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Nonadiabatic Molecular Dynamics: Concepts, Methods, and Emerging Tools

III– Framing molecules in a bigger context

What does happen to a quantum state when it is measured?

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)


Can Particles be Quantum Entangled Across Time?
Brian Greene
World Science Festival
9:22 / 35:18 • History of the Beginnings of Quantum Mechanics ›
Scroll for details


World Science Festival
Elise Crull
• Decoherence
tinyurl.com/wsf-crull

Sean Carroll

- Many worlds
- Objective collapse

tinyurl.com/wsf-caroll

Carlo Rovelli

- Relational interpretation

tinyurl.com/wsf-rovelli

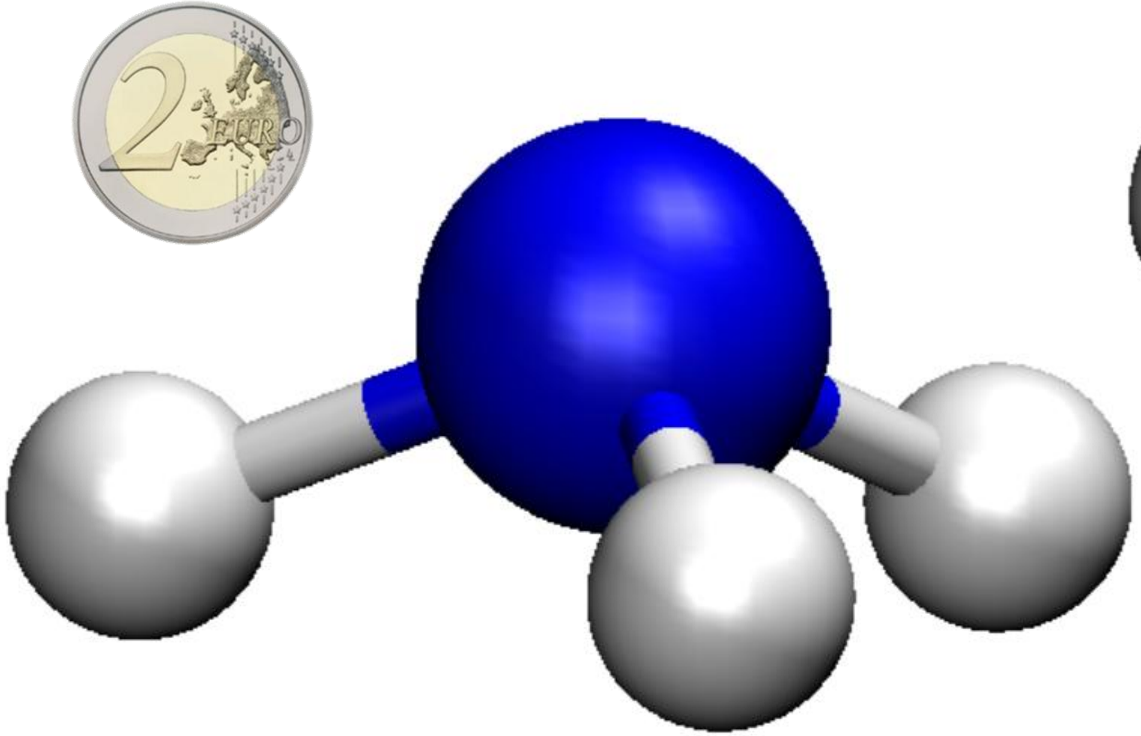
Decoherence
Many worlds
Objective collapse
Relational interpretation
. . .

Proposed Solutions to the Measurement Problem

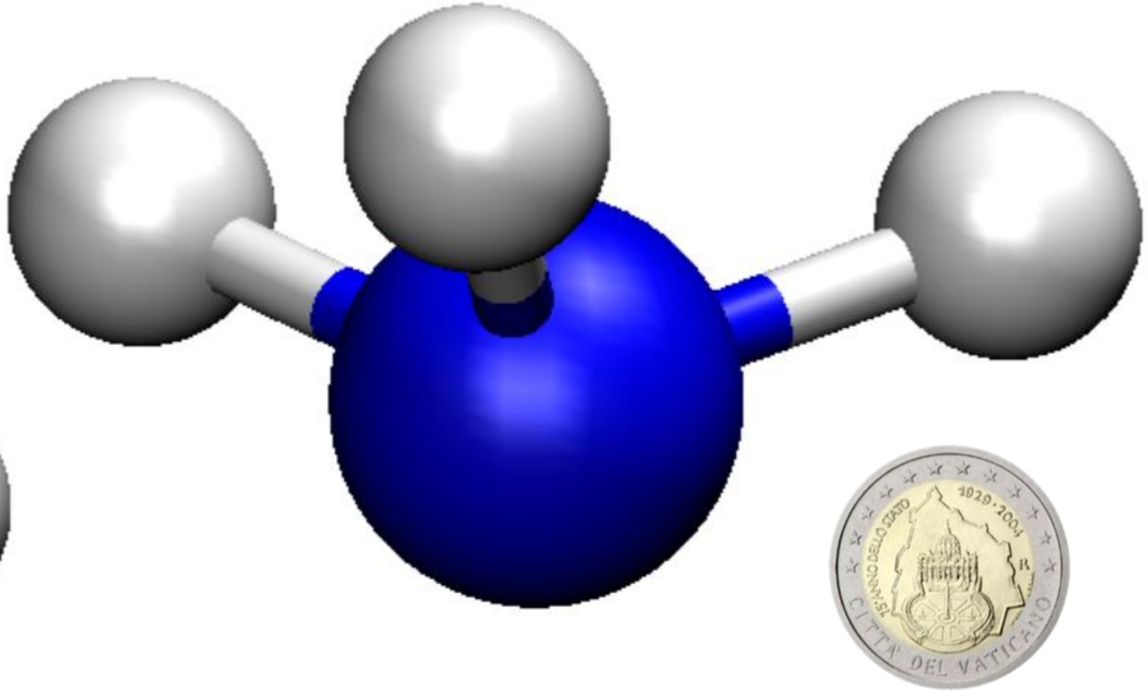
Interpretation	Year published	Author(s)	Deterministic?	Ontic wave-function?	Unique history?	Hidden variables?	Collapsing wave-functions?	Observer role?	Local dynamics?	Counter-factually definite?	Extant universal wave-function?
Consciousness causes collapse	1961–1993	John von Neumann, Eugene Wigner, Henry Stapp	No	Yes	Yes	No	Yes	Causal	No	No	Yes
Consistent histories	1984	Robert B. Griffiths	No	No	No	No	No	No	Yes	No	Yes
Copenhagen interpretation	1927–	Niels Bohr, Werner Heisenberg	No	Some	Yes	No	Some	No	Yes	No	No
de Broglie–Bohm theory	1927–1952	Louis de Broglie, David Bohm	Yes	Yes	Yes	Yes	Phenomen-ological	No	No	Yes	Yes
Ensemble interpretation	1926	Max Born	Agnostic	No	Yes	Agnostic	No	No	No	No	No
Many-minds interpretation	1970	H. Dieter Zeh	Yes	Yes	No	No	No	Interpre-tational	Yes	Ill-posed	Yes
Many-worlds interpretation	1957	Hugh Everett	Yes	Yes	No	No	No	No	Yes	Ill-posed	Yes
Objective-collapse theories	1986–1989	Ghirardi–Rimini–Weber, Penrose interpretation	No	Yes	Yes	No	Yes	No	No	No	No
QBism	2010	Christopher Fuchs, Rüdiger Schack	No	No	Agnostic	No	Yes	Intrinsic	Yes	No	No
Quantum logic	1936	Garrett Birkhoff	Agnostic	Agnostic	Yes	No	No	Interpre-tational	Agnostic	No	No
Relational interpretation	1994	Carlo Rovelli	No	No	Agnostic	No	Yes	Intrinsic	Possibly	No	No
Time-symmetric theories	1955	Satosi Watanabe	Yes	No	Yes	Yes	No	No	No	No	Yes
Transactional interpretation	1986	John G. Cramer	No	Yes	Yes	No	Yes	No	No	Yes	No

