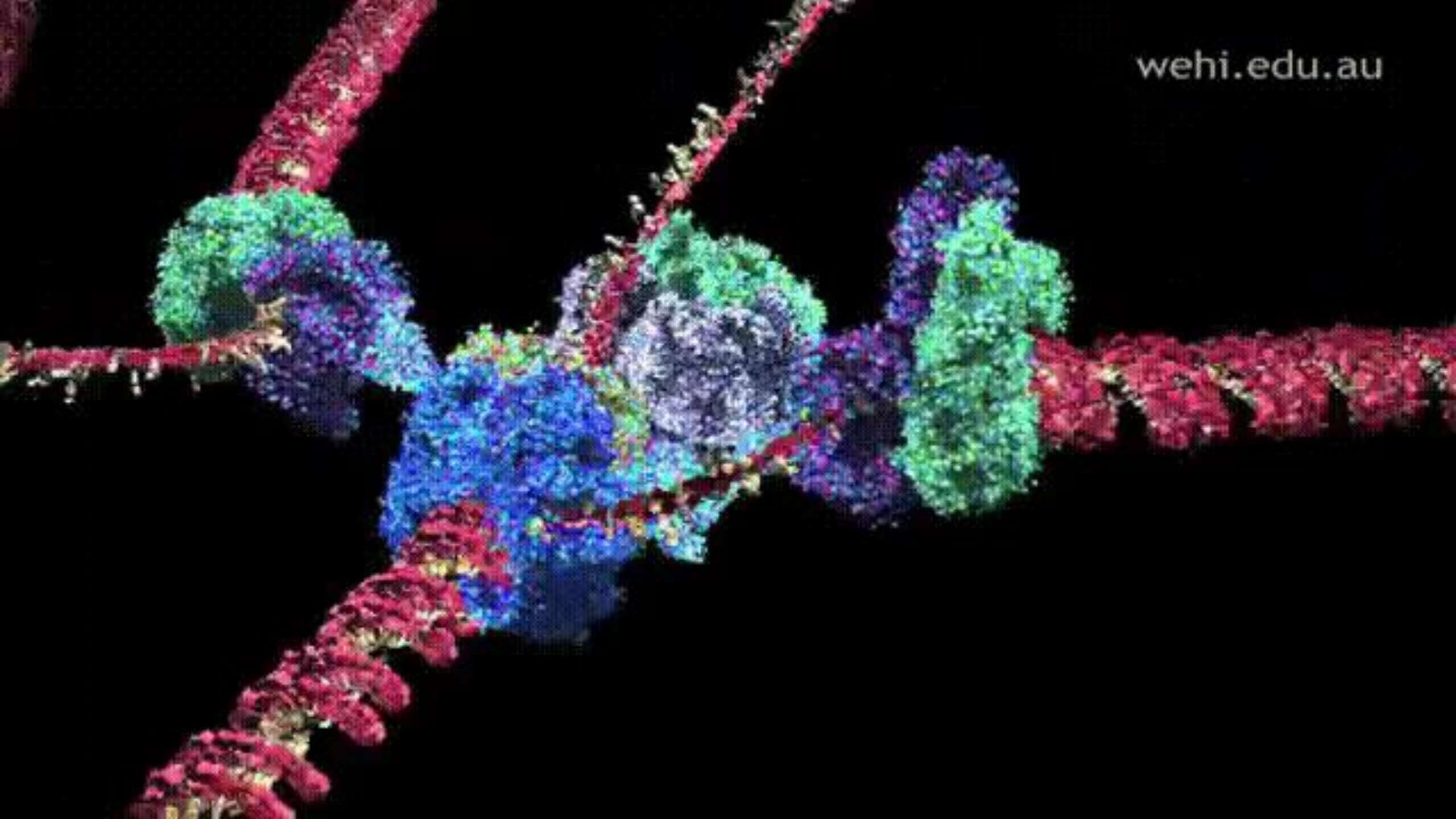




# L4 – Quantum Mechanics 4

Quantum mechanics in context

# The classical nuclear motion



Quantum nuclear motion

$\hbar \rightarrow 0$

Classical nuclear motion

Born-Oppenheimer nuclear equation

$$T_{nuc}(\mathbf{R})h_n(\mathbf{R},t) + E_n(\mathbf{R})h_n(\mathbf{R},t) - i\hbar \frac{\partial h_n(\mathbf{R},t)}{\partial t} = 0$$

Newton's nuclear equation

$$M_\alpha \frac{d^2 \mathbf{R}_\alpha}{dt^2} = \mathbf{F}_\alpha$$

# Hamilton-Jacobi formulation of classical mechanics

$$M_{\alpha} \frac{d^2 \mathbf{R}_{\alpha}}{dt^2} = \mathbf{F}_{\alpha}$$



$$\frac{\partial S}{\partial t} + H(\mathbf{R}, \nabla S, t) = 0$$

$$S(\mathbf{R}, t) = \int_{t_0}^t L d\tau$$

$$\mathbf{p} = \nabla S$$

$S$ : Action

$L = T - V$ : Lagrangian

$H = T + V$ : Hamiltonian

1. Start with the Nuclear Schrödinger equation in TD-BOA:

$$T_{nuc}(\mathbf{R})h_n(\mathbf{R},t) + E_n(\mathbf{R})h_n(\mathbf{R},t) - i\hbar \frac{\partial h_n(\mathbf{R},t)}{\partial t} = 0$$

2. Assume the nuclear wave function in polar form

$$h_n(\mathbf{R},t) = A(\mathbf{R},t) \exp\left(\frac{i}{\hbar} S(\mathbf{R},t)\right)$$

3. Use the nuclear kinetic energy operator

$$T_{nuc} = -\frac{\hbar^2}{2\mathbf{M}} \nabla^2$$

4. After a lot of algebra, we get ....

(See the demonstration at the end of the presentation)

$$\frac{\partial S(\mathbf{R}, t)}{\partial t} + \frac{1}{2\mathbf{M}} (\nabla S(\mathbf{R}, t))^2 + E_n(\mathbf{R}) - \frac{\hbar^2}{2\mathbf{M}} \frac{\nabla^2 A(\mathbf{R}, t)}{A(\mathbf{R}, t)} = 0$$

$$\frac{\partial A(\mathbf{R}, t)^2}{\partial t} + \frac{1}{\mathbf{M}} \nabla \cdot (A^2(\mathbf{R}, t) \nabla S(\mathbf{R}, t)) = 0$$

$$\frac{\partial S(\mathbf{R}, t)}{\partial t} + \frac{1}{2\mathbf{M}} (\nabla S(\mathbf{R}, t))^2 + E_n(\mathbf{R}) - \frac{\hbar^2}{2\mathbf{M}} \frac{\nabla^2 A(\mathbf{R}, t)}{A(\mathbf{R}, t)} = 0$$

$\lim \hbar \rightarrow 0$

$$\frac{\partial S(\mathbf{R}, t)}{\partial t} + \frac{1}{2\mathbf{M}} \underbrace{(\nabla S(\mathbf{R}, t))^2}_{\mathbf{p}(\mathbf{R}, t)} + E_n(\mathbf{R}) = 0$$

$$\underbrace{\hspace{10em}}_{T_{nuc}}$$

$$\underbrace{\hspace{15em}}_{H(\mathbf{R}, \nabla S, t)}$$

$$\frac{\partial S}{\partial t} + H(\mathbf{R}, \nabla S, t) = 0$$

*Classical Hamilton-Jacobi equation!*

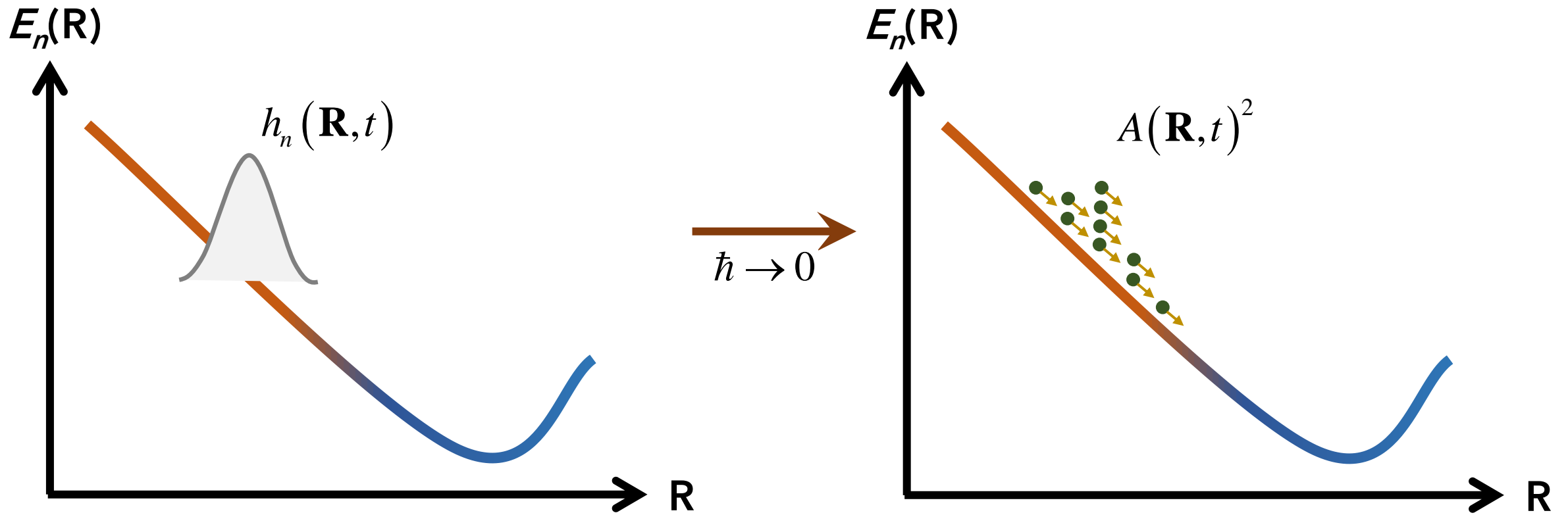


$$\frac{\partial S(\mathbf{R}, t)}{\partial t} + H(\mathbf{R}, \nabla S, t) = 0$$

$$\frac{\partial A(\mathbf{R}, t)^2}{\partial t} + \frac{1}{\mathbf{M}} \nabla \cdot (A^2(\mathbf{R}, t) \nabla S(\mathbf{R}, t)) = 0$$

“In the classical approximation,  $h_n(\mathbf{R}, t)$  describes a fluid of non-interacting classical particles of mass  $\mathbf{M}$  (statistical mixture) and subject to the potential  $E_n(\mathbf{R})$ . The density and current density at each point of space are at all times respectively equal to the probability density  $A^2$  and the probability current density  $A^2 \nabla S / \mathbf{M}$  of the quantum particles at that point.”

Messiah, 1961, p. 223



“In the classical approximation,  $h_n(\mathbf{R}, t)$  describes a fluid of non-interacting classical particles of mass  $\mathbf{M}$  (statistical mixture) and subject to the potential  $E_n(\mathbf{R})$ . The density and current density at each point of space are at all times respectively equal to the probability density  $A^2$  and the probability current density  $A^2 \nabla S / \mathbf{M}$  of the quantum particles at that point.”

Messiah, 1961, p. 223

This classical limit of the nuclear Schrödinger equation is the formal reason we can do molecular dynamics of molecules.

