho_{AB} \middle| B_i \right\rangle$ **Reduced density** of A

ρ_A contains, exhaustively and correctly, all information (i.e., all measurement statistics) that the observer of system A can extract.

Quantization

Suppose a **time-independent Hamiltonian** $H(\mathbf{r})$.

We can separate **r** and t in the wave function:

$$\Psi(\mathbf{r},t)=\psi(\mathbf{r})\phi(t)$$

Replace in the Schrödinger equation

$$i\hbar\frac{\partial\Psi}{\partial t}=\hat{H}(\mathbf{r})\Psi\rightarrow i\hbar\frac{\partial\psi(\mathbf{r})\phi(t)}{\partial t}=\hat{H}(\mathbf{r})\psi(\mathbf{r})\phi(t)$$

$$i\hbar\psi(\mathbf{r})\frac{d\phi(t)}{dt}=\hat{H}(\mathbf{r})\psi(\mathbf{r})\phi(t)$$

Separate the variables:

$$i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt}=\frac{\hat{H}(\mathbf{r})\psi(\mathbf{r})}{\psi(\mathbf{r})}=E$$

$$\begin{cases} i\hbar\dfrac{d\phi(t)}{dt}=E\phi(t) \\ \hat{H}(\mathbf{r})\psi(\mathbf{r})=E\psi(\mathbf{r}) \end{cases}$$

The first equation

$$i\hbar \frac{d\phi(t)}{dt} = E\phi(t)$$

gives

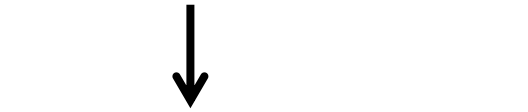
$$\phi(t) = \exp\left(-i\frac{Et}{\hbar}\right)$$

The second equation

$$\hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

is called the **Time-Independent Schrödinger equation**.

Eigenvector

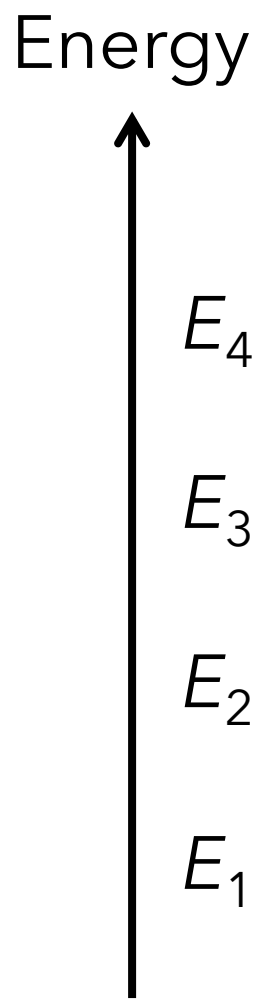


$$\hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Eigenvalue

$$\hat{H}(\mathbf{r})\psi_1(\mathbf{r}) = E_1\psi_1(\mathbf{r})$$ Ground state

$$\hat{H}(\mathbf{r})\psi_2(\mathbf{r}) = E_2\psi_2(\mathbf{r})$$
$$\vdots$$
$$\hat{H}(\mathbf{r})\psi_N(\mathbf{r}) = E_N\psi_N(\mathbf{r})$$
Excited states



A standard procedure to determine the system evolution is to first solve a stationary case, and use the eigenvectors to expand the time-dependent Ψ.

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.

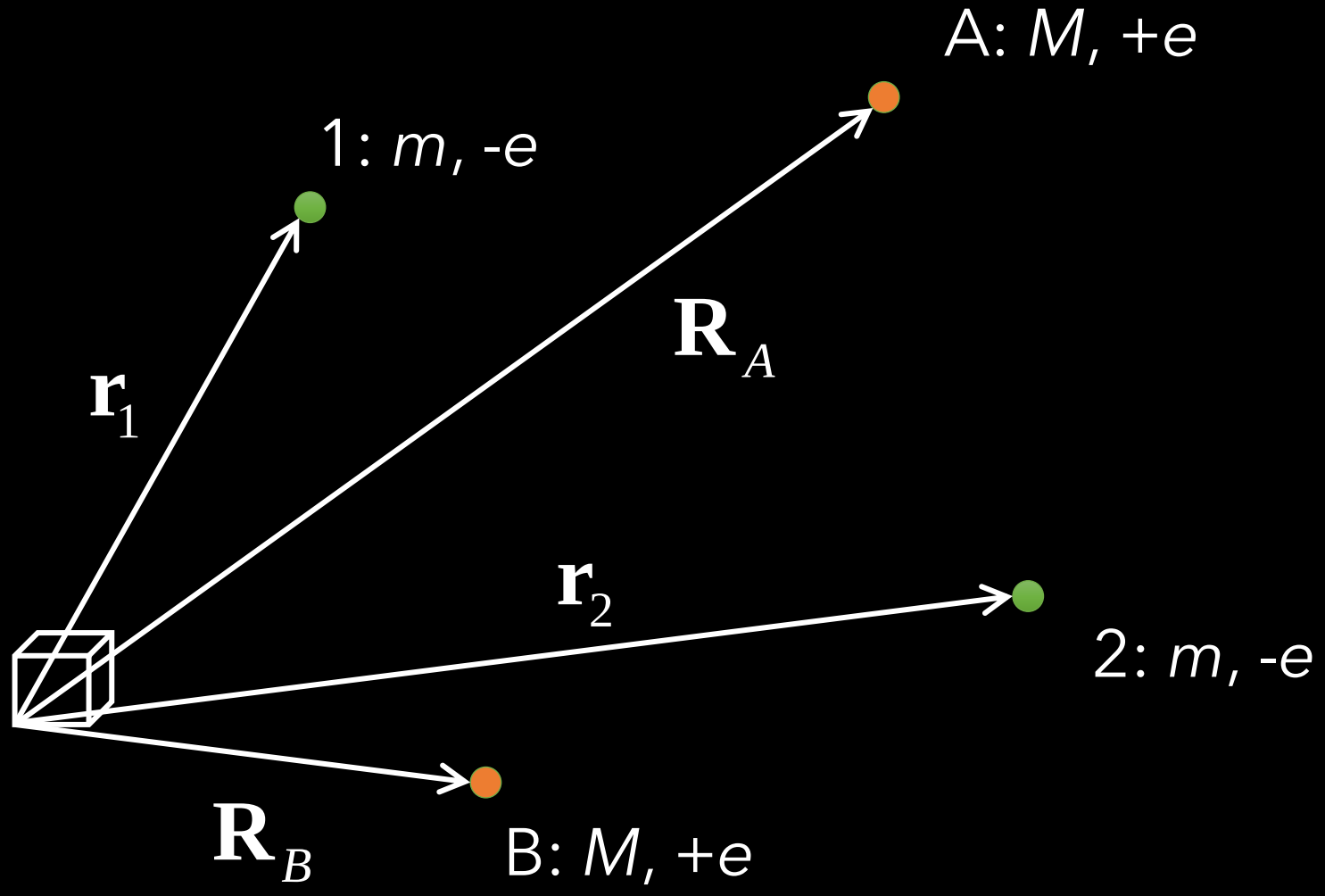
“Without the Born-Oppenheimer approximation as a foundation, there would be **no molecular structure**, solid-state crystal structure, molecular vibrations, phonons, electronic band structure, and so on.

