



# L1 – Quantum Mechanics 1

Foundations

# The quantum state

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

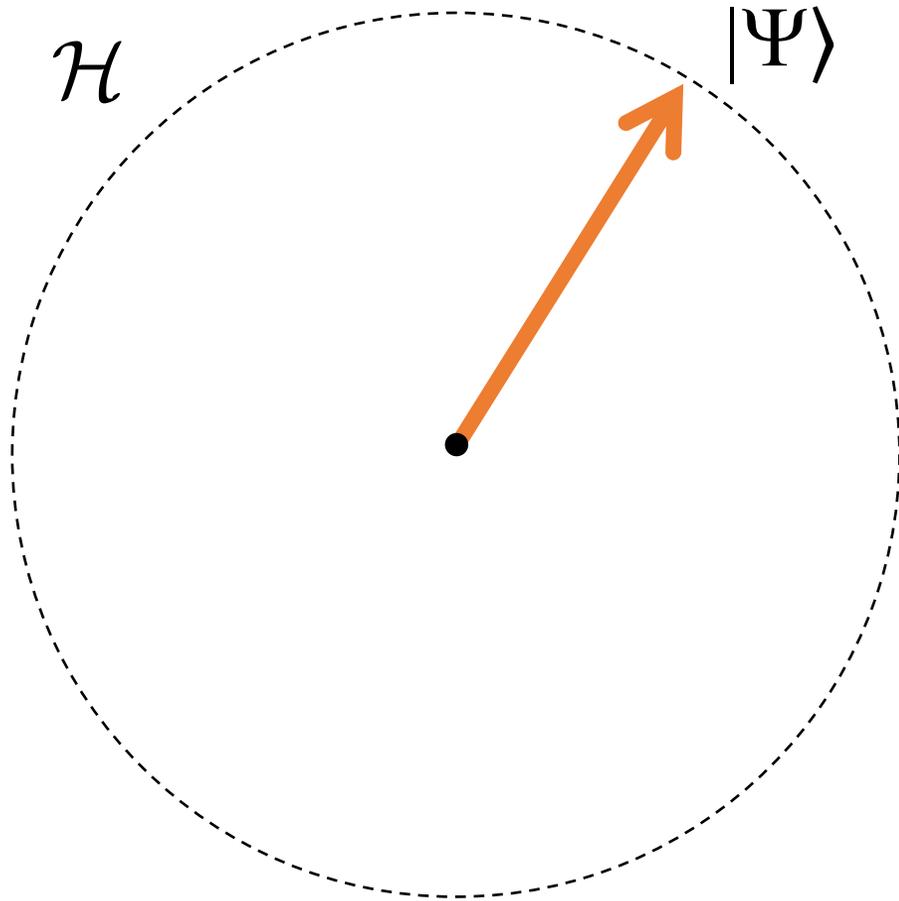
$$= c_1|E_1\rangle + c_2|E_2\rangle + \dots$$

$$|\Psi\rangle$$

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

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

# Quantum state in the Hilbert space

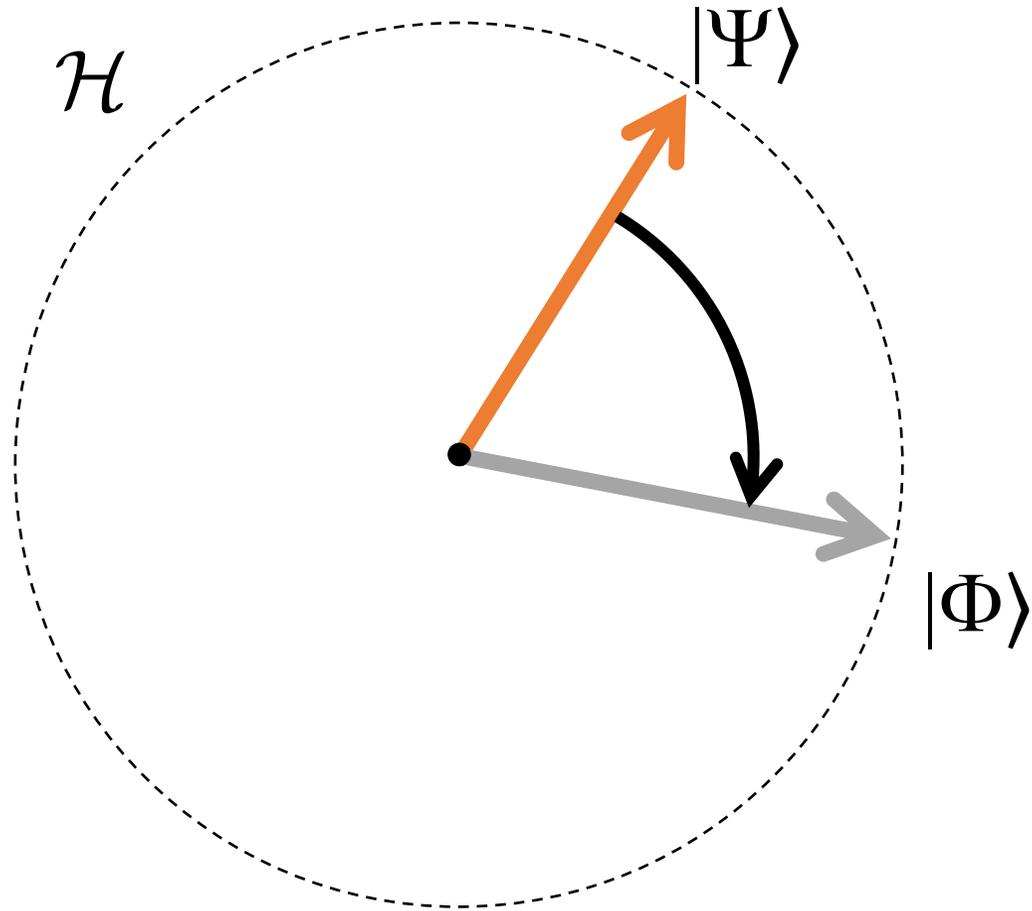


The number of dimensions is the number of possible outputs.