# Decoherence & collapse

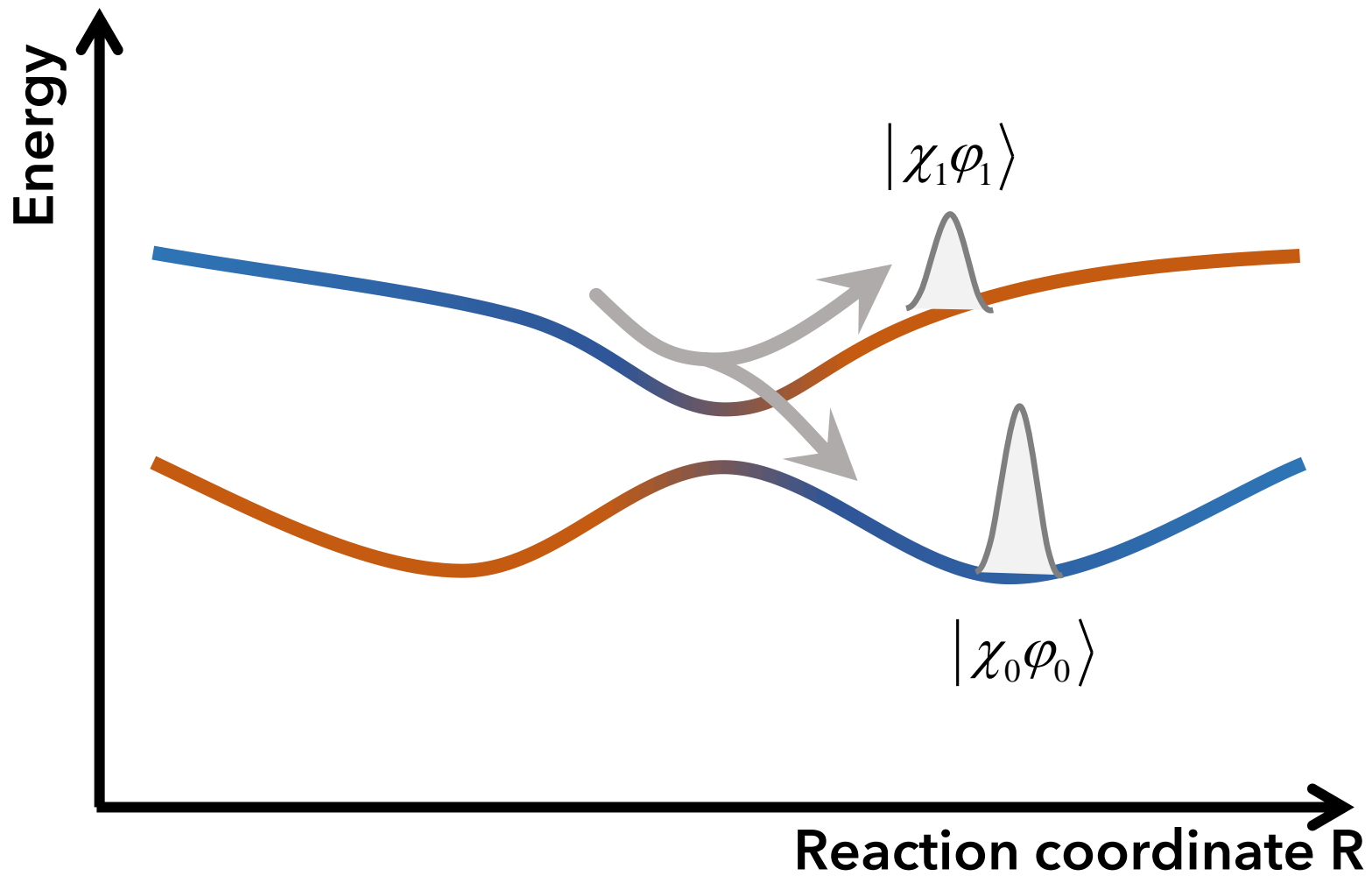
# Understanding Quantum Mechanics #5

# Decoherence

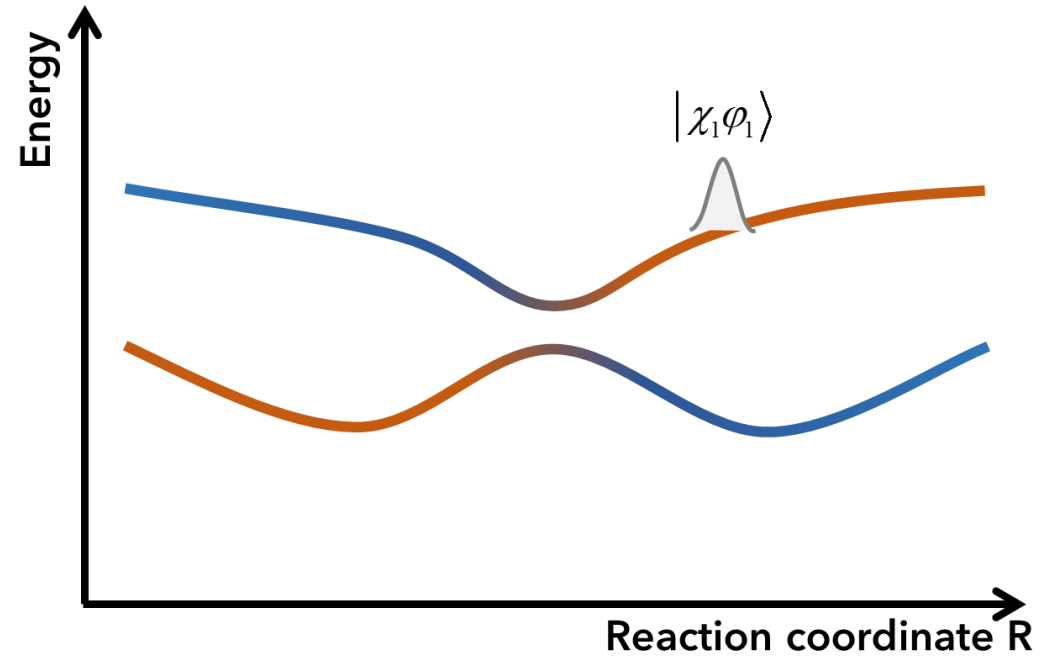
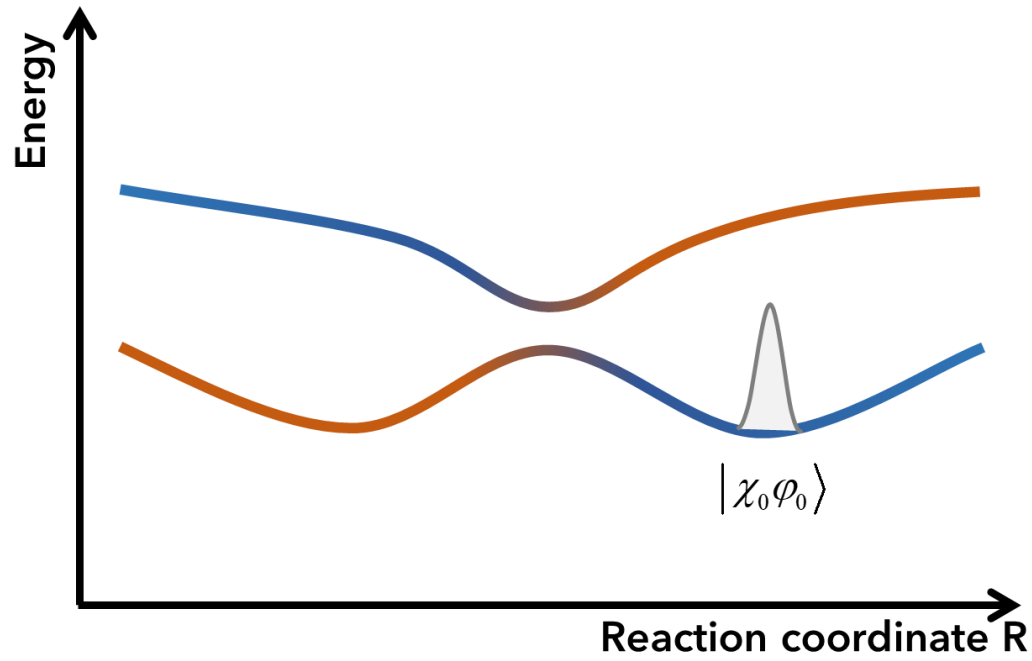
$$|\Psi\rangle = \frac{1}{\sqrt{2}}|1\rangle + \frac{1}{\sqrt{2}}e^{i\theta}|2\rangle$$



$$|\Psi\rangle = a_0(t)|\chi_0\phi_0\rangle + a_1(t)|\chi_1\phi_1\rangle$$



# Result of a measurement



We say that the wave function collapsed into one state.

But we should distinguish between two distinct effects:  
decoherence and collapse

- **Decoherence** selects which states can be measured
- **Collapse** define the states that are actually measured



To discuss decoherence, we need the **density matrix**

$$\rho \equiv |\Psi\rangle\langle\Psi|$$

Suppose the system is a superposition of two states

$$|\Psi\rangle = a_0|\psi_0\rangle + a_1|\psi_1\rangle$$

The density matrix is

$$\begin{aligned}\rho &= |\Psi\rangle\langle\Psi| = (a_0|\psi_0\rangle + a_1|\psi_1\rangle)(a_0^*\langle\psi_0| + a_1^*\langle\psi_1|) \\ &= a_0a_0^*|\psi_0\rangle\langle\psi_0| + a_0a_1^*|\psi_0\rangle\langle\psi_1| + a_1a_0^*|\psi_1\rangle\langle\psi_0| + a_1a_1^*|\psi_1\rangle\langle\psi_1| \\ &= |a_0|^2|\psi_0\rangle\langle\psi_0| + a_0a_1^*|\psi_0\rangle\langle\psi_1| + a_1a_0^*|\psi_1\rangle\langle\psi_0| + |a_1|^2|\psi_1\rangle\langle\psi_1|\end{aligned}$$

$$\rho = |a_0|^2 |\psi_0\rangle\langle\psi_0| + a_0 a_1^* |\psi_0\rangle\langle\psi_1| + a_1 a_0^* |\psi_1\rangle\langle\psi_0| + |a_1|^2 |\psi_1\rangle\langle\psi_1|$$

$$\rho = \begin{bmatrix} |a_0|^2 & a_0 a_1^* \\ a_1 a_0^* & |a_1|^2 \end{bmatrix}$$

$|a_i|^2$  population of state  $|\psi_i\rangle$

$a_i a_j^*$  coherence between  $|\psi_i\rangle$  and  $|\psi_j\rangle$

Forming the **molecular density matrix** for

$$|\Psi_{mol}\rangle = a_0(t)|\chi_0\varphi_0\rangle + a_1(t)|\chi_1\varphi_1\rangle$$

$|\chi_i\rangle$  – nuclei

$|\varphi_i\rangle$  – electrons

$$\begin{aligned}\rho_{mol} &= \left[ a_0(t)|\chi_0\varphi_0\rangle + a_1(t)|\chi_1\varphi_1\rangle \right] \left[ a_0^*(t)\langle\chi_0\varphi_0| + a_1^*(t)\langle\chi_1\varphi_1| \right] \\ &= \begin{bmatrix} |a_0(t)|^2 & a_0(t)a_1^*(t) \\ a_1(t)a_0^*(t) & |a_1(t)|^2 \end{bmatrix}\end{aligned}$$

Molecular coherences  $a_i(t)a_j^*(t)$  survive forever.  
They never tend to zero.

Forming the **electronic density** matrix for

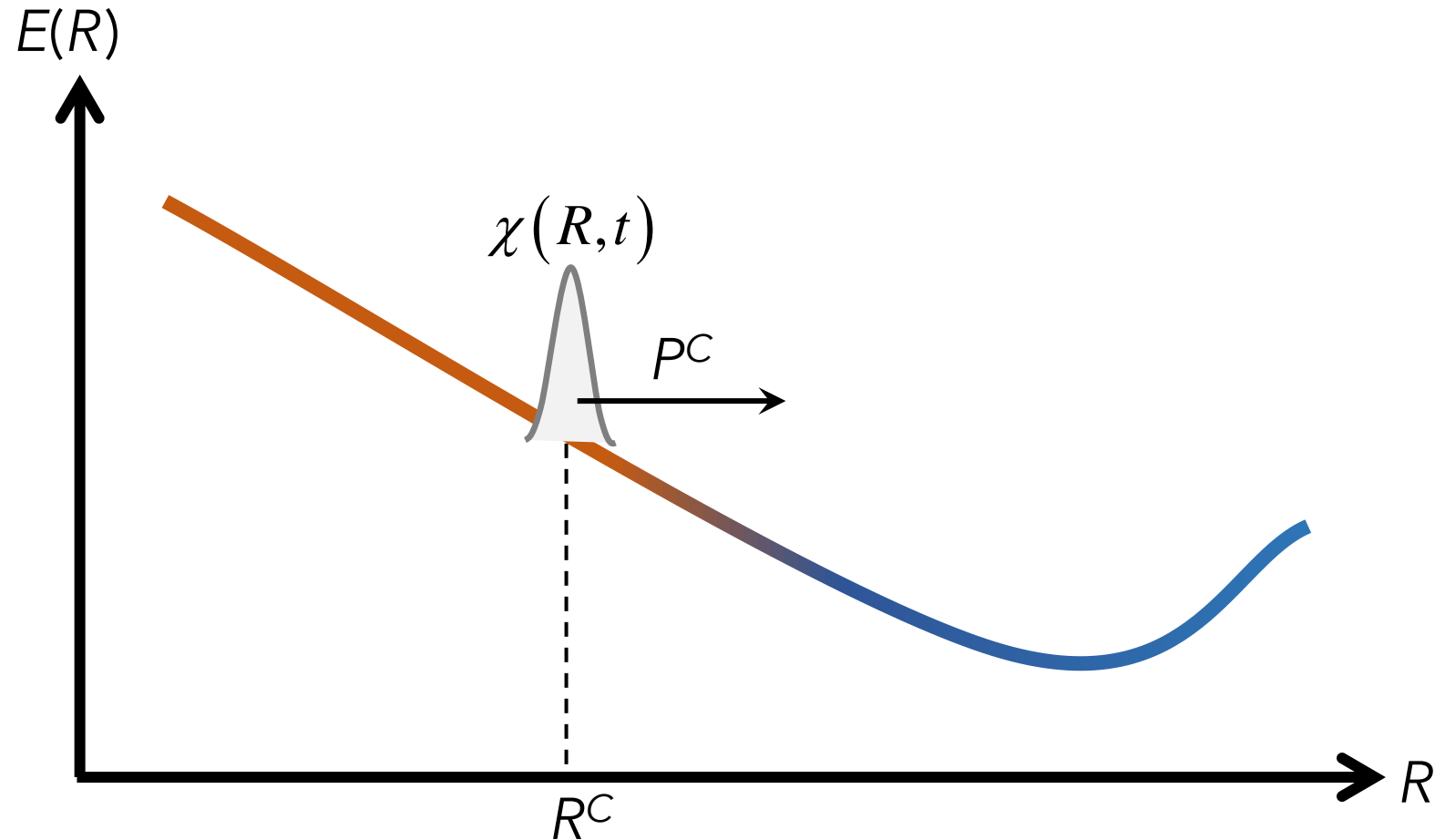
$$|\Psi_{el}\rangle = \chi_0(\mathbf{R}, t)|\varphi_0\rangle + \chi_1(\mathbf{R}, t)|\varphi_1\rangle$$

$$\begin{aligned}\rho_{el} &= \left[ \chi_0(\mathbf{R}, t)|\varphi_0\rangle + \chi_1(\mathbf{R}, t)|\varphi_1\rangle \right] \left[ \chi_0^*(\mathbf{R}, t)\langle\varphi_0| + \chi_1^*(\mathbf{R}, t)\langle\varphi_1| \right] \\ &= \begin{bmatrix} |\chi_0(\mathbf{R}, t)|^2 & \chi_0(\mathbf{R}, t)\chi_1^*(\mathbf{R}, t) \\ \chi_1(\mathbf{R}, t)\chi_0^*(\mathbf{R}, t) & |\chi_1(\mathbf{R}, t)|^2 \end{bmatrix}\end{aligned}$$

Will electronic coherences  $\chi_i(\mathbf{R}, t)\chi_j^*(\mathbf{R}, t)$  also survive forever?

