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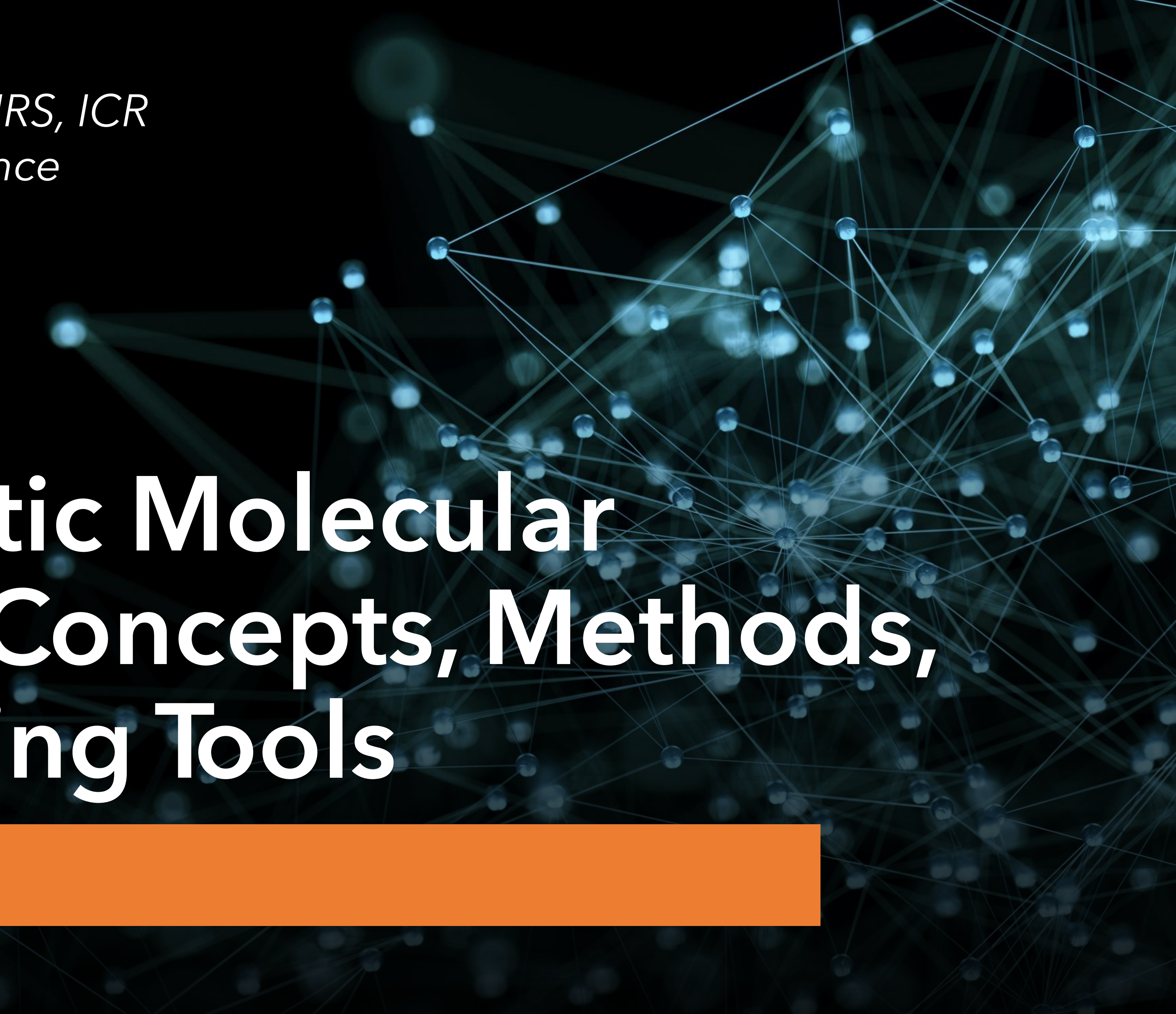


Nonadiabatic Molecular Dynamics: Concepts, Methods, and Emerging Tools

I – Quantum Mechanics

The quantum state

$$a_1|x_1\rangle + a_2|x_2\rangle + \cdots =$$

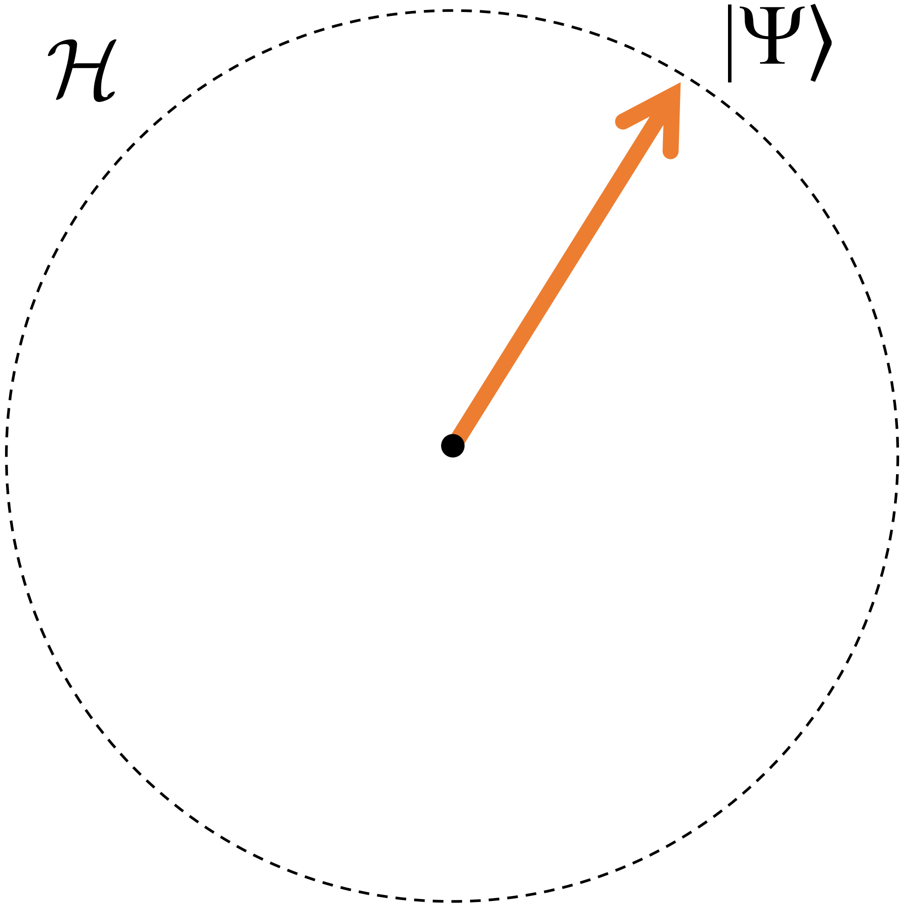
$$= c_1|E_1\rangle + c_2|E_2\rangle + \cdots$$

$$|\Psi\rangle$$

$$b_1|p_1\rangle + b_2|p_2\rangle + \cdots =$$

$$= d_1|L_1\rangle + d_2|L_2\rangle + \cdots$$

Quantum state in the Hilbert space

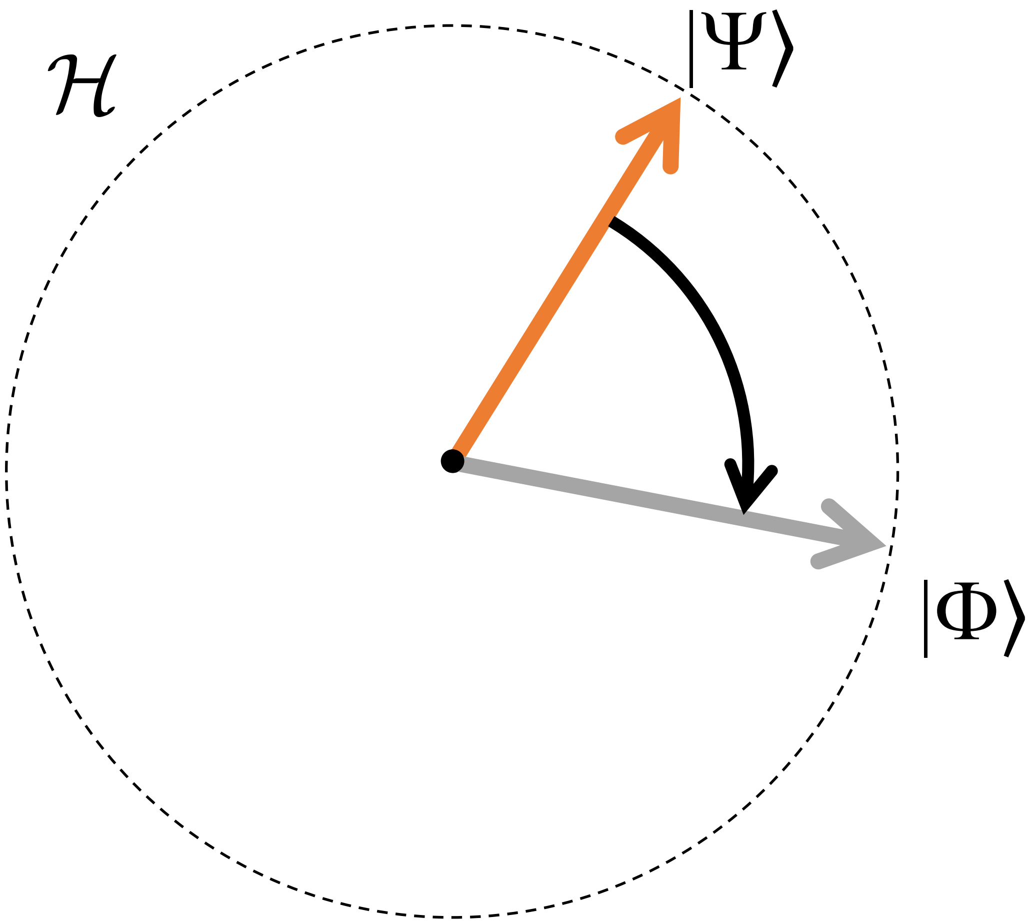


The number of dimensions is the number of possible outputs.

Kets can be represented as column vectors

$$|\Psi\rangle = \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix}$$

Operators in the Hilbert space



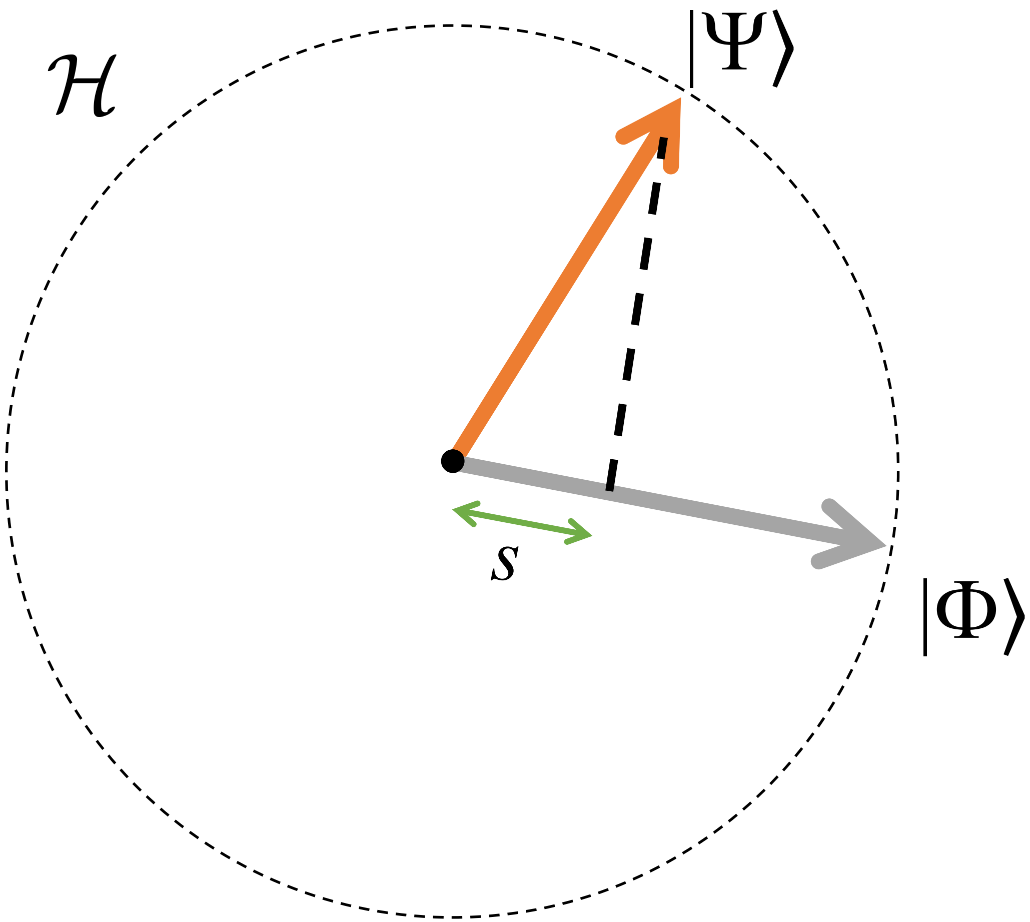
An operator acts on the vector creating a new vector in $\mathcal{H}$

$$\hat{A}|\Psi\rangle = |\Phi\rangle$$

Operators can be represented as matrices

$$|\Phi\rangle = \begin{bmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & \ddots & \\ \vdots & & \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix}$$

Inner product in the vector space



The inner product of two vectors

$$s = \langle\Phi|\cdot|\Psi\rangle = \langle\Phi|\Psi\rangle$$

encodes their overlap

Bras can be represented as complex-conjugate row vectors

$$\langle\Phi|\Psi\rangle = \begin{bmatrix} b_1^* & b_2^* & \cdots \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix}$$