en.wikipedia.org/wiki/Interpretations_of_quantum_mechanics

Stating the Measurement Problem



$|\mathrm{up}\rangle$



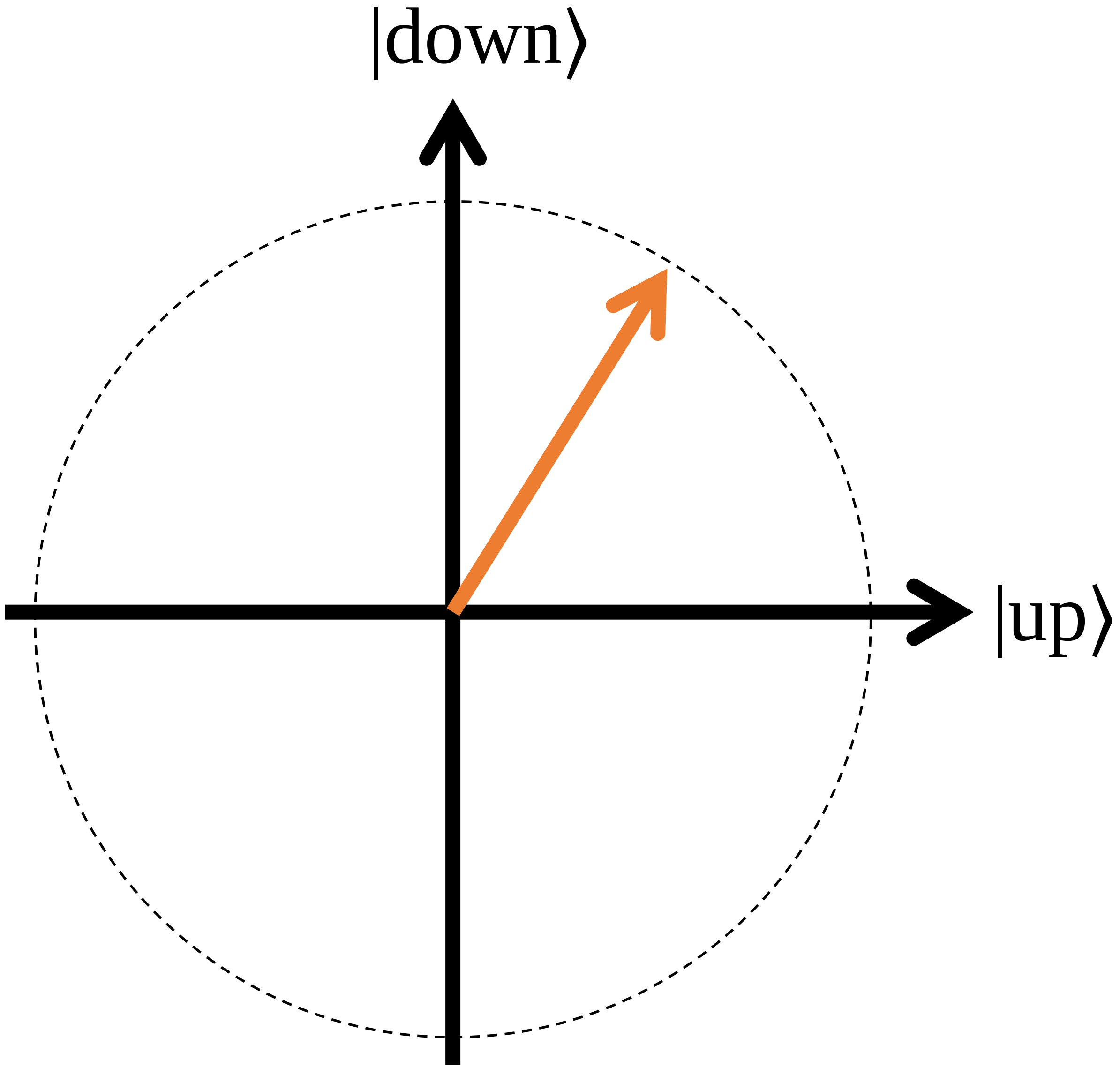
$|\mathrm{down}\rangle$

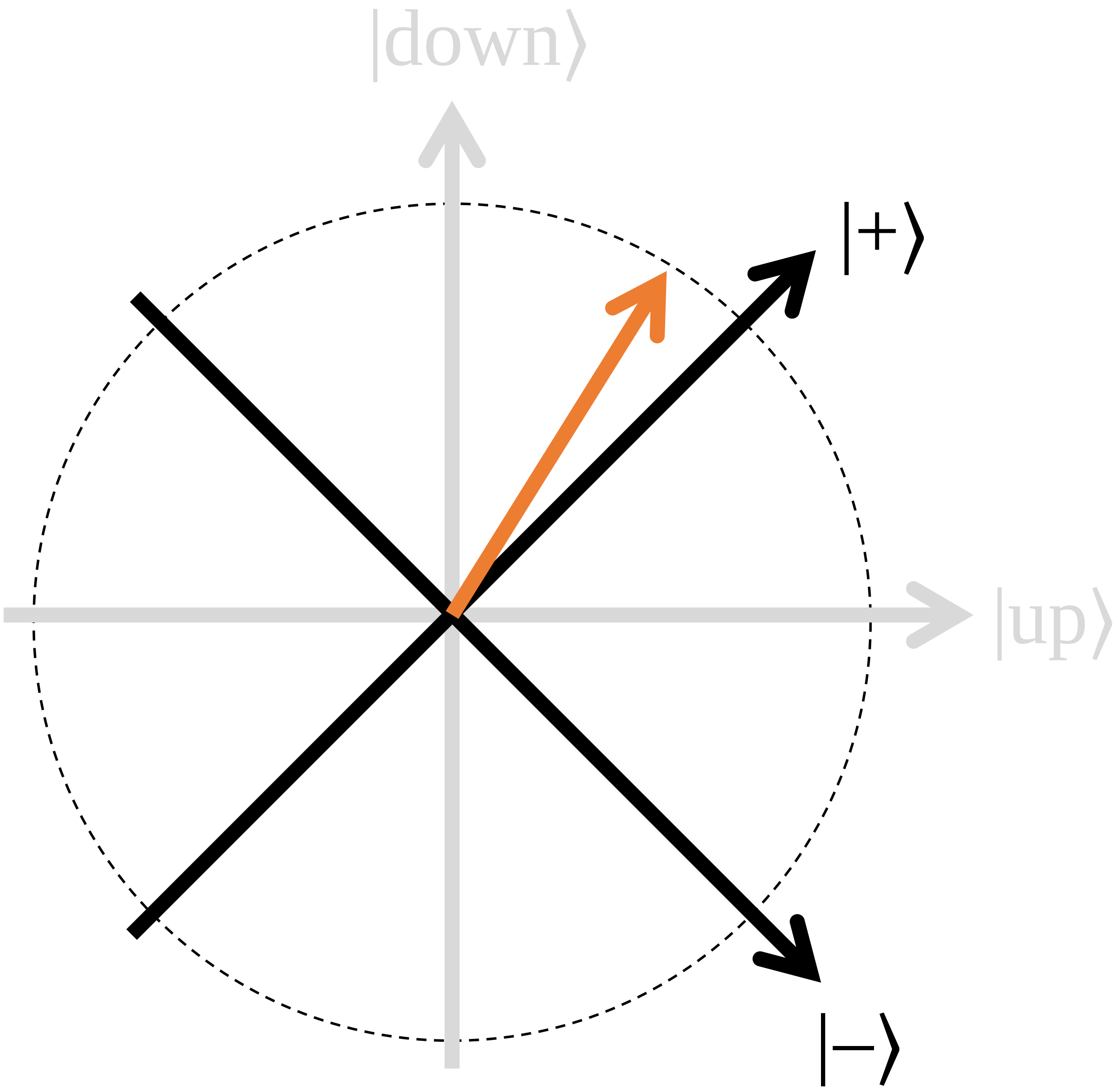
The Feynman Lectures on Physics III, Ch. 8 & 9

The Measurement Problem

- The problem of **outcomes**:
  How and why a single outcome is chosen?

Schlosshauer. *Decoherence,* **2007**


|down⟩
|up⟩



The quantum state can be written in any basis in the Hilbert space

$$|+\rangle = |up\rangle + |down\rangle$$

$$|-\rangle = |up\rangle - |down\rangle$$

The Measurement Problem

- The problem of **outcomes**:
  How and why a single outcome is chosen?

- The problem of **preferred basis**:
  What singles out preferred outcomes in nature?