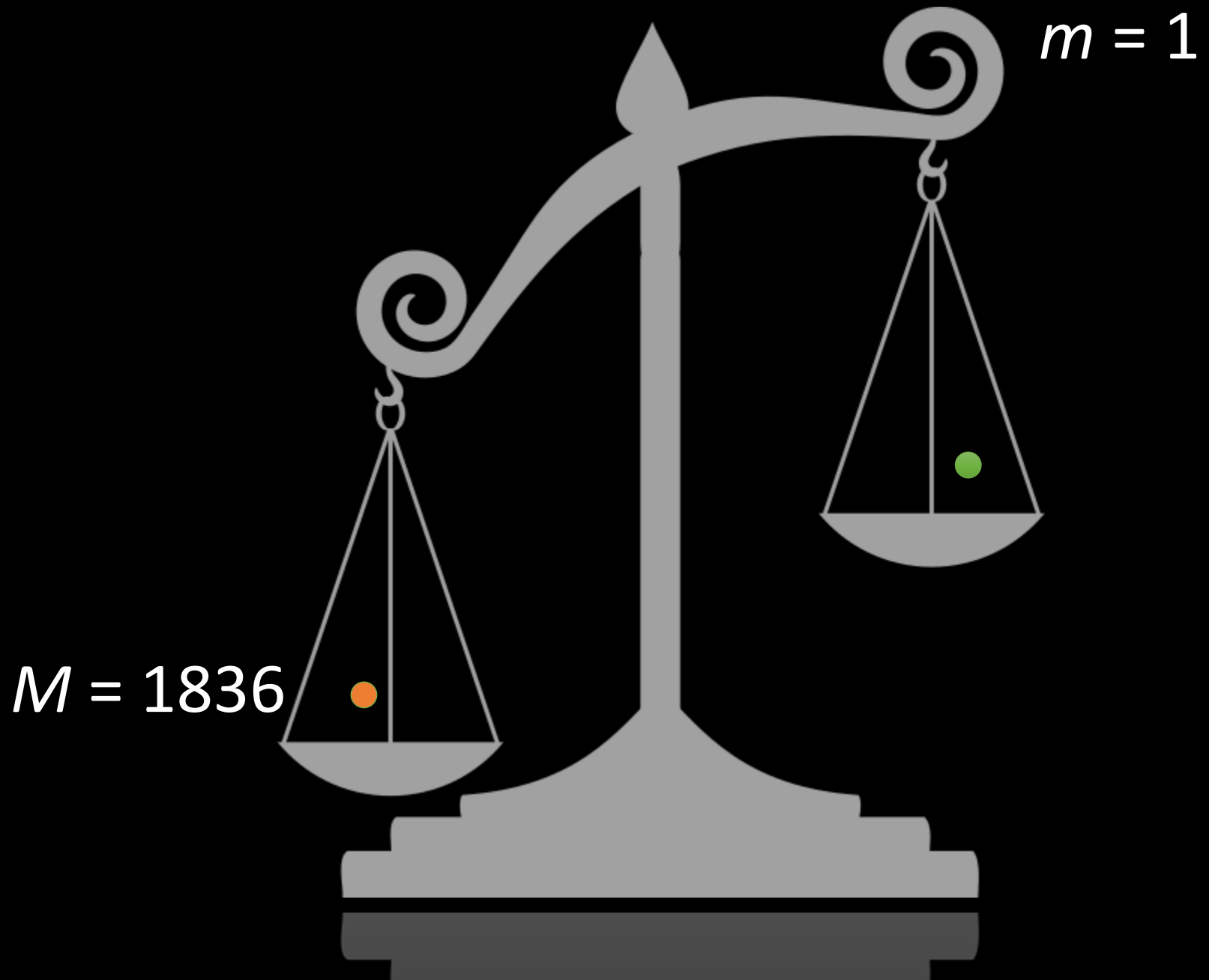
“Why? Because it is the Born-Oppenheimer approximation that allows separation of electronic from nuclear motion. Without it, we appear to be lost in a soggy many-body ‘pea soup’ or plasma of electrons and nuclei, where there is seemingly no structure at all, save the kind of structure one finds in a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

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

$$\Psi\left(\mathbf{R}_A, \mathbf{R}_B, \mathbf{r}_1, \mathbf{r}_2\right)$$

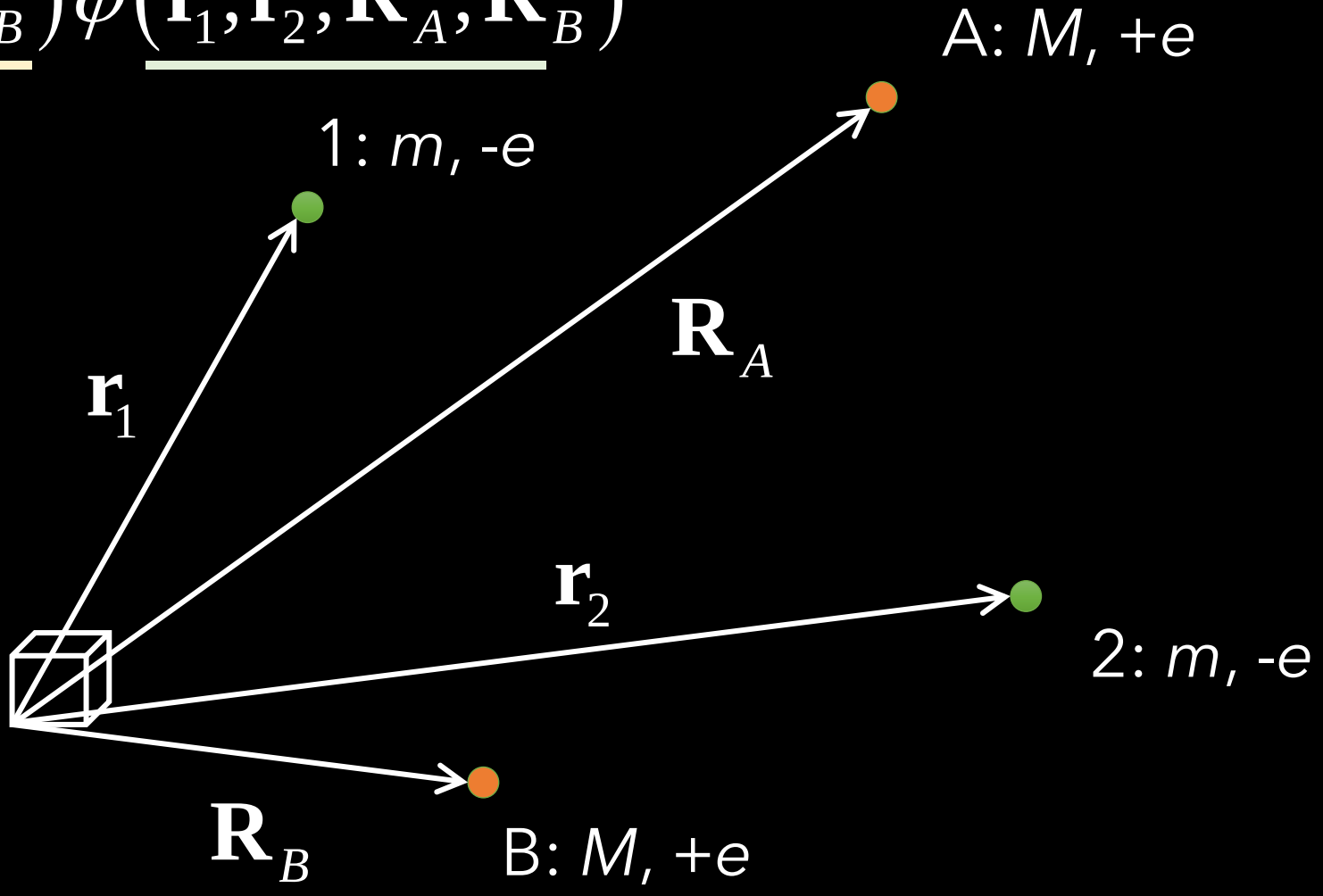
$$\hat{H}\Psi = \varepsilon\Psi$$




$m = 1$
$M = 1836$

$$\Psi(\mathbf{R}_A,\mathbf{R}_B,\mathbf{r}_1,\mathbf{r}_2)$$

$$= \chi(\mathbf{R}_A,\mathbf{R}_B)\varphi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}_A,\mathbf{R}_B)$$



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

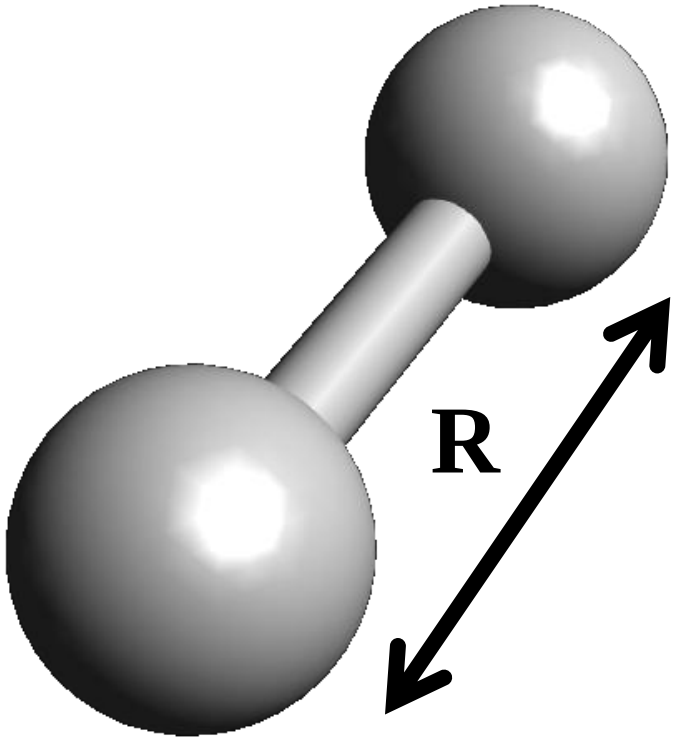
$$\left(\hat{T}_{elec}(\mathbf{r}) + V(\mathbf{r},\mathbf{R})\right)\varphi(\mathbf{r};\mathbf{R}) = E(\mathbf{R})\,\varphi(\mathbf{r};\mathbf{R})$$