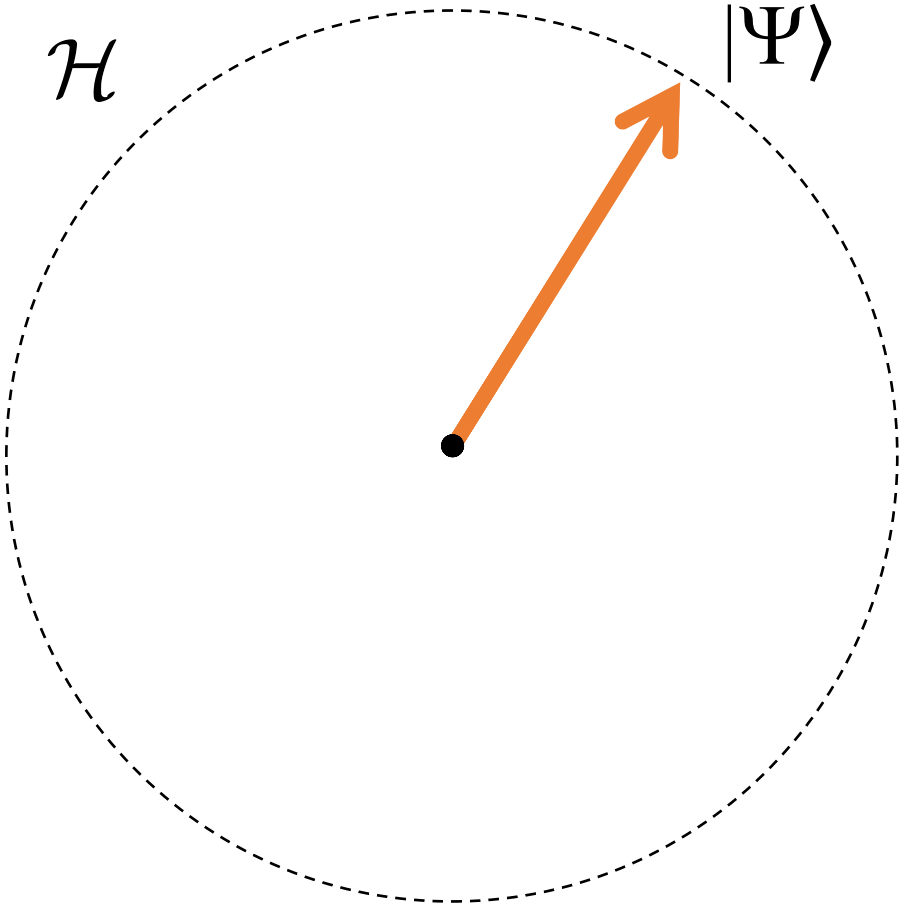
Any observable is represented as a self-adjoint operator Ô in $\mathcal{H}$

$$\left\langle \Phi \middle| \hat{\mathrm{O}}\Psi \right\rangle = \left\langle \hat{\mathrm{O}}\Phi \middle| \Psi \right\rangle$$

The expected value of Ô when the system is state $|\Psi\rangle$ is

$$O = \left\langle \Psi \middle| \hat{O} \middle| \Psi \right\rangle$$

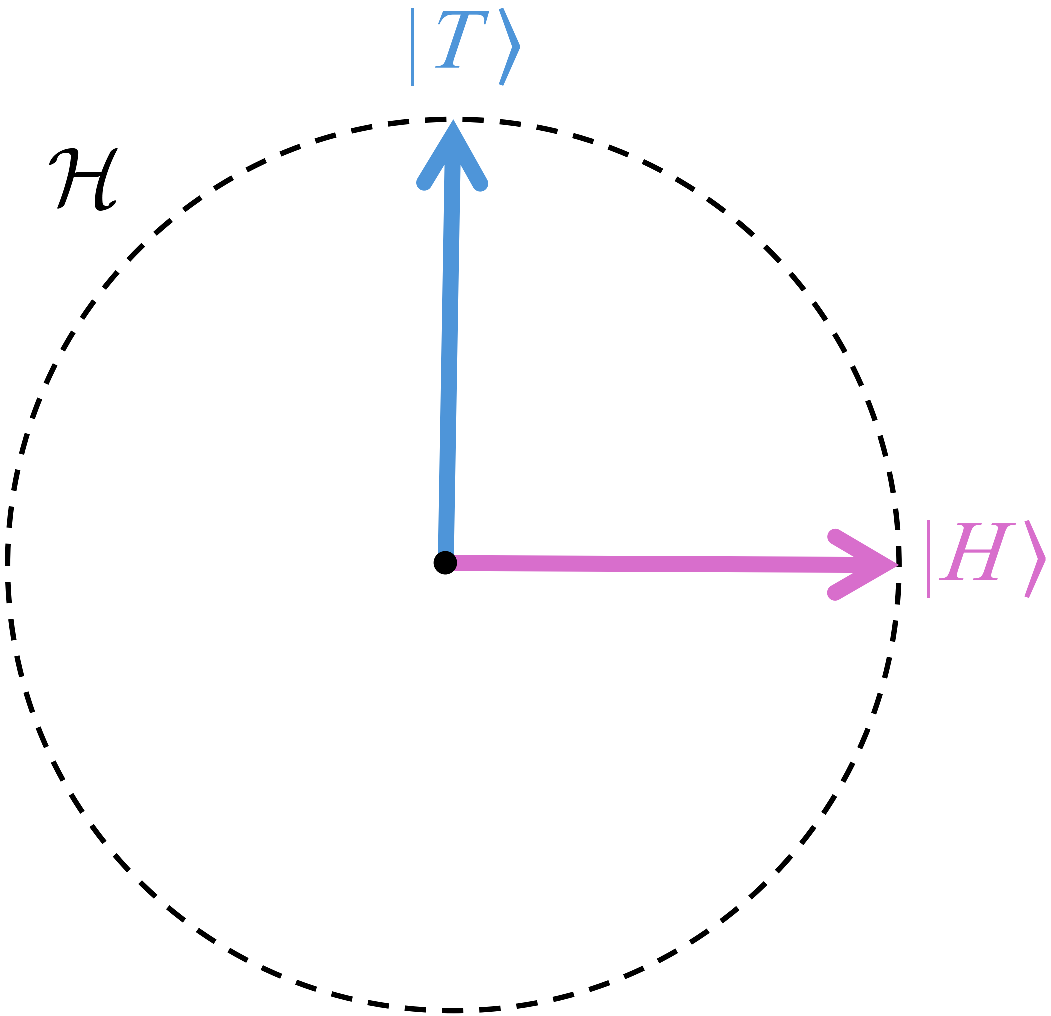
Qubit in the Hilbert space



2 outputs

The number of dimensions is two.

Observables



Example: Observable "Side"

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

Basis

$$\hat{S}|H\rangle = c_H|H\rangle \quad \hat{S}|T\rangle = c_T|T\rangle \quad c_H, c_T \in \mathbb{R}$$

Complete

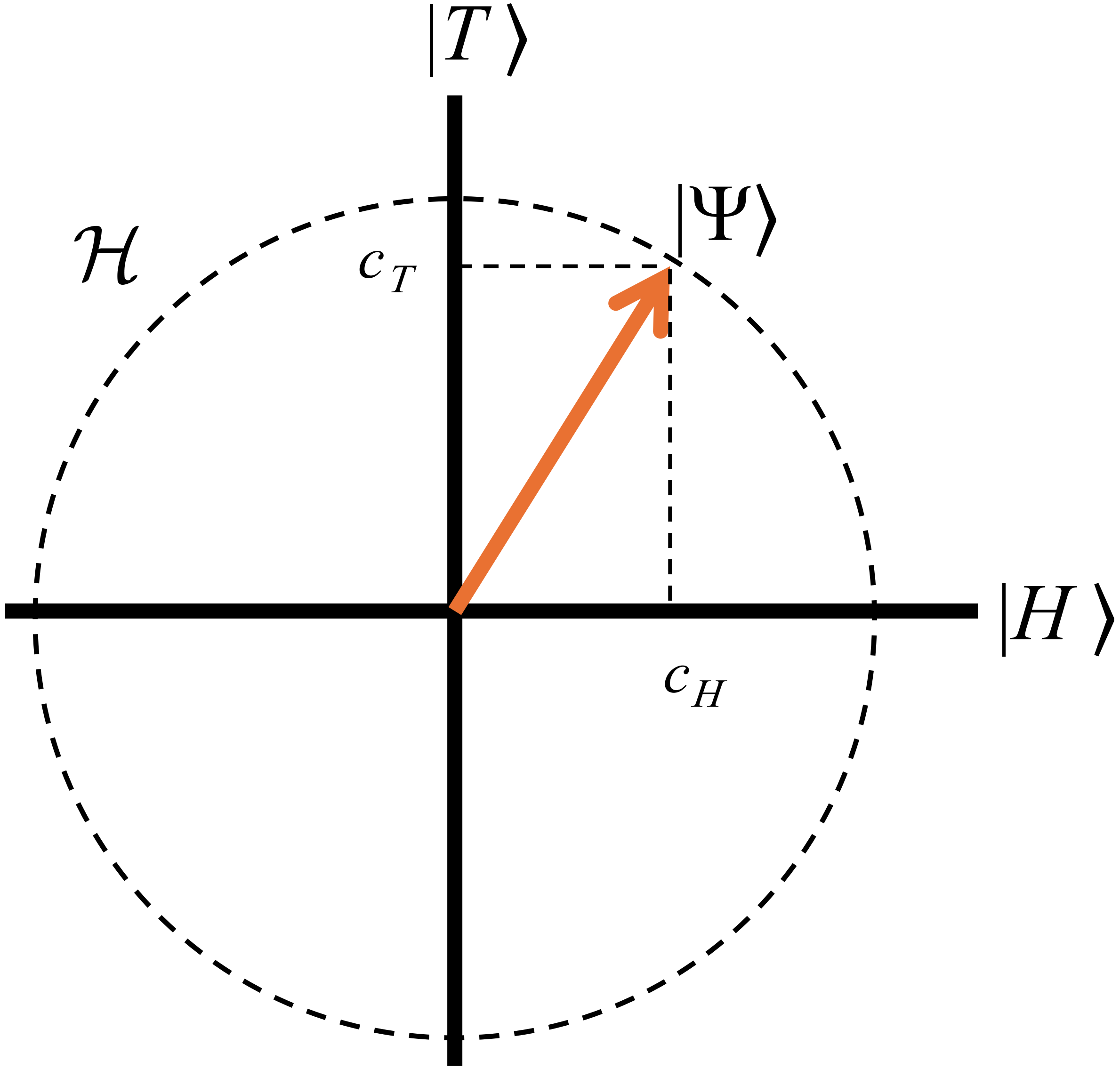
$$|H\rangle\langle H| + |T\rangle\langle T| = \hat{\mathrm{I}}$$

Orthonormal

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

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

Superposition



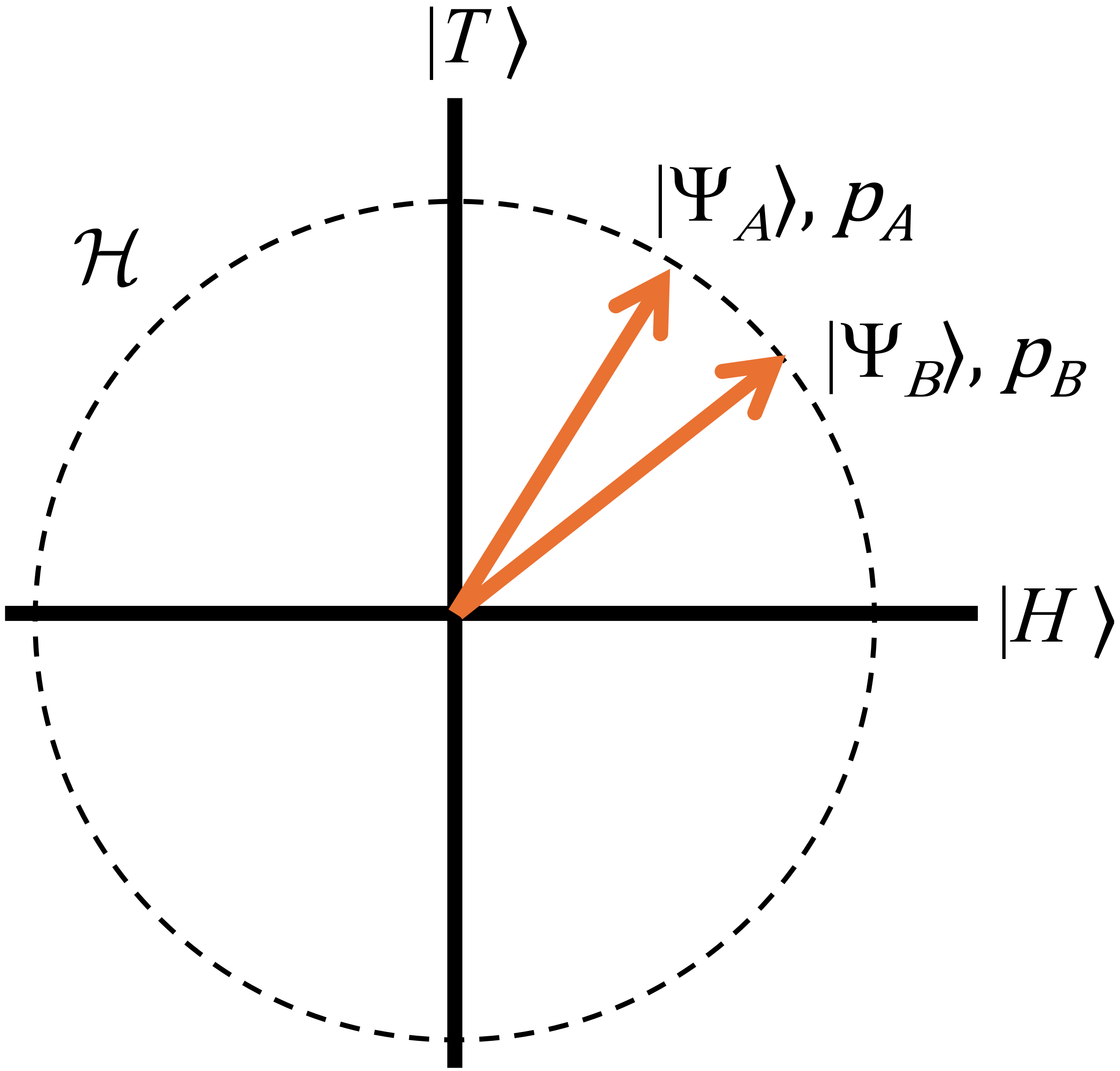
Any unit vector in $\mathcal{H}$ is a possible state