Kets can be represented as column vectors

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

# Operators in the Hilbert space



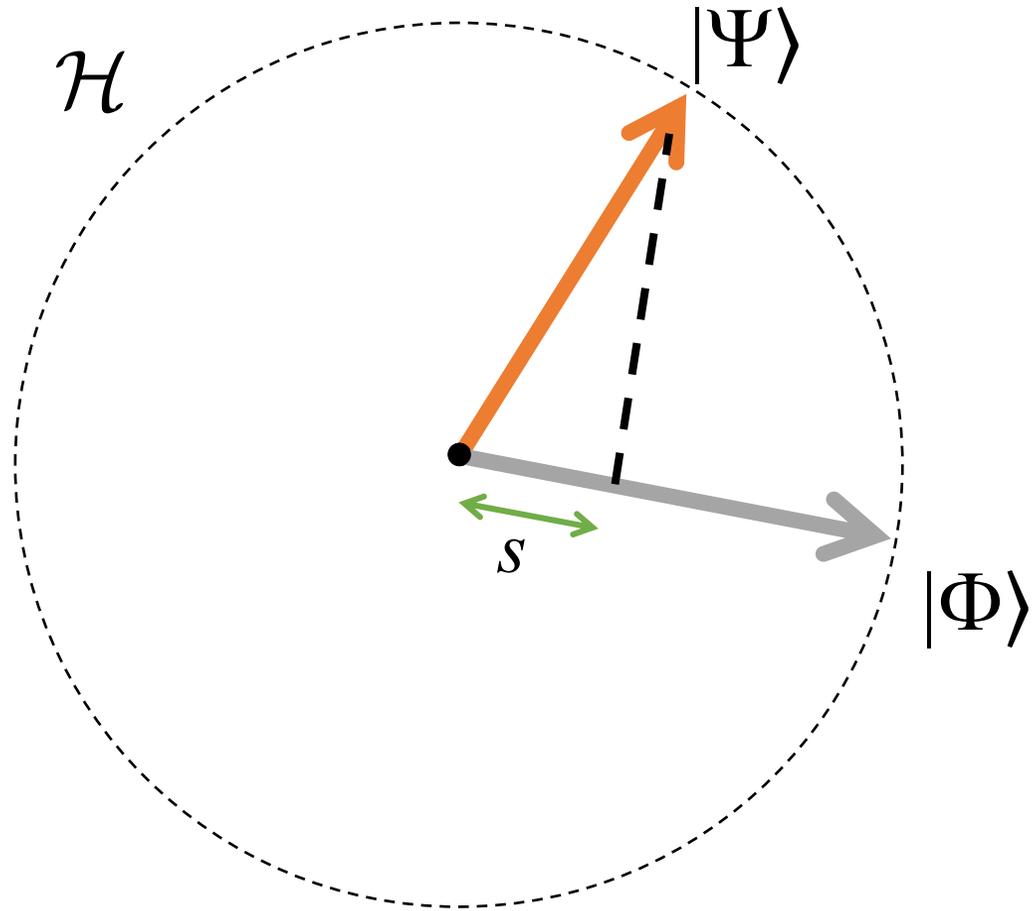
An operator acts on the vector creating a new vector in  $\mathcal{H}$

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

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

$$\langle \Phi | \Psi \rangle = [b_1^* \quad b_2^* \quad \dots] \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix}$$

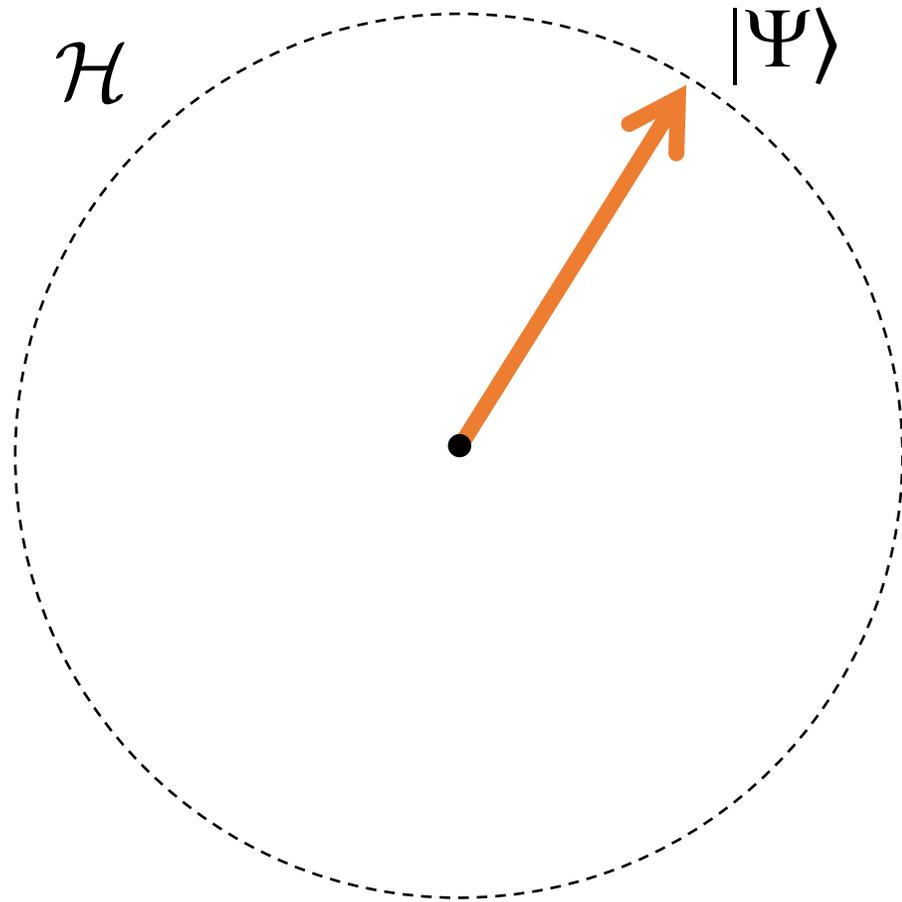
Any observable is represented as a self-adjoint operator  $\hat{O}$  in  $\mathcal{H}$

$$\langle \Phi | \hat{O} \Psi \rangle = \langle \hat{O} \Phi | \Psi \rangle$$

The expected value of  $\hat{O}$  when the system is state  $|\Psi\rangle$  is

$$O = \langle \Psi | \hat{O} | \Psi \rangle$$

# Qubit in the Hilbert space



Head



Tail

**2 outputs**

The number of dimensions is two.

# Observables

Example: Observable "Side"