Schlosshauer. *Decoherence,* **2007**

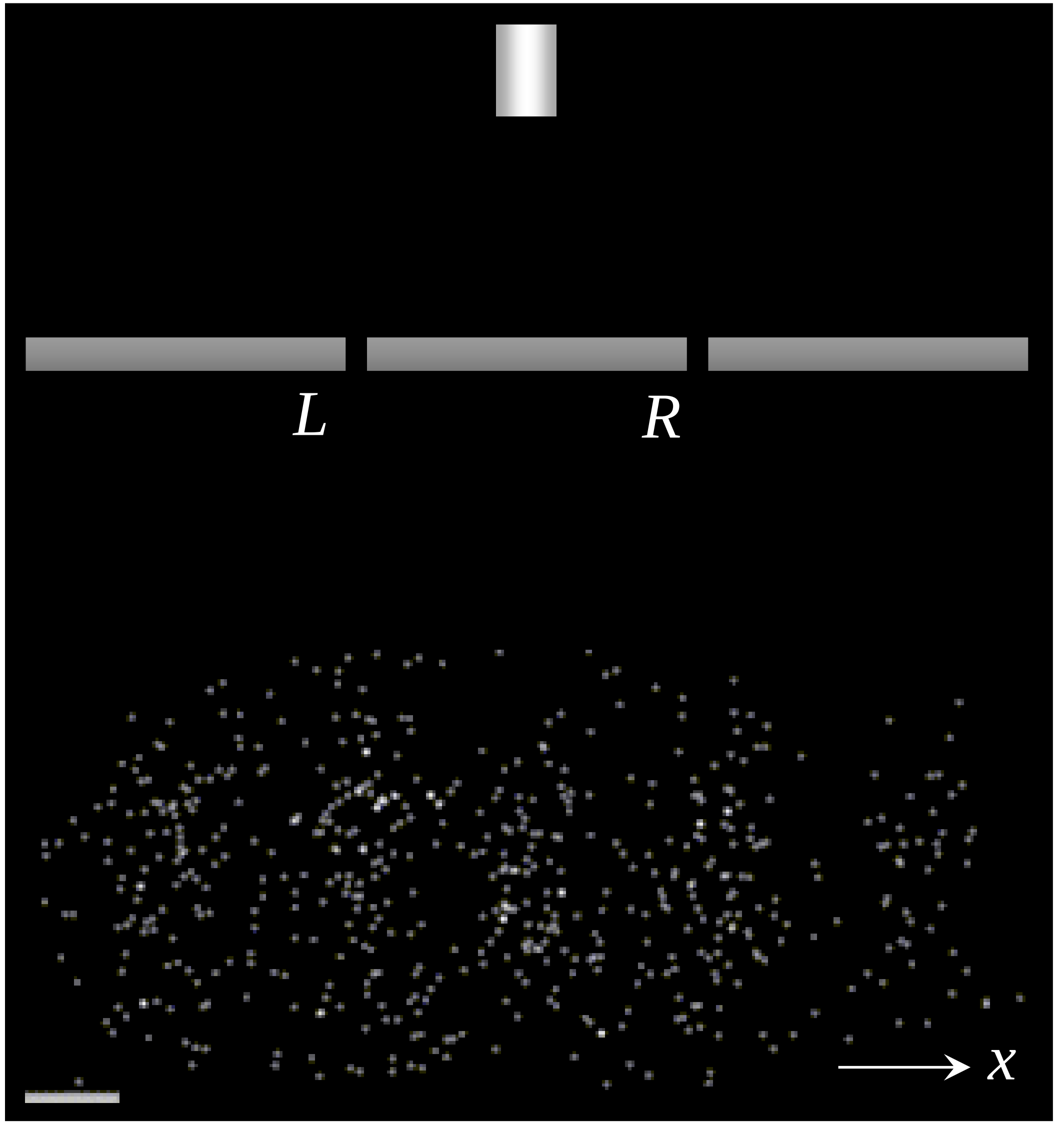
Double-slit experiment

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\left(|\psi_L\rangle + |\psi_R\rangle\right)$$

$$\varrho(x) = \frac{1}{2}\left|\psi_L(x) + \psi_R(x)\right|^2$$

$$= \frac{1}{2}\left|\psi_L(x)\right|^2 + \frac{1}{2}\left|\psi_R(x)\right|^2$$

$$+\mathrm{Re}\left[\psi_L(x)\psi_R^*(x)\right]$$



The Measurement Problem

- The problem of **outcomes**:
  How and why a single outcome is chosen?

- The problem of **preferred basis**:
  What singles out preferred outcomes in nature?

- The problem of **nonobservability of interference**:
  Why don't we see superposition effects everywhere?

Schlosshauer. *Decoherence,* **2007**

Decoherence:
A Quantum World in Disguise

Decoherence transfers quantum information to the environment and suppresses the interference terms

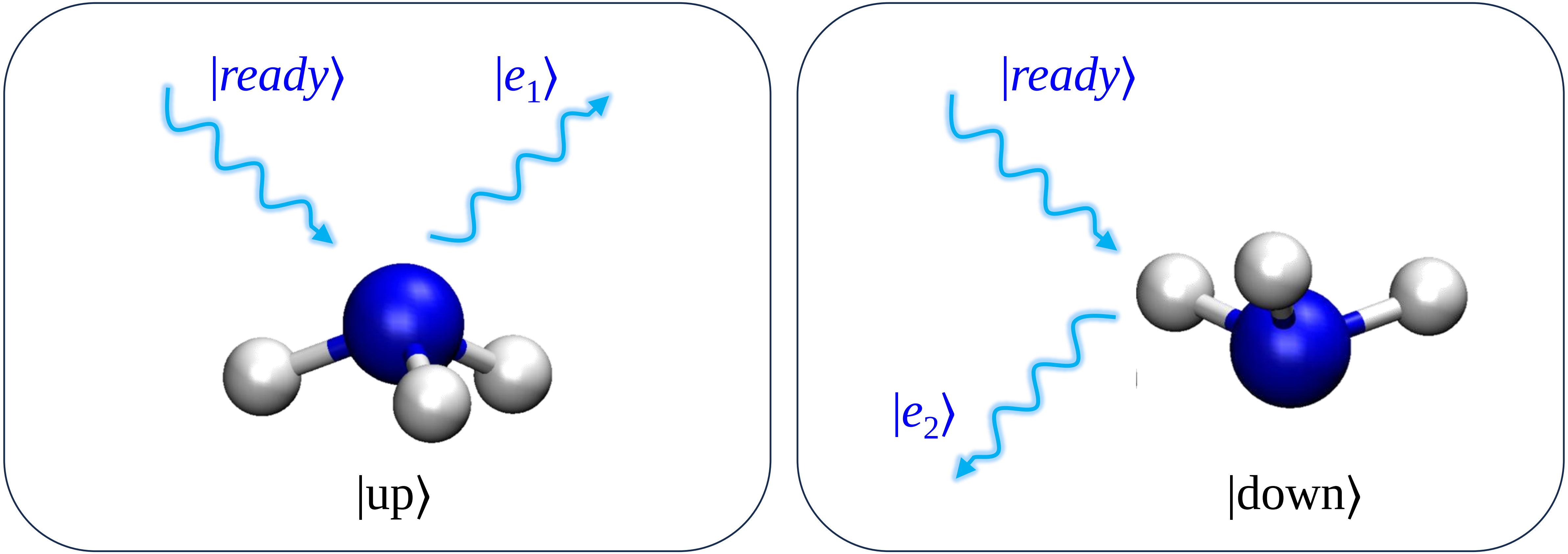
$$\left|\Psi\right\rangle = \overbrace{\left(a\left|up\right\rangle + b\left|down\right\rangle\right)}^{\text{System}} \otimes \overbrace{\left|ready\right\rangle}^{\text{Environment}}$$

$$= a\left|up\right\rangle\left|e_1\right\rangle + b\left|down\right\rangle\left|e_2\right\rangle$$

System's reduced density matrix

$$\rho_S = \mathrm{Tr}_E\left[\left|\Psi\right\rangle\left\langle\Psi\right|\right]$$

$$= \begin{bmatrix} \left|a\right|^2 & ab^*\left\langle e_2|e_1\right\rangle \\ ba^*\left\langle e_1|e_2\right\rangle & \left|b\right|^2 \end{bmatrix}$$



$$\langle e_1 | e_2 \rangle \to 0$$

$$\left|\Psi\right\rangle = \underbrace{\left(a\left|up\right\rangle + b\left|down\right\rangle\right)}_{\text{System}} \otimes \underbrace{\left|ready\right\rangle}_{\text{Environment}}$$

$$= a\left|up\right\rangle\left|e_1\right\rangle + b\left|down\right\rangle\left|e_2\right\rangle$$

System's reduced density matrix

$$\rho_S = \mathrm{Tr}_E\left[\left|\Psi\right\rangle\left\langle\Psi\right|\right]$$

$$= \begin{bmatrix} |a|^2 & ab^*\left\langle e_2|e_1\right\rangle \\ ba^*\left\langle e_1|e_2\right\rangle & |b|^2 \end{bmatrix} \xrightarrow{\text{Decoherence}} \begin{bmatrix} |a|^2 & 0 \\ 0 & |b|^2 \end{bmatrix}$$

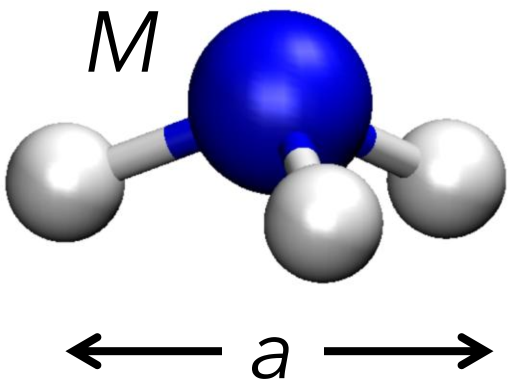
Decoherence is fast!