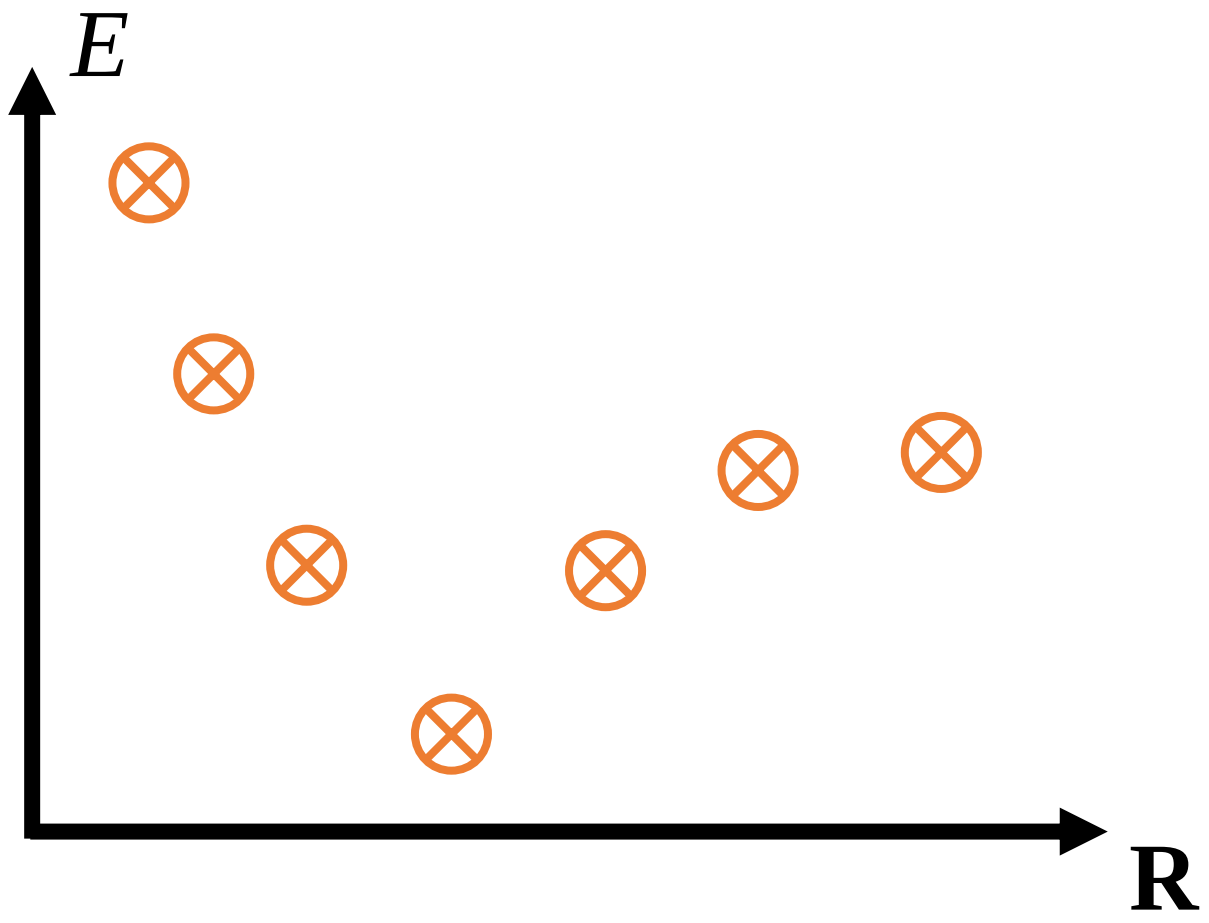
Potential Energy Surface

BO molecular wave function

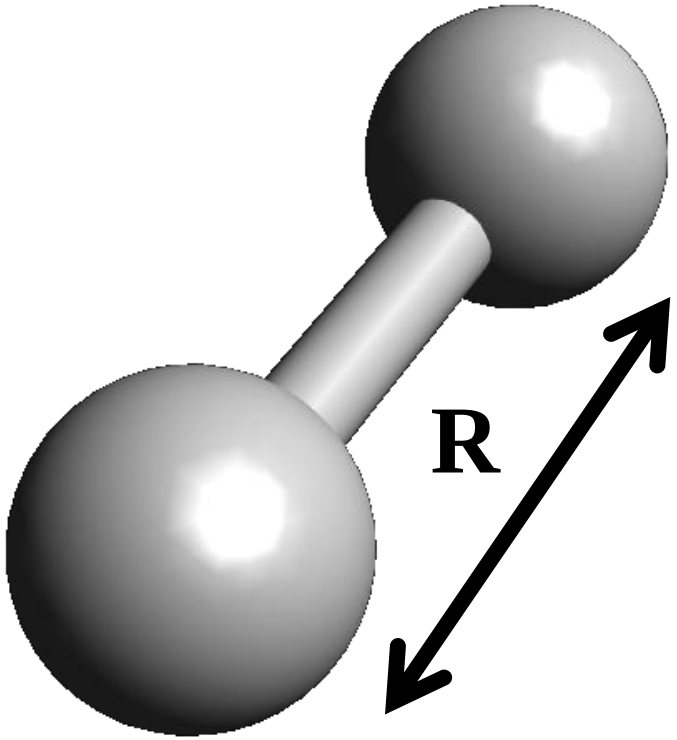
$$\Psi^{BO}(\mathbf{R},\mathbf{r}) = \varphi(\mathbf{r};\mathbf{R})\,\chi(\mathbf{R})$$