Suppose the nuclear wave function is a 1-D Gaussian wave packet

$$\chi(R,t) = \left(\frac{2\alpha}{\pi}\right)^{1/4} \exp\left[-\alpha(R - R^C(t))^2 + \frac{i}{\hbar} P^C(t)(R - R^C(t))\right]$$



Assuming a 1-D Gaussian nuclear wave packet

$$\chi_k(R, t) = \left( \frac{2\alpha}{\pi} \right)^{1/4} \exp \left[ -\alpha (R - R_k^C(t))^2 + \frac{i}{\hbar} P_k^C(t) (R - R_k^C(t)) \right]$$

Electronic populations

$$|\chi_k(R, t)|^2 = \left( \frac{2\alpha}{\pi} \right)^{1/2} \exp \left[ -2\alpha (R - R_k^C(t))^2 \right]$$

Electronic coherences

$$\begin{aligned} \chi_k^*(R, t) \chi_l(R, t) &= \left( \frac{2\alpha}{\pi} \right)^{1/2} \exp \left[ -\frac{\alpha}{2} (R_k^C(t) - R_l^C(t))^2 \right] \times \\ &\exp \left[ -2\alpha \left( R - \frac{R_k^C(t) + R_l^C(t)}{2} \right)^2 \right] \exp \left[ -\frac{i}{\hbar} (P_k^C(t) (R - R_k^C(t)) - P_l^C(t) (R - R_l^C(t))) \right] \end{aligned}$$

$$\chi_k^*(R,t) \chi_l(R,t) = \left( \frac{2\alpha}{\pi} \right)^{1/2} \exp \left[ -\frac{\alpha}{2} (R_k^C(t) - R_l^C(t))^2 \right] \times$$

$$\exp \left[ -2\alpha \left( R - \frac{R_k^C(t) + R_l^C(t)}{2} \right)^2 \right] \exp \left[ -\frac{i}{\hbar} (P_k^C(t)(R - R_k^C(t)) - P_l^C(t)(R - R_l^C(t))) \right]$$

Classical uniform velocity motion of the Gaussian center  $R_k^C(t) = R_k^C(0) + v_k^C t$

$$\exp \left[ -\frac{\alpha}{2} (R_k^C(t) - R_l^C(t))^2 \right] \propto \exp \left[ -\frac{\alpha}{2} (v_k^C - v_l^C)^2 t^2 \right]$$

The electronic coherence tends to zero with time.

That's called **decoherence**.

## Decoherence

$$\rho(t_\infty) \rightarrow \begin{bmatrix} |\chi_0(R, t_\infty)|^2 & 0 \\ 0 & |\chi_1(R, t_\infty)|^2 \end{bmatrix}$$

$$t_\infty \gg \tau_D = \frac{1}{|v_k^C - v_l^C|} \sqrt{\frac{2}{\alpha}}$$

$$\rho(t_\infty) = |\chi_0(R, t_\infty)|^2 |\varphi_0\rangle\langle\varphi_0| + |\chi_1(R, t_\infty)|^2 |\varphi_1\rangle\langle\varphi_1|$$

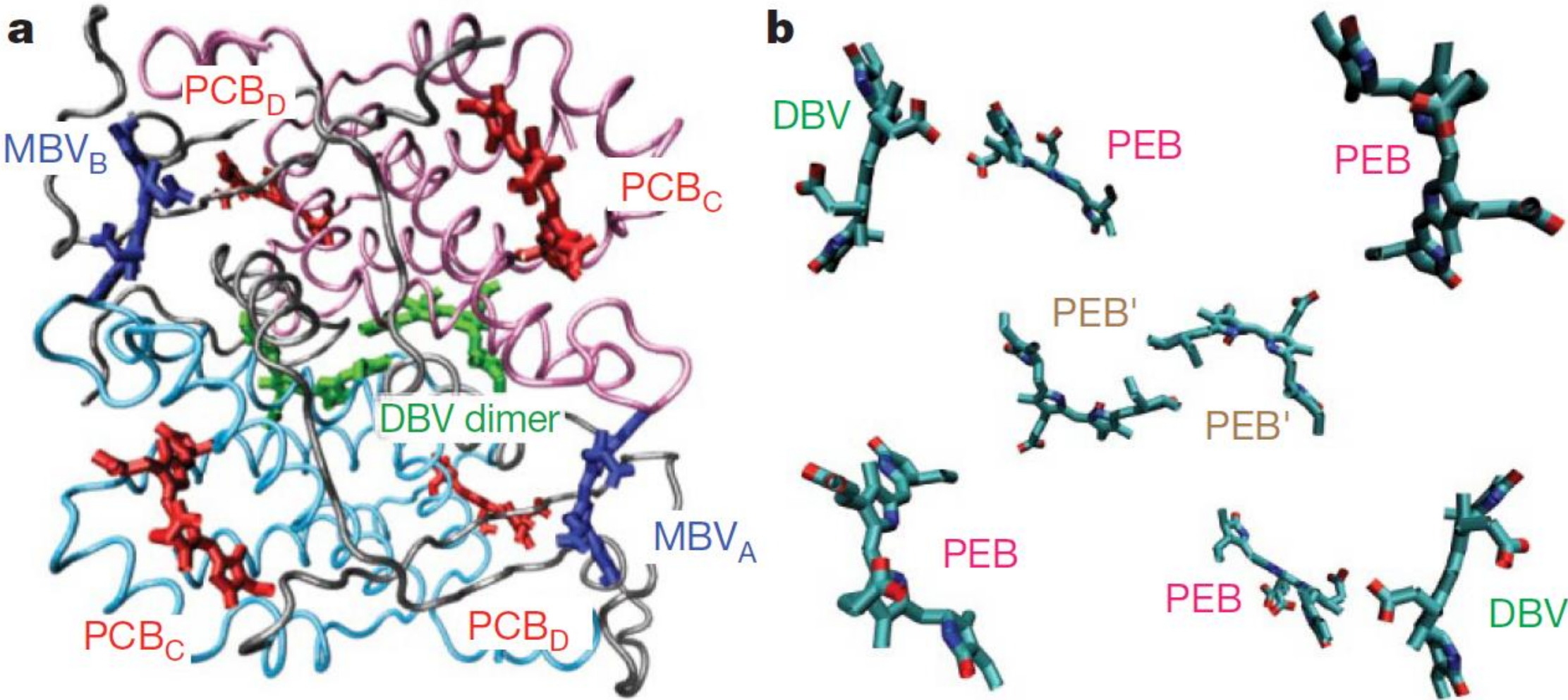
Einselection (*Quantum Darwinism*):

$|\varphi_0\rangle, |\varphi_1\rangle$  are **pointer states**.

States like  $\chi_0|\varphi_0\rangle + \chi_1|\varphi_1\rangle$  disappear and cannot be measured.



# Photosynthetic centers have long-lived coherences

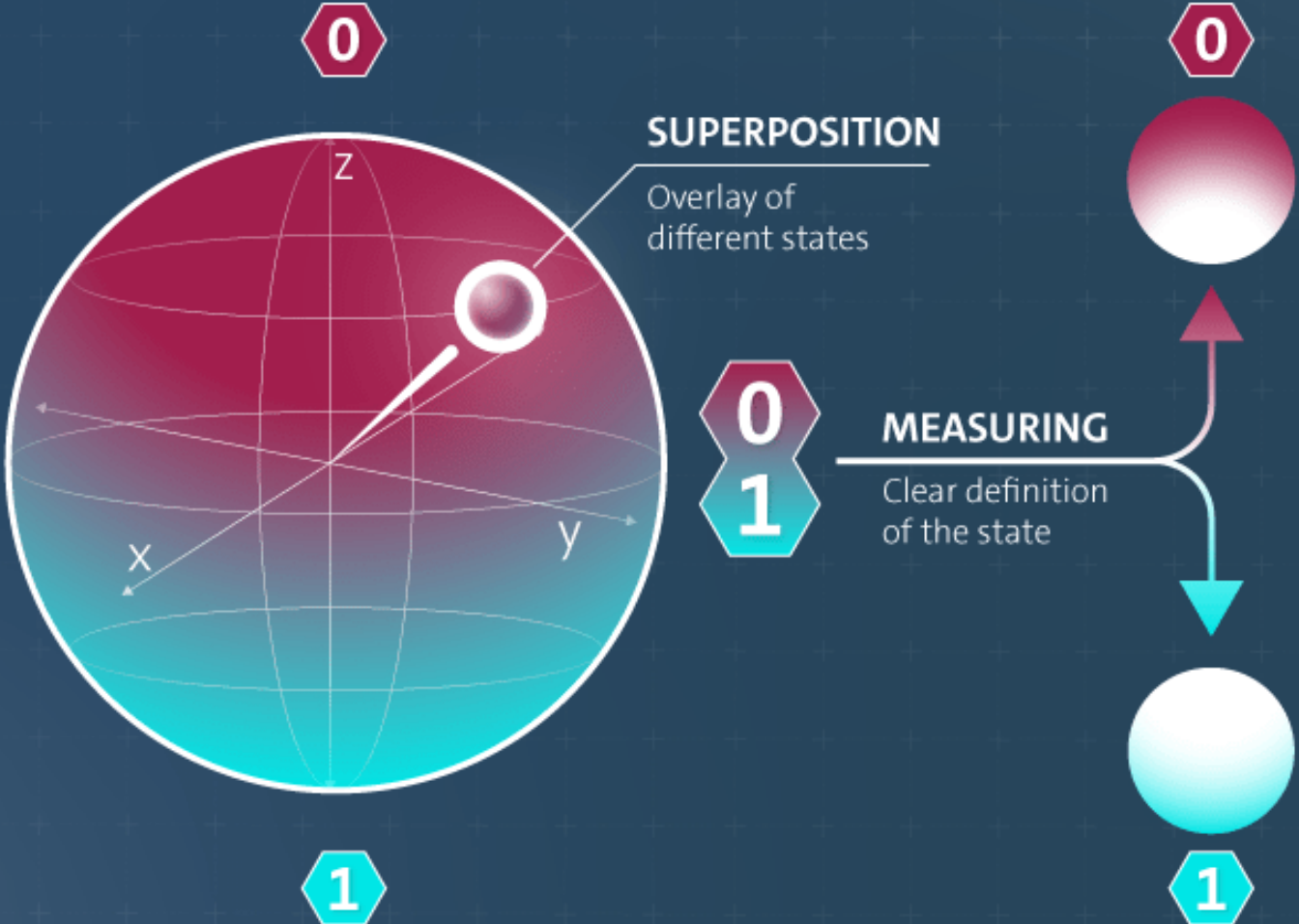


# Long-lived coherences are the heart of quantum computing

**Classical Bit**  
Binary system



**quantum bit "qubit"**  
Arbitrarily manipulable two-state quantum system



- Parallel arithmetic operations possible
- Exponential multiplication per qubit
- Massive amounts of data can be handled in plausible time

## Decoherence

$$\rho(t) \rightarrow \begin{bmatrix} |\chi_0(R,t)|^2 & 0 \\ 0 & |\chi_1(R,t)|^2 \end{bmatrix}$$