$$|\Psi\rangle = c_H |H\rangle + c_T |T\rangle$$

$$c_H = \langle H|\Psi\rangle$$

$$c_T = \langle T|\Psi\rangle$$

Density operator



Unsure which state we have…

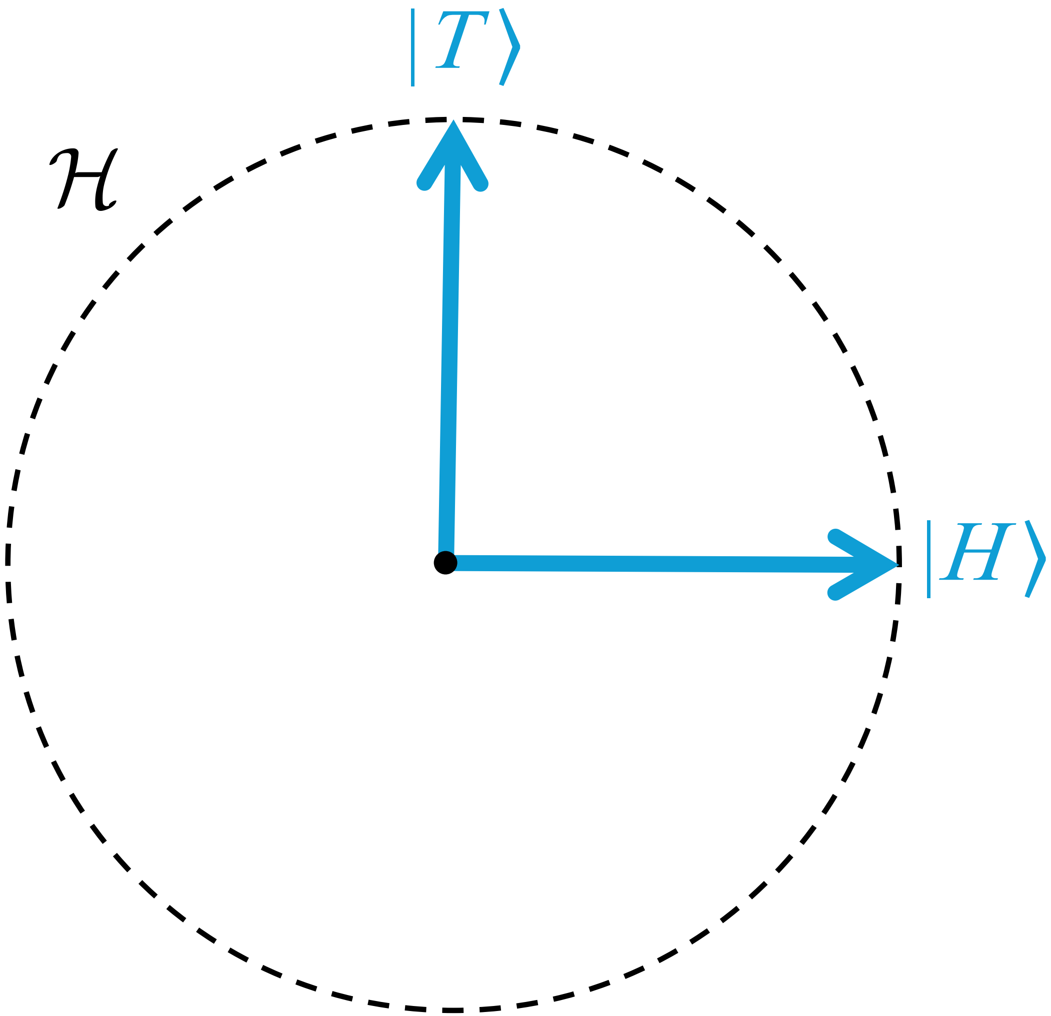
$$\rho = p_A |\Psi_A\rangle\langle\Psi_A| + p_B |\Psi_B\rangle\langle\Psi_B|$$

$$p_A + p_B = 1$$

The density operator will also be central for description of **open quantum systems**.

Commutation

Commutation relations

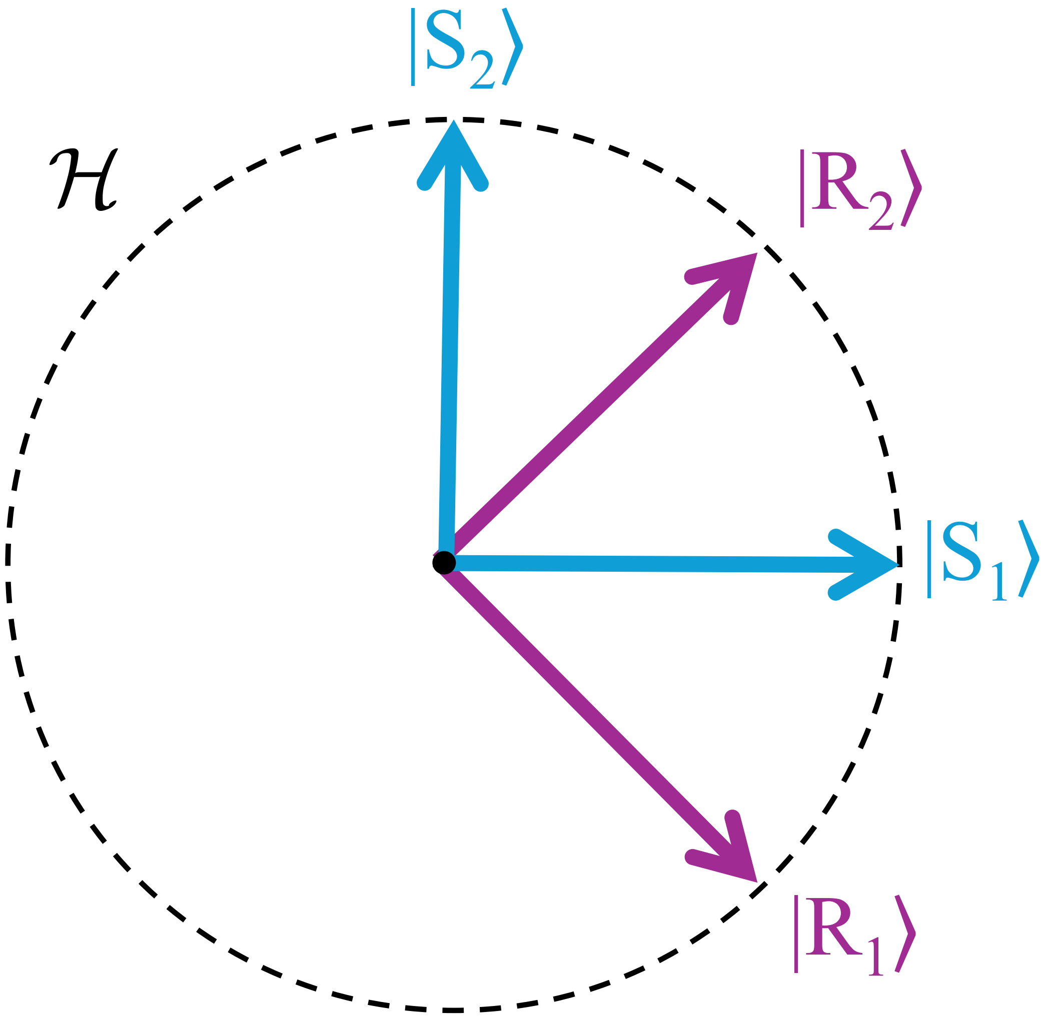


$$\left[\hat{S},\hat{R}\right]|\Psi\rangle = \hat{S}\hat{R}|\Psi\rangle - \hat{R}\hat{S}|\Psi\rangle = 0$$

Commuting operators **share** the same eigenvectors.

The system **can** have well-defined values for the observables *R* and *S* simultaneously.

Commutation relations



$$\left[\hat{S},\hat{R}\right]|\Psi\rangle = \hat{S}\hat{R}|\Psi\rangle - \hat{R}\hat{S}|\Psi\rangle \neq 0$$

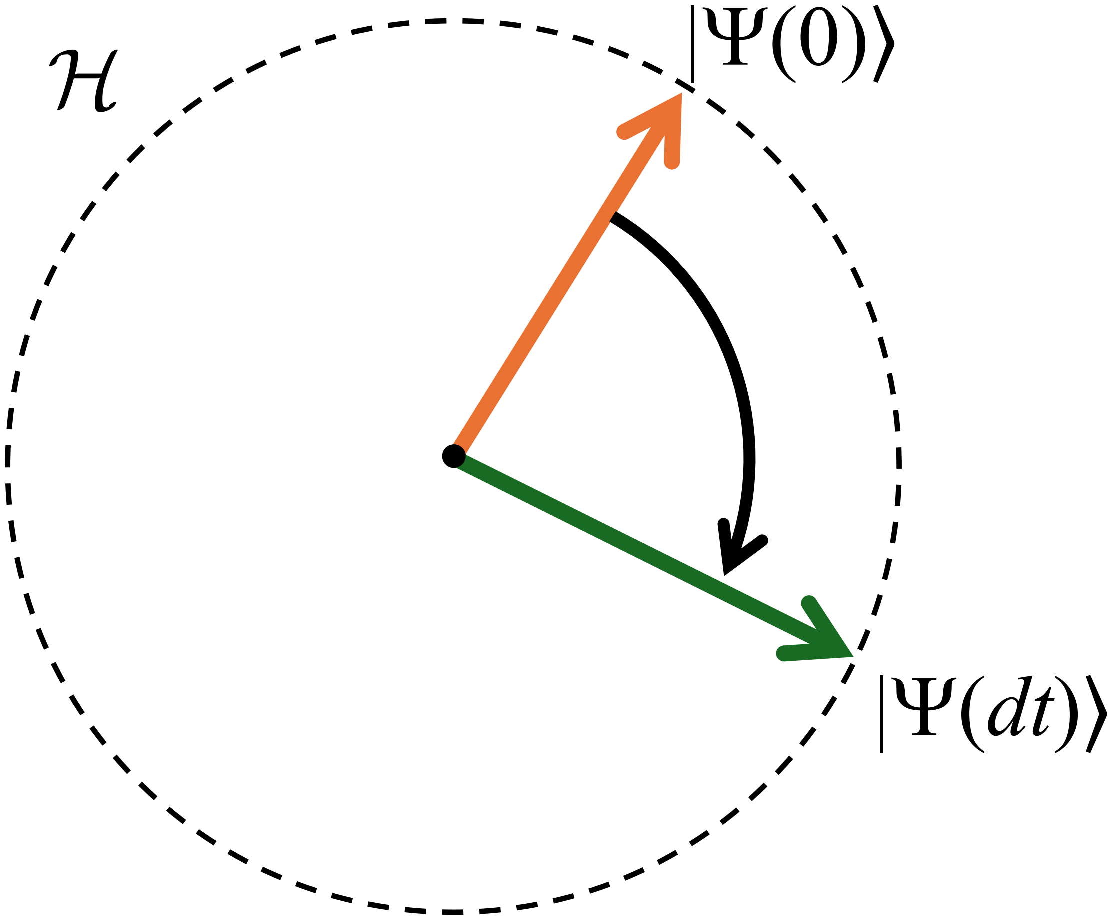
Non-commuting operators **do not share** eigenvectors.

The system **cannot** have well-defined values for the observables *R* and *S* simultaneously.