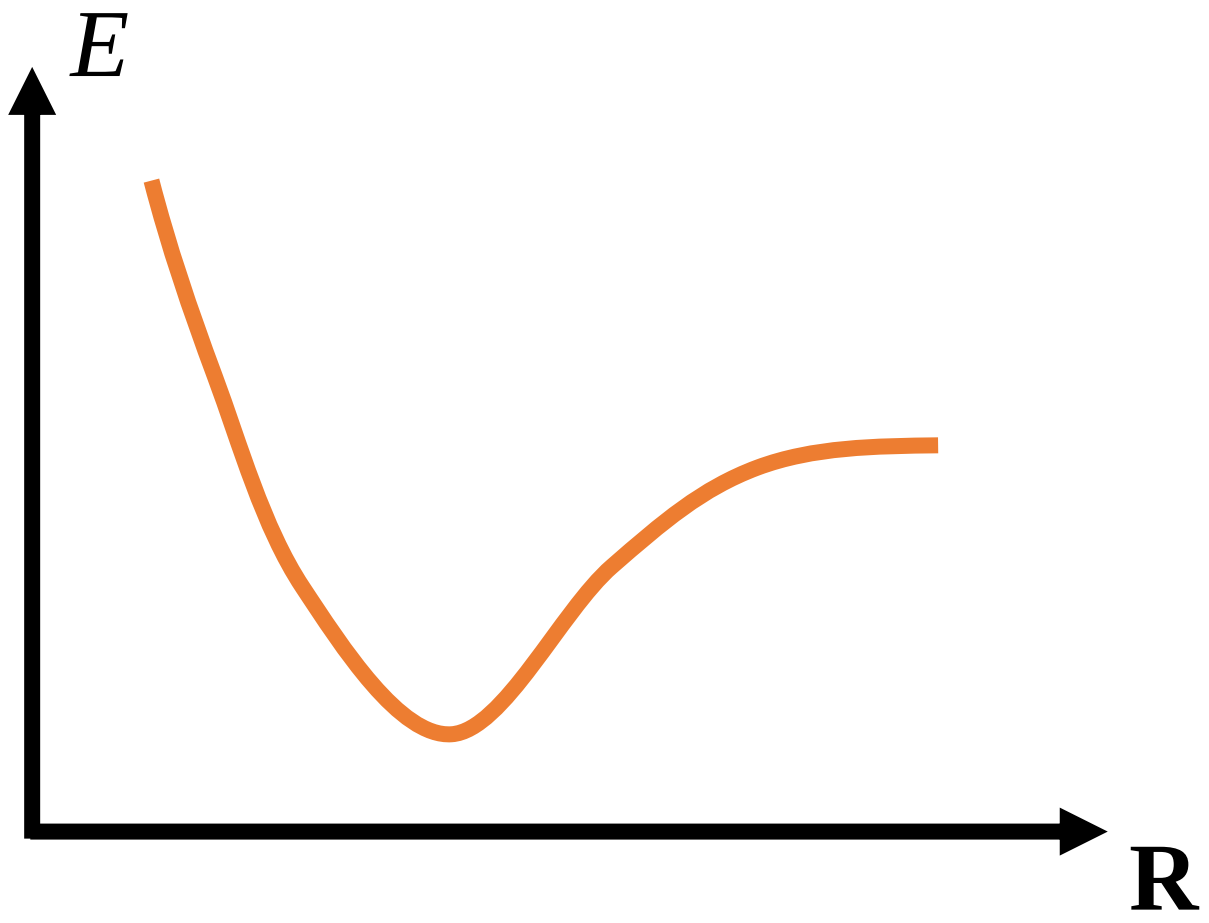
Check the derivation in the appendix





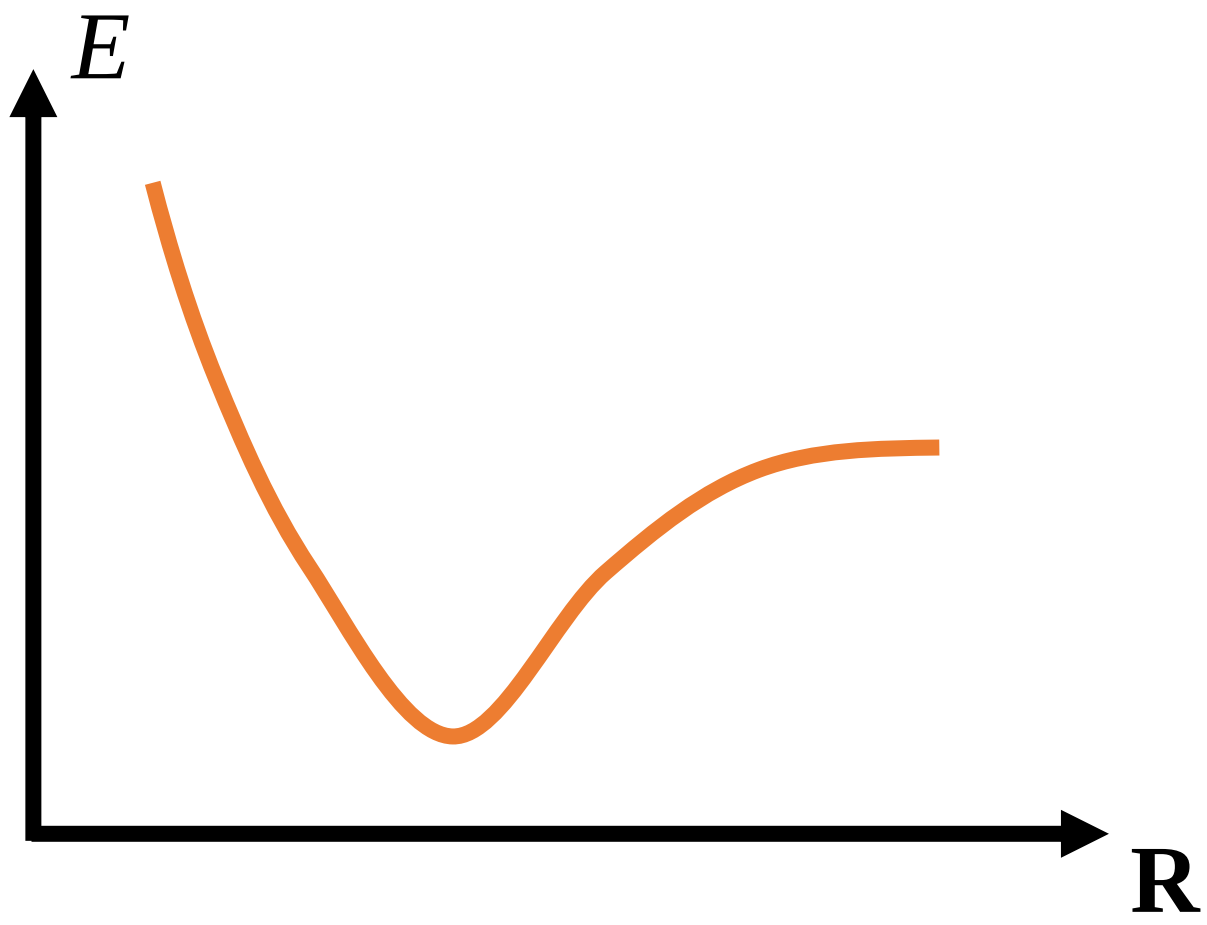
$$\hat{H}_{elec}\varphi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}) = E(\mathbf{R})\varphi(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R})$$