Decoherence time

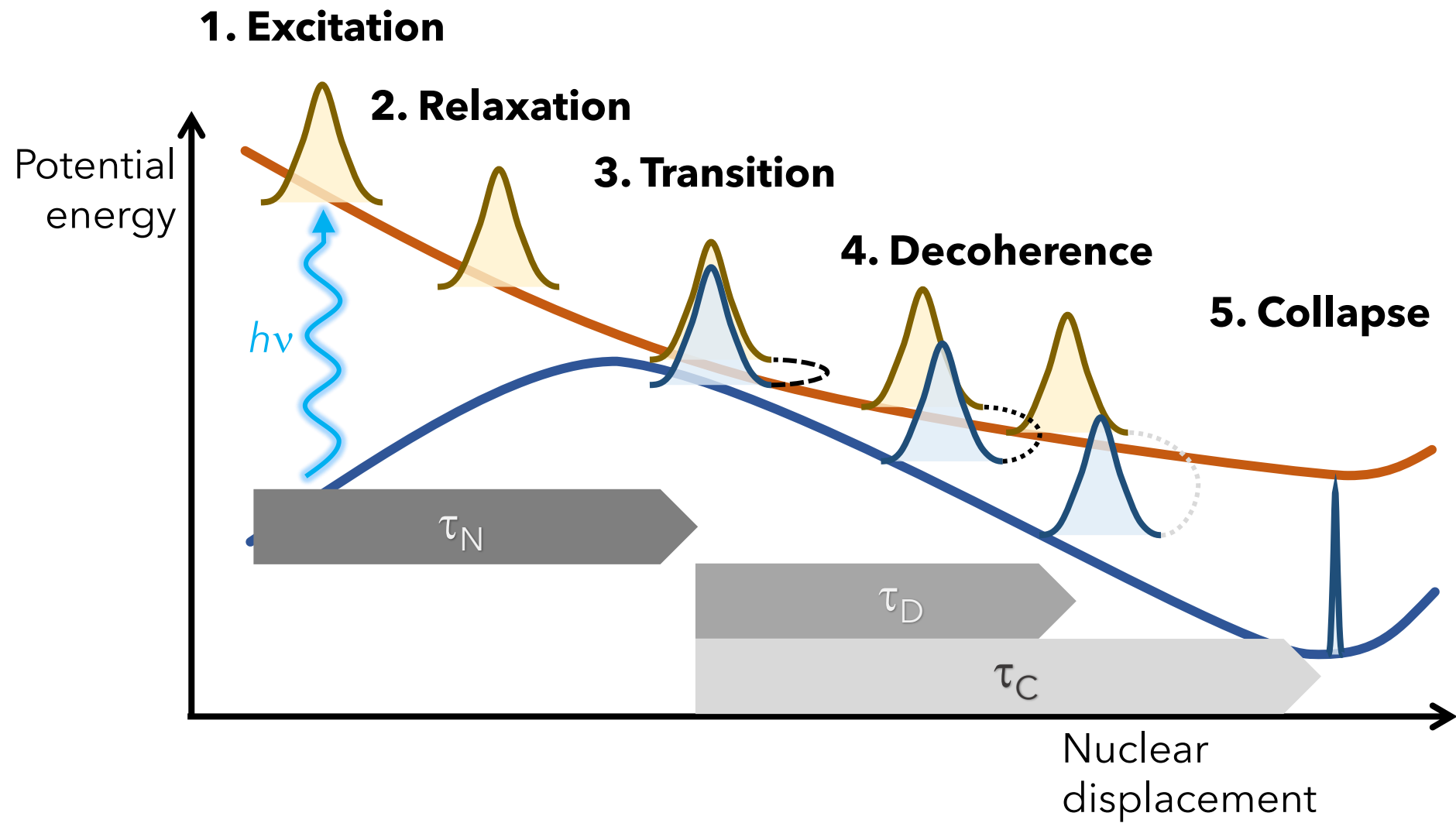
$$\tau_D = \frac{1}{|v_k^C - v_l^C|} \sqrt{\frac{2}{\alpha}}$$

## Collapse

$$\rho(t) \rightarrow \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \text{ or } \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$$

Collapse time

$$\tau_C = ?$$



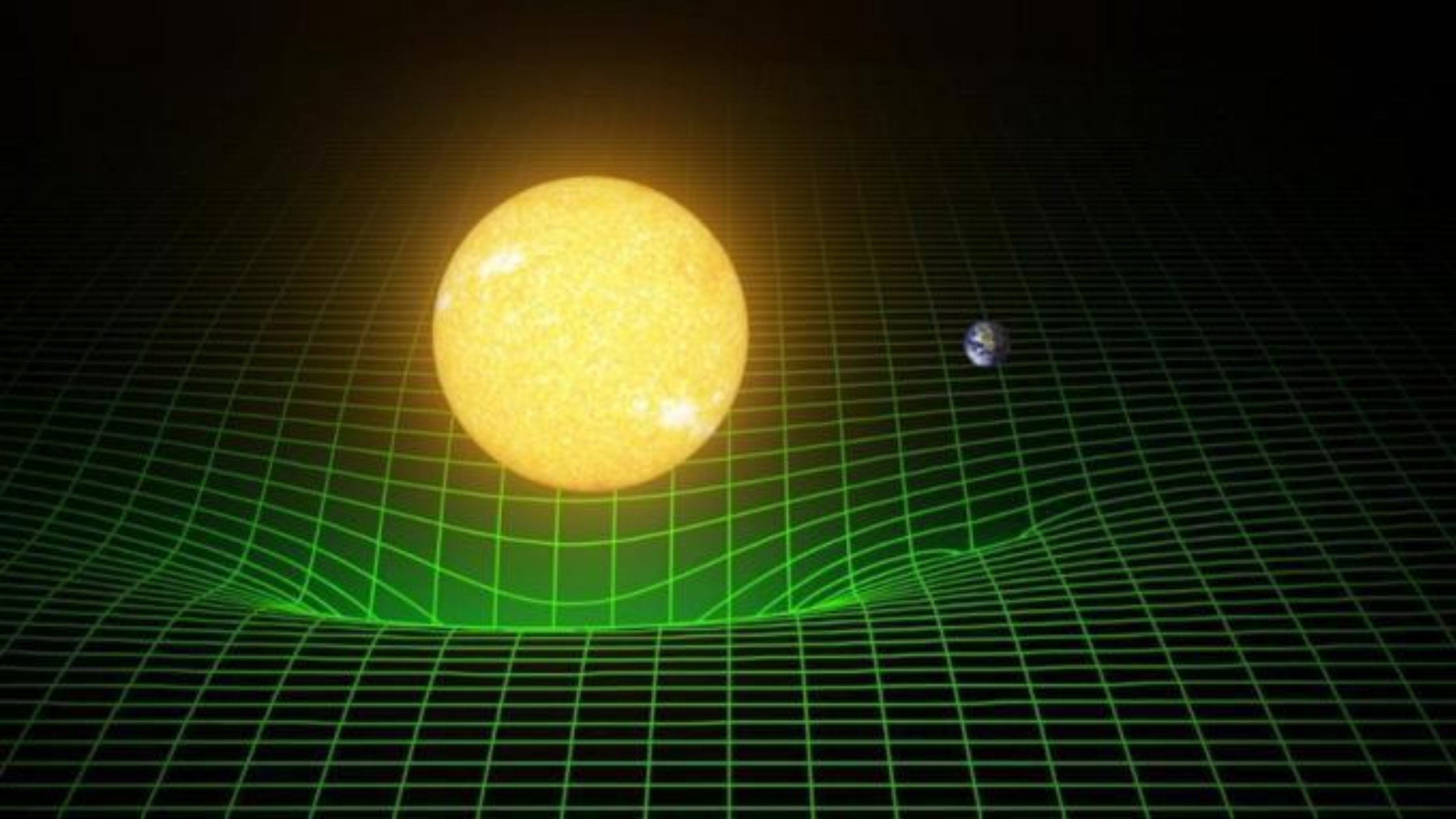
# Collapse theories

- Copenhagen interpretation  
"Shut up and calculate!"
- Many worlds (parallel lives)  
The Wave function never collapses. All states happen in different universes
- Qbism  
The wave function represents our lack of knowledge about the system
- Pilot waves  
The wave function guides a corpuscle, which is finally measured
- Objective collapse  
The wave function collapses induced by environmental perturbations

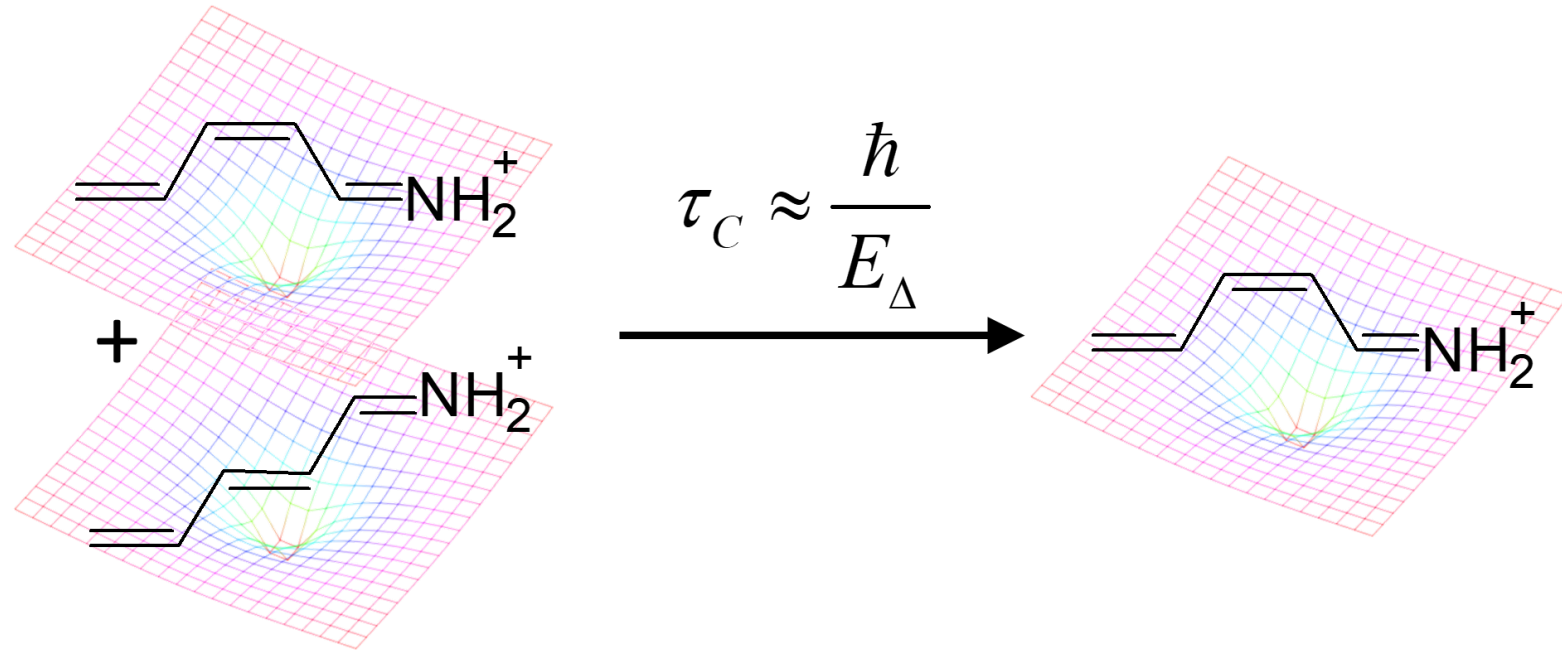
# Interpretations of quantum mechanics

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

[en.wikipedia.org/wiki/Interpretations\\_of\\_quantum\\_mechanics](https://en.wikipedia.org/wiki/Interpretations_of_quantum_mechanics)



# Diósi-Penrose model



$$\tau_C = \frac{\hbar}{4\pi G \left[ \int d\mathbf{r} d\mathbf{r}' \frac{(\mu_A(\mathbf{r}') - \mu_B(\mathbf{r}'))(\mu_A(\mathbf{r}) - \mu_B(\mathbf{r}))}{|\mathbf{r} - \mathbf{r}'|} \right]}$$



**The most complex place  
in the universe**



[youtu.be/Unl1jXFnzgo](https://youtu.be/Unl1jXFnzgo)