Non-commutation leads to the **Heisenberg uncertainty principle.**

Deterministic evolution of the quantum state

Schrödinger evolution



We assume that:

1) Time evolution is **unitary** (conserves total probability) and **reversible**:

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

2) The Hamiltonian is the **generator** of time translation:

$$\frac{d\hat{U}}{dt} = -\frac{i}{\hbar}\hat{H}$$

In the non-relativistic limit, they imply:

Schrödinger Equation

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

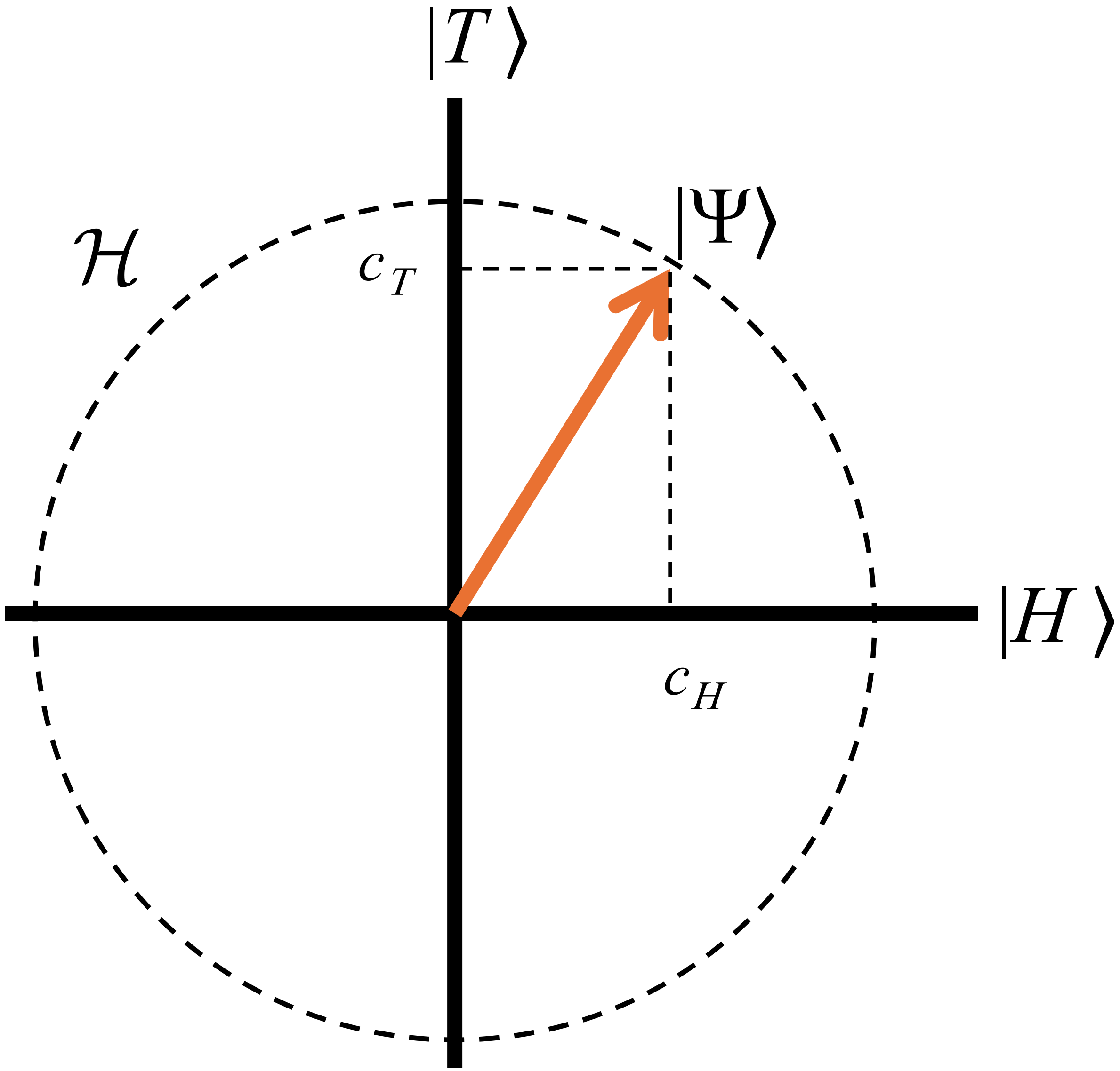
Von Neumann evolution

$$\rho = \sum_k p_k \left|\Psi_k\right\rangle\left\langle\Psi_k\right|$$

Von Neumann Equation

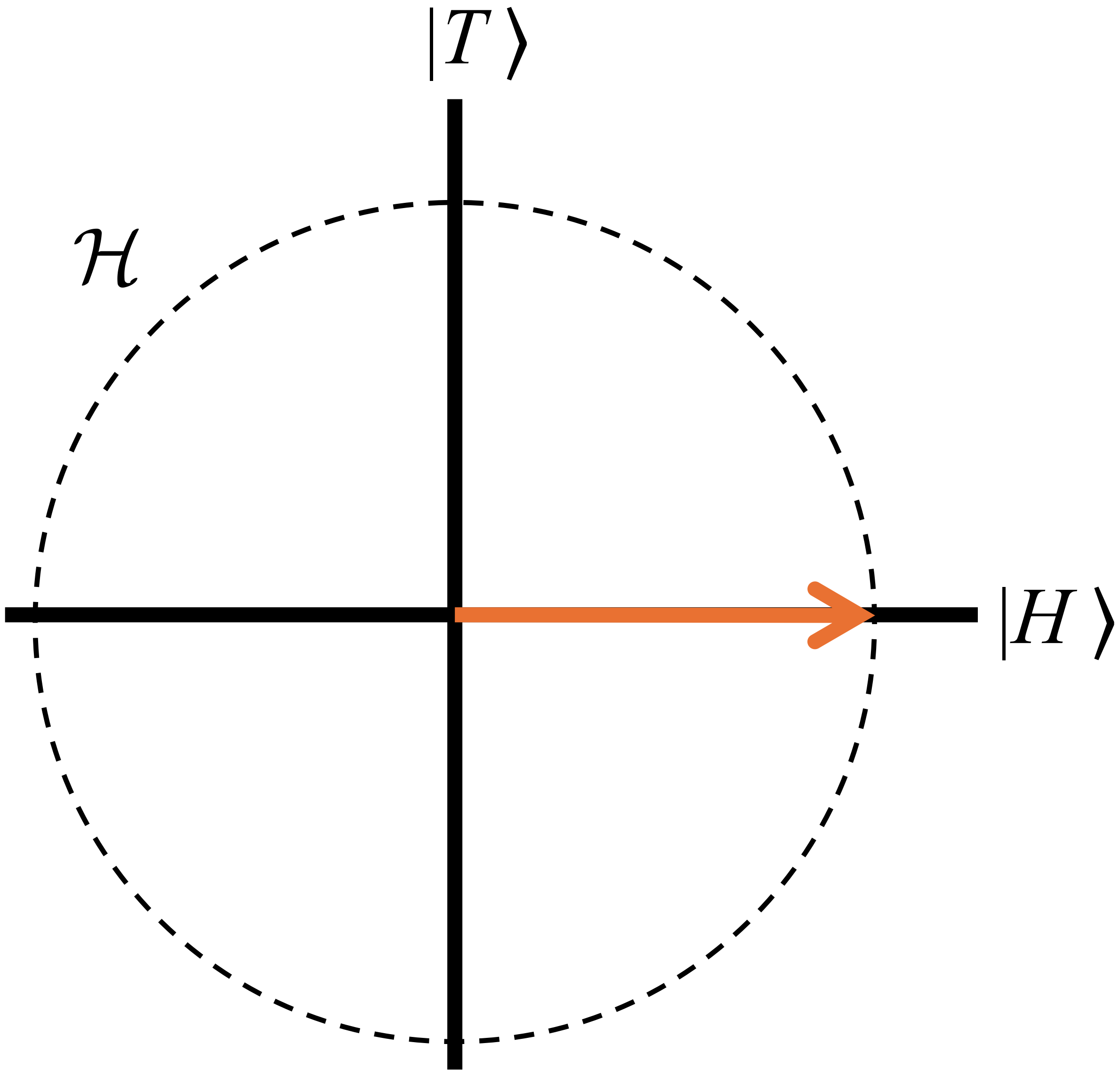
$$i\hbar \frac{d\rho}{dt} = \left[\hat{H}, \rho\right]$$

Stochastic evolution of the quantum state



$$|\Psi\rangle = c_H|H\rangle + c_T|T\rangle$$

Quantum state measurement



$$|\Psi\rangle = c_H|H\rangle + c_T|T\rangle$$

$$\downarrow$$

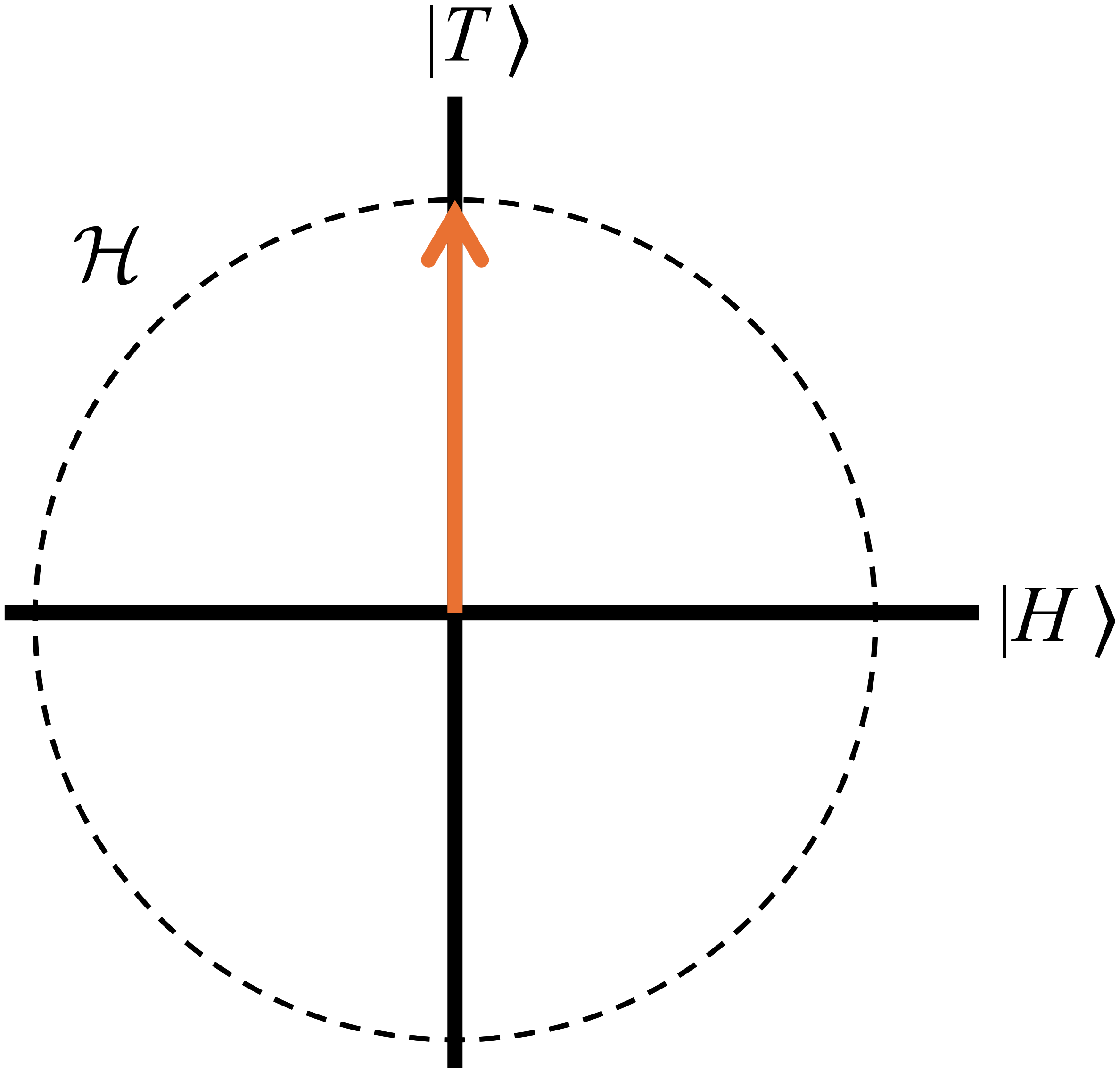
$$|\Psi\rangle = |H\rangle$$

$$P(H) = \left|\langle H|\Psi\rangle\right|^2 = |c_H|^2$$

or

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

Quantum state measurement



$$|\Psi\rangle = c_H|H\rangle + c_T|T\rangle$$

$$\downarrow$$

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

$$P(T) = \left|\langle T|\Psi\rangle\right|^2 = |c_T|^2$$

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)

Gleason's theorem shows that the Born rule can be derived from the usual mathematical representation of the quantum state.

Generalization 1: Multidimensional systems & position basis

How many outputs?

6 outputs

∞ outputs

$$|\Psi\rangle = c_1|1\rangle + c_2|2\rangle + \cdots + c_6|6\rangle = \sum_{k=1}^{6} c_k|k\rangle$$

countable outputs

$$|\Psi\rangle = \sum_{k=1}^{\infty} {\color{blue}c_k}|x\rangle$$

uncountable ∞ outputs

$$|\Psi\rangle = c_1|1\rangle + c_2|2\rangle + \cdots + c_6|6\rangle = \sum_{k=1}^{6} c_k|k\rangle$$

countable outputs

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

0 5 m

uncountable ∞ outputs

State vector ⟶

$$\left|\Psi\right\rangle = \int \Psi\left(x\right)\left|x\right\rangle dx$$

Wave function ↑

↑ Base vector

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

$$\langle x'||\Psi\rangle = \langle x'|\int \Psi(x)|x\rangle dx$$

$$\langle x'|\Psi\rangle = \int \Psi(x)\langle x'|x\rangle dx$$

$$= \int \Psi(x)\delta(x'-x)dx$$

$$\boxed{\Psi(x) = \langle x|\Psi\rangle}$$

Time evolution in the position basis

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

$$\left\langle x\right|i\hbar\frac{d\left|\Psi\right\rangle}{dt}=\left\langle x\right|\hat{H}\left|\Psi\right\rangle$$

$$=i\hbar\frac{\partial\left\langle x|\Psi\right\rangle}{\partial t}=i\hbar\frac{\partial\Psi\left(x,t\right)}{\partial t}$$

Assuming that

$$\Psi\left(x\to\pm\infty\right)\to 0$$

$$\hat{H}\left(x\right)\Psi\left(x,t\right)=$$

Position-basis Schrödinger equation

$$i\hbar\frac{\partial\Psi\left(x,t\right)}{\partial t}=\hat{H}\left(x\right)\Psi\left(x,t\right)$$