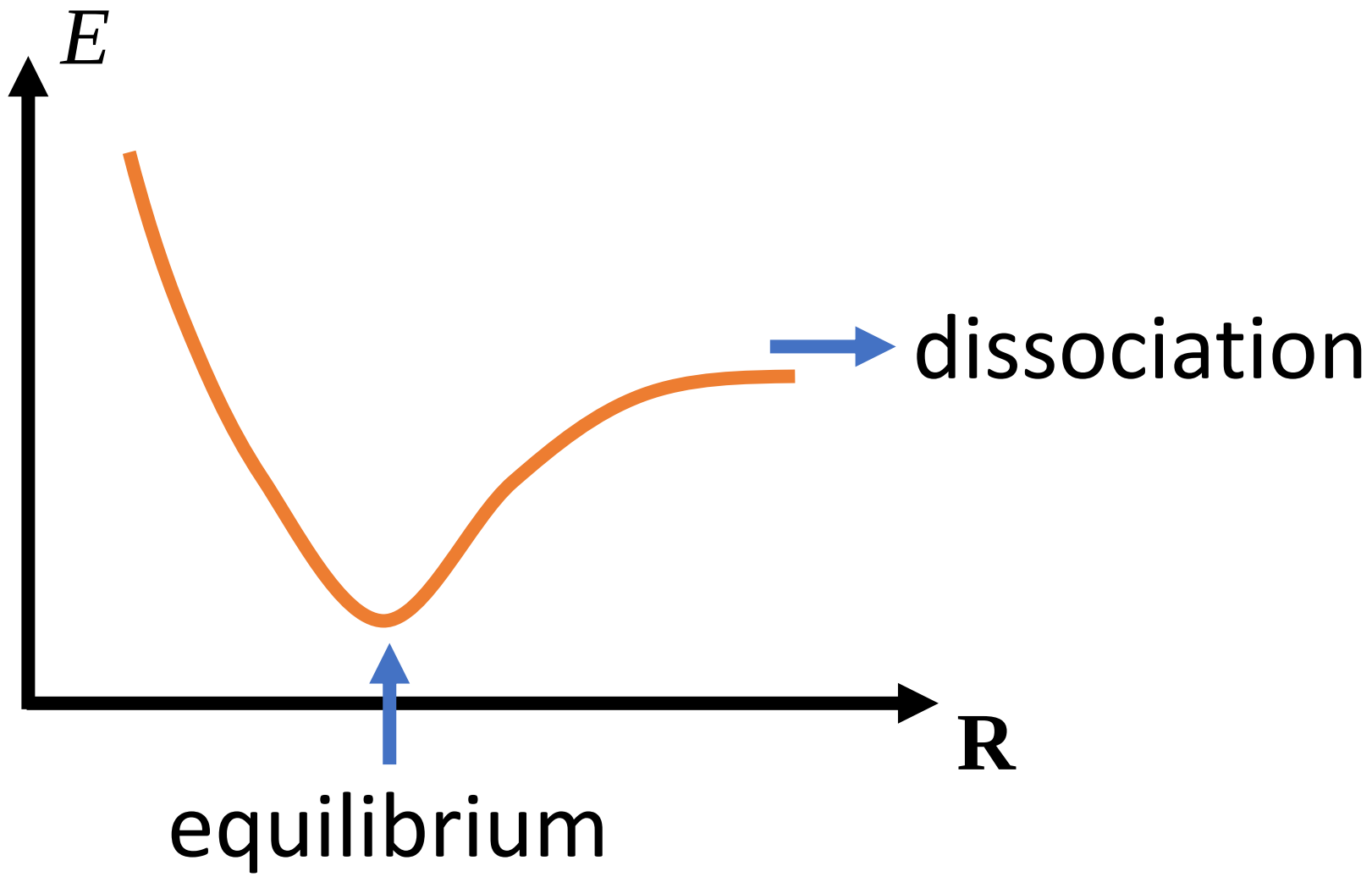


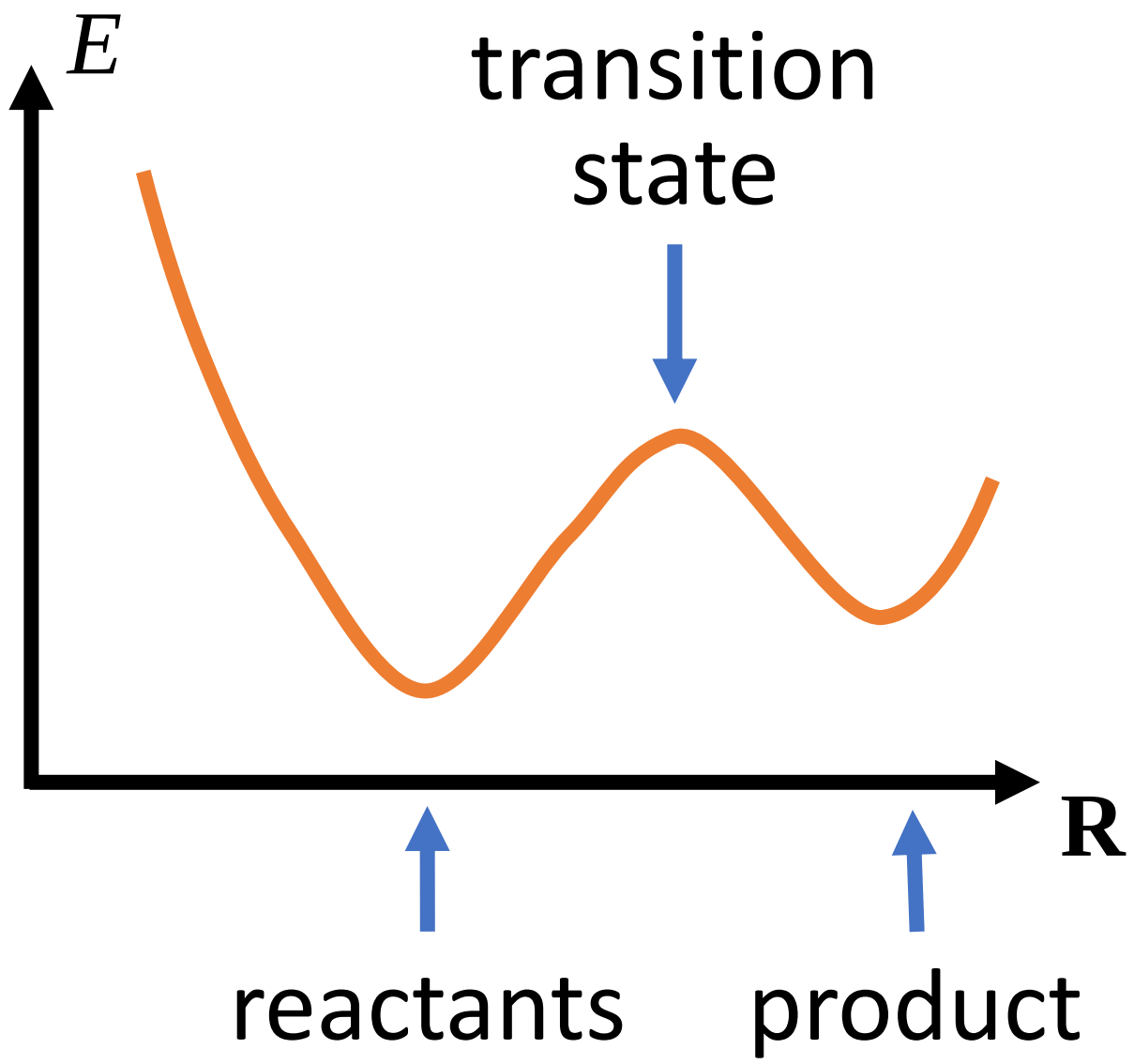


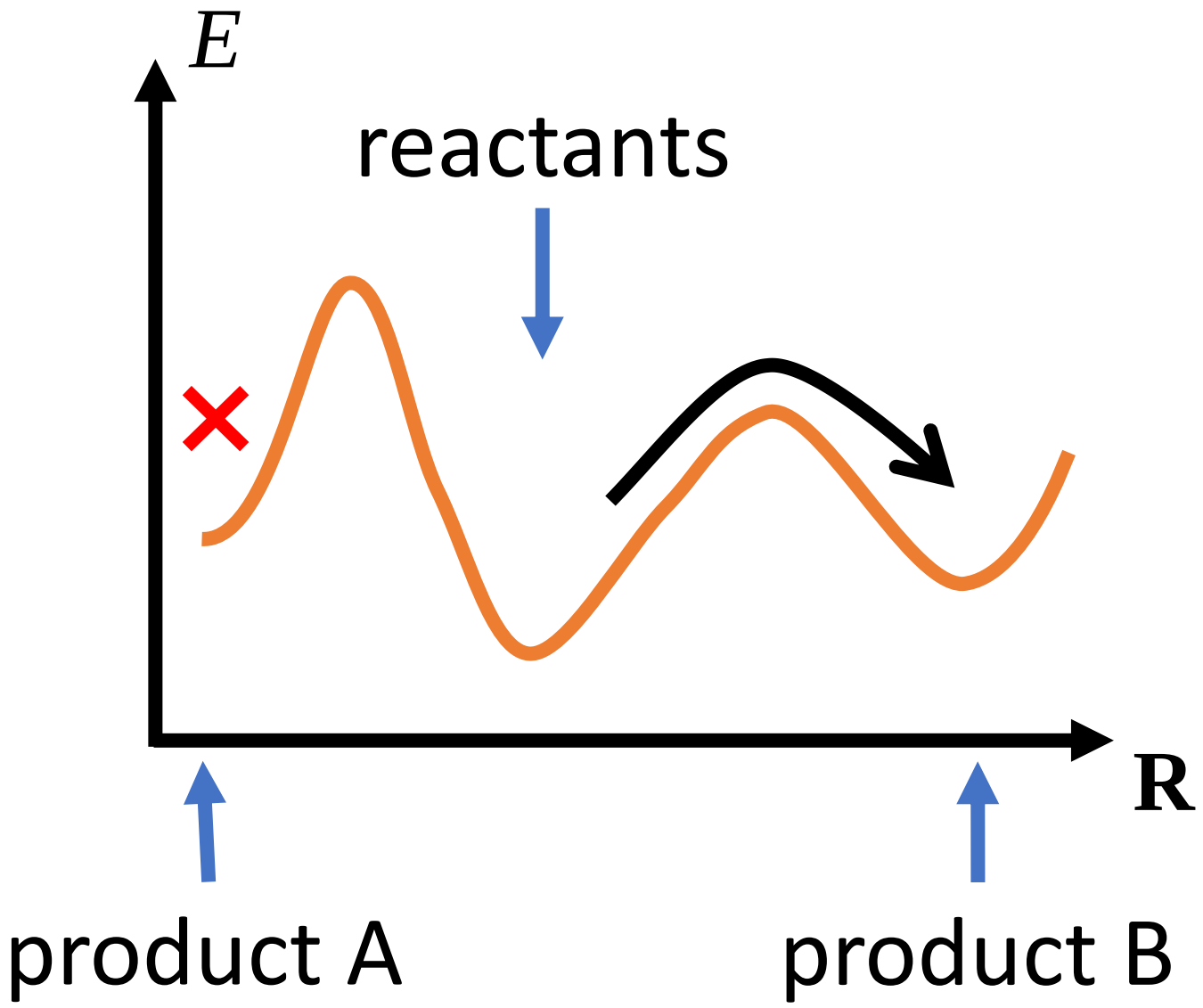
$$H_{elec}\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)=E\left(\mathbf{R}\right)\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)$$