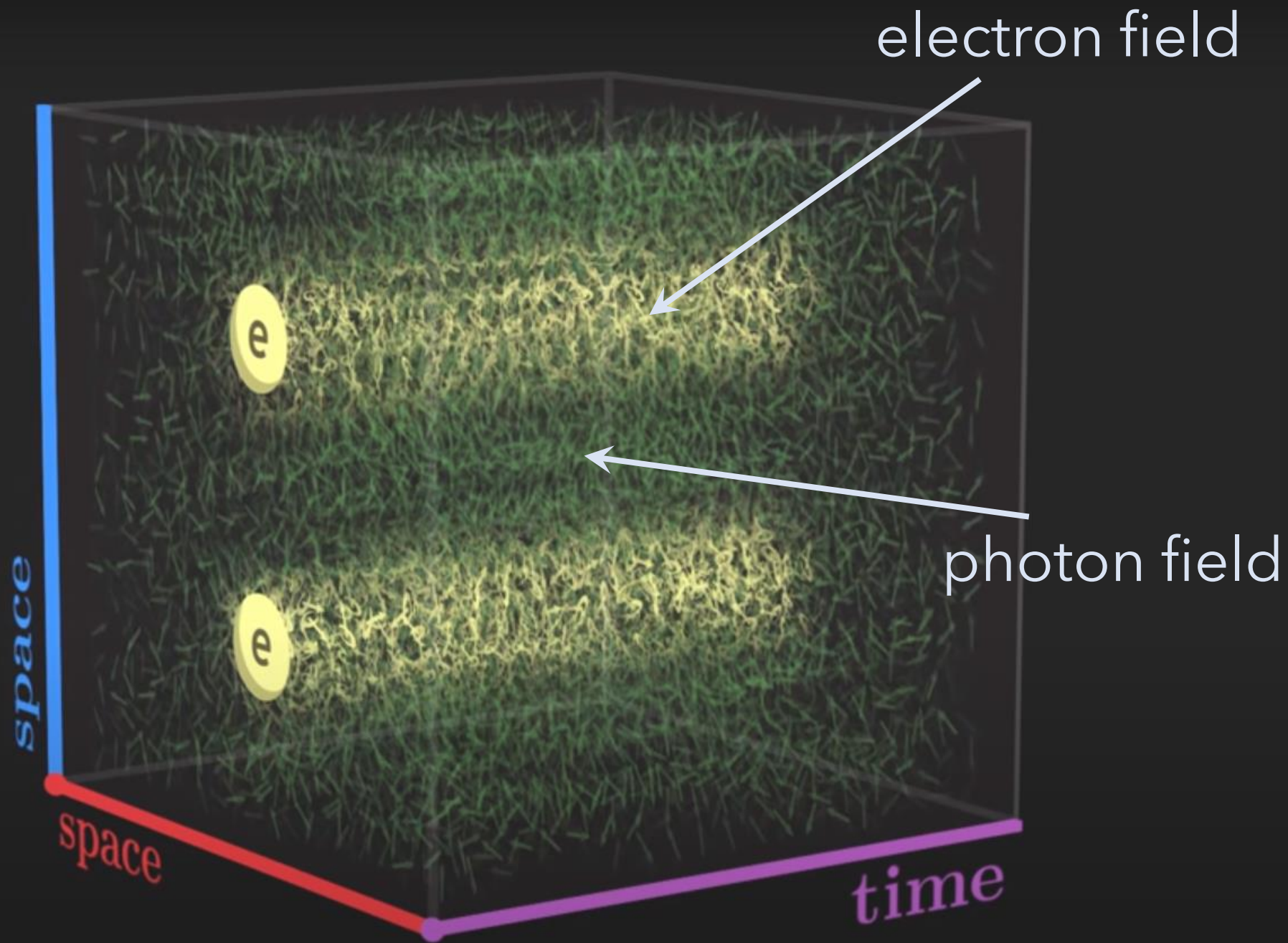


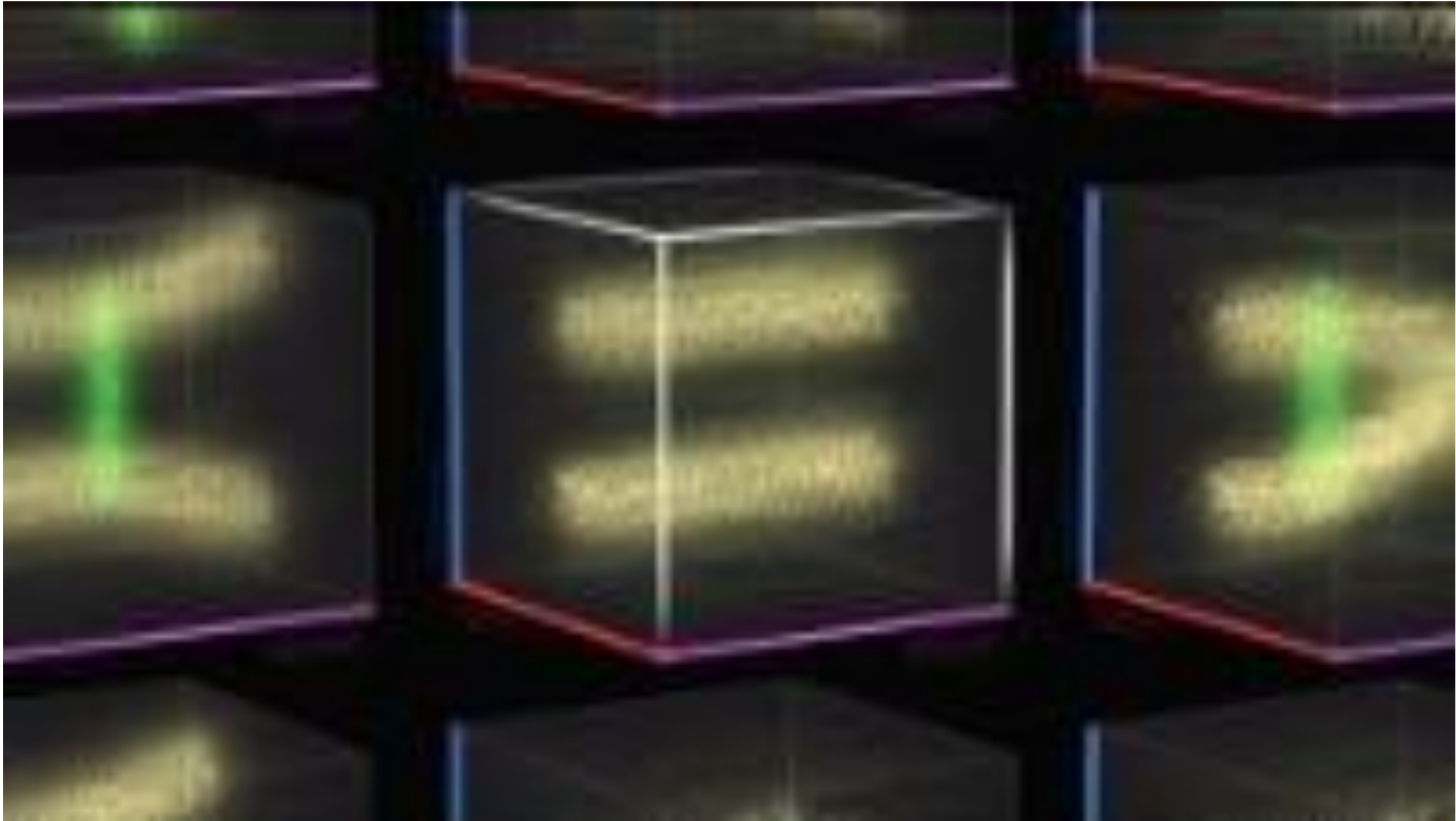
Why don't we ever speak of these particles  
when discussing molecules?

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

(second quantization)







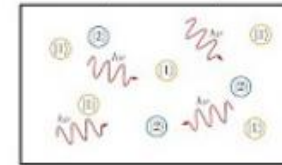
[tinyurl.com/sciclickqft](https://tinyurl.com/sciclickqft)



Course on quantum field theory  
ViaScience, [tinyurl.com/viasciQFT](https://tinyurl.com/viasciQFT)

On the Quantum Theory of Radiation, Einstein, 1917

thermal equilibrium at temperature  $T$



**emission:** atoms in higher energy state can *spontaneously* emit a photon and transition to lower energy state.

**absorption:** atoms in lower energy state can absorb a photon and transition to higher energy state.

$N_1, N_2$  atoms in quantum states (1), (2) with energy  $E_1, E_2$  and  $E_2 - E_1 = h\nu$

## Quantum Field Theory

ViaScience

19 videos 91,441 views Last updated on Sep 25, 2021

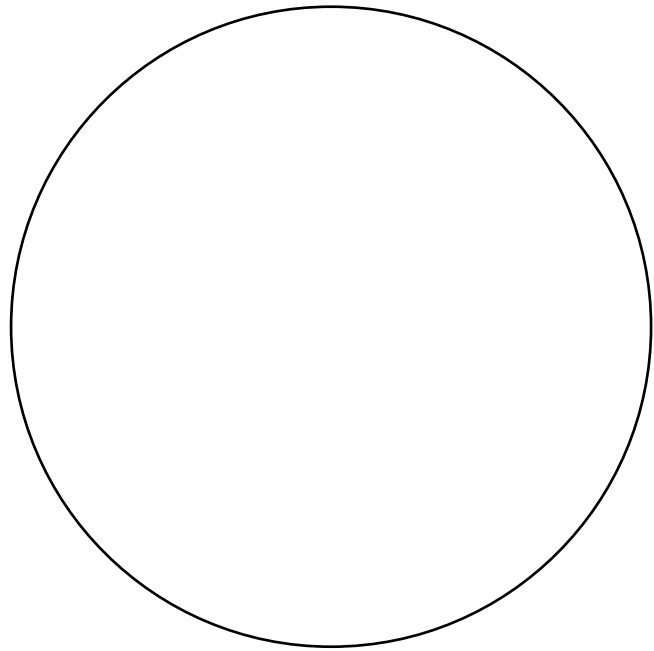


▶ Play all

↻ Shuffle

This series draws from several sources, but especially from E. G. Harris, *A Pedestrian Approach to Quantum Field Theory*, Dover Publications, 2014, ISBN 978-0-486-78022-1; and M. D. Schwartz, *Quantum Field Theory and the Standard Model*, Cambridge, 2014, ISBN 978-1-107-03473-0.