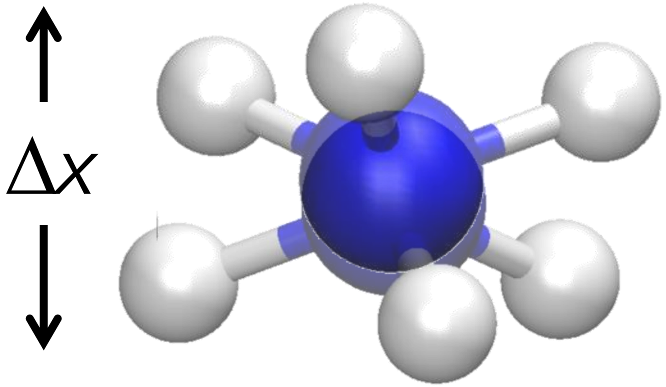
Off-diagonal terms

$$\rho_S(up, down, t) = \rho_S(up, down, 0)e^{-t/\tau_D}$$

$$\tau_D = \frac{1}{\frac{8}{3\hbar^2}\frac{N}{V}(2\pi M)^{1/2} a^2 \Delta x^2 (k_B T)^{3/2}}$$

$$= 10^{-19}\ \mathrm{s}$$

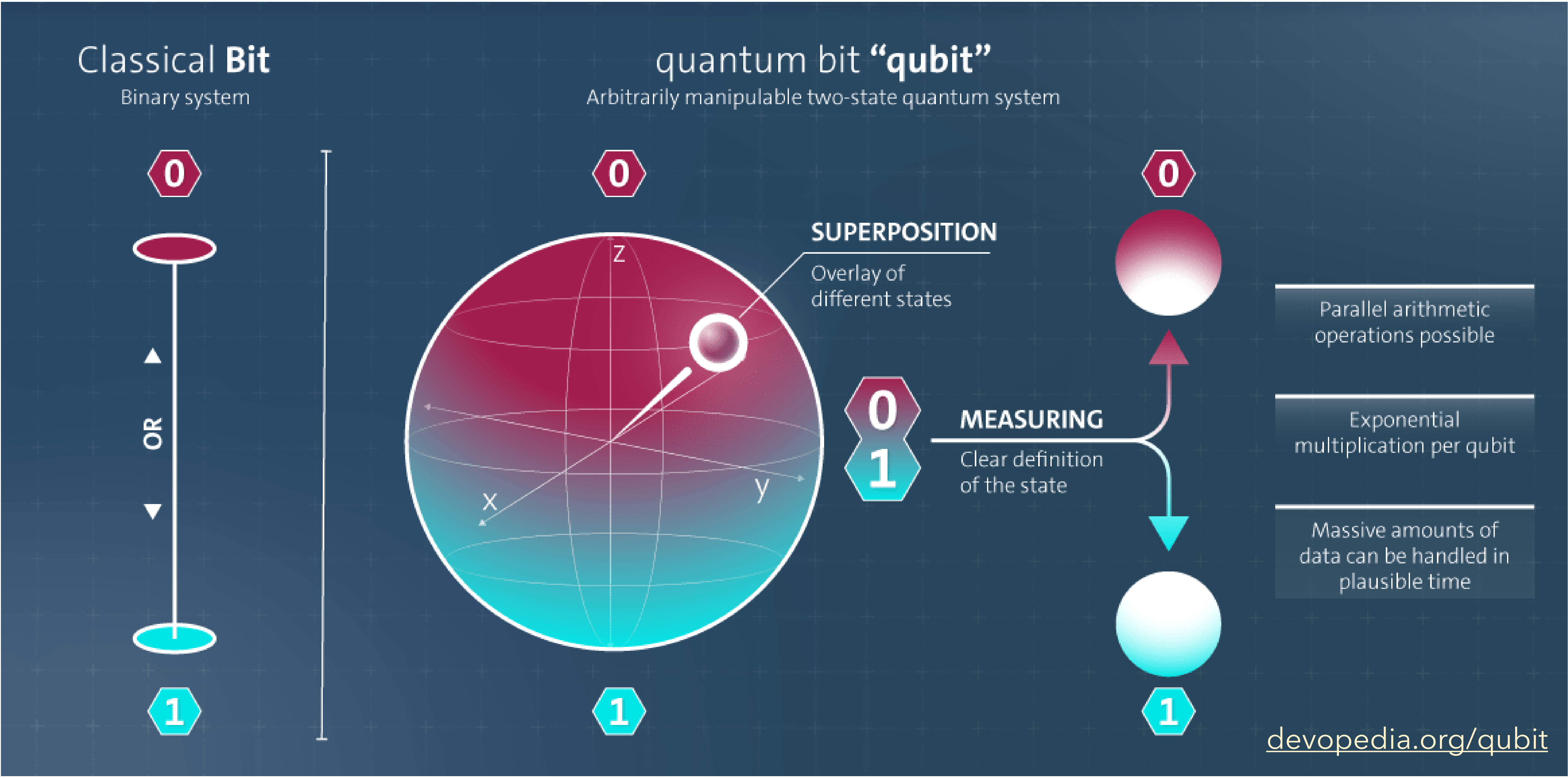




Joos; Zeh. *Z Phys B* **1985**, *59*, 223

But sometimes,
decoherence may take longer

Long-lived coherences are the heart of quantum computing



On which basis does decoherence occur?

Einselection:
Decoherence drives the quantum state to the basis **least entangled** with the environment

Zurek. *Phys Rev D* **1981**, *24*, 1516

In a molecule, electrons lose coherence to nuclear vibrations because $\hat{H}_{elec} \gg \hat{H}_{vib}$

The *least entangled basis* is $\hat{H}_{elec}$ eigenstates (**electronic energy**)

In a gas, a molecule loses coherence to the environment because $\hat{H}_{int} \gg \hat{H}_{mol}$

The *least entangled basis* is $\hat{H}_{int}$ eigenstates (**molecular position**)

Paz; Zurek. *Phys Rev Lett* **1999**, *82*, 5181

Decoherence solves:

- The problem of **preferred basis**:
  What singles out preferred outcomes in nature?

- The problem of **nonobservability of interference**:
  Why don’t we see superposition effects everywhere?