Potential energy surface

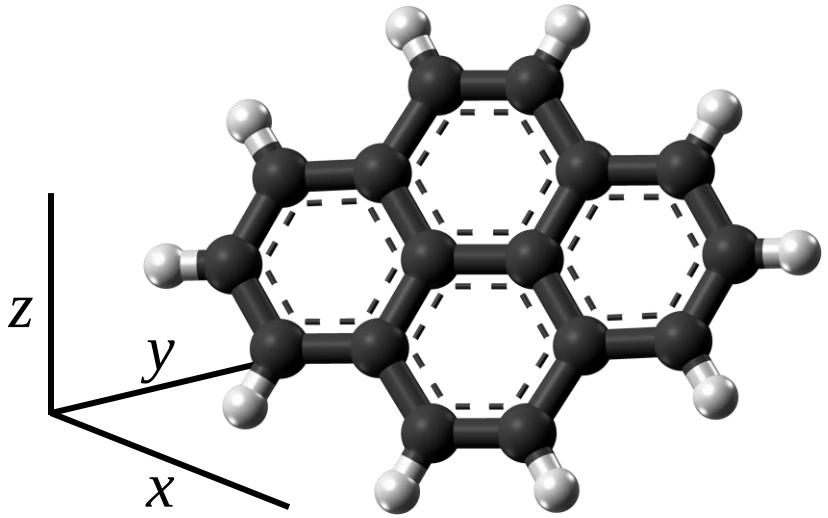


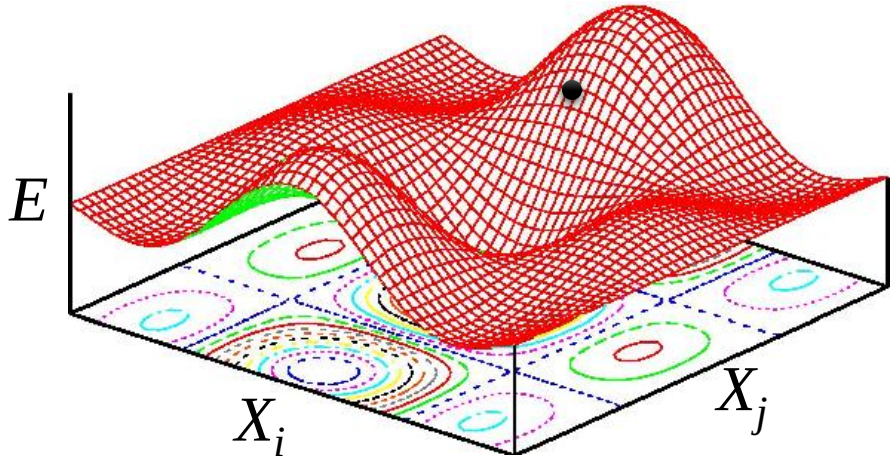

E
dissociation
R
equilibrium


E
transition
state
R
reactants
product

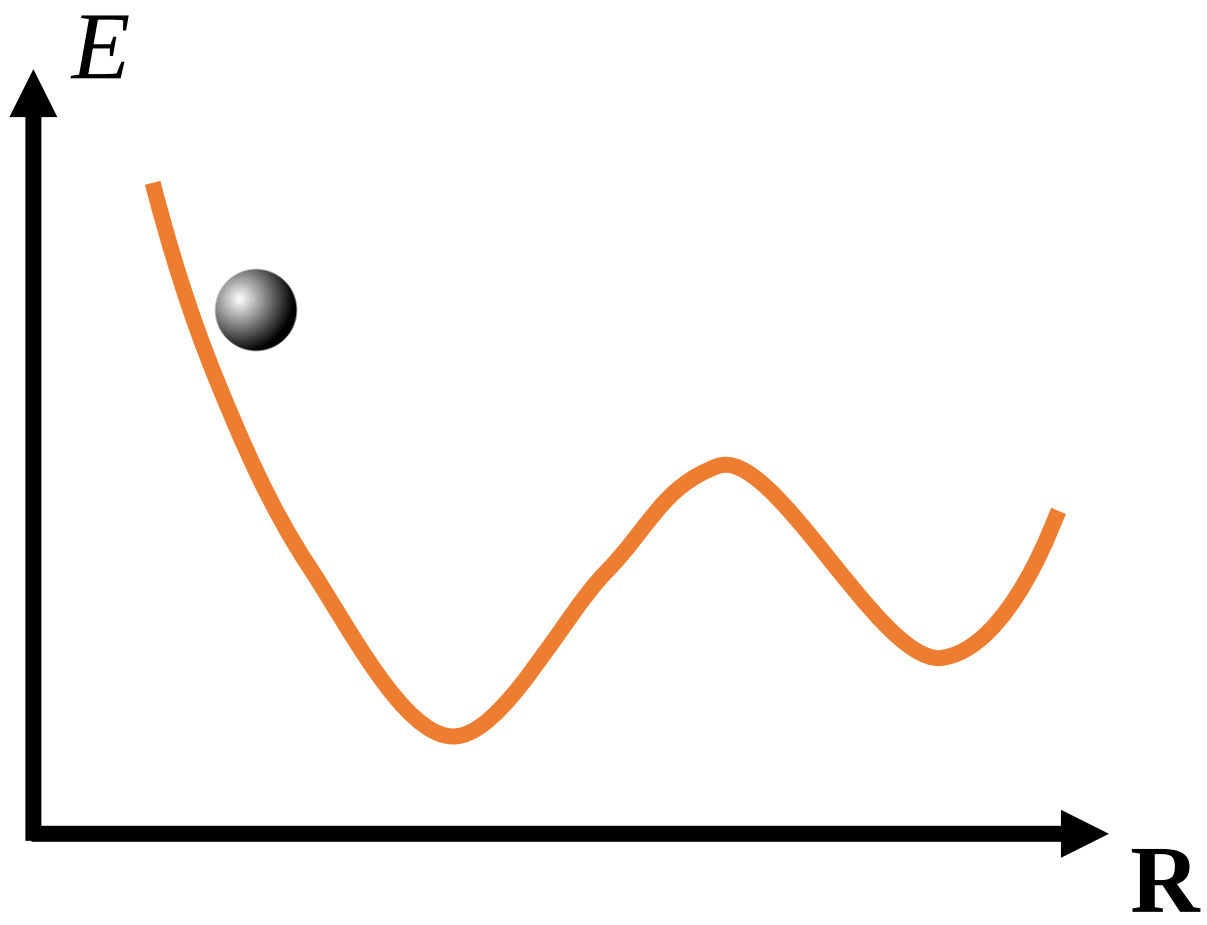

E
reactants
R
product A
product B

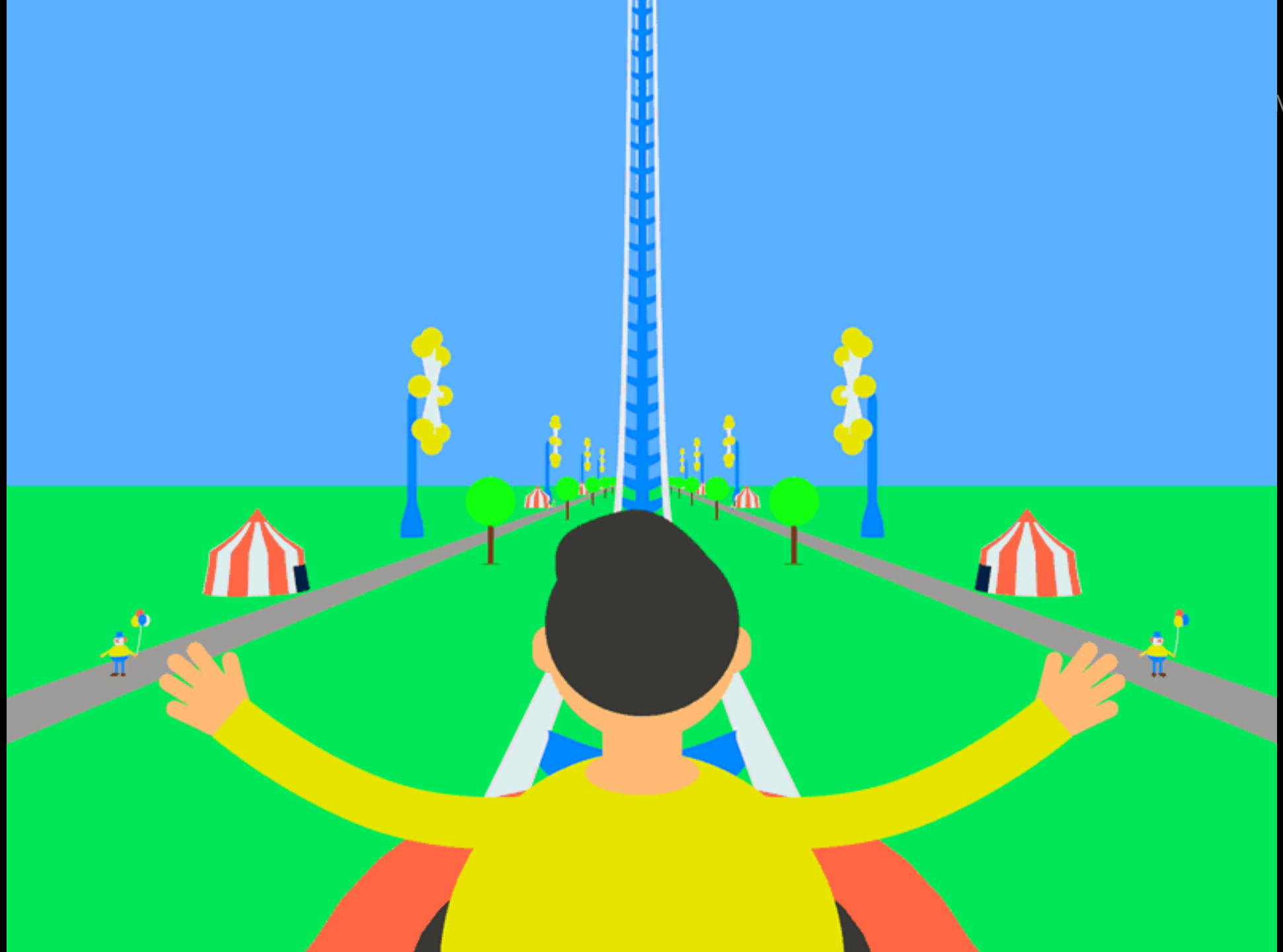
$$E(\mathbf{R}) \equiv E(X_1, Y_1, Z_1, \cdots, X_N, Y_N, Z_N)$$