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

**Basis**

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

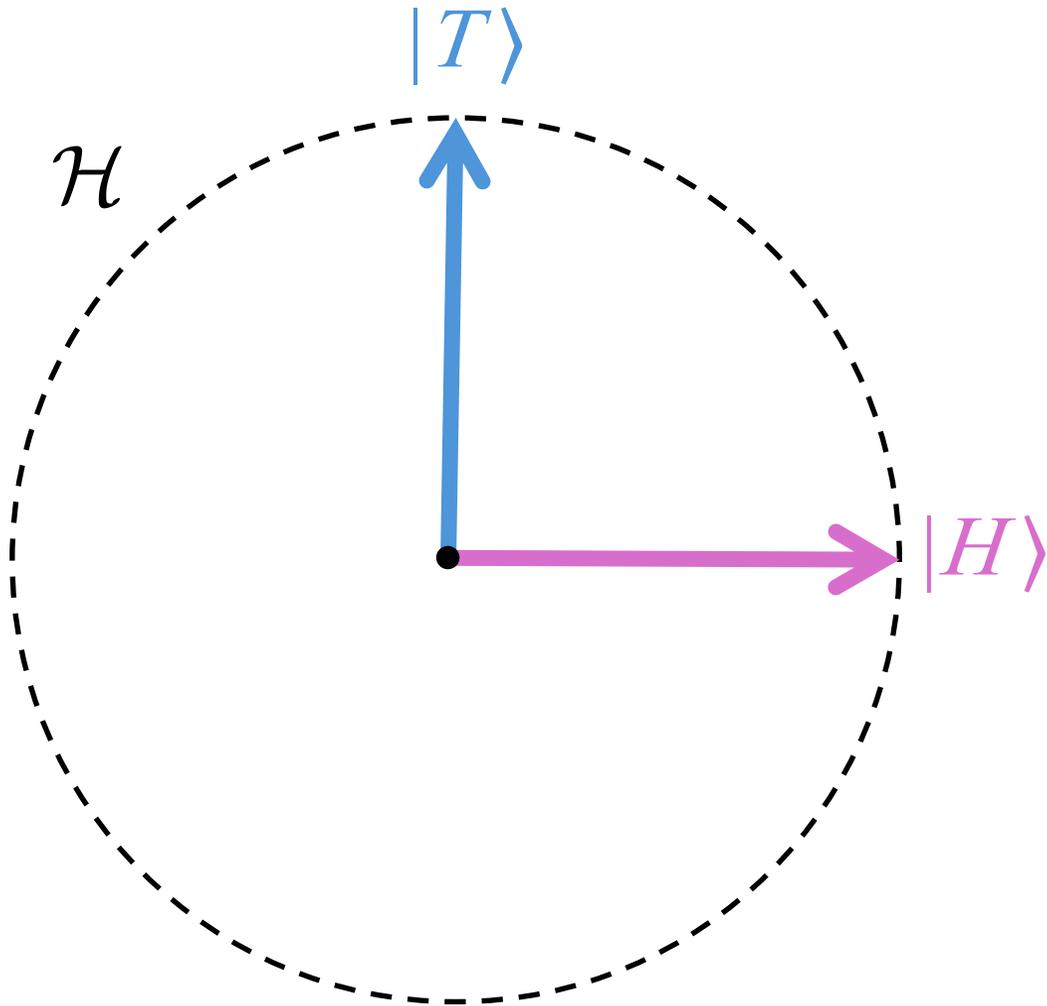
**Complete**

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

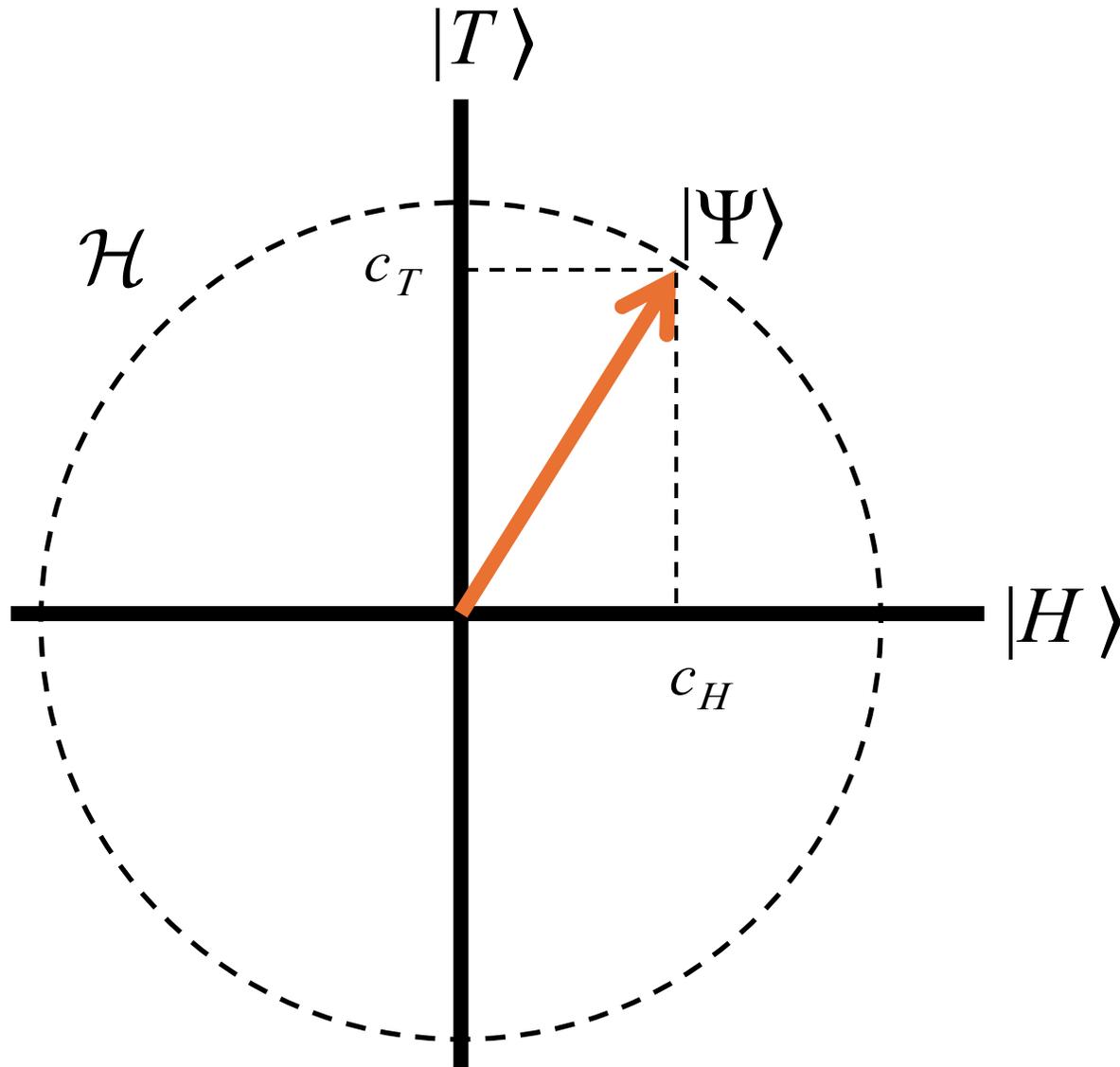
**Orthonormal**

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

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



# Superposition



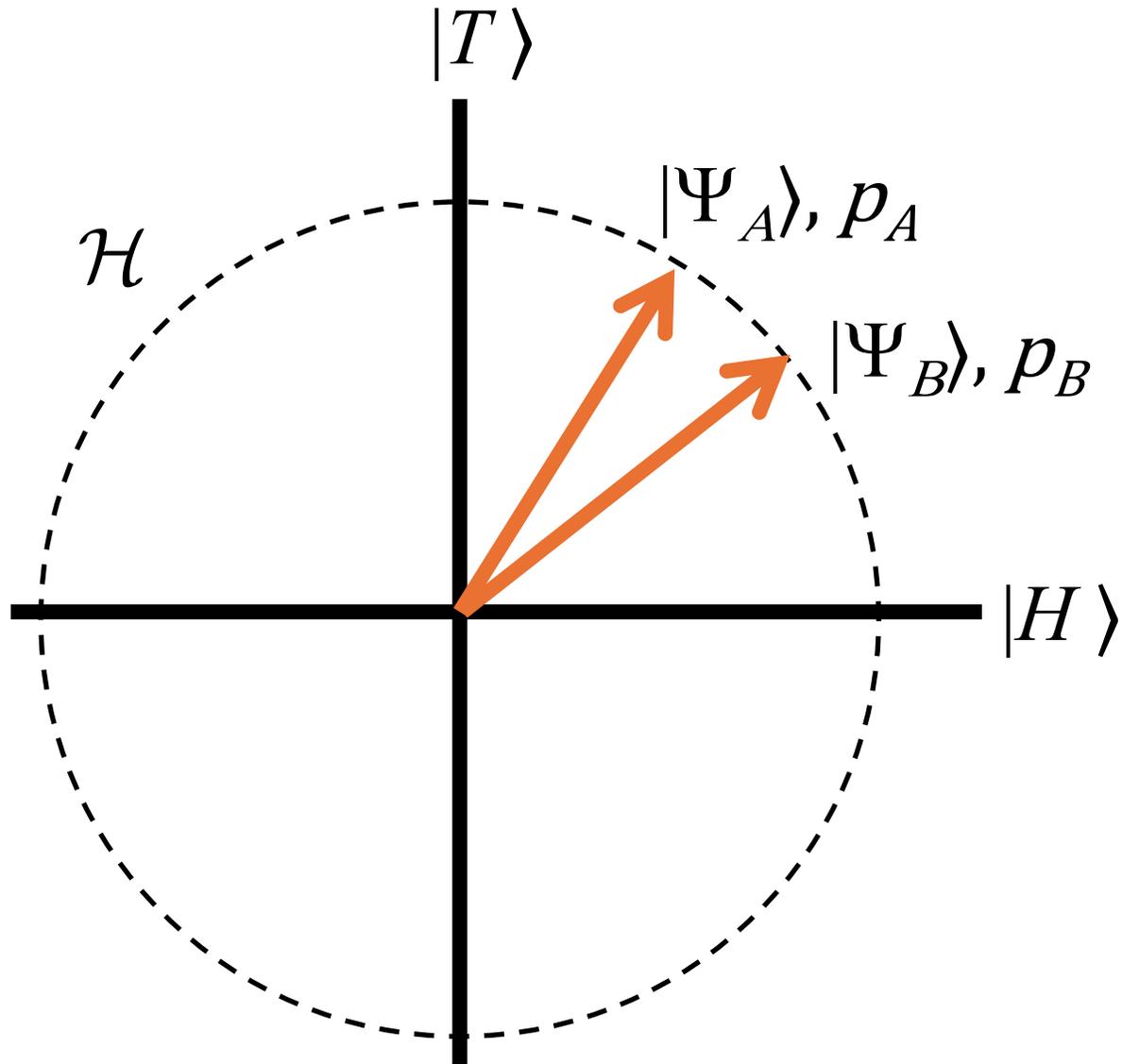