Decoherence does NOT solve:

- The problem of **outcomes**:
  How and why a single outcome is chosen?

$$\rho_S = \mathrm{Tr}_E\left[\hat{\rho}\right]$$

$$= \begin{bmatrix} |a|^2 & ab^*\langle e_2|e_1\rangle \\ ba^*\langle e_1|e_2\rangle & |b|^2 \end{bmatrix} \xrightarrow{\text{Decoherence}} \begin{bmatrix} |a|^2 & 0 \\ 0 & |b|^2 \end{bmatrix}$$

Collapse

$$\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \qquad \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$$

Collapse is not a consensus

Many-Worlds Interpretation

$$\rho_S = \mathrm{Tr}_S\left[\hat{\rho}\right]$$

$$= \begin{bmatrix} |a|^2 & ab^*\langle e_2|e_1\rangle \\ ba^*\langle e_1|e_2\rangle & |b|^2 \end{bmatrix} \xrightarrow{\text{Decoherence}} \begin{bmatrix} |a|^2 & 0 \\ 0 & |b|^2 \end{bmatrix}_S$$

Universe branching

$$\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}_{S+O} \qquad \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}_{S+O}$$

Objective Collapse

$$\rho_S = \mathrm{Tr}_S\left[\hat{\rho}\right]$$

$$= \begin{bmatrix} |a|^2 & ab^*\langle e_2|e_1\rangle \\ ba^*\langle e_1|e_2\rangle & |b|^2 \end{bmatrix} \xrightarrow{\text{Decoherence}} \begin{bmatrix} |a|^2 & 0 \\ 0 & |b|^2 \end{bmatrix}_S$$

Field perturbation

$$\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \qquad \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$$

QBism

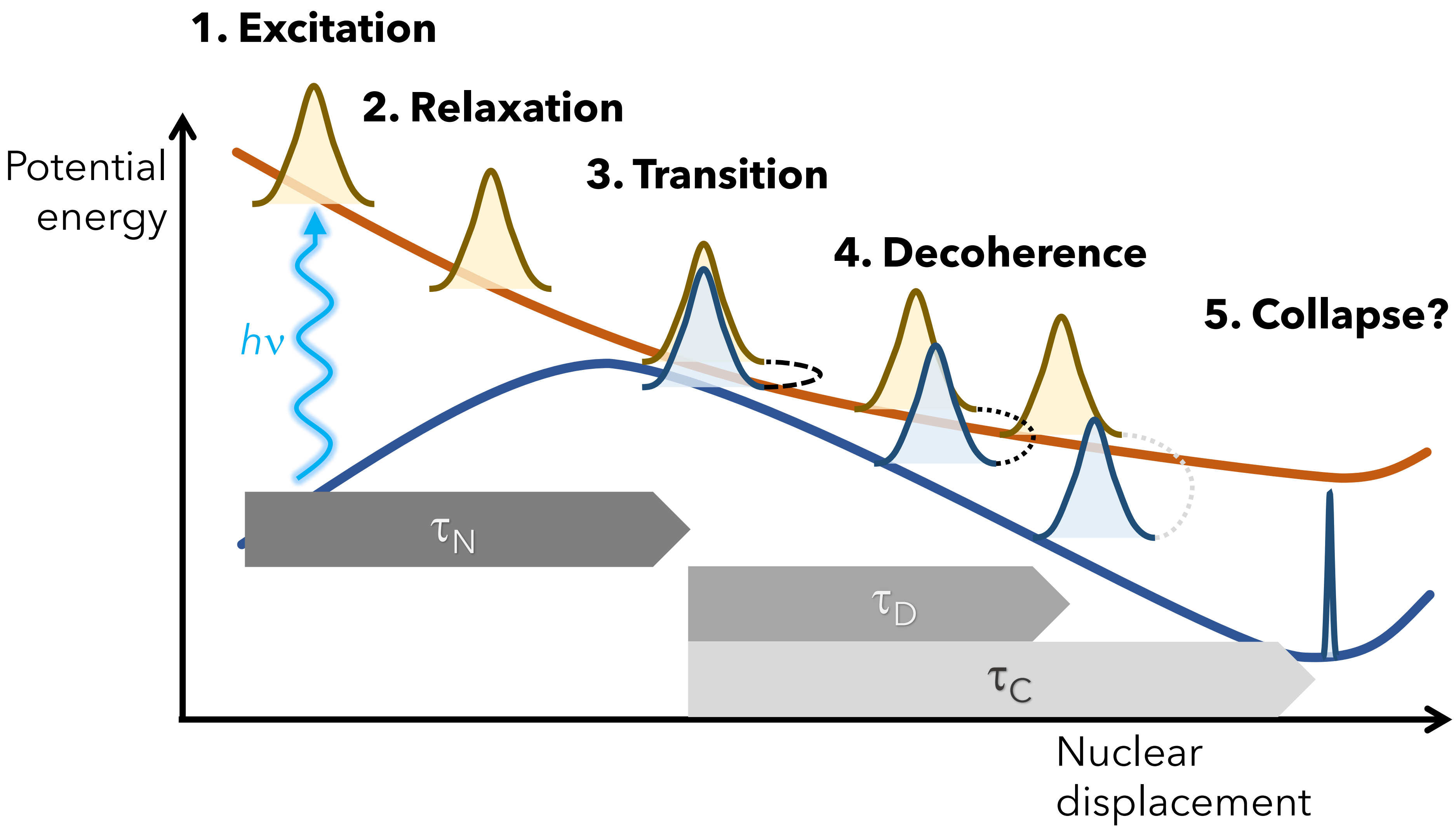
$$\rho_S = \mathrm{Tr}_S\left[\hat{\rho}\right]$$

$$= \begin{bmatrix} |a|^2 & ab^*\langle e_2|e_1\rangle \\ ba^*\langle e_1|e_2\rangle & |b|^2 \end{bmatrix} \xrightarrow{\text{Decoherence}} \begin{bmatrix} |a|^2 & 0 \\ 0 & |b|^2 \end{bmatrix}_S$$

Knowledge update

$$\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \qquad \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$$

A Quasi-Classical World



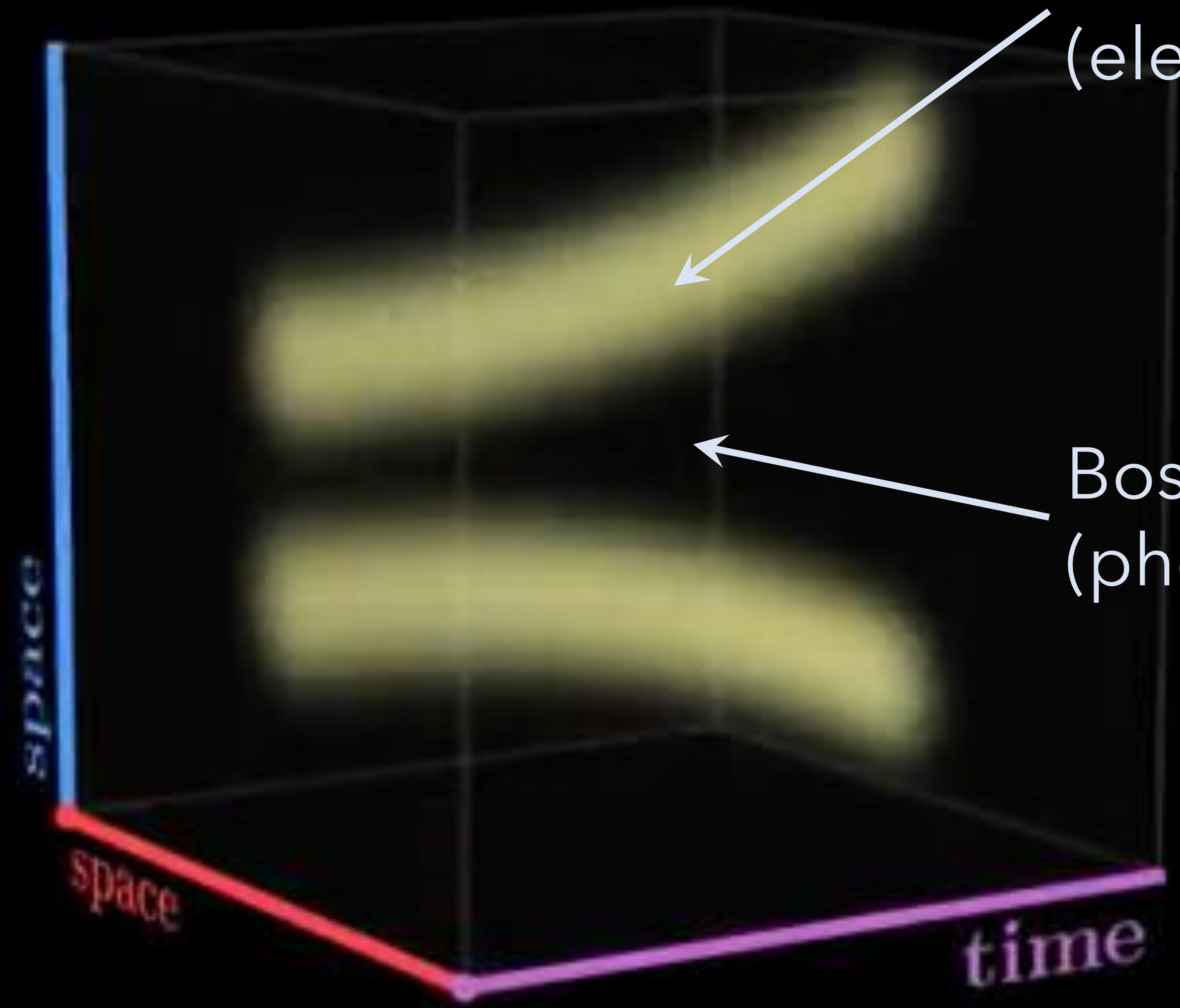
Shu; Truhlar. *JCTC* **2023**, *19*, 380