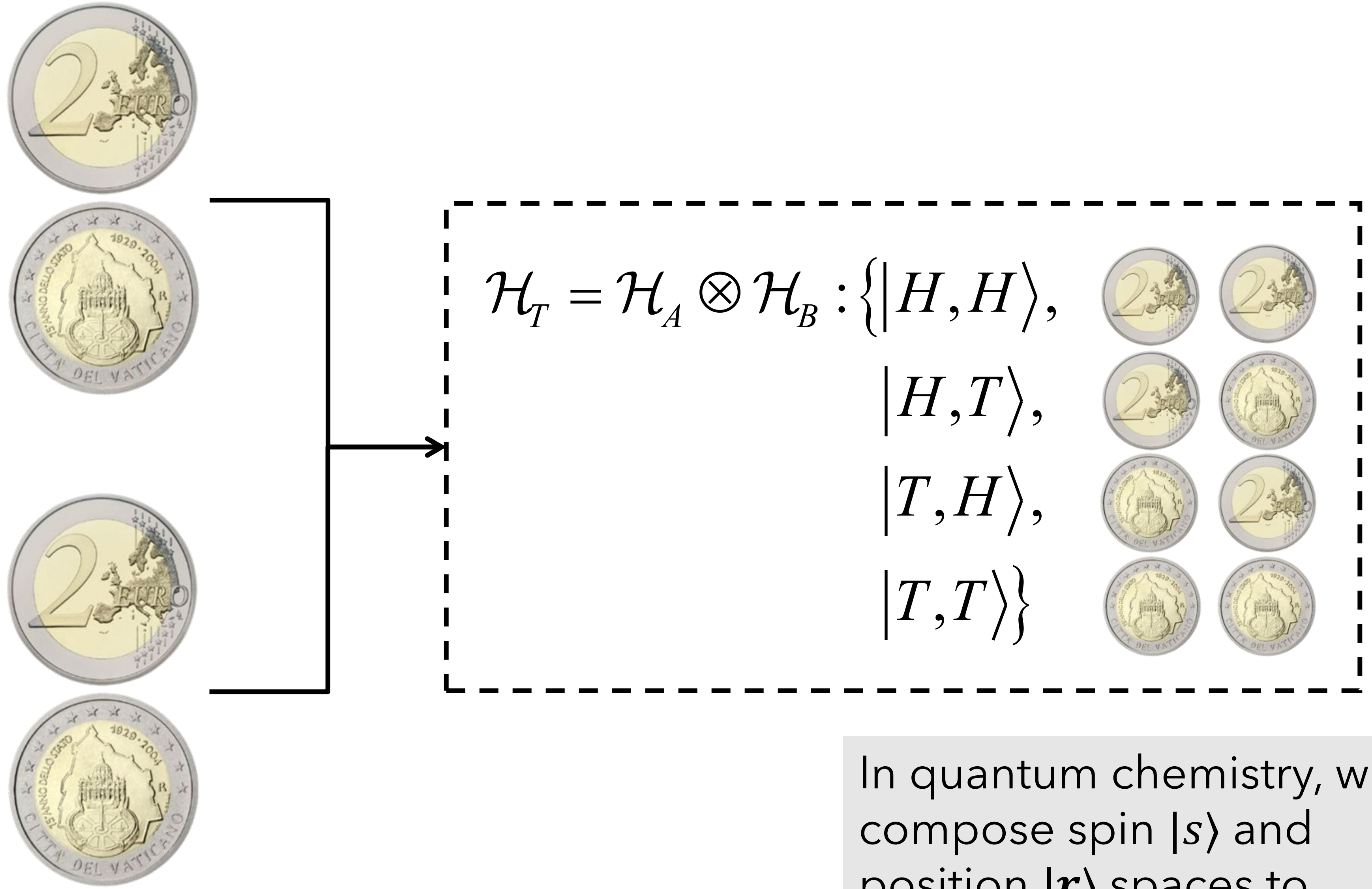
Generalization 2: Composite systems

1 Qubit

2 outputs

2 Qubits

4 outputs



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

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

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

In quantum chemistry, we compose spin $|s\rangle$ and position $|\boldsymbol{r}\rangle$ spaces to describe electron's spin orbitals $|\chi\rangle = |s, \boldsymbol{r}\rangle$.

Entanglement

$$\left|\Psi\right\rangle = \sum_{i,j} c_{ij} \left|A_i, B_j\right\rangle$$

Entangled state

$$\left|\Psi\right\rangle = \left|A_i, B_i\right\rangle = \left|A_i\right\rangle \otimes \left|B_i\right\rangle$$

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

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

Fermion’s antisymmetry leads to the **Pauli exclusion principle**.

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.

Lindblad evolution

$$\rho_A = \mathrm{Tr}_B\left[\rho_{AB}\right]$$

Lindblad Equation

$$\frac{d\rho_A}{dt} = -\frac{i}{\hbar}\left[\hat{H},\rho_A\right] + \sum_k \Gamma_k\left(\hat{L}_k\rho_A\hat{L}_k^\dagger - \frac{1}{2}\left\{\hat{L}_k^\dagger\hat{L}_k,\rho_A\right\}\right)$$

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

$$\left\{\hat{L}_k^\dagger\hat{L}_k,\rho_A\right\} = \hat{L}_k^\dagger\hat{L}_k\rho_A + \rho_A\hat{L}_k^\dagger\hat{L}_k$$

The Lindblad equation **conserves the total probability** and always yields **positive probabilities**.

Quantization

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

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

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

Replace it in the position-basis Schrödinger equation

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

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

Separate the variables:

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

The first equation

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

gives

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

$|\phi(t)|^2 = 1$: This phase factor does **not** impact probabilities

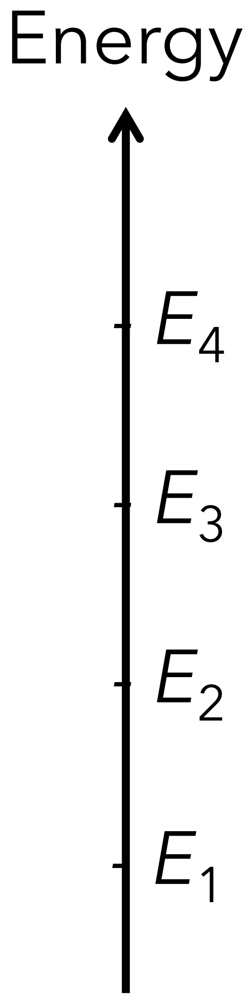
The second equation

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

is the **Time-Independent Schrödinger equation**
(on the position basis)

$$\left.\begin{array}{c}\hat{H}(\mathbf{r})\psi_N(\mathbf{r}) = E_N\psi_N(\mathbf{r}) \\ \vdots \\ \hat{H}(\mathbf{r})\psi_2(\mathbf{r}) = E_2\psi_2(\mathbf{r})\end{array}\right\} \text{Excited states}$$

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



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

$$\text{Molecular wave function} \longrightarrow \Psi\left(\underset{\substack{\uparrow\\ \text{nuclei}}}{\mathbf{R}}, \overset{\substack{\text{electrons}\\ \downarrow}}{\mathbf{r}}\right) \approx \underset{\substack{\uparrow \\ \text{Electronic wave function}}}{\varphi}\left(\mathbf{r};\mathbf{R}\right) \otimes \overset{\substack{\text{Nuclear wave function}\\ \downarrow}}{\chi}\left(\mathbf{R}\right)$$

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

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

Electronic Schrödinger equation

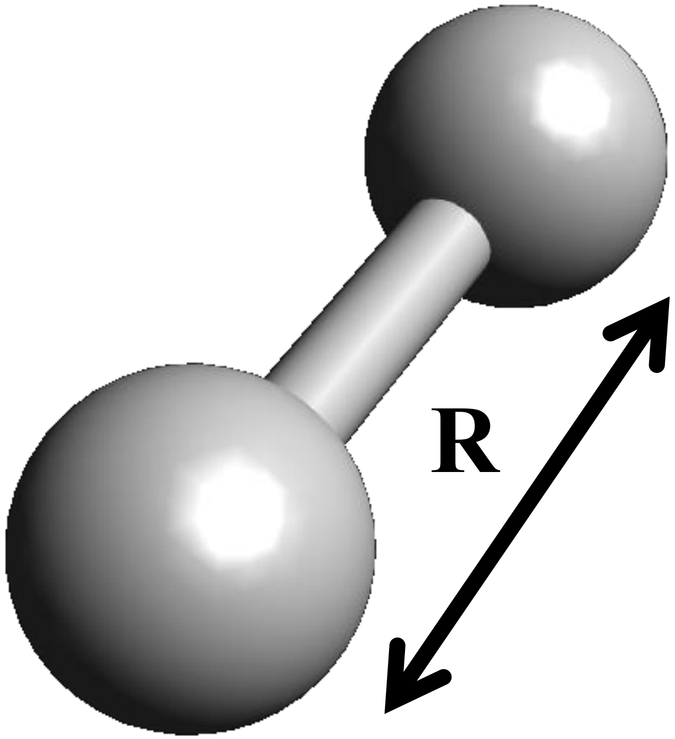
$$\left(\hat{T}_{elec}(\mathbf{r}) + V(\mathbf{r},\mathbf{R})\right)\varphi(\mathbf{r};\mathbf{R}) = \underline{E(\mathbf{R})}\varphi(\mathbf{r};\mathbf{R})$$

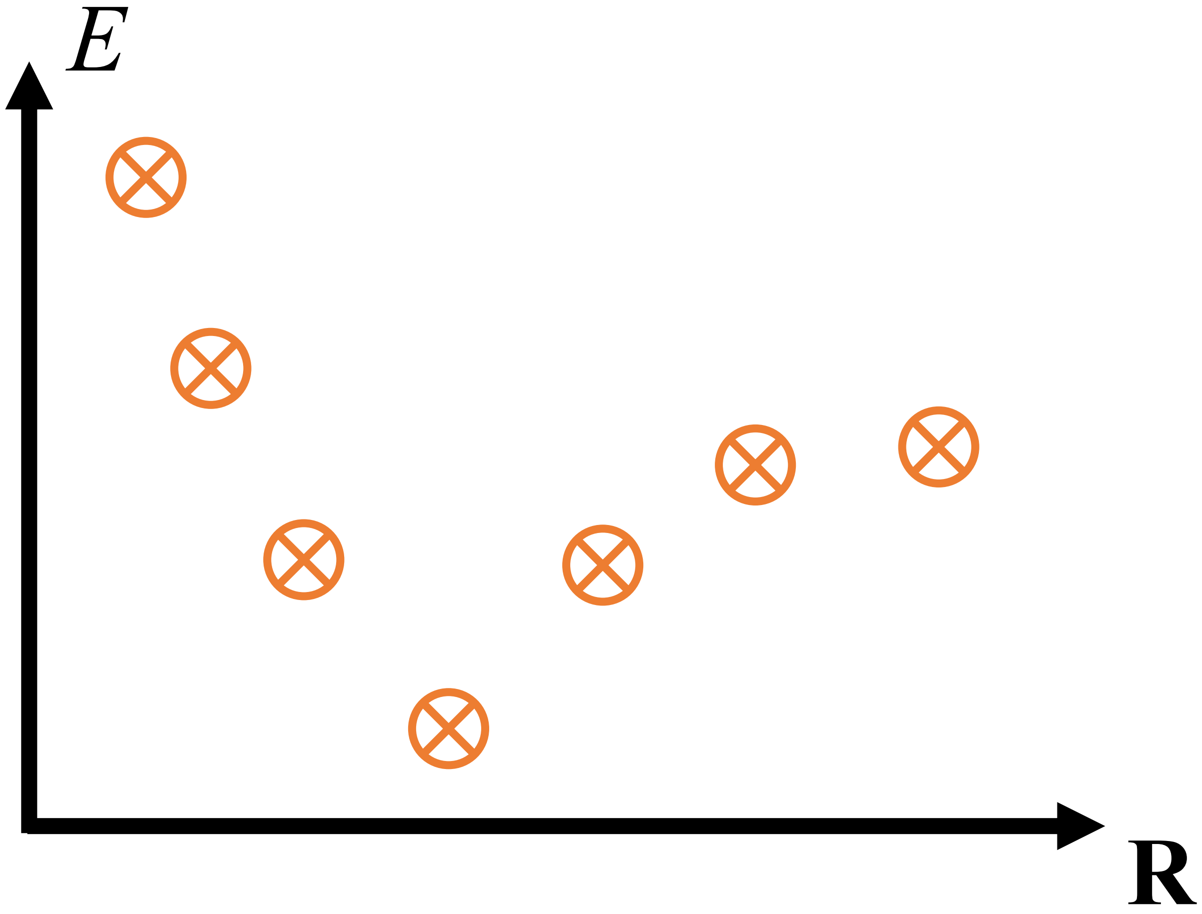
Potential Energy Surface

BO molecular wave function

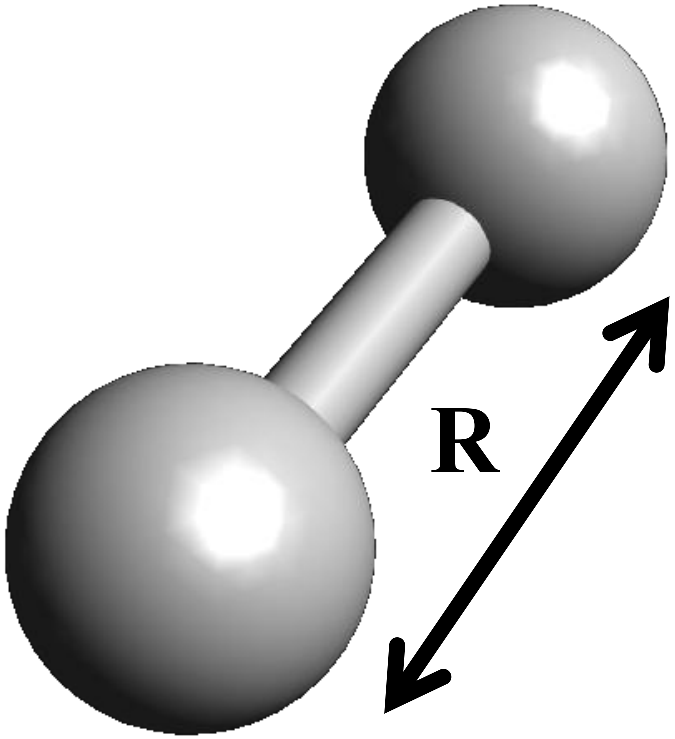
$$\Psi^{BO}(\mathbf{R},\mathbf{r}) = \varphi(\mathbf{r};\mathbf{R})\chi(\mathbf{R})$$