# electron



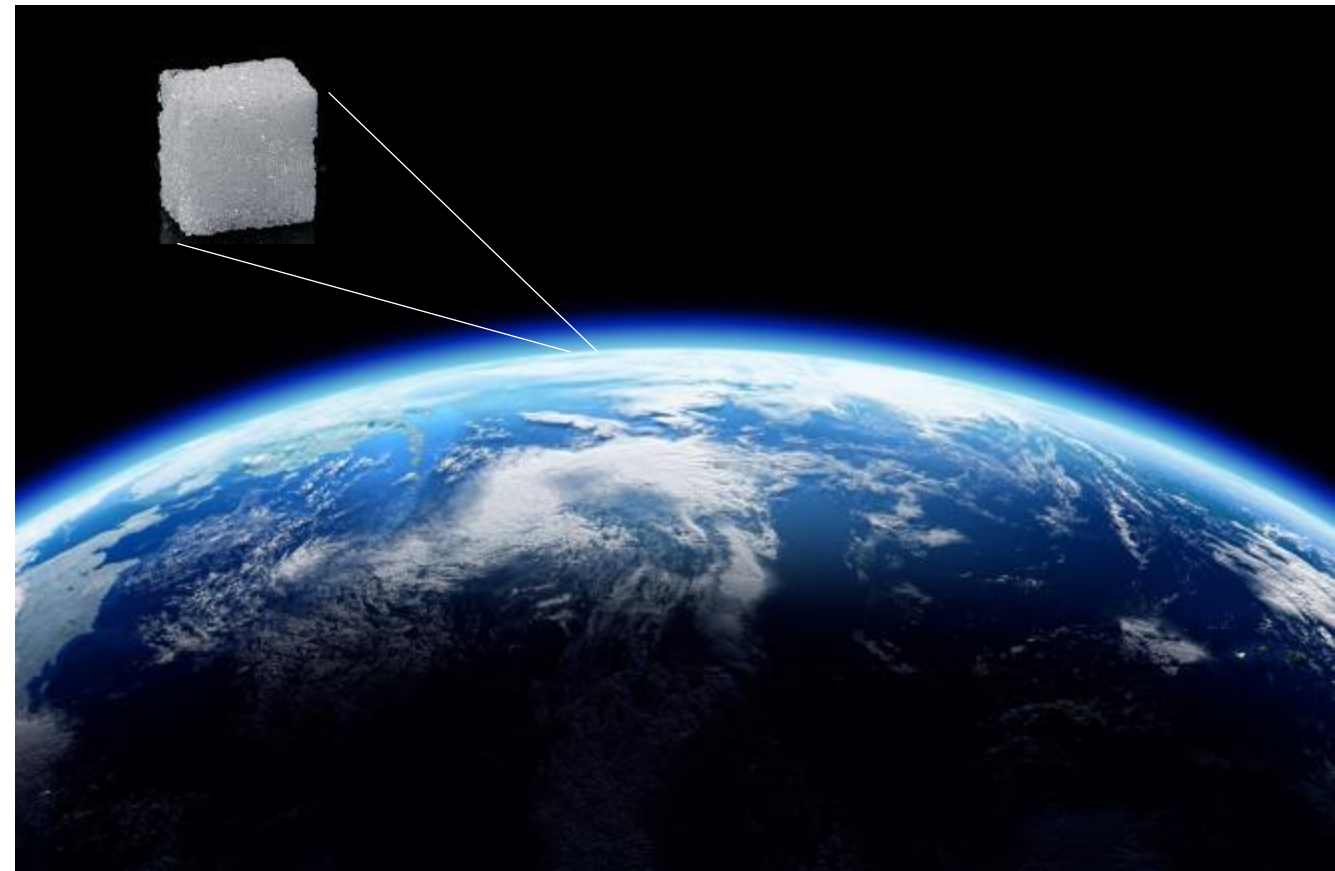
←————→  
< 0.1  $\mu\text{\AA}$

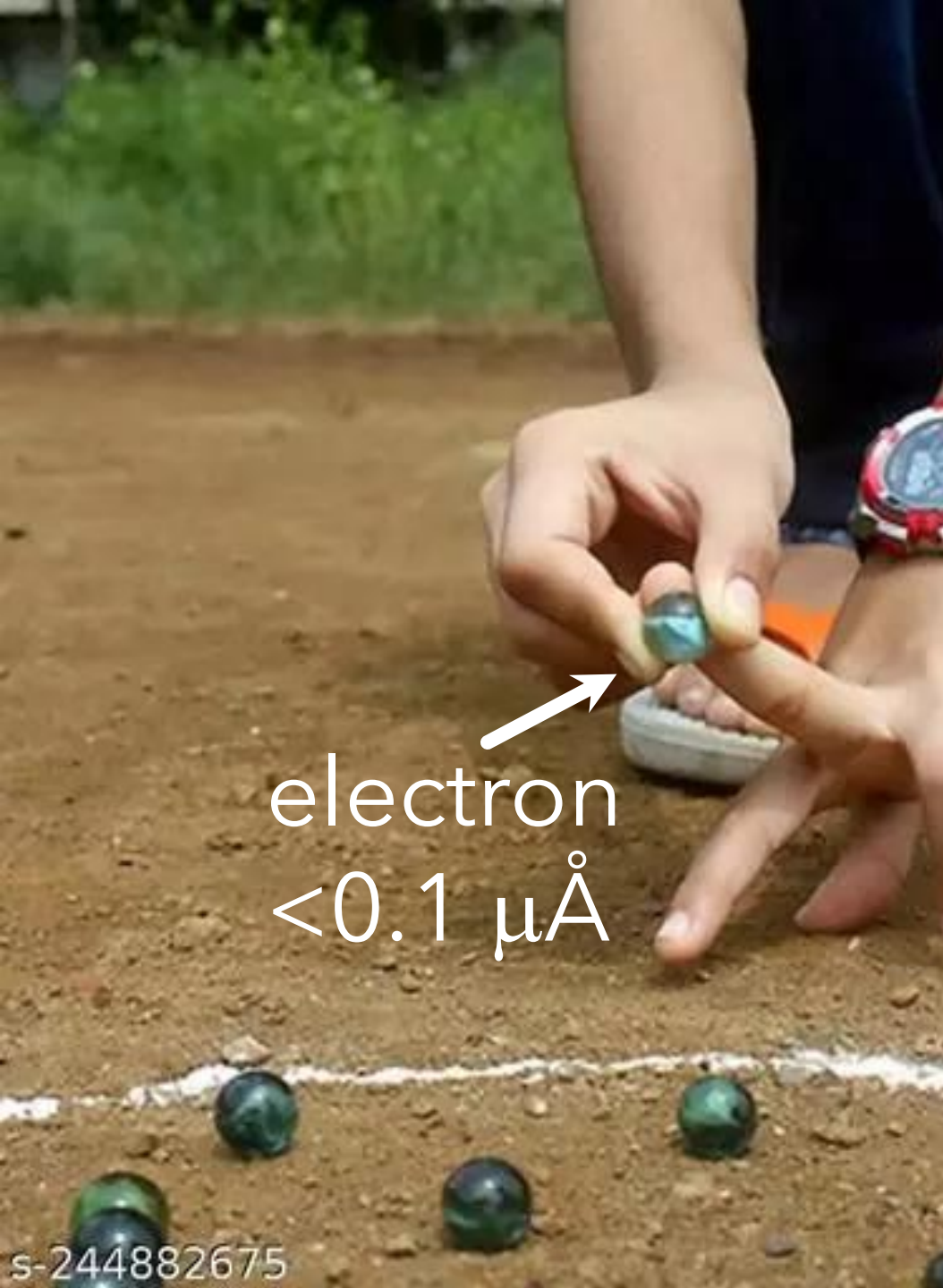
lifetime  $6.6 \times 10^{28}$  years

mass 1

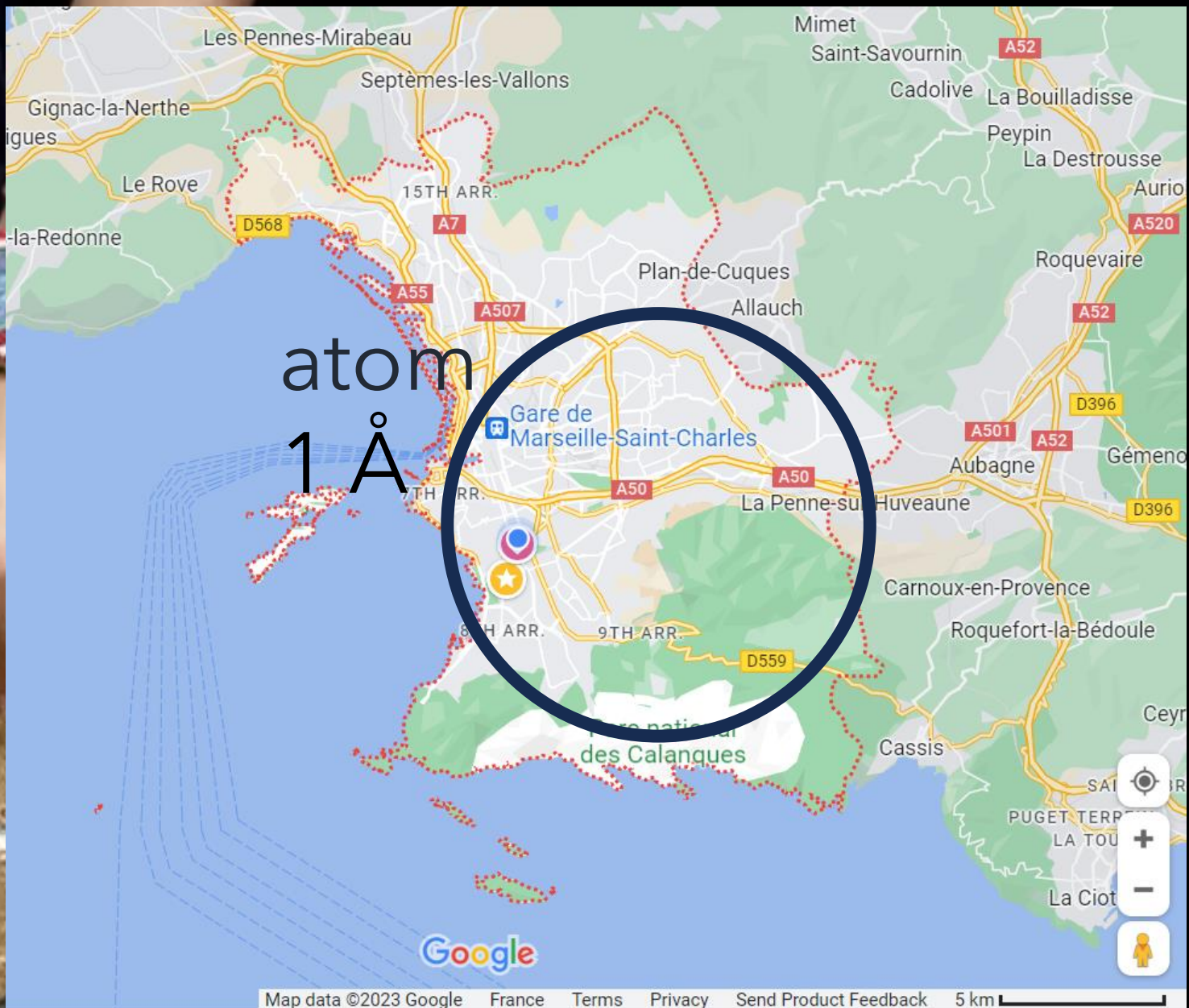
charge -1

spin 1/2



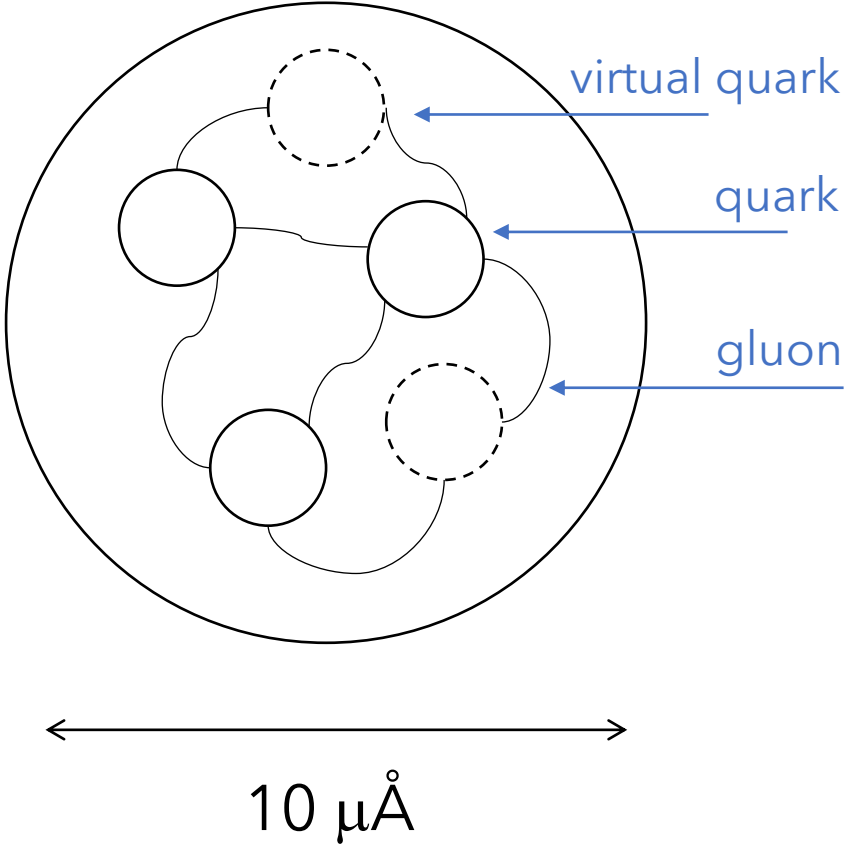