Where are the quarks?


u
Up quark
d
Down quark
c
Charm quark
s
Strange quark
t
Top quark
b
Bottom quark
γ
Photon
g
Gluon
H
Higgs boson
graviton
τ
Tau
W
W boson
Z
Z boson
Tau neutrino
μ
Muon
Muon neutrino
e
Electron
Electron neutrino

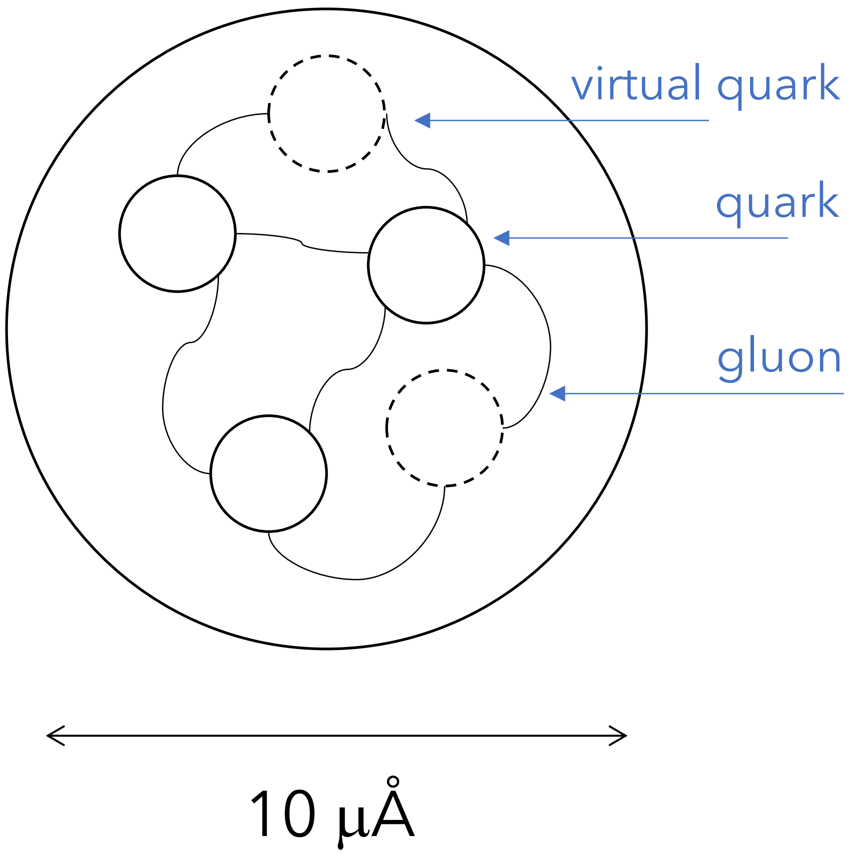
Quantum field theory: quantum waves $\rightarrow$ quantum particles

(second quantization)

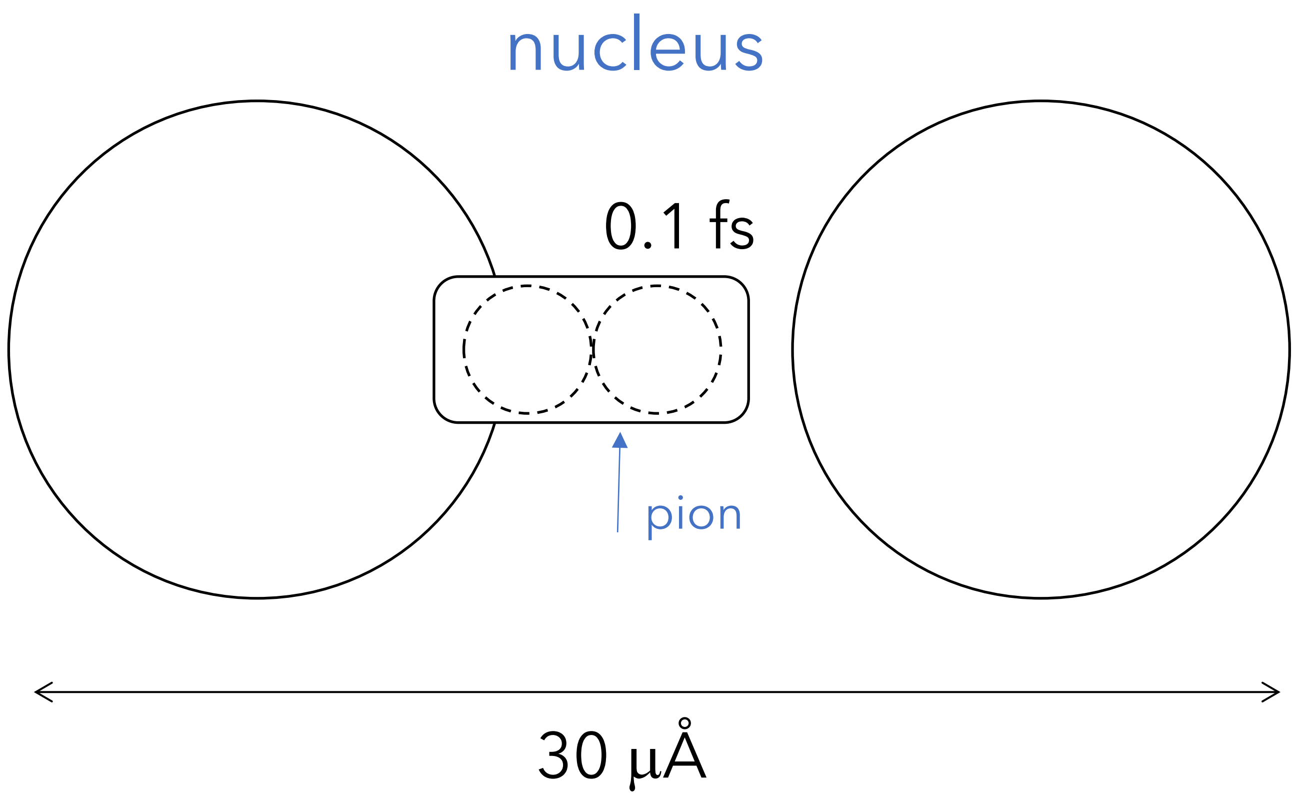


tinyurl.com/sciclickqft

proton/neutron



lifetime 10^{34} years
mass 1836
charge 1 (proton) / 0 (neutron)
spin 1/2


nucleus
0.1 fs
pion
30 μÅ

From the molecular perspective, subnuclear effects are so localized that nuclei and electrons can be treated as **point-like particles**

A molecule is a **stable collection** of point-like nuclei and point-like electrons