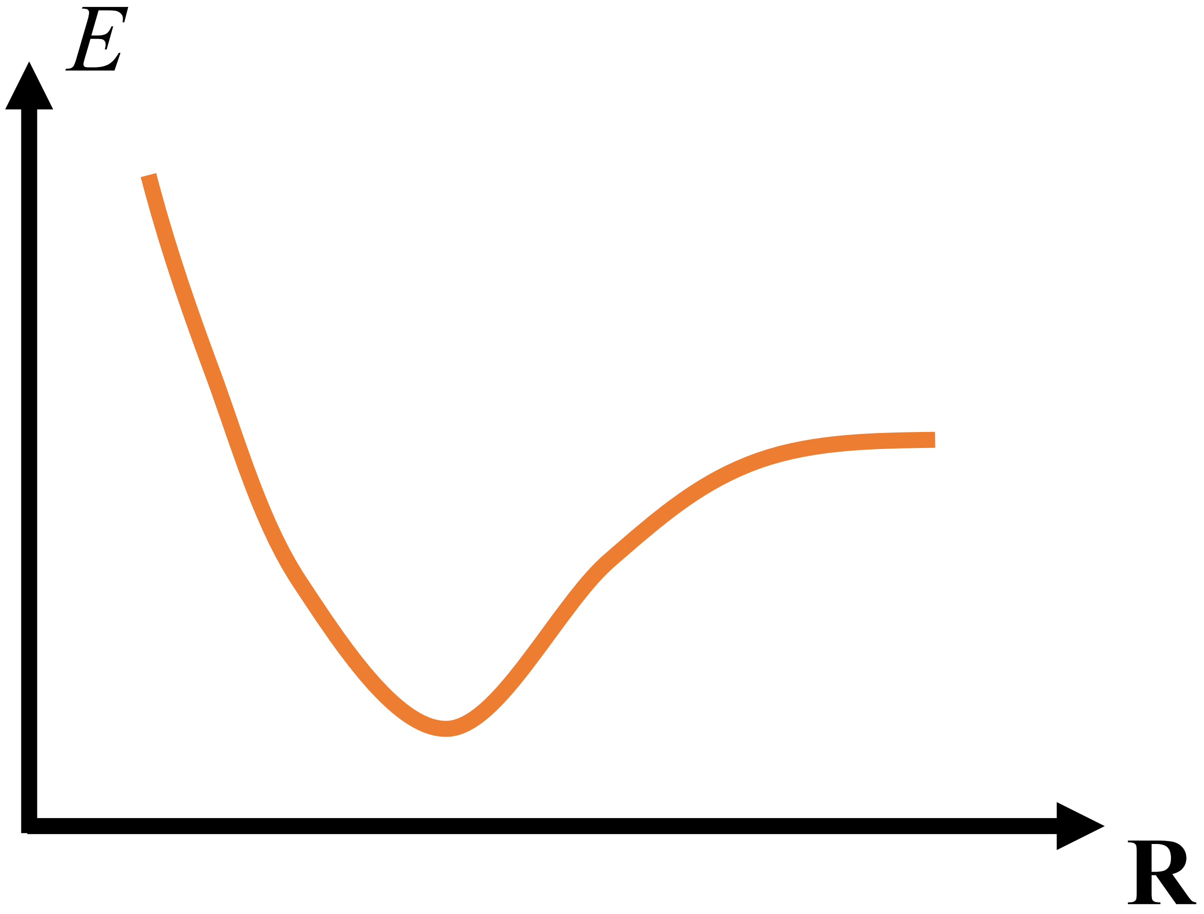
Check the derivation in the appendix





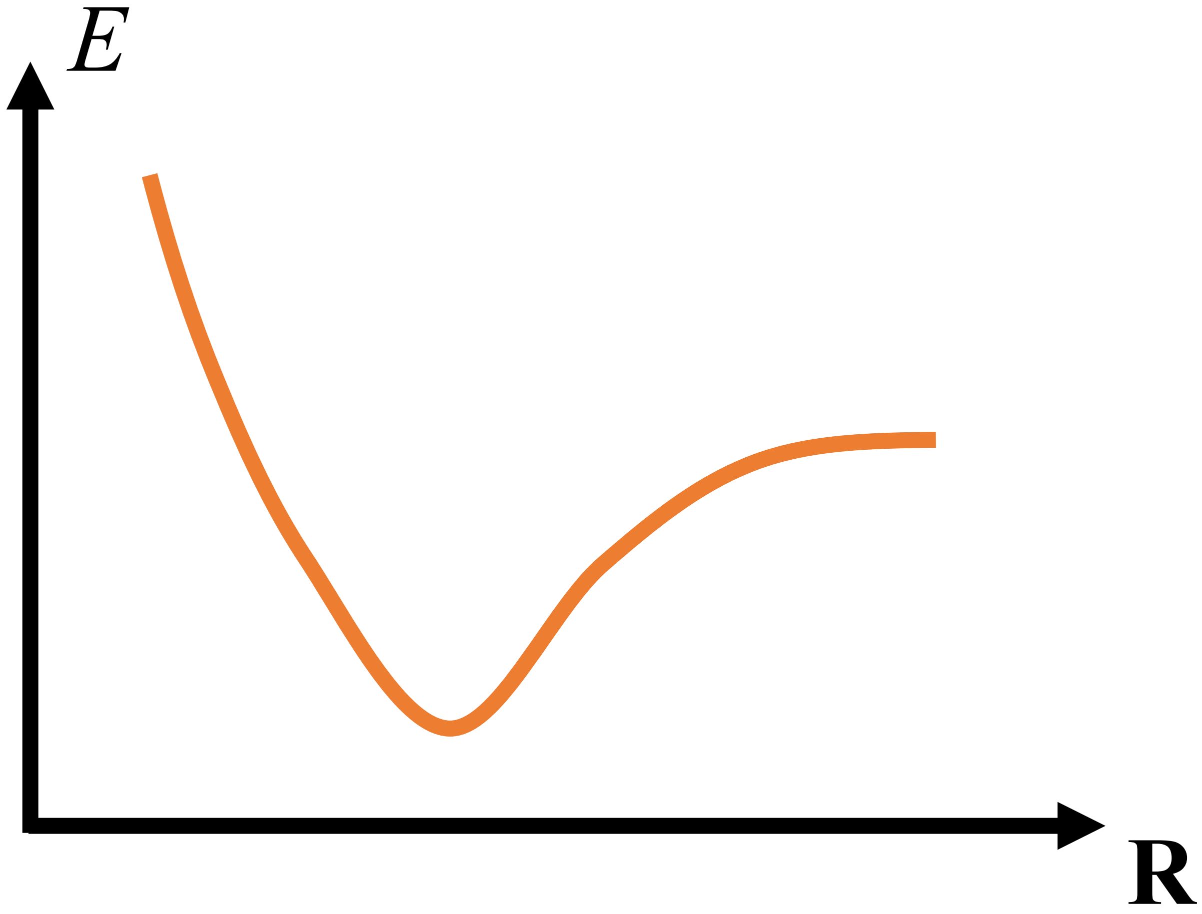
$$\hat{H}_{elec}\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)=E\left(\mathbf{R}\right)\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)$$