electron  
 $< 0.1 \mu\text{\AA}$



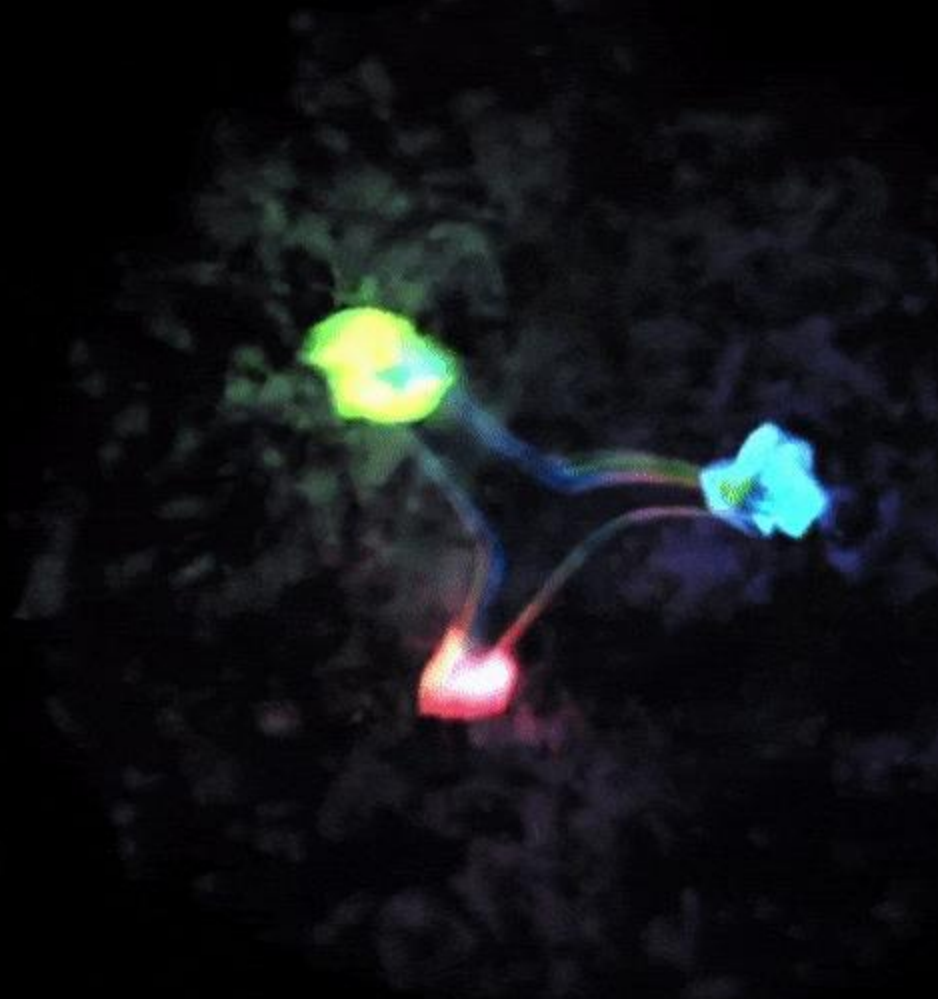
s-244882675

# proton/neutron

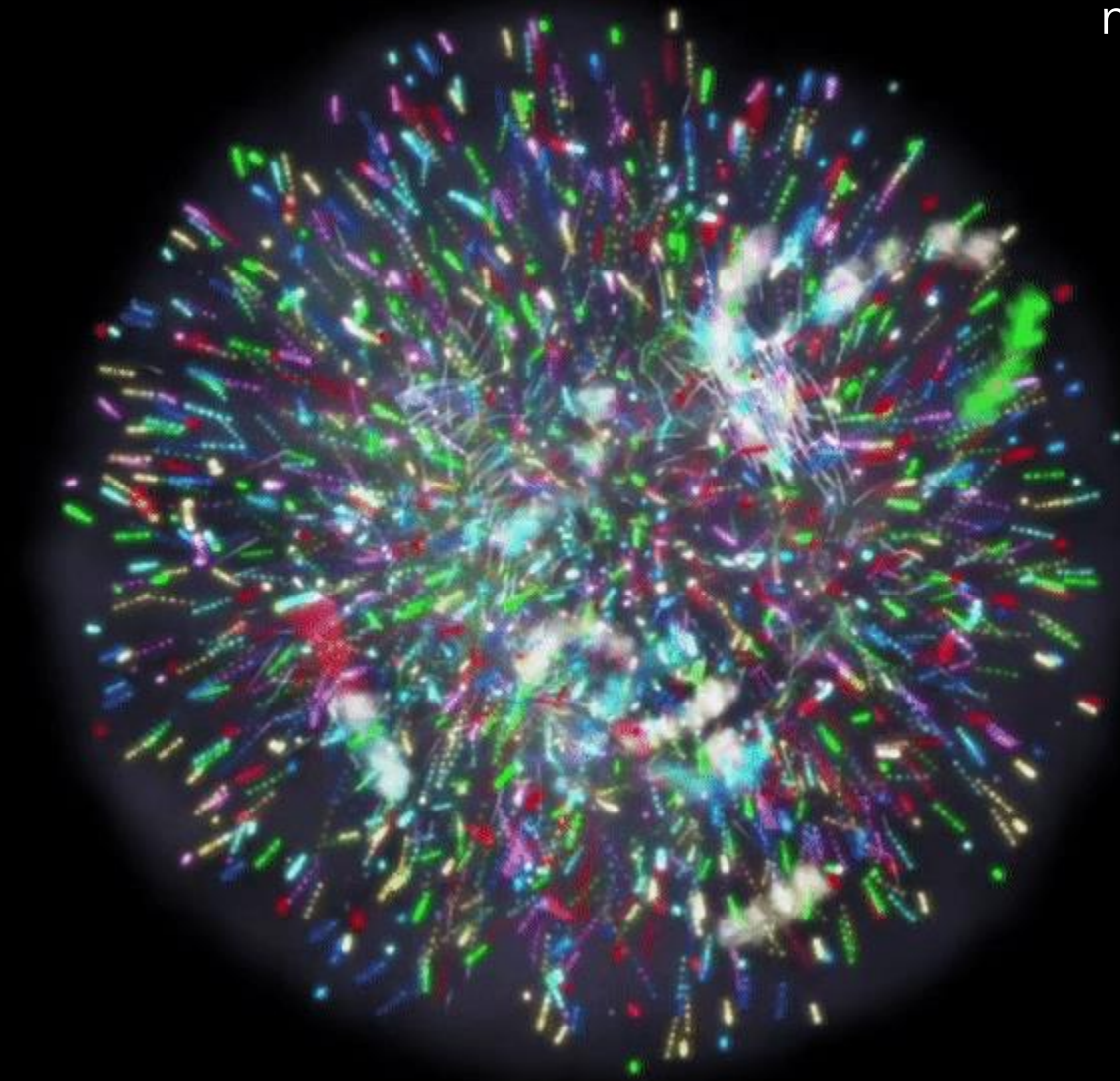


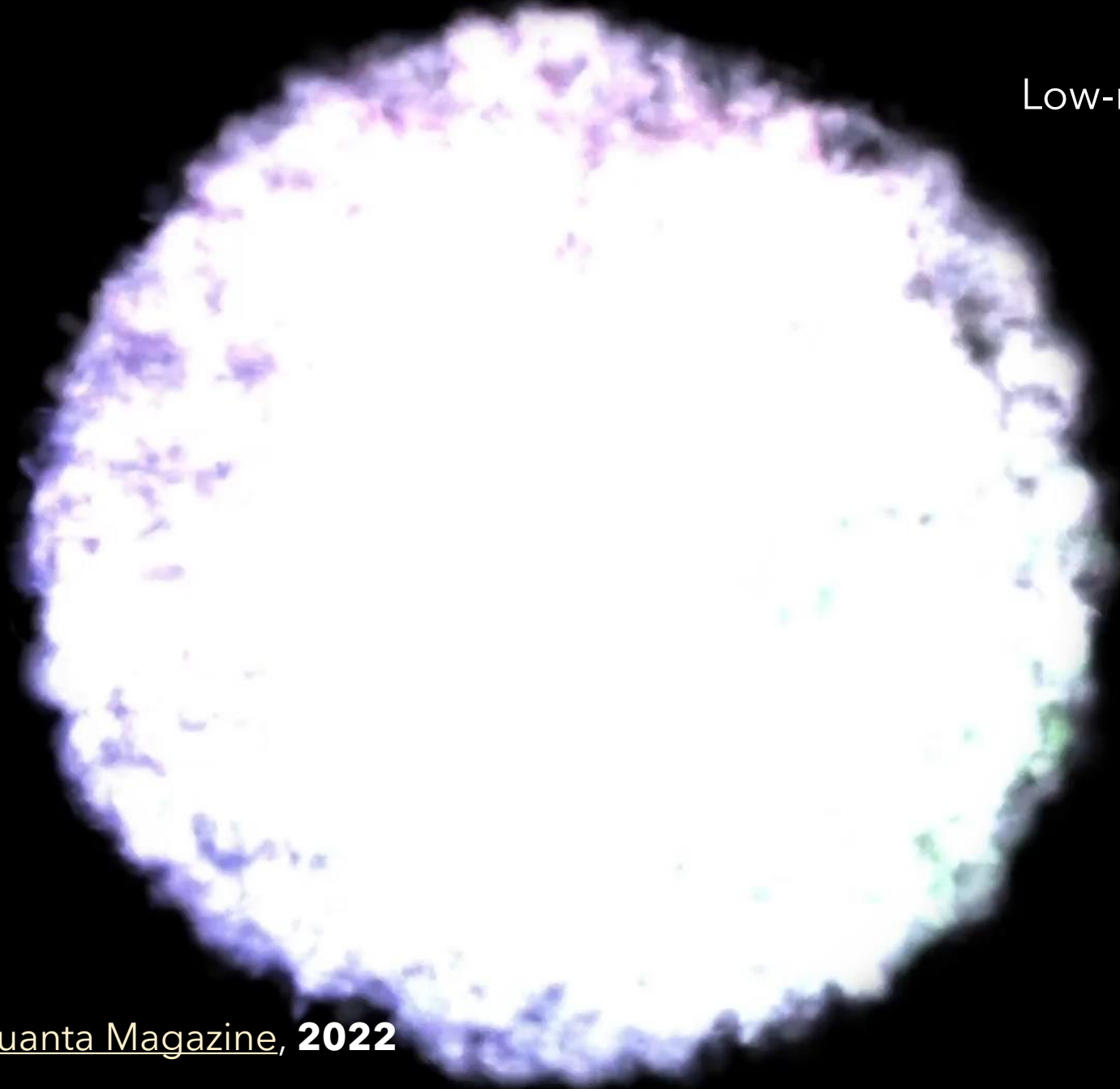
lifetime  $10^{34}$  years  
mass 1836  
charge 1 (proton) / 0 (neutron)  
spin 1/2