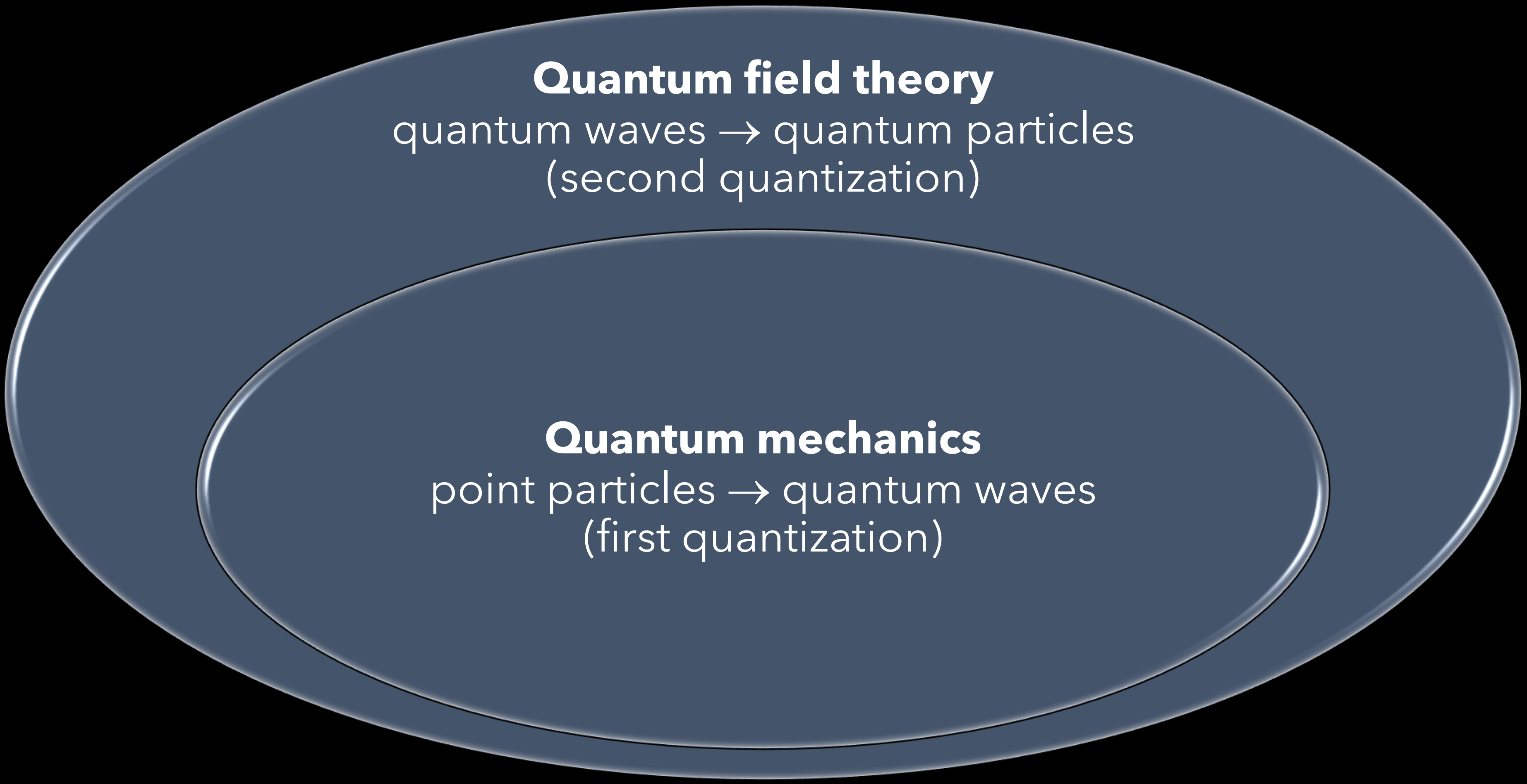
Quantum mechanics: point particles → quantum waves

(first quantization)

$$\hat{H}\left(\mathbf{R},\mathbf{r}\right)=T_{nuc}\left(\mathbf{R}\right)+T_{elec}\left(\mathbf{r}\right)+\sum_{ab}\frac{Z_aZ_b}{\left|\mathbf{R}_a-\mathbf{R}_b\right|}-\sum_{a,i}\frac{Z_a}{\left|\mathbf{R}_a-\mathbf{r}_i\right|}+\sum_{ij}\frac{Z_aZ_b}{\left|\mathbf{r}_i-\mathbf{r}_j\right|}$$

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

Quantum theory



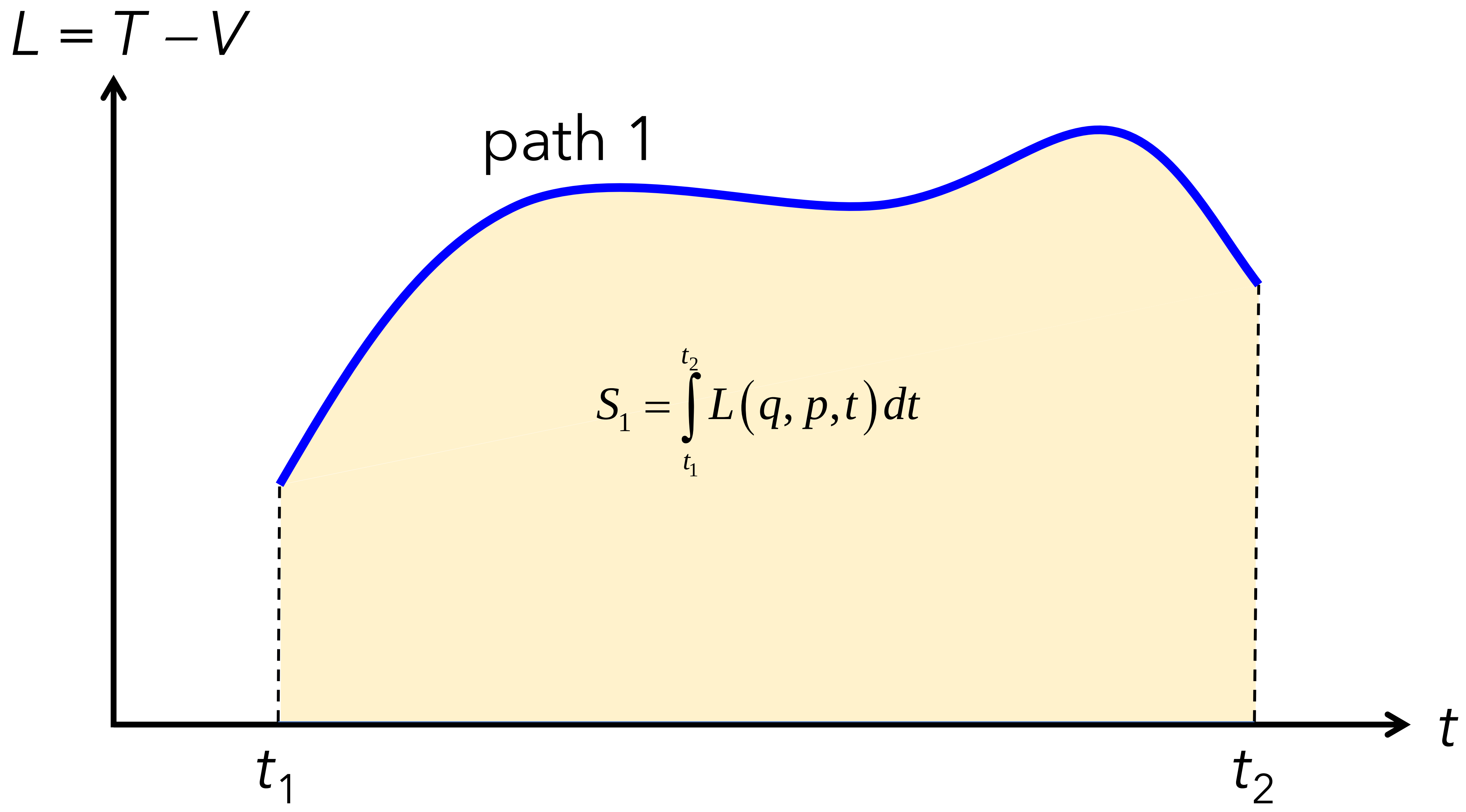
Framing molecules in the Core Theory

The **Core** Theory (Frank Wilczek)