Any unit vector in  $\mathcal{H}$  is a possible state

$$|\Psi\rangle = c_H |H\rangle + c_T |T\rangle \quad c_H, c_T \in \mathbb{C}$$

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

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

# Density operator



Unsure which state we have...

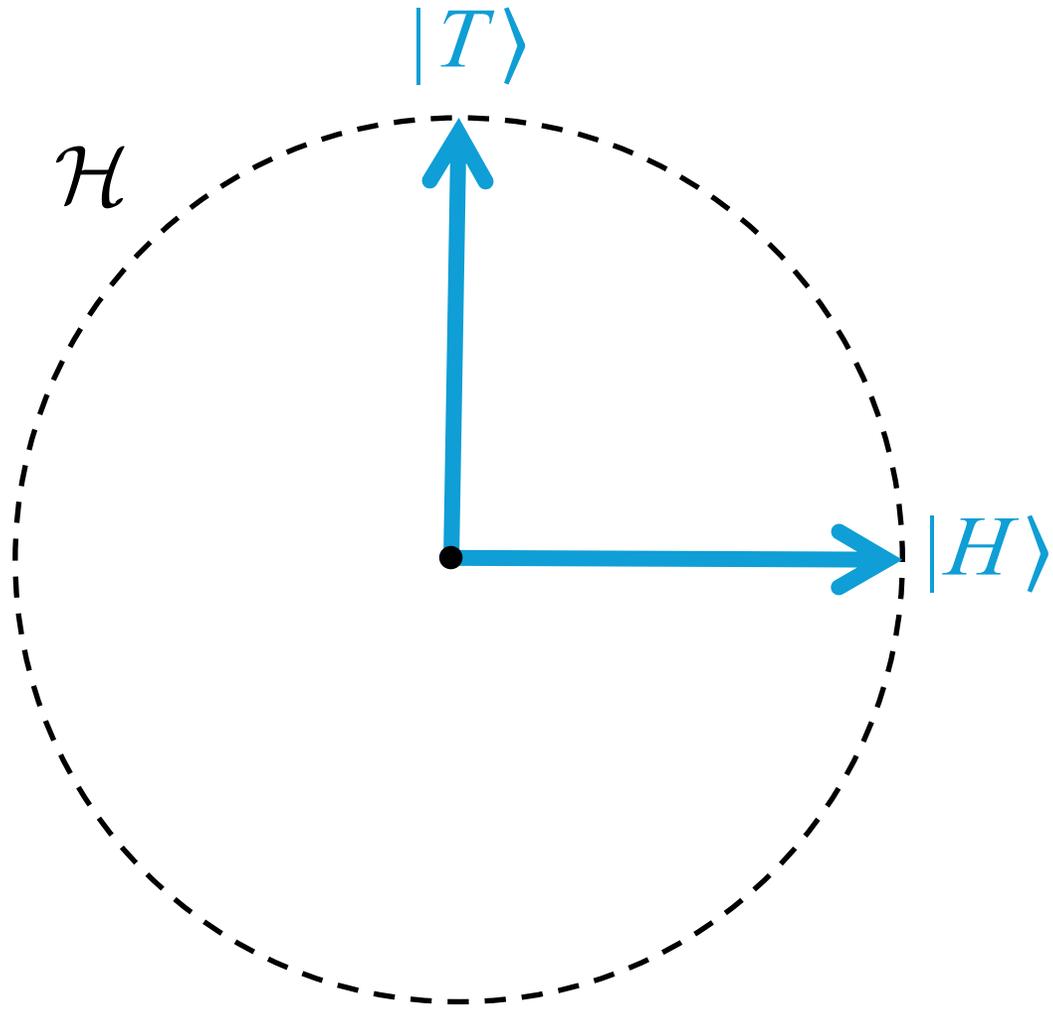
$$\rho = p_A |\Psi_A\rangle\langle\Psi_A| + p_B |\Psi_B\rangle\langle\Psi_B|$$