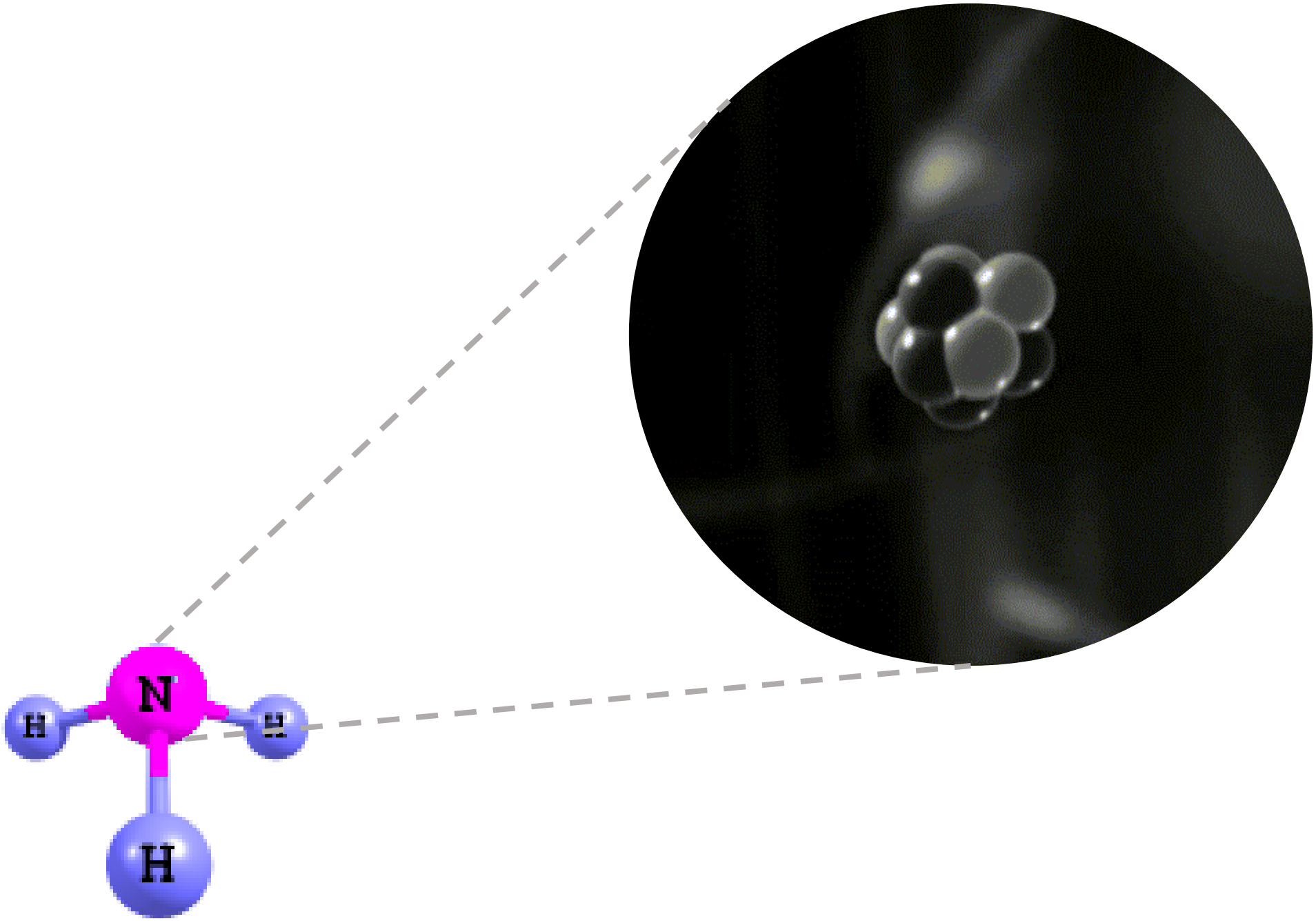
N points × 3 dimensions → 1 point × 3*N* dimensions


E
R



LIGHT AND
MOLECULES

A note about molecular time


N
H
H
H

There's **no time** dependency.

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

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

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

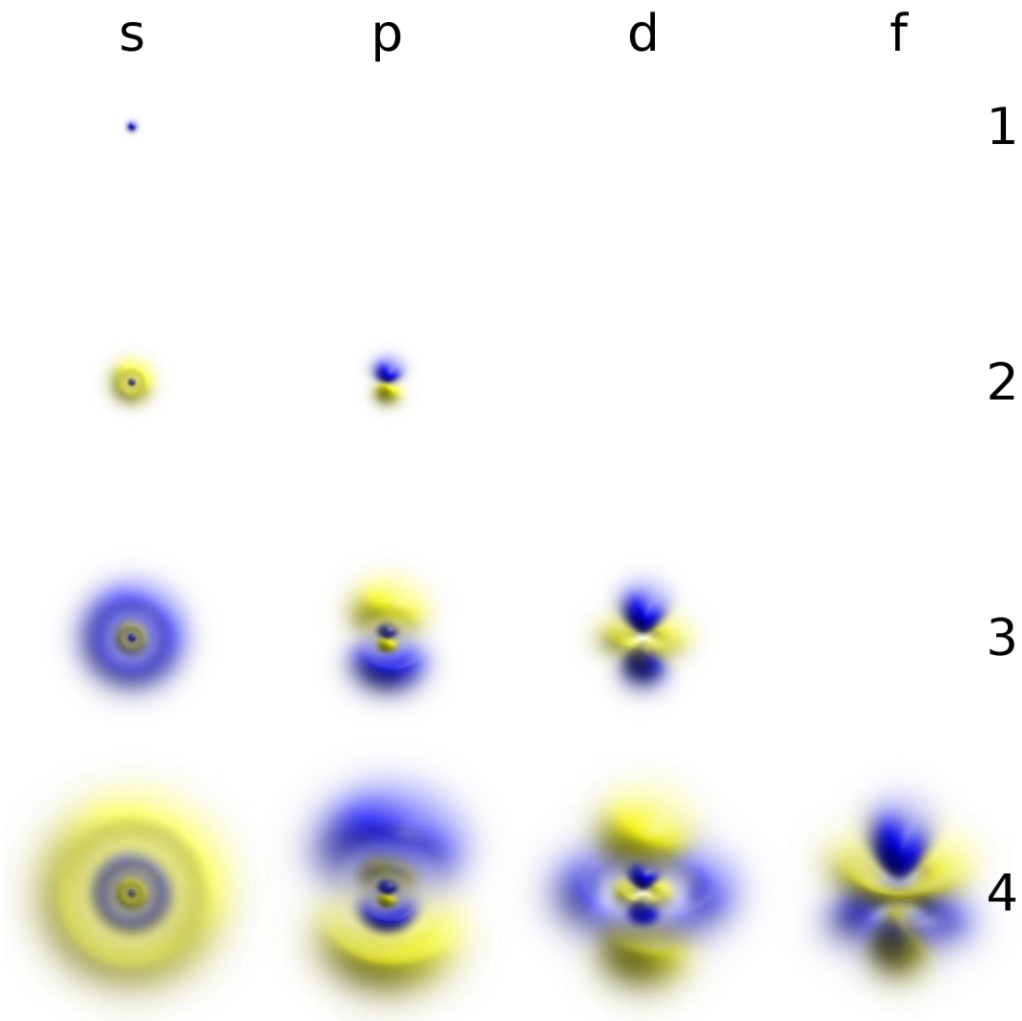
Barbatti, Aeon Magazine **2023**, tinyurl.com/emptyatom

For a stationary state

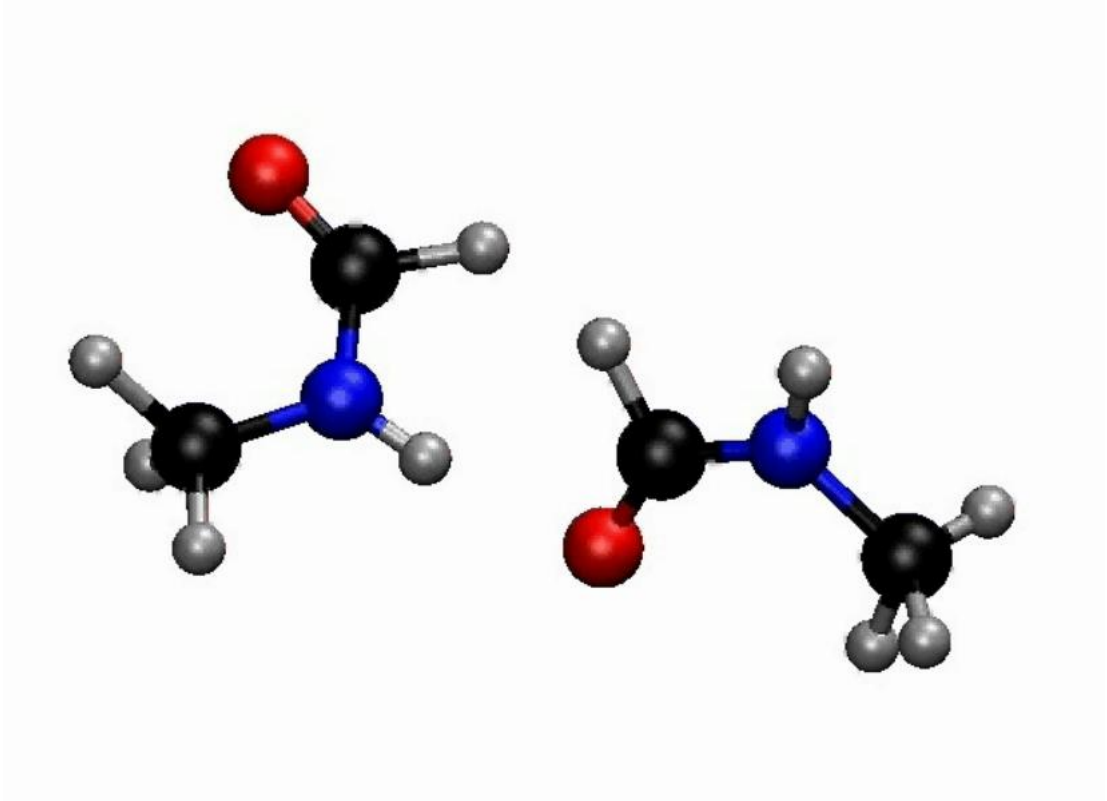
- Momentum = wave function steepness $\left[-i\hbar\nabla\psi\right]$
- Kinetic energy = field stress (how much the wave function differs from the mean) $\left[-\frac{\hbar^2}{2M}\nabla^2\psi\right]$
- Spin = curl of the electron density * $\left[\frac{\hbar}{4}\nabla\times\left(\tilde{\psi}^{\dagger}\boldsymbol{\sigma}\tilde{\psi}\right)\right]$