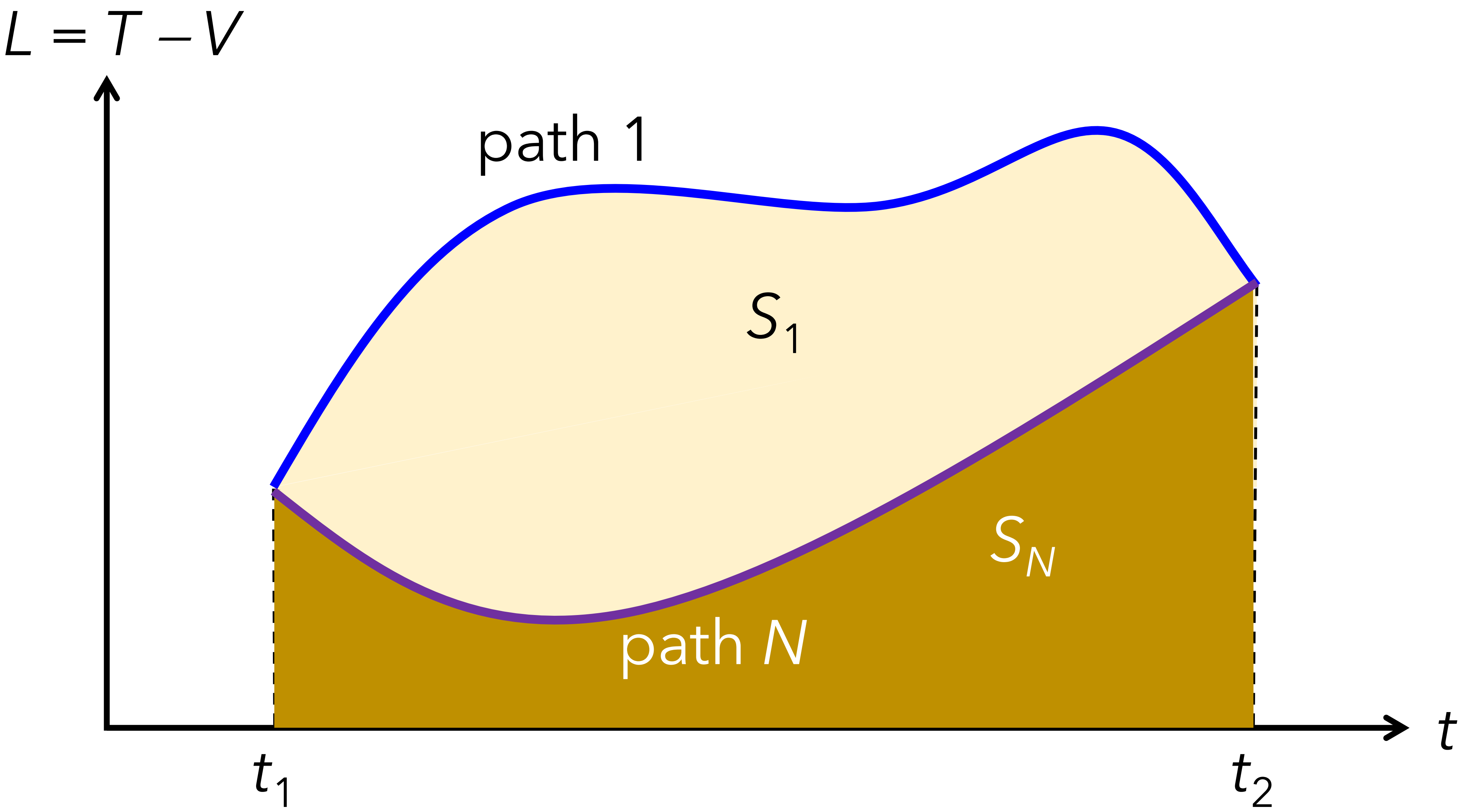
The Core Theory encompasses

- the standard model of elementary particles
- their interactions
- and general relativity

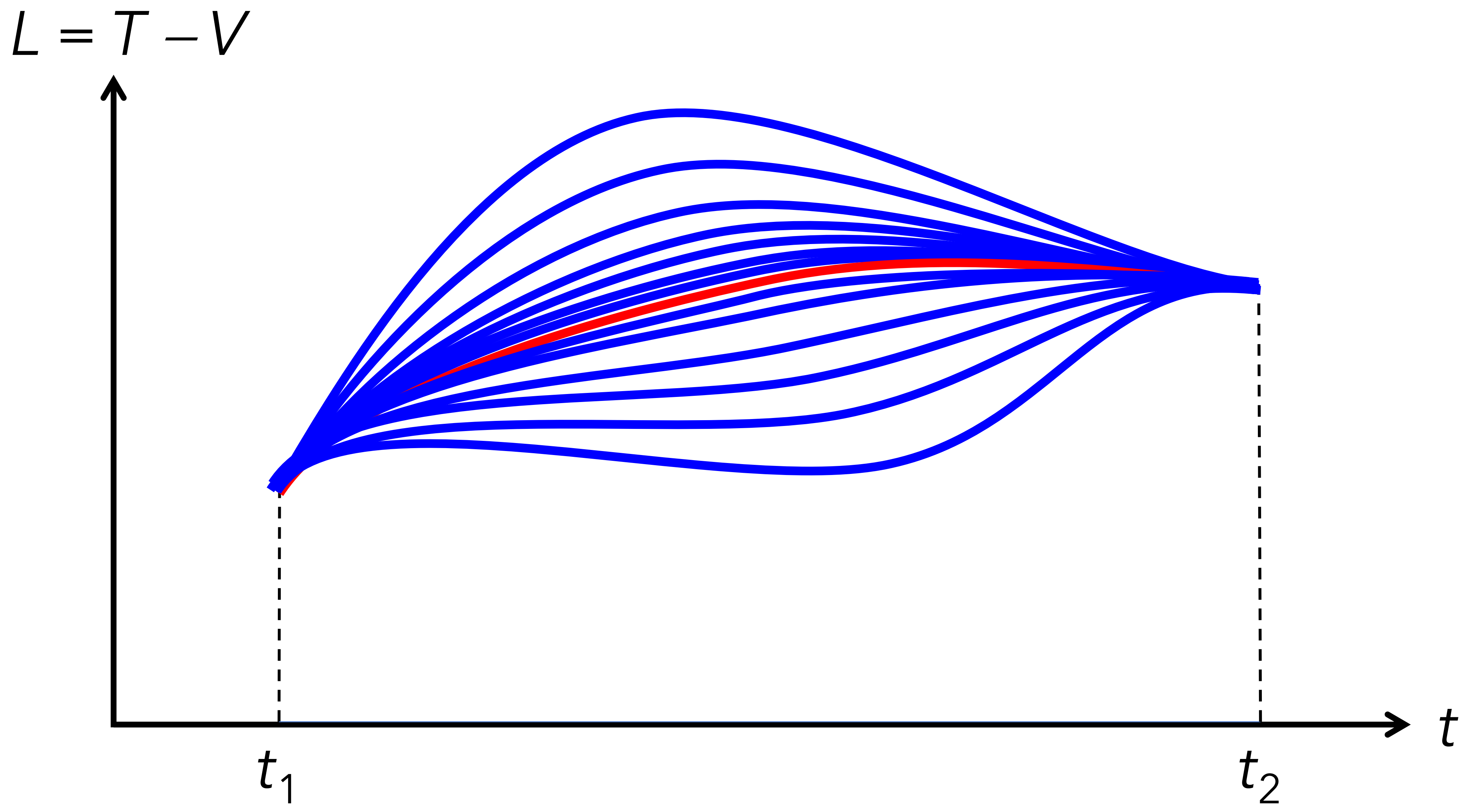
We can express the Core Theory in the language of path integrals



S is the Action



$L = T - V$
path 1
S_1
S_N
path N
t
t_1
t_2


$L = T - V$
t
t_1
t_2

Path integral formulation of quantum mechanics

Action in the entire space and time

$$W = \int D\varphi \exp\{iS[\varphi]\}$$

Integral over every field configurations

The Core Theory (Frank Wilczek)

quantum theory — spacetime

$$W = \int_{k<\Lambda} [Dg][DA][D\psi][D\Phi] \exp\left\{ i \int d^4x \sqrt{-g} \times \right.$$

$$\left. \left[\frac{m_p^2}{2} R - \frac{1}{4} F^a_{\mu\nu} F^{a\mu\nu} + i\bar{\psi}^i \gamma^\mu D_\mu \psi^i + \left(\bar{\psi}^i_L V_{ij} \Phi \psi^j_R + h.c.\right) - \left|D_\mu \Phi\right|^2 - V(\Phi) \right] \right\}$$

gravity — strong nuclear, weak nuclear, electromagnetic forces — matter — Higgs

quantum chemistry
& molecular physics

Carroll. *The Big Picture*, **2016**

"As science continues to learn more about the universe, we will keep adding to the Core Theory, and perhaps we will even find a more comprehensive theory underlying it that doesn't refer to quantum field theory at all. But none of that will change the fact that the Core Theory is an accurate description of nature in its claimed domain. The fact that we have successfully put together such a theory is one of the greatest triumphs of human intellectual history."

- Carroll. *The Big Picture*, **2016**


epistemological
pale blue dot

To know more:

Decoherence

- Sabine Hossenfeld, youtu.be/igsulul_HAQ
- Phillip Ball, Aeon Magazine, **2017**

Many worlds interpretation

- PBS Space Time, youtu.be/z-syaCoqkZA

Pilot wave

- PBS Space Time, youtu.be/RlXdsyctD50

Objective collapse

- PBS Space Time, youtu.be/FP6iyVJ70OU

QBism

- Corin S. Powell, Aeon Magazine, **2017**

Inside the proton

- Wood and Shreman, Quanta Magazine, **2022**
- Quanta Magazine, youtu.be/Unl1jXFnzgo

Quantum field theory

- Science click, tinyurl.com/sciclickqft
- ViaScience, tinyurl.com/viasciQFT (full course)
- Carroll, *The Biggest Ideas in the Universe*, v. 2, **2024**

The Core theory

- Carroll. *The Big Picture,* ***2016***