$$p_A + p_B = 1$$

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

# Commutation

# Commutation relations

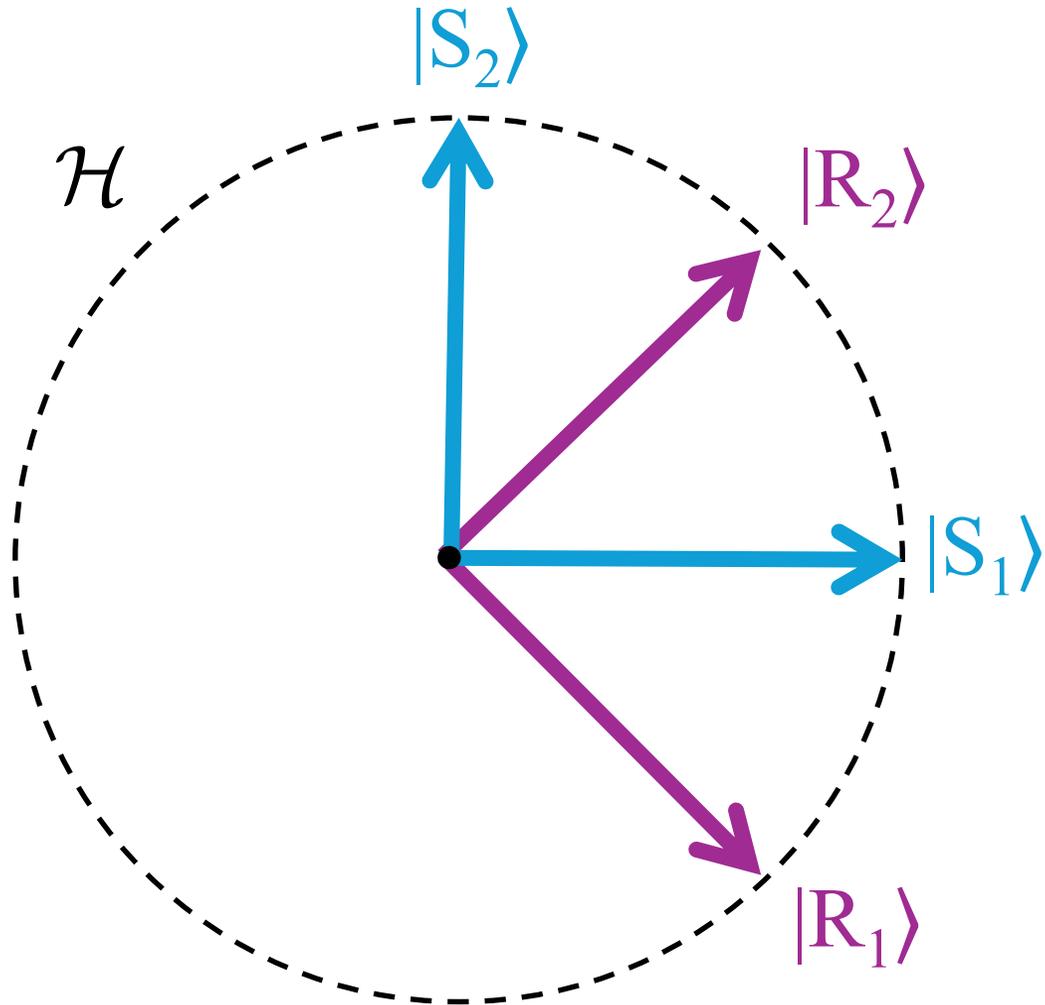


$$[\hat{S}, \hat{R}]|\Psi\rangle = \hat{S}\hat{R}|\Psi\rangle - \hat{R}\hat{S}|\Psi\rangle = 0$$

Commuting operators **share** the same eigenvectors.

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

# Commutation relations



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

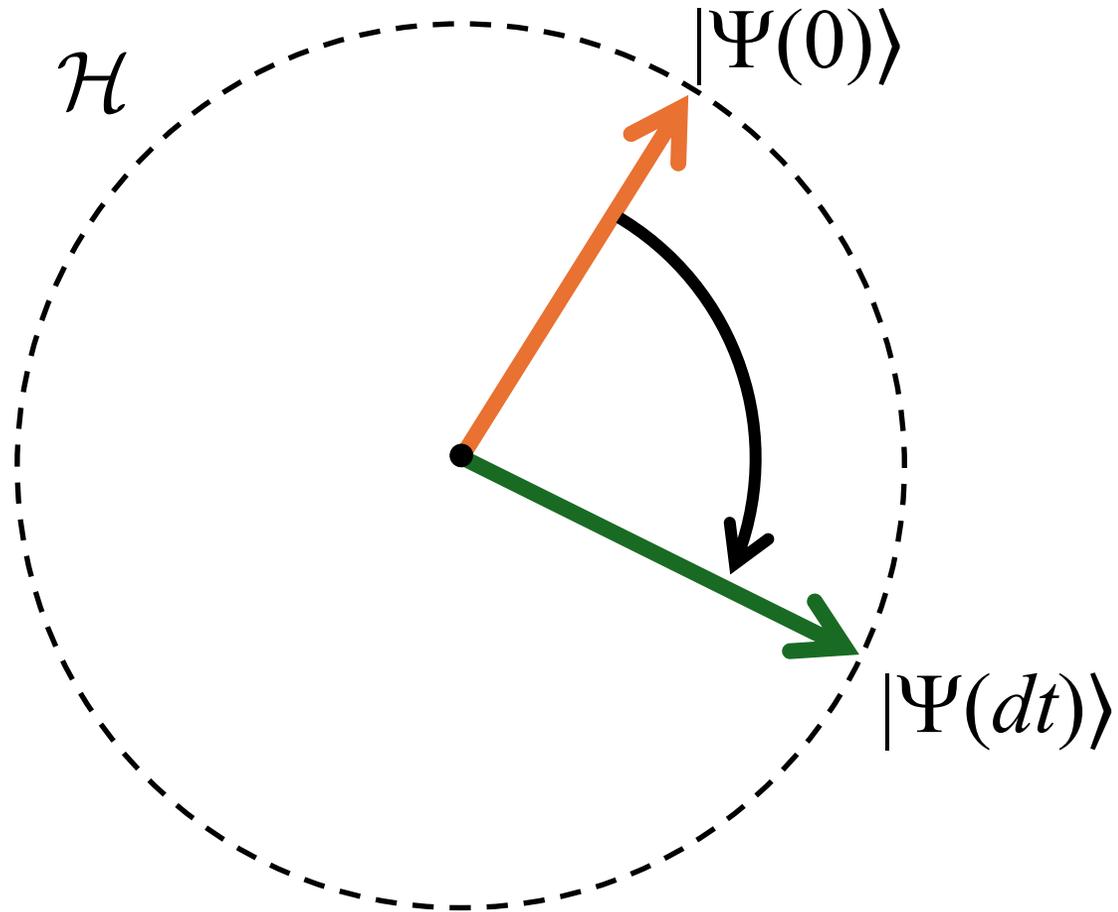
Non-commuting operators **do not share** eigenvectors.

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**:

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

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

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

# The Hamiltonian operator

Potential energy  
operator



$$\hat{H} = \hat{T} + \hat{V}$$



Kinetic energy  
operator

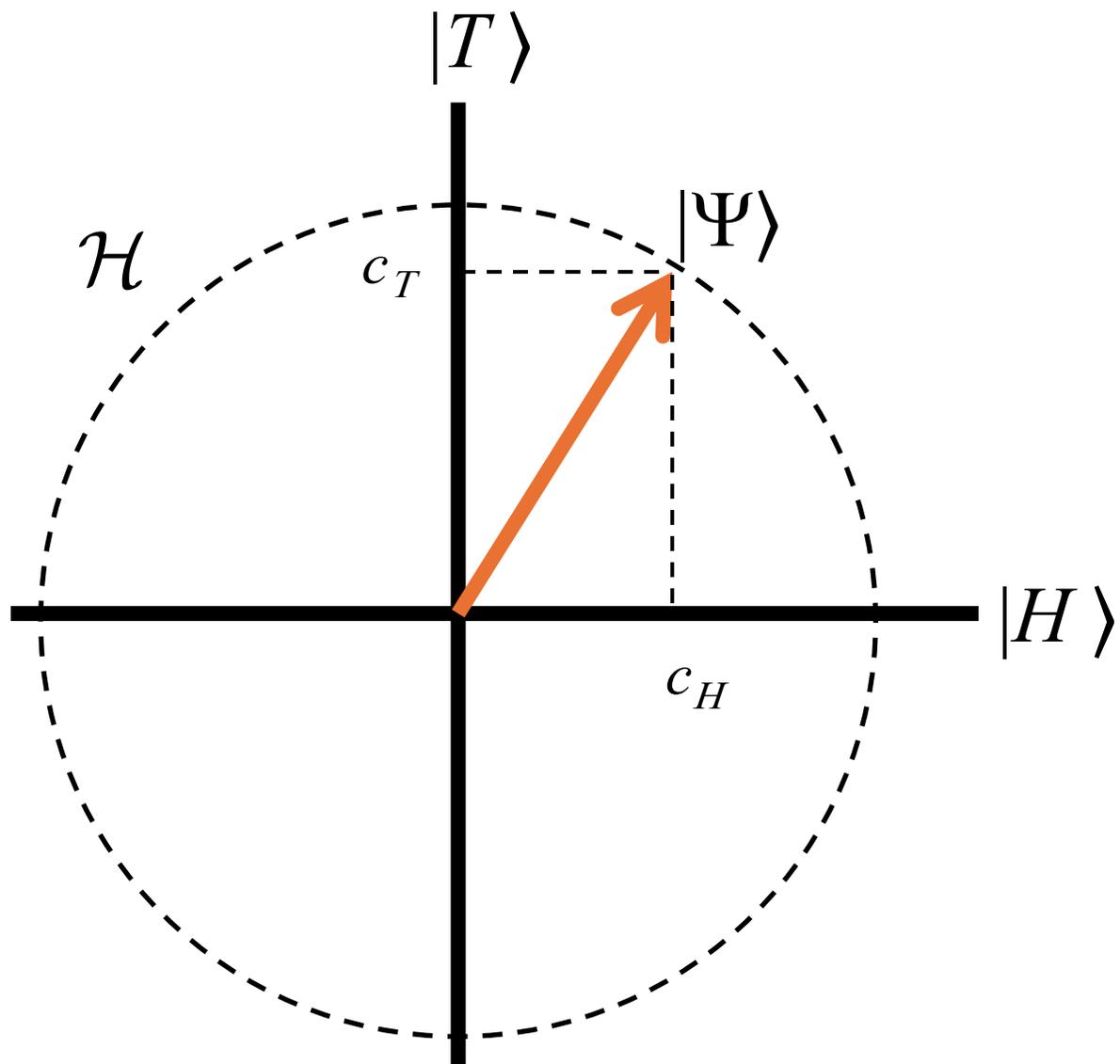
# Von Neumann evolution

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

## Von Neumann Equation

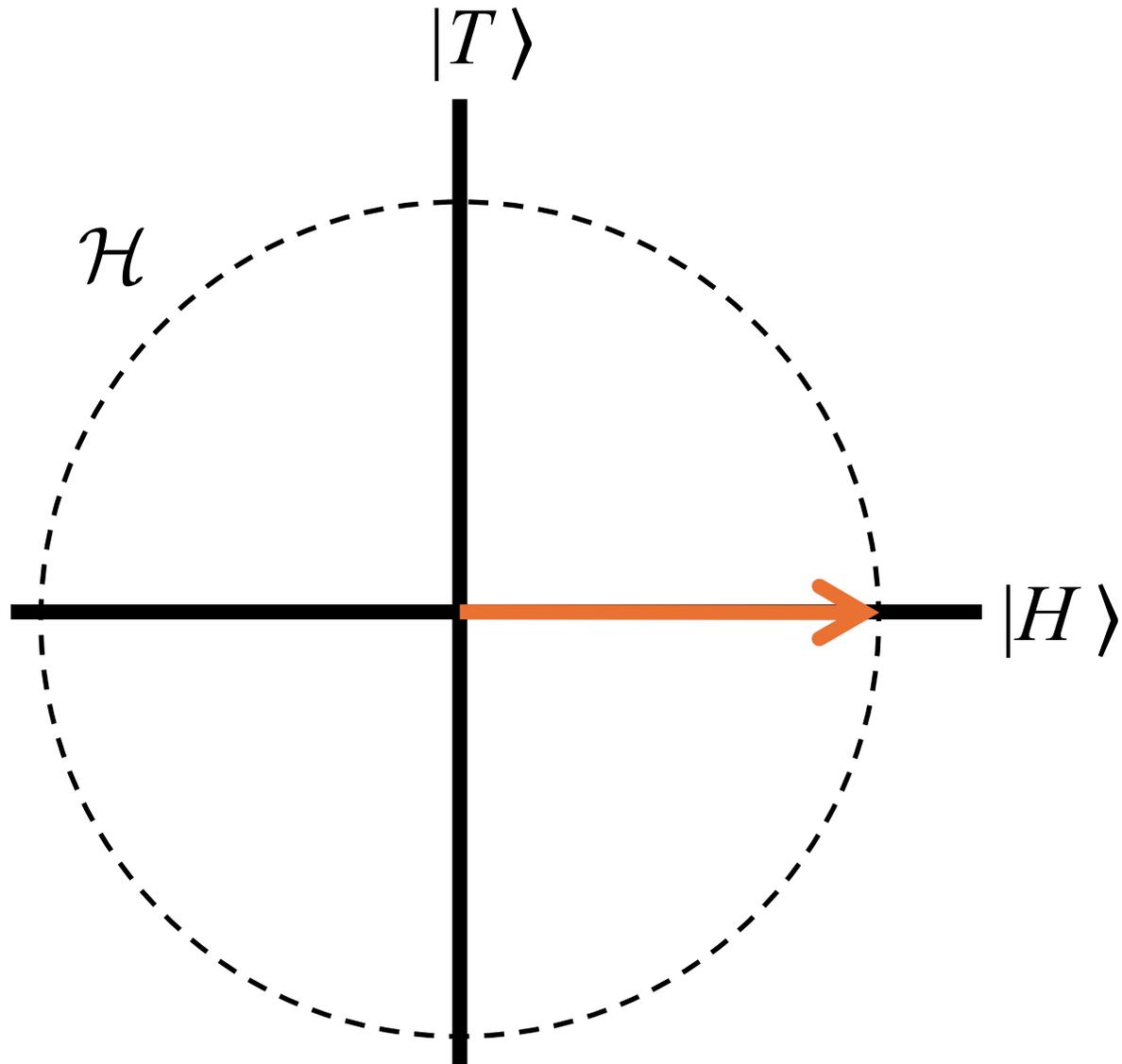
$$i\hbar \frac{d\rho}{dt} = [\hat{H}, \rho]$$