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

- Angular momentum = wave function blobs and nodes



Time becomes important again during chemical reactions or field interactions



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

To know more:

Quantum mechanics

- Abide by Reason, tinyurl.com/hilbertspace
- ViaScience, tinyurl.com/viasciQM
- Manzano. *AIP Advances* **2020,** *10*, 025106

The BO approximation

- Eric J Heller, *The semiclassical way*, **2018**. Ch 16

About molecular time

- Barbatti, Aeon Magazine **2023**, tinyurl.com/emptyatom
- Minute Physics, tinyurl.com/minutephysatom

Appendix: Derivation of the Born-Oppenheimer Formulation

Field-free non-relativistic molecular problem

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

with

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

Born-Huang wave function

$$\Psi\left(\mathbf{R},\mathbf{r}\right)=\sum_{n}\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)\chi_{n}\left(\mathbf{R}\right)$$

Solving the **electronic** part

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

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

Solving the **nuclear** part

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

with

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

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

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

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

$$\left(\hat{T}_{nuc}+\hat{T}_{elec}+\hat{V}\right)\left(\sum_n \varphi_n\chi_n\right)=\varepsilon\left(\sum_n \varphi_n\chi_n\right)$$

Working on the left-side term

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

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}\left(\sum_n \varphi_n\chi_n\right)+\sum_n E_n\varphi_n\chi_n$$

$$\hat{T}_{nuc}=-\frac{\hbar^2}{2}\sum_\alpha \frac{1}{M_\alpha}\nabla^2_{\mathbf{R}}$$

$$\sum_\alpha \frac{1}{M_\alpha} f(\mathbf{R}_\alpha)\rightarrow\frac{1}{\mathbf{M}} f(\mathbf{R})$$

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}\left(\sum_n \varphi_n(\mathbf{r};\mathbf{R})\chi_n(\mathbf{R})\right)+\sum_n E_n\varphi_n\chi_n = \varepsilon\left(\sum_n \varphi_n\chi_n\right)$$

Expanding the blue term

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}\left(\sum_n \varphi_n\chi_n\right)=$$

$$-\frac{\hbar^2}{2\mathbf{M}}\sum_n\left[\left(\nabla^2_{\mathbf{R}}\varphi_n\right)\chi_n+2\nabla_{\mathbf{R}}\varphi_n\cdot\nabla_{\mathbf{R}}\chi_n+\varphi_n\nabla^2_{\mathbf{R}}\chi_n\right]$$

$$-\frac{\hbar^2}{2\mathbf{M}}\sum_n\left[\left(\nabla^2_{\mathbf{R}}\varphi_n\right)\chi_n+2\nabla_{\mathbf{R}}\varphi_n\cdot\nabla_{\mathbf{R}}\chi_n+\varphi_n\nabla^2_{\mathbf{R}}\chi_n\right]$$

$$+\sum_n E_n\varphi_n\chi_n=\varepsilon\left(\sum_n\varphi_n\chi_n\right)$$

Projecting on n′

$$-\left\langle\varphi_{n'}\left|\frac{\hbar^2}{2\mathbf{M}}\sum_n\left[\left(\nabla^2_{\mathbf{R}}\varphi_n\right)\chi_n+2\nabla_{\mathbf{R}}\varphi_n\cdot\nabla_{\mathbf{R}}\chi_n+\varphi_n\nabla^2_{\mathbf{R}}\chi_n\right]\right\rangle_{\mathbf{r}}\right.$$

$$+\left\langle\varphi_{n'}\left|\sum_n E_n\varphi_n\chi_n\right\rangle_{\mathbf{r}}\right.=\left\langle\varphi_{n'}\left|\varepsilon\left(\sum_n\varphi_n\chi_n\right)\right\rangle_{\mathbf{r}}\right.$$

$$-\left\langle \varphi_{n'} \left| \frac{\hbar^2}{2\mathbf{M}} \sum_n \left[\left(\nabla^2_{\mathbf{R}} \varphi_n \right) \chi_n + 2 \nabla_{\mathbf{R}} \varphi_n \cdot \nabla_{\mathbf{R}} \chi_n + \varphi_n \nabla^2_{\mathbf{R}} \chi_n \right] \right| \right\rangle_{\mathbf{r}}$$

$$+\left\langle \varphi_{n'} \left| \sum_n E_n \varphi_n \chi_n \right| \right\rangle_{\mathbf{r}} = \left\langle \varphi_{n'} \left| \varepsilon \left(\sum_n \varphi_n \chi_n \right) \right| \right\rangle_{\mathbf{r}}$$

Using orthonormality

$$\left\langle \varphi_{n'} \middle| \varphi_n \right\rangle_{\mathbf{r}} = \delta_{nn'}$$

$$-\frac{\hbar^2}{2\mathbf{M}} \sum_n \left[\left\langle \varphi_{n'} \left| \nabla^2_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} \chi_n + 2 \left\langle \varphi_{n'} \left| \nabla_{\mathbf{R}} \varphi_n \right\rangle_{\mathbf{r}} \cdot \nabla_{\mathbf{R}} \chi_n \right] \right.$$

$$-\frac{\hbar^2}{2\mathbf{M}} \nabla^2_{\mathbf{R}} \chi_n + E_{n'} \chi_{n'} = \varepsilon \chi_{n'}$$

Time-independent Born-Huang formulation

$$\hat{H}_{n'}\chi_{n'} - \varepsilon\chi_{n'} + \sum_{n}\hat{N}_{n'n}\chi_{n'} = 0$$

$$\hat{H}_{n'} = -\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}} + E_{n'}$$

$$\hat{N}_{n'n} = -\frac{\hbar^2}{2\mathbf{M}}\left[\left\langle\varphi_{n'}\middle|\nabla^2_{\mathbf{R}}\varphi_n\right\rangle_{\mathbf{r}} + 2\left\langle\varphi_{n'}\middle|\nabla_{\mathbf{R}}\varphi_n\right\rangle_{\mathbf{r}}\cdot\nabla_{\mathbf{R}}\right]$$

$$\begin{pmatrix} \hat{H}_1(\mathbf{R})-\varepsilon & \hat{N}_{12}(\mathbf{R}) & \hat{N}_{13}(\mathbf{R}) & \cdots \\ \hat{N}_{21}(\mathbf{R}) & \hat{H}_2(\mathbf{R})-\varepsilon & \hat{N}_{23}(\mathbf{R}) & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix}\begin{pmatrix} \chi_1(\mathbf{R}) \\ \chi_2(\mathbf{R}) \\ \chi_3(\mathbf{R}) \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

Adiabatic approximation

$$\hat{N}_{n'n}(\mathbf{R}) = 0$$

$$\begin{pmatrix} H_1(\mathbf{R}) - \varepsilon & 0 & 0 & \cdots \\ 0 & H_2(\mathbf{R}) - \varepsilon & 0 & \cdots \\ \vdots & \vdots & \vdots & \cdots \end{pmatrix} \begin{pmatrix} \chi_1(\mathbf{R}) \\ \chi_2(\mathbf{R}) \\ \chi_3(\mathbf{R}) \\ \vdots \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

$$\hat{H}_n(\mathbf{R})\chi_n(\mathbf{R}) - \varepsilon\chi_n(\mathbf{R}) = 0$$

$$-\frac{\hbar^2}{2\mathbf{M}}\nabla^2_{\mathbf{R}}\chi_n(\mathbf{R}) + E_n(\mathbf{R})\chi_n(\mathbf{R}) = \varepsilon\chi_n(\mathbf{R})$$

Time-independent BO adiabatic formulation

Nuclear Schrödinger equation

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

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

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