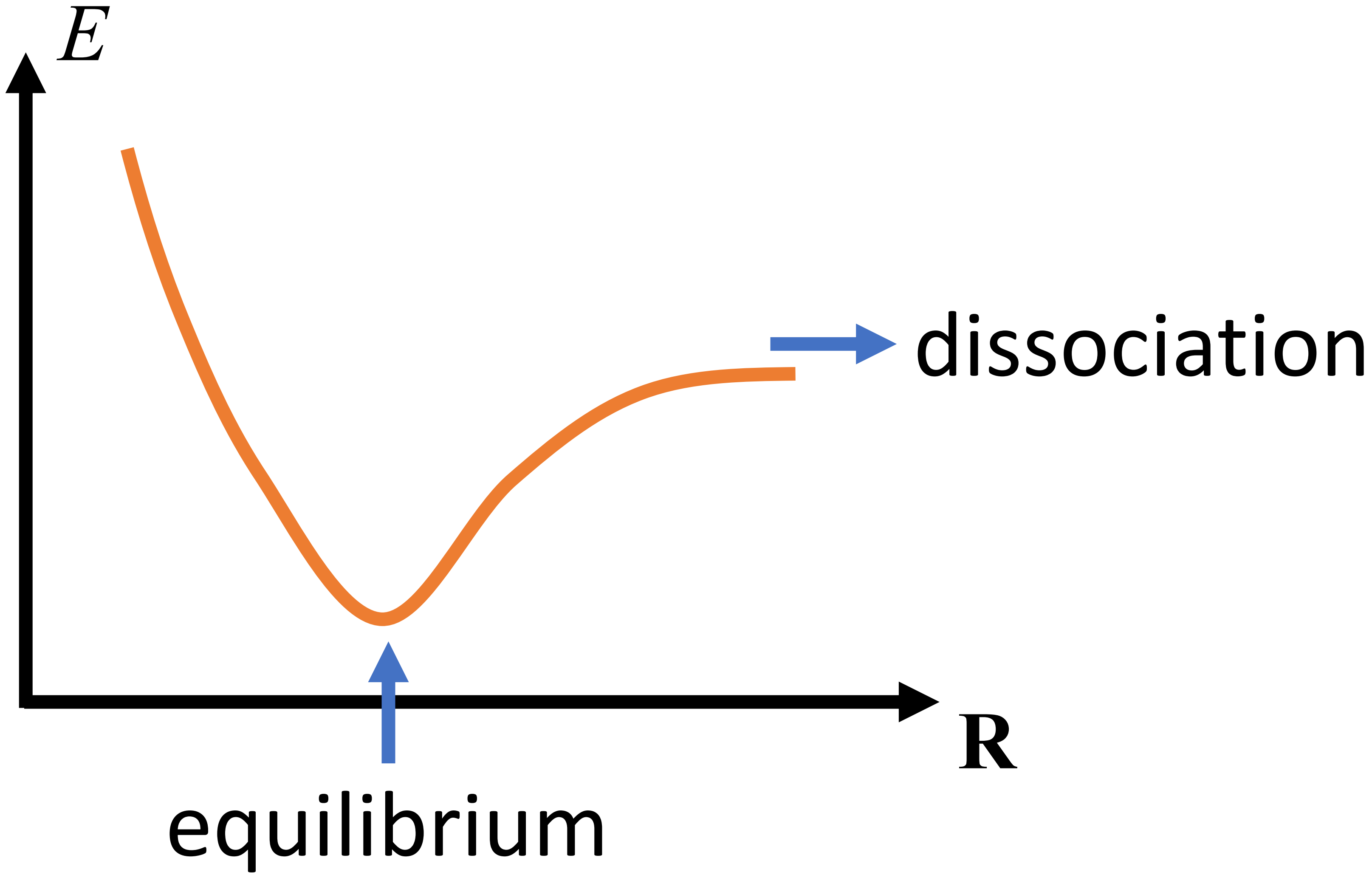


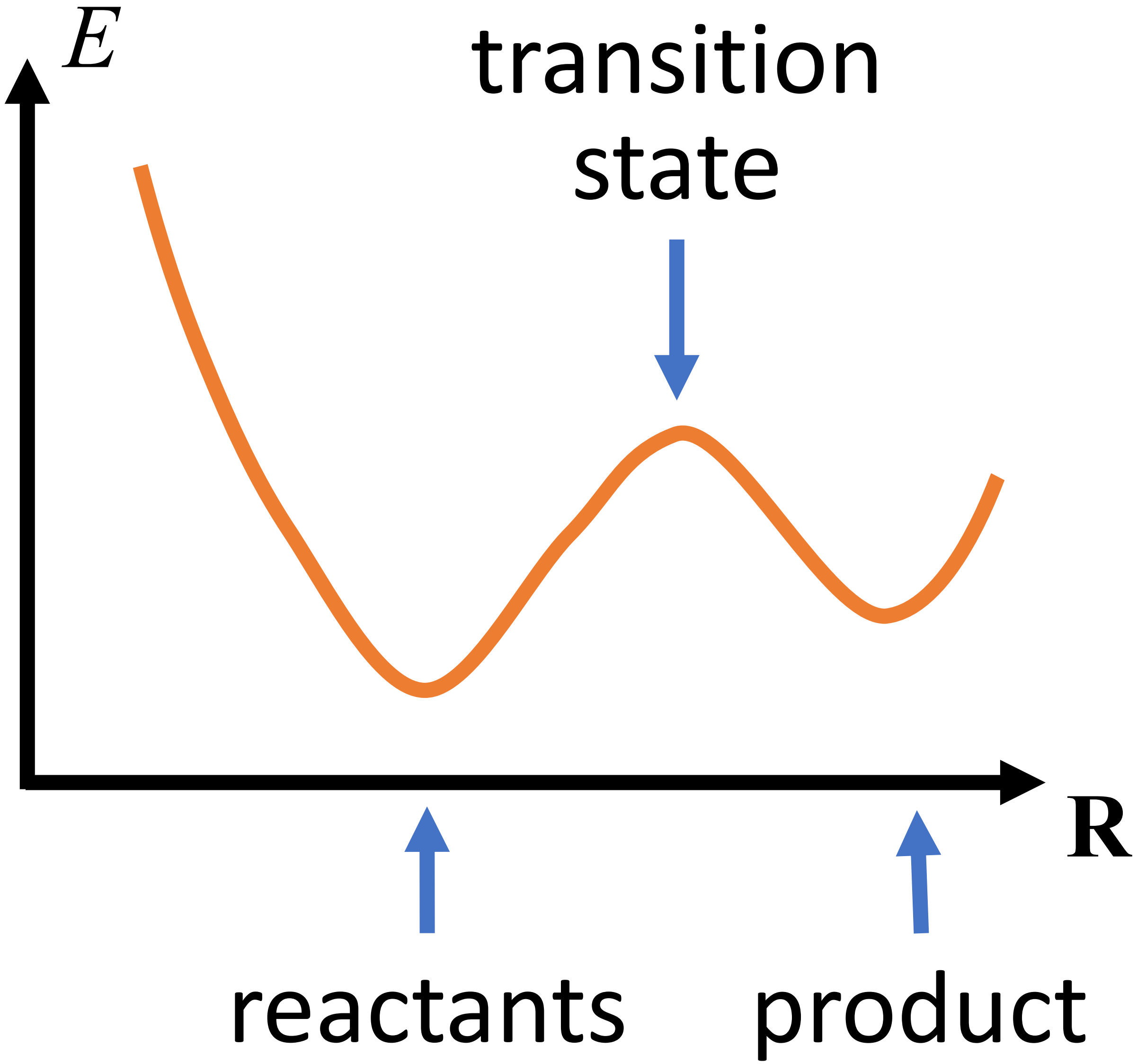


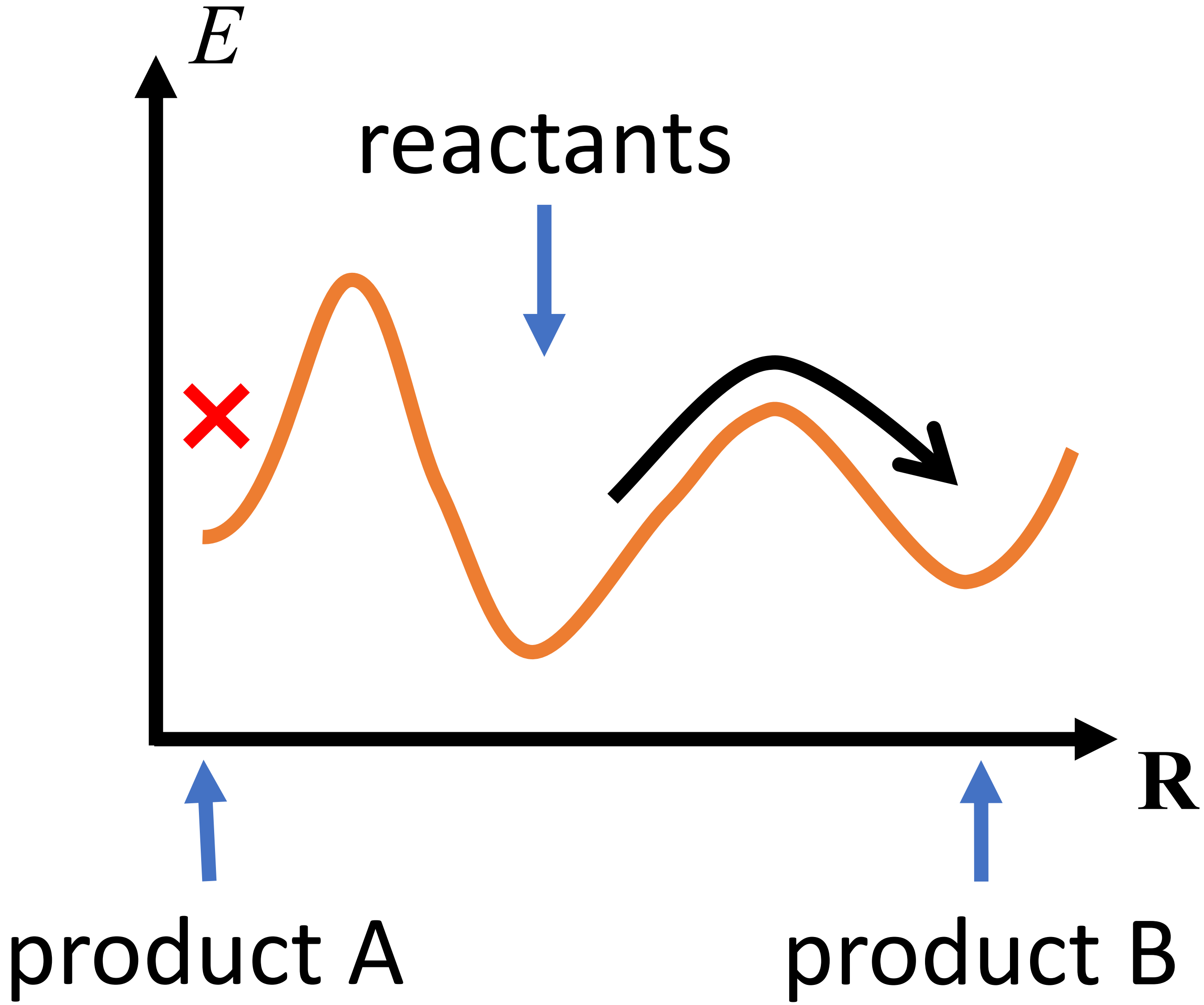
$$\hat{H}_{elec}\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)=E\left(\mathbf{R}\right)\varphi\left(\mathbf{r}_1,\mathbf{r}_2;\mathbf{R}\right)$$