# Stochastic evolution of the quantum state



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

# Quantum state measurement



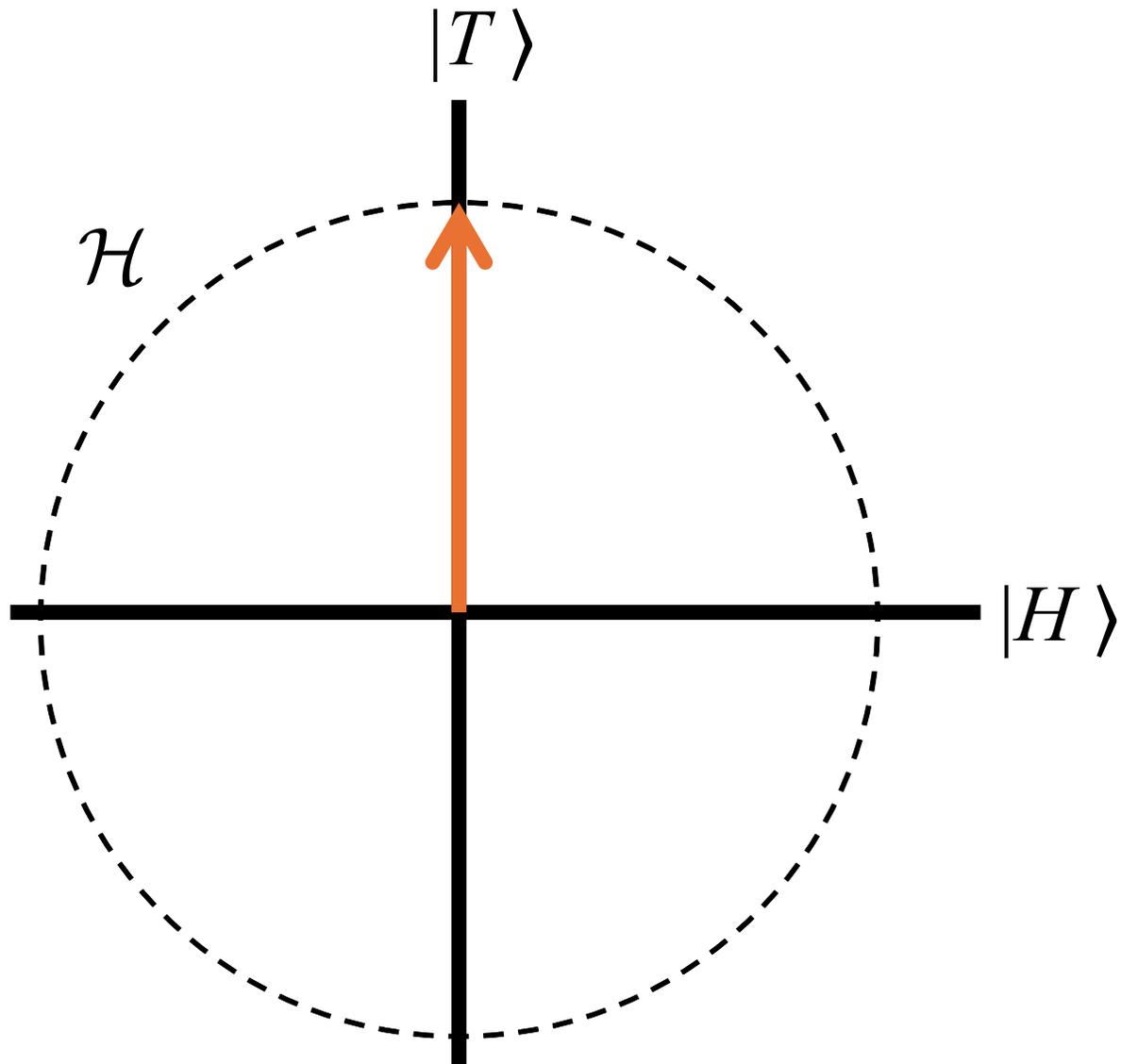
$$|\Psi\rangle = c_H |H\rangle + c_T |T\rangle$$



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

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

# Quantum state measurement



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



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

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

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**



**$\infty$  outputs**

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



**countable outputs**

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



0

5 m

**uncountable  $\infty$  outputs**

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



**countable outputs**

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



0

5 m

**uncountable  $\infty$  outputs**

State vector  $\longrightarrow$   $|\Psi\rangle = \int \Psi(x) |x\rangle dx$

Wave function  $\uparrow$   $\uparrow$  Base vector

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

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

$$\begin{aligned}\langle x'|\Psi\rangle &= \int \Psi(x)\langle x'|x\rangle dx \\ &= \int \Psi(x)\delta(x'-x) dx\end{aligned}$$

$$\Psi(x) = \langle x|\Psi\rangle$$

# Time evolution in the position basis

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

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

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

$$\hat{H}(x) \Psi(x,t) \leftarrow$$

Assuming that

$$\int |f(x)|^2 dx < \infty$$

$$f = \Psi; \frac{d\Psi}{dx}; \frac{d^2\Psi}{dx^2}$$

**Position-basis Schrödinger equation**

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

# Generalization 2: Composite systems

# 1 Qubit



**2 outputs**

# 2 Qubits



**4 outputs**

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



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



$$\mathcal{H}_T = \mathcal{H}_A \otimes \mathcal{H}_B : \left\{ \begin{array}{l} |H, H\rangle, \\ |H, T\rangle, \\ |T, H\rangle, \\ |T, T\rangle \end{array} \right\}$$



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

# 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

$$|\Psi\rangle = \sum_{i,j} c_{ij} |i, j\rangle$$

$$\begin{aligned} \hat{P}_{ij} |\Psi\rangle &= \sum_{i,j} c_{ij} |j, i\rangle \\ &= \sum_{i,j} c_{ji} |i, j\rangle \end{aligned}$$

Fermions

$$\hat{P}_{ij} |\Psi\rangle = -|\Psi\rangle$$

Bosons

$$\hat{P}_{ij} |\Psi\rangle = +|\Psi\rangle$$

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

# Info from a subsystem

$\rho_{AB}$  Density of a composite system AB

$$\rho_A = \text{Tr}_B [\rho_{AB}] = \sum_i \langle B_i | \rho_{AB} | B_i \rangle \quad \textbf{Reduced density} \text{ of A}$$

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

# Lindblad evolution

$$\rho_A = \text{Tr}_B [\rho_{AB}]$$

## Lindblad Equation

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

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

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

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  $\mathbf{r}$  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:

$$i\hbar \frac{1}{\phi(t)} \frac{d\phi(t)}{dt} = \frac{\hat{H}(\mathbf{r})\psi(\mathbf{r})}{\psi(\mathbf{r})} = E \quad \left\{ \begin{array}{l} i\hbar \frac{d\phi(t)}{dt} = E\phi(t) \\ \hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r}) \end{array} \right.$$

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

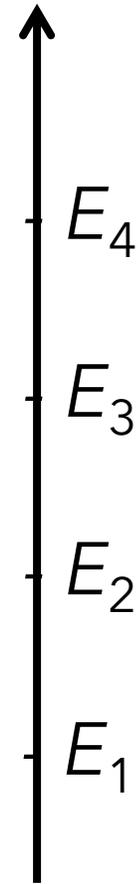
$$\hat{H}(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