Potential energy surface

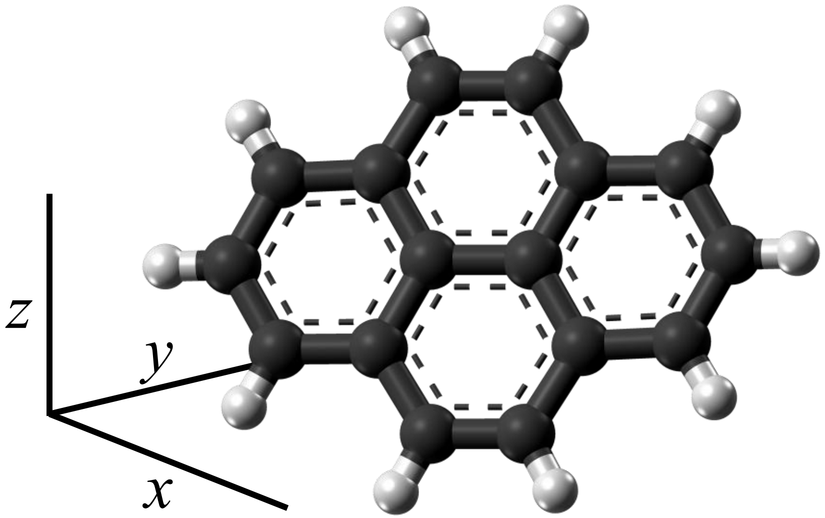


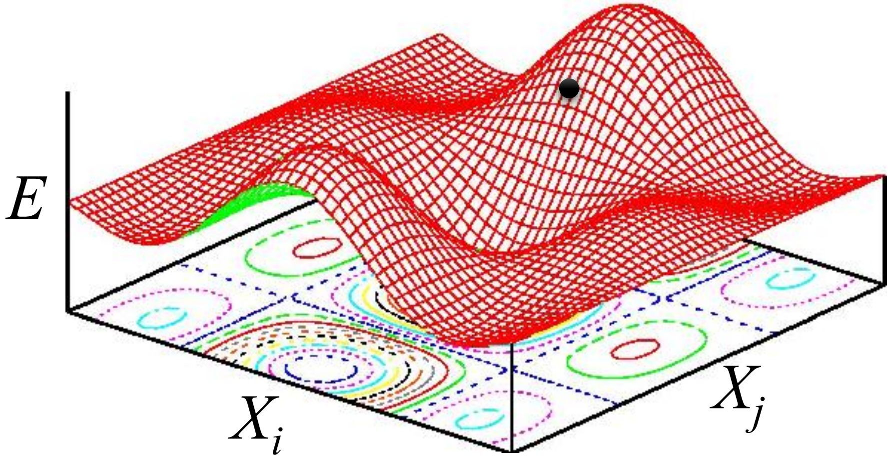

E
dissociation
R
equilibrium


E
transition state
R
reactants
product

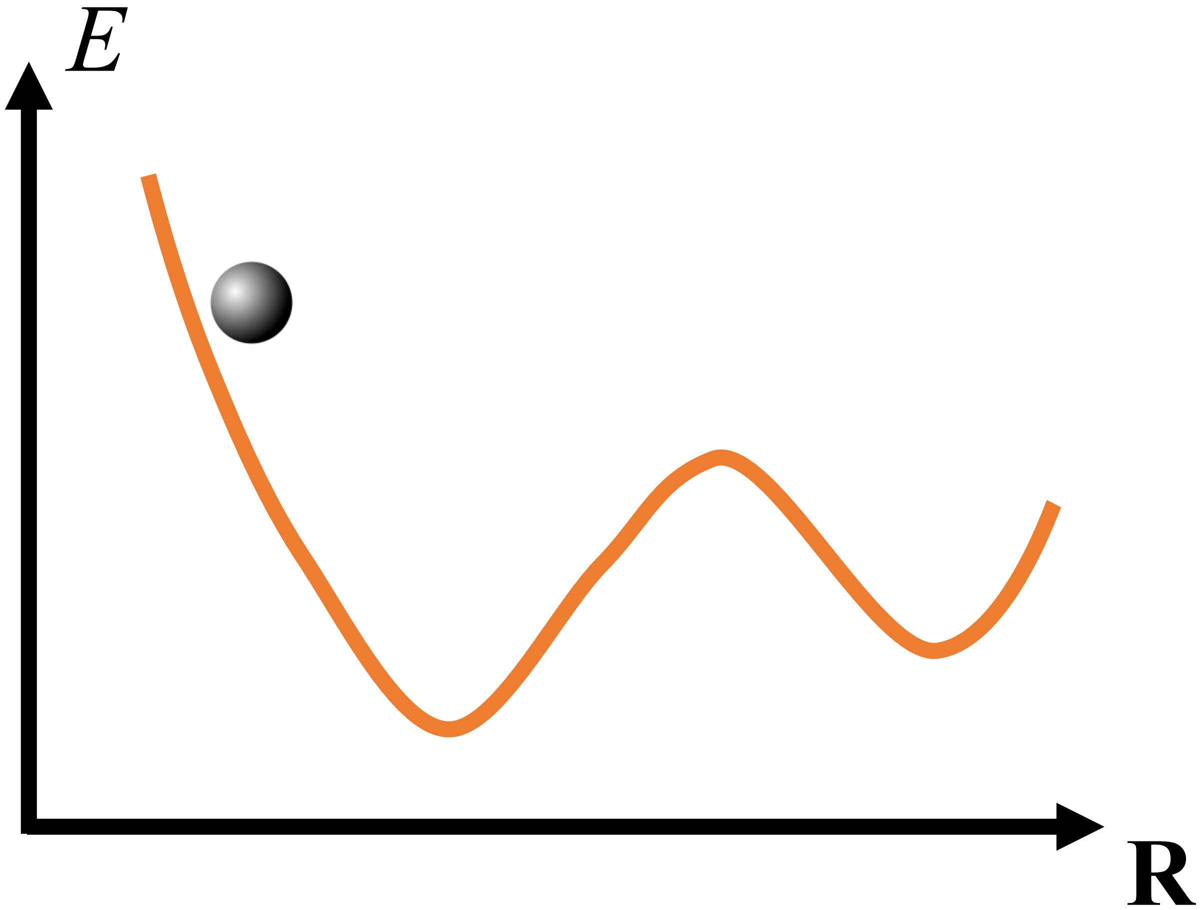

E
reactants
✕
R
product A
product B

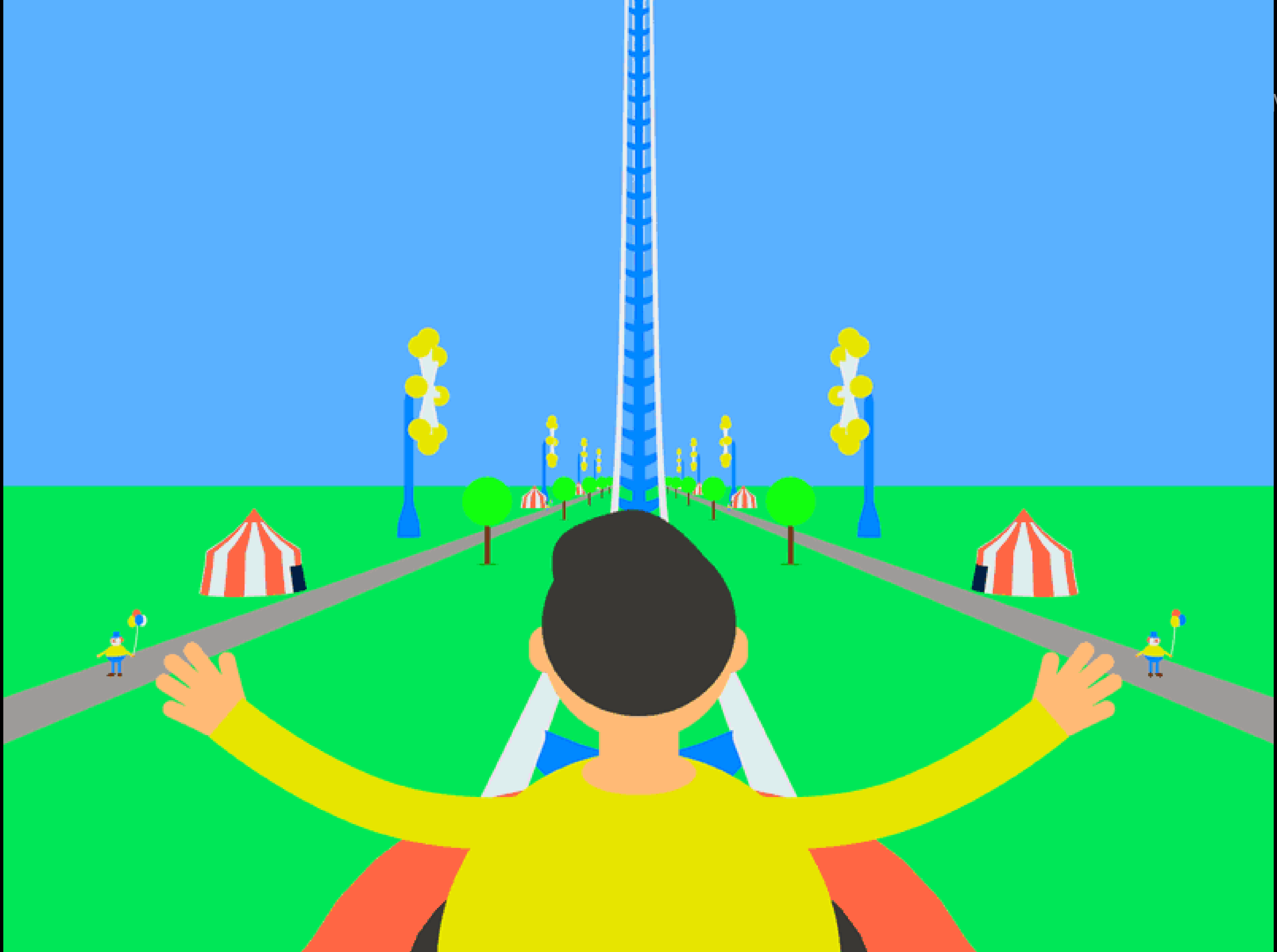
$$E(\mathbf{R}) \equiv E\left(X_1, Y_1, Z_1, \cdots, X_N, Y_N, Z_N\right)$$



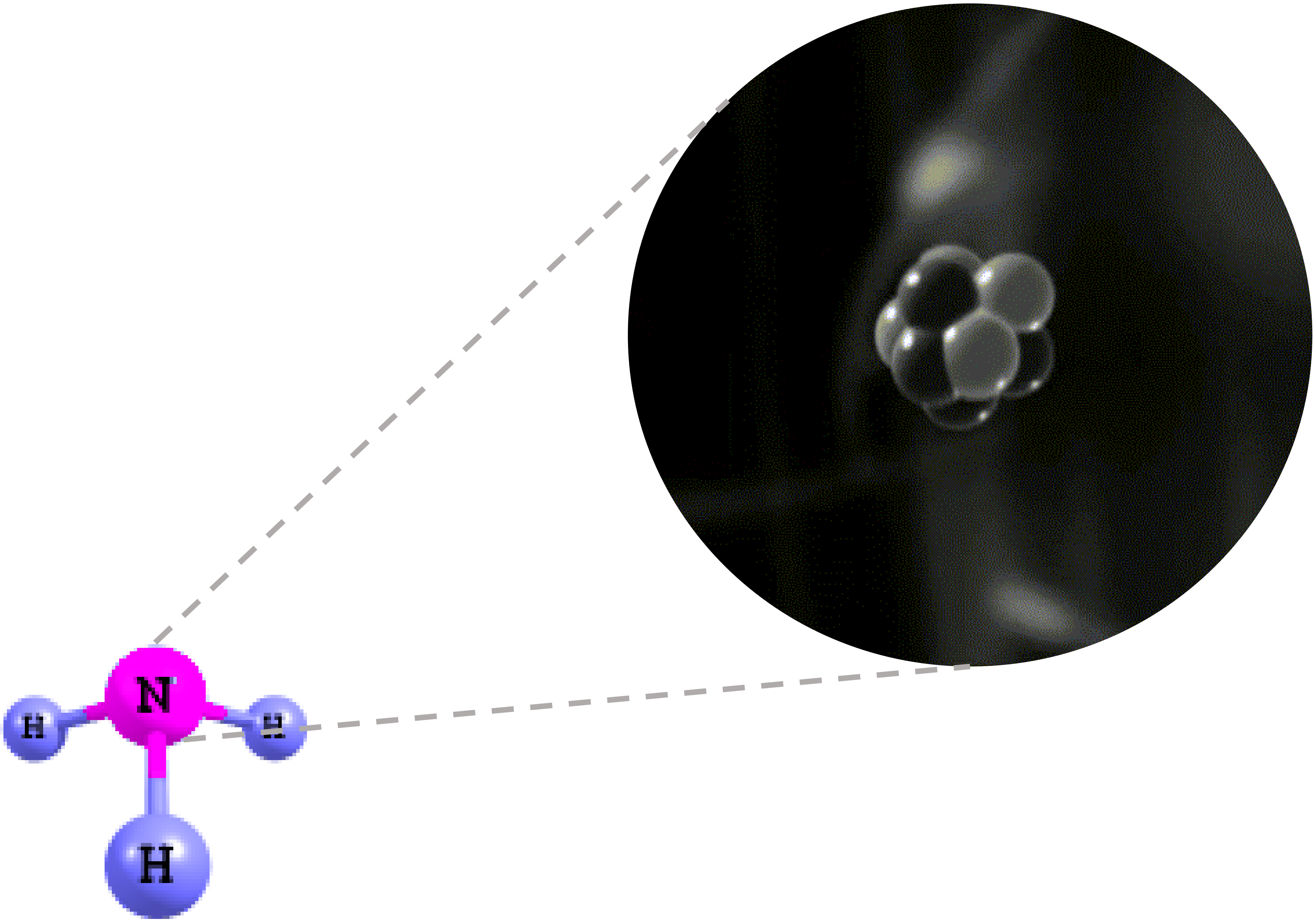


N points × 3 dimensions → 1 point × $3N$ dimensions


E
R



A note about molecular time


N
H
H
H

There's **no time** dependency.

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

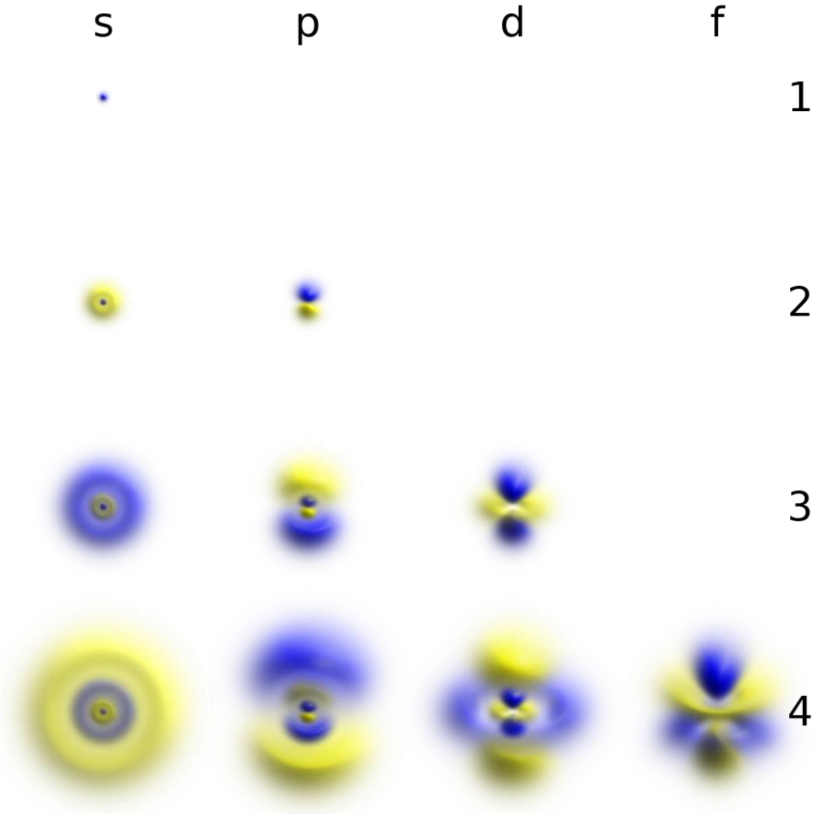
$$\left(\hat{T}_{elec}(\mathbf{r})+V(\mathbf{r},\mathbf{R})\right)\varphi(\mathbf{r};\mathbf{R})=E(\mathbf{R})\varphi(\mathbf{r};\mathbf{R})$$

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

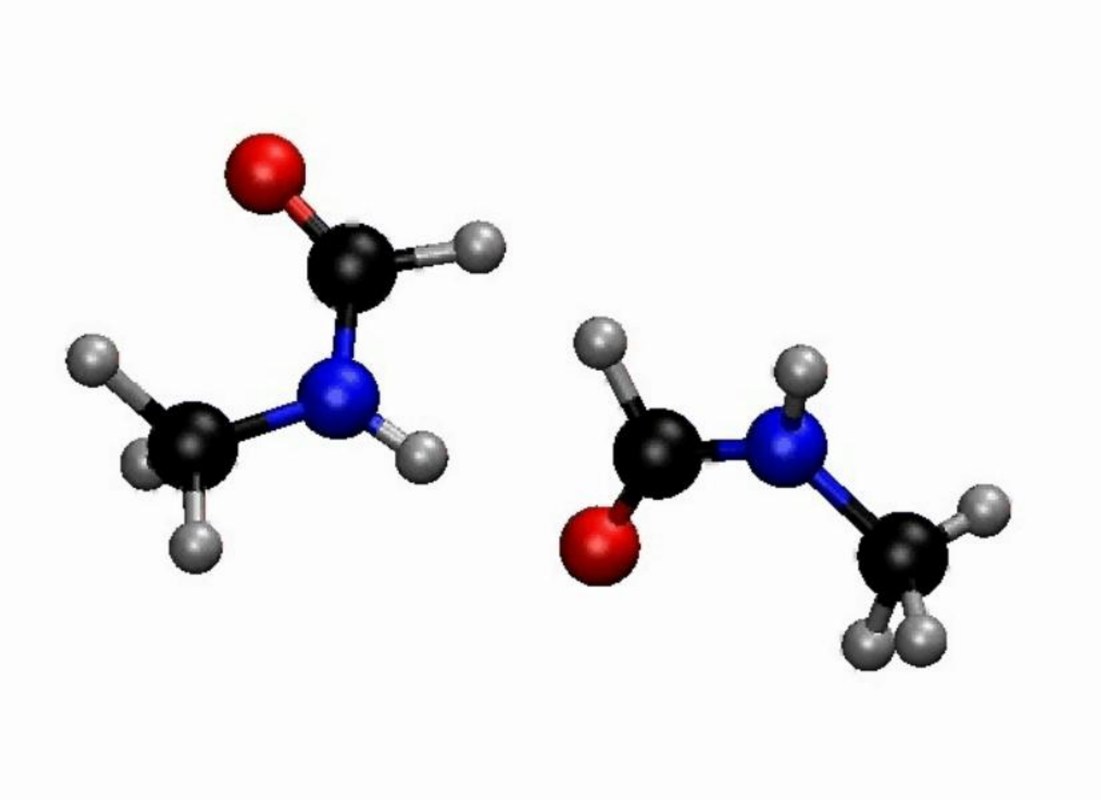
Barbatti, Aeon Magazine **2023**, tinyurl.com/emptyatom

For a molecule in a well-defined energy state:

- Momentum = wave function steepness $\left[-i\hbar\nabla\psi\right]$
- Kinetic energy = field stress (how much the wave function differs from the mean) $\left[-\frac{\hbar^2}{2M}\nabla^2\psi\right]$
- Angular momentum = wave function blobs and nodes $\left[-i\hbar\,\hat{\mathbf{r}}\times\nabla\psi\right]$



Time becomes important again during chemical reactions or field interactions



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

We need dynamics.

To know more:

Quantum mechanics

- **Linear algebra:** 3Blue1Brown, tinyurl.com/3b1bLA
- **Mathematical concepts of QM:** Quantum Sense, tinyurl.com/quantumsense
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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

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

with

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

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

$$\left(\hat{T}_{nuc}\left(\mathbf{R}\right)+\hat{T}_{elec}\left(\mathbf{r}\right)+\hat{V}\left(\mathbf{r},\mathbf{R}\right)\right)\left(\sum_{n}\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)\chi_{n}\left(\mathbf{R}\right)\right)=\varepsilon\left(\sum_{n}\varphi_{n}\left(\mathbf{r};\mathbf{R}\right)\chi_{n}\left(\mathbf{R}\right)\right)$$

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

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

Working on the left-side term

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

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

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

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

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

Expanding the blue term

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

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

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

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

Projecting on n′

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

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

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

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

Using orthonormality

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

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

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

Time-independent Born-Huang formulation

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

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

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

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

Adiabatic approximation

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

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

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

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

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

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

Appendix:
General unitary transformations

General unitary evolution

Time evolution

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

Spatial translation

$$i\hbar \frac{d\left|x\right\rangle}{dx} = \hat{p}\left|x\right\rangle$$

General unitary evolution

$$i\hbar \frac{d\left|\Psi\right\rangle}{d\alpha} = \hat{g}\left|\Psi\right\rangle$$

Momentum translation

$$i\hbar \frac{d\left|p\right\rangle}{dp} = -\hat{x}\left|p\right\rangle$$

Rotation

$$i\hbar \frac{d\left|\theta\right\rangle}{d\theta} = \hat{L}\left|\theta\right\rangle$$