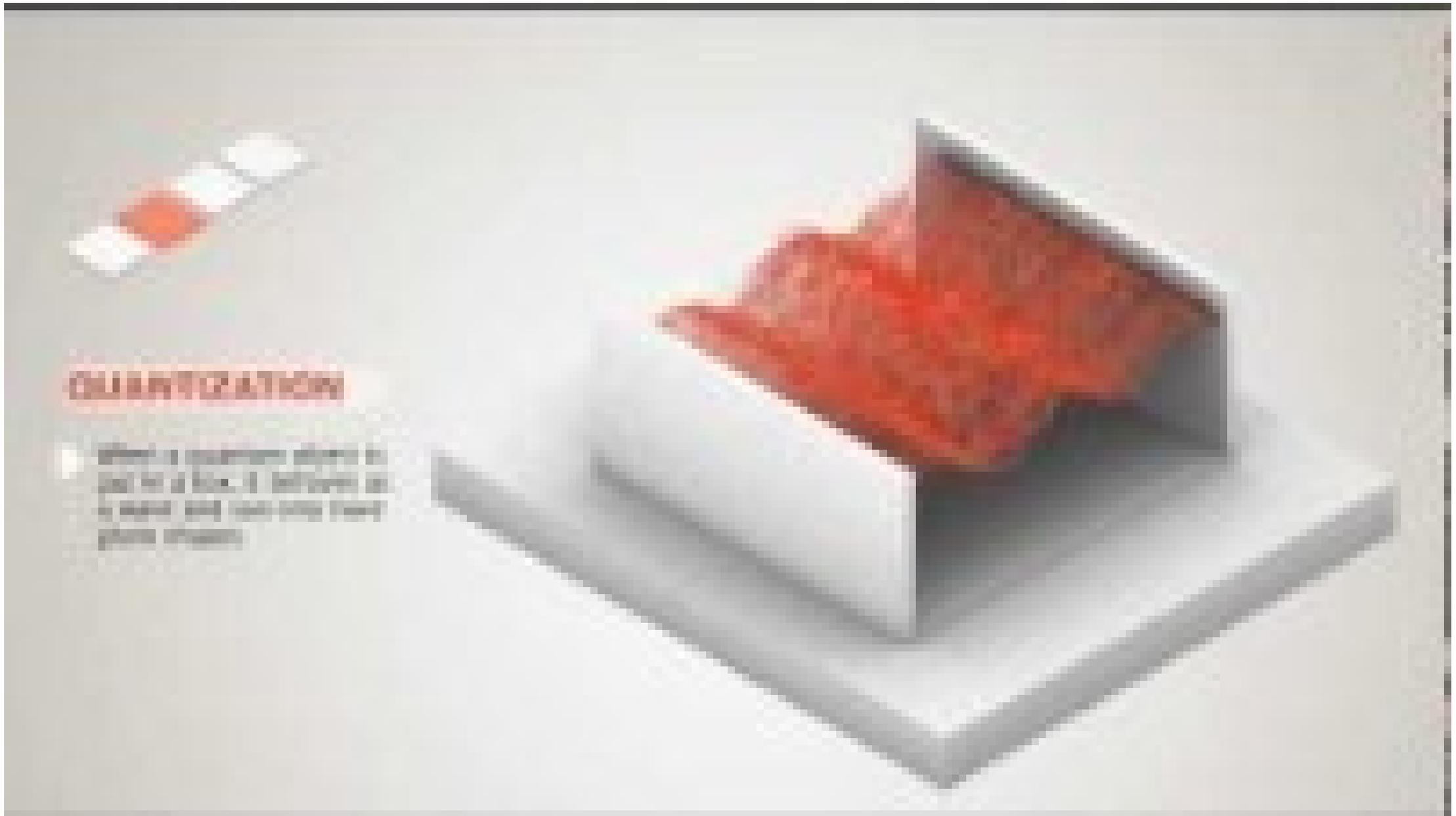
is the **Time-Independent Schrödinger equation**  
(on the position basis)

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

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

Energy





### COMPARISON OF ACTORS

- Actor 1: ...
- Actor 2: ...
- Actor 3: ...
- Actor 4: ...

To know more:

Quantum mechanics

- **Linear algebra:** 3Blue1Brown, [tinyurl.com/3b1bLA](https://tinyurl.com/3b1bLA)
- **Mathematical concepts of QM:** Quantum Sense, [tinyurl.com/quantumsense](https://tinyurl.com/quantumsense)
- **Hilbert space:** Abide by Reason, [tinyurl.com/hilbertspace](https://tinyurl.com/hilbertspace)
- **Course on QM:** ViaScience, [tinyurl.com/viasciQM](https://tinyurl.com/viasciQM)
- **Density operator:** Wu; Scholes. *J Phys Chem Lett* **2024**, 15, 4056
- **Lindblad evolution:** Manzano. *AIP Adv* **2020**, 10, 025106

The BO approximation

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

# **Appendix: Derivation of the Born- Oppenheimer Formulation**

Field-free non-relativistic molecular problem

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

*with*

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

Born-Huang wave function

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

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

$$\begin{aligned} \hat{T}_{nuc} \left(\sum_n \varphi_n \chi_n\right) + \left(\hat{T}_{elec} + \hat{V}\right) \left(\sum_n \varphi_n \chi_n\right) = \\ -\frac{\hbar^2}{2\mathbf{M}} \nabla_{\mathbf{R}}^2 \left(\sum_n \varphi_n \chi_n\right) + \sum_n E_n \varphi_n \chi_n \end{aligned}$$

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

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

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

Expanding the blue term

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

$$\begin{aligned}
& -\frac{\hbar^2}{2\mathbf{M}} \sum_n \left[ \left( \nabla_{\mathbf{R}}^2 \varphi_n \right) \chi_n + 2 \nabla_{\mathbf{R}} \varphi_n \cdot \nabla_{\mathbf{R}} \chi_n + \varphi_n \nabla_{\mathbf{R}}^2 \chi_n \right] \\
& + \sum_n E_n \varphi_n \chi_n = \mathcal{E} \left( \sum_n \varphi_n \chi_n \right)
\end{aligned}$$

Projecting on  $n'$

$$\begin{aligned}
& - \left\langle \varphi_{n'} \left| \frac{\hbar^2}{2\mathbf{M}} \sum_n \left[ \left( \nabla_{\mathbf{R}}^2 \varphi_n \right) \chi_n + 2 \nabla_{\mathbf{R}} \varphi_n \cdot \nabla_{\mathbf{R}} \chi_n + \varphi_n \nabla_{\mathbf{R}}^2 \chi_n \right] \right\rangle_{\mathbf{r}} \\
& + \left\langle \varphi_{n'} \left| \sum_n E_n \varphi_n \chi_n \right\rangle_{\mathbf{r}} = \left\langle \varphi_{n'} \left| \mathcal{E} \left( \sum_n \varphi_n \chi_n \right) \right\rangle_{\mathbf{r}}
\end{aligned}$$

$$\begin{aligned}
& - \left\langle \varphi_{n'} \left| \frac{\hbar^2}{2\mathbf{M}} \sum_n \left[ (\nabla_{\mathbf{R}}^2 \varphi_n) \chi_n + 2 \nabla_{\mathbf{R}} \varphi_n \cdot \nabla_{\mathbf{R}} \chi_n + \varphi_n \nabla_{\mathbf{R}}^2 \chi_n \right] \right\rangle_{\mathbf{r}} \\
& + \left\langle \varphi_{n'} \left| \sum_n E_n \varphi_n \chi_n \right\rangle_{\mathbf{r}} = \left\langle \varphi_{n'} \left| \varepsilon \left( \sum_n \varphi_n \chi_n \right) \right\rangle_{\mathbf{r}}
\end{aligned}$$

Using orthonormality

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

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

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

# Time-independent Born-Huang formulation

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

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

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

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

# Adiabatic approximation

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

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

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

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

## Time-independent BO adiabatic formulation

Nuclear Schrödinger equation

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

Electronic Schrödinger equation

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

BO molecular wave function

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

# **Appendix:**

# **General unitary transformations**

# General unitary evolution

## Time evolution

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

## Spatial translation

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

## General unitary evolution

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

## Momentum translation

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

## Rotation

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