High-momentum quarks

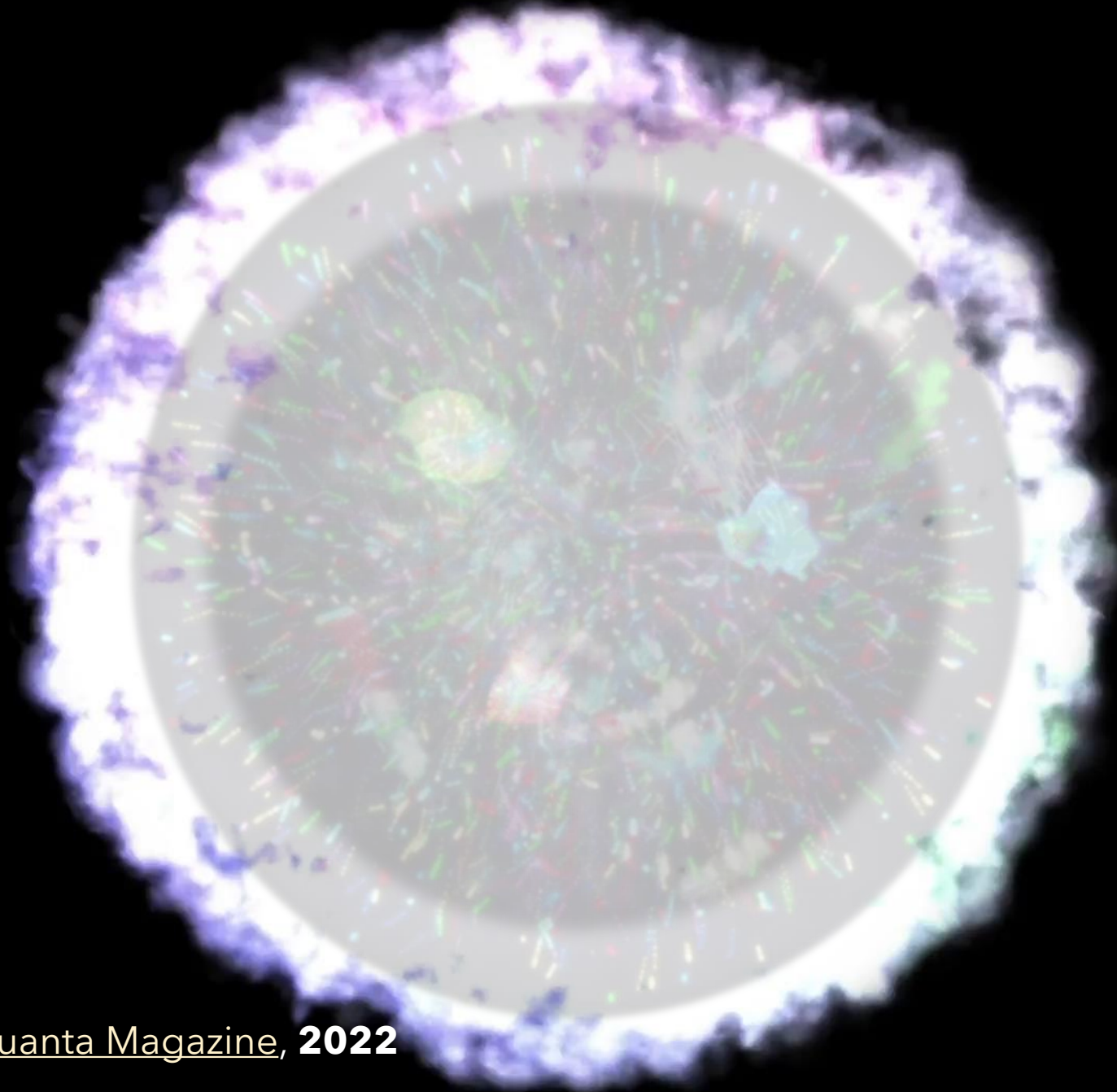


medium-momentum quarks





Low-momentum quarks

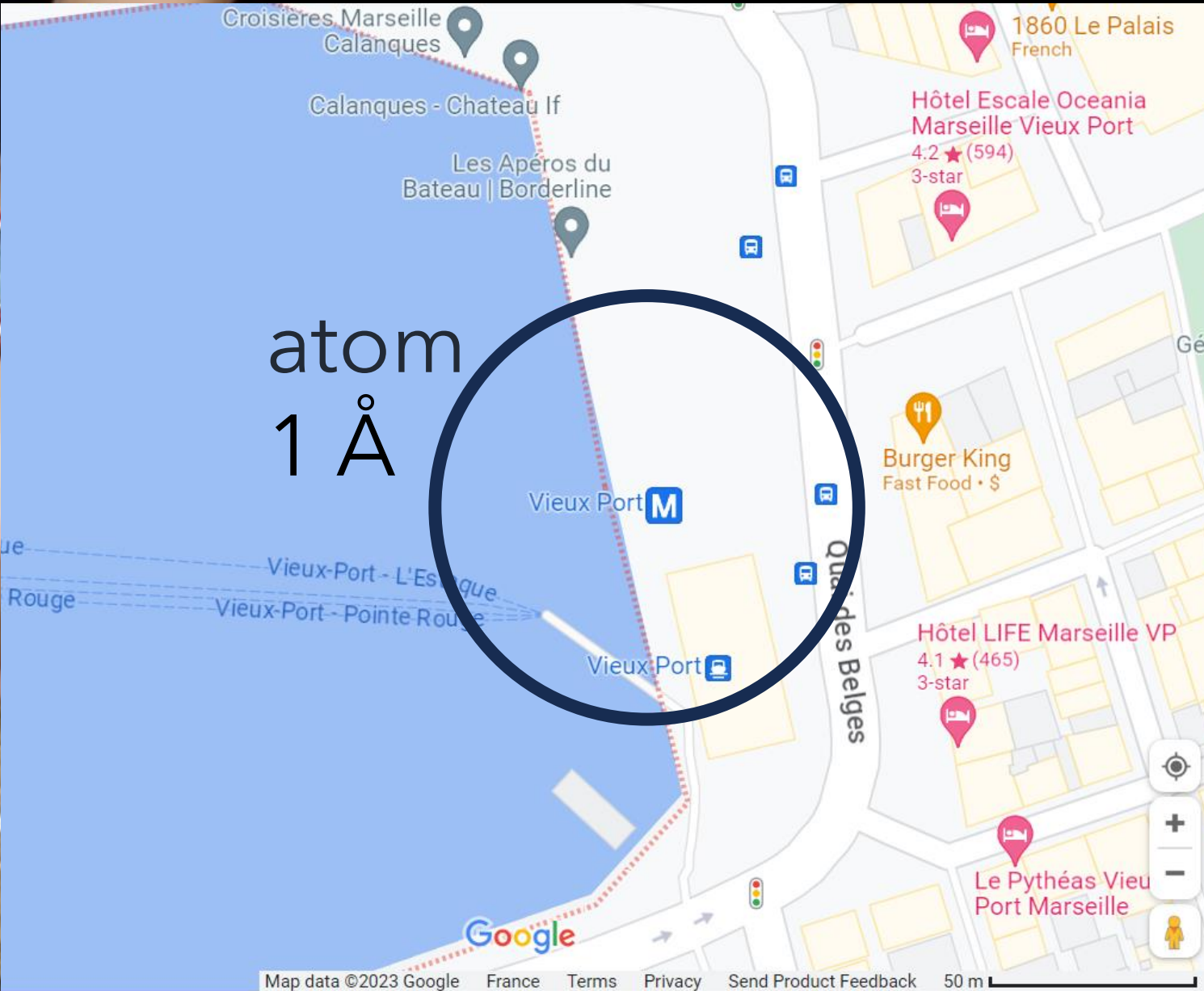


Wood and Shreman, [Quanta Magazine](#), **2022**

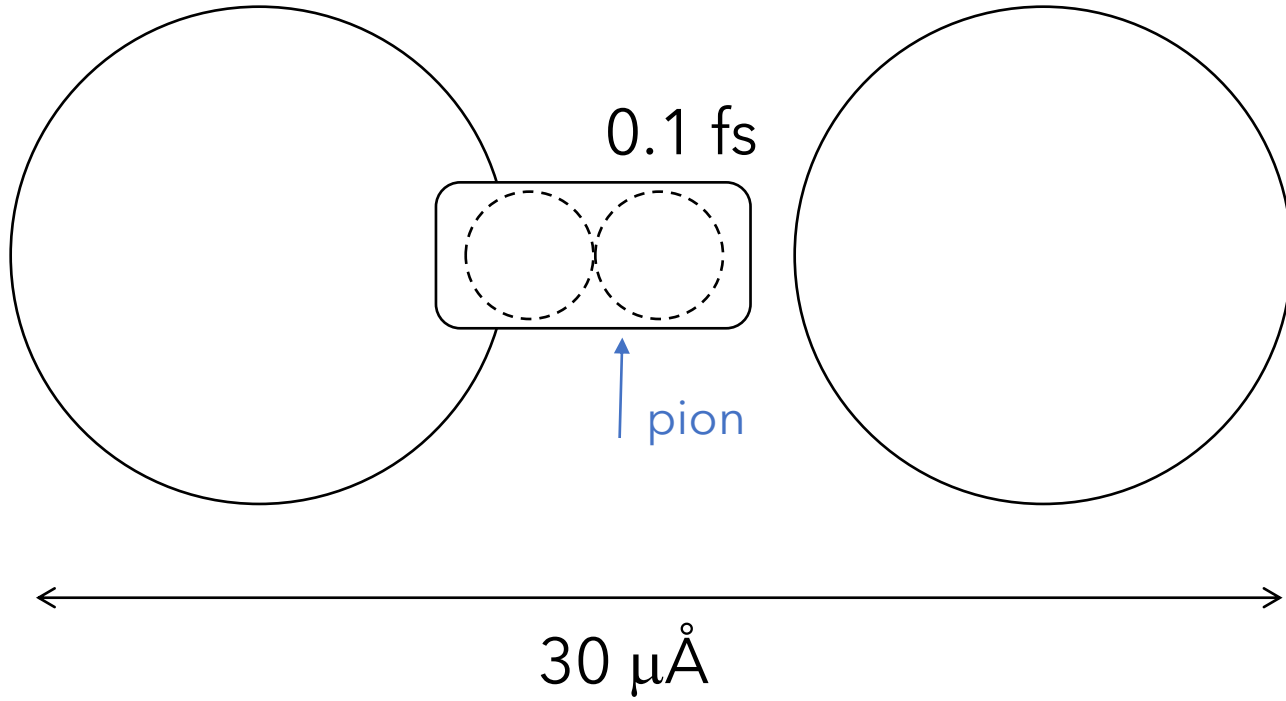




proton  
 $10 \mu\text{\AA}$



nucleus



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  $\rightarrow$  quantum waves

(first quantization)

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

$$H(\mathbf{R}, \mathbf{r}) \Psi^k(\mathbf{R}, \mathbf{r}) = i\hbar \frac{\partial \Psi^k(\mathbf{R}, \mathbf{r})}{\partial t}$$

# Quantum theory

## **Quantum field theory**

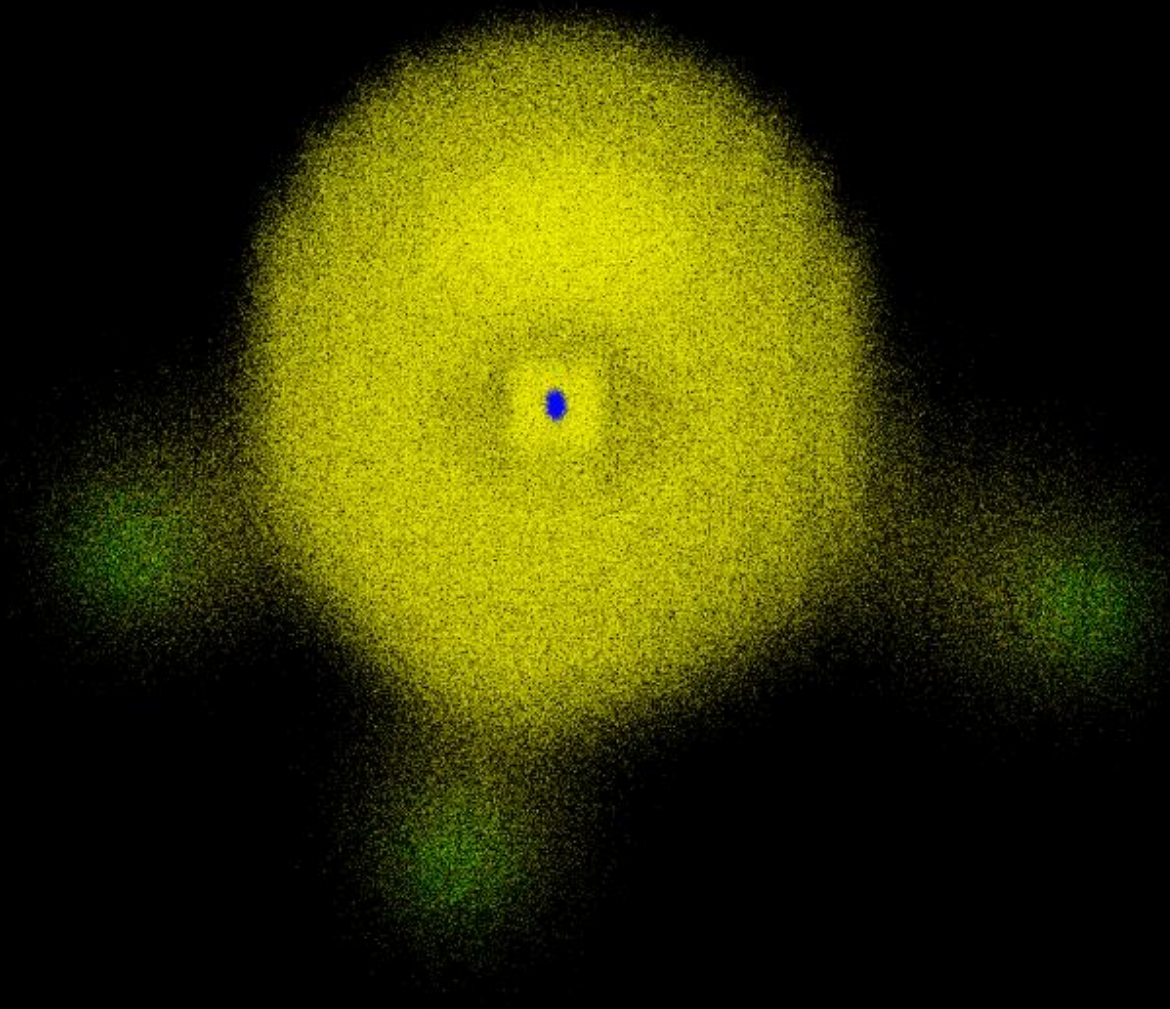
quantum waves  $\rightarrow$  quantum particles  
(second quantization)

## **Quantum mechanics**

point particles  $\rightarrow$  quantum waves  
(first quantization)

**Delocalization** predicted by quantum mechanics is central to describing molecules.

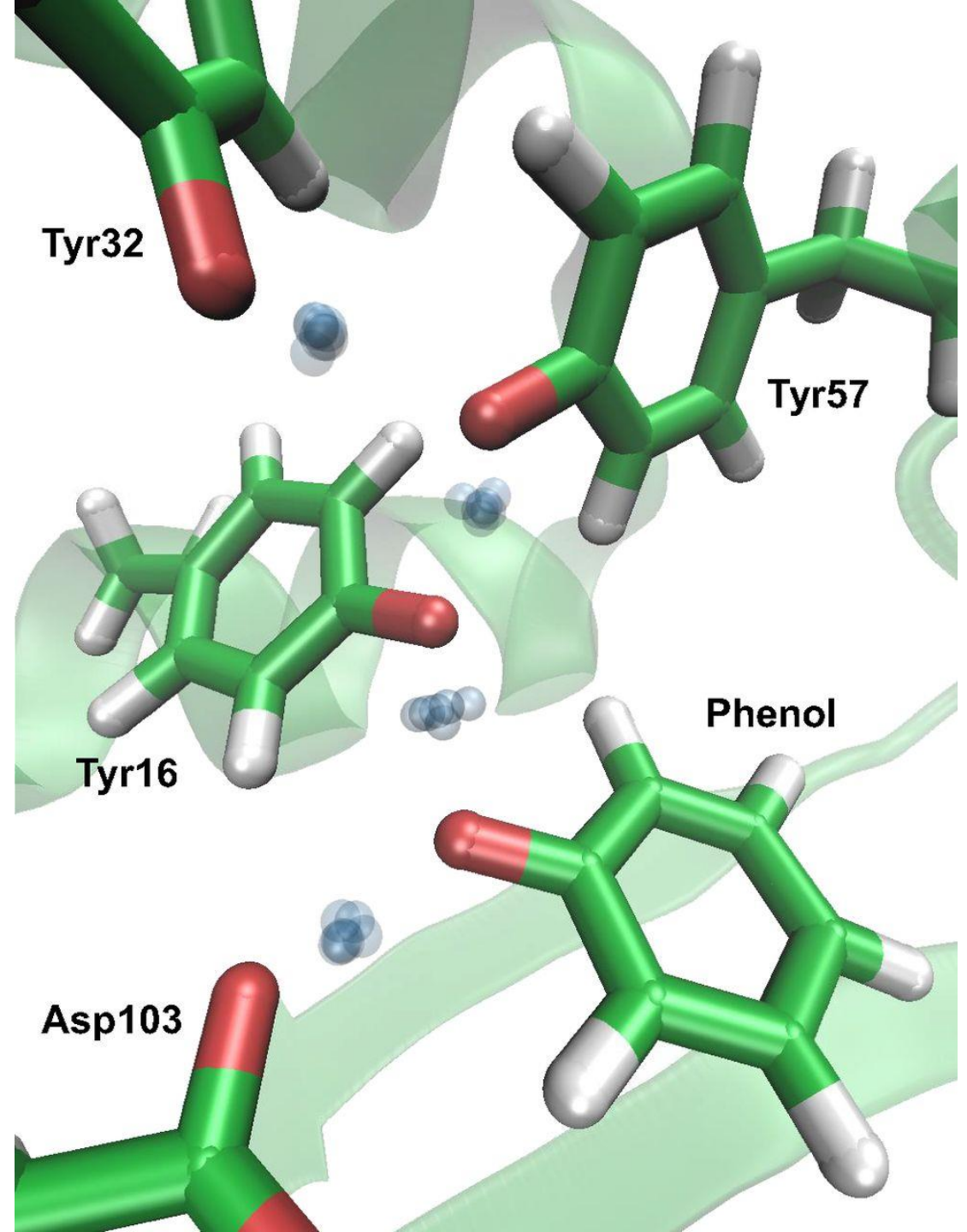
It affects both **electrons** and **nuclei**.



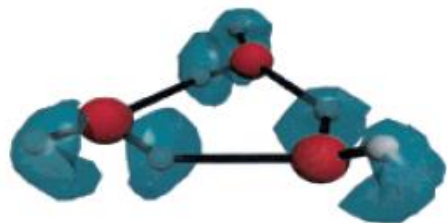


“[extensive quantum proton delocalization] leads to a 10,000-fold increase in the acidity of an active-site residue compared with the limit where the nuclei are classical particles”

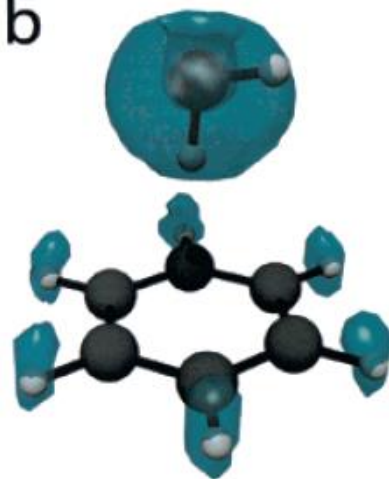
Wang *et al.* *PNAS* **2014**, 111, 18454



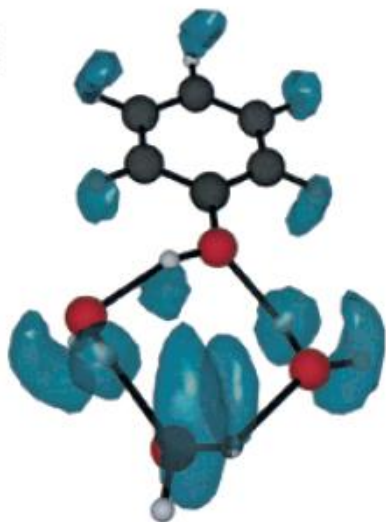
a



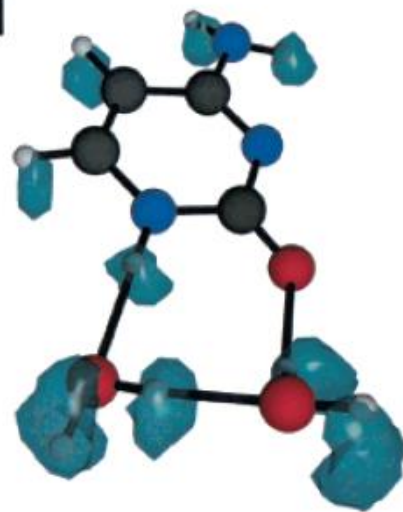
b



c



d



# Nuclear-Electronic Orbital methods

BO molecular wave function

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

NEO molecular wave function

$$\Psi^{NEO}(\mathbf{R}, \mathbf{r}) = \varphi(\mathbf{r}^e, \mathbf{R}^p; \mathbf{R}') \chi(\mathbf{R}')$$

# Framing molecules in the Core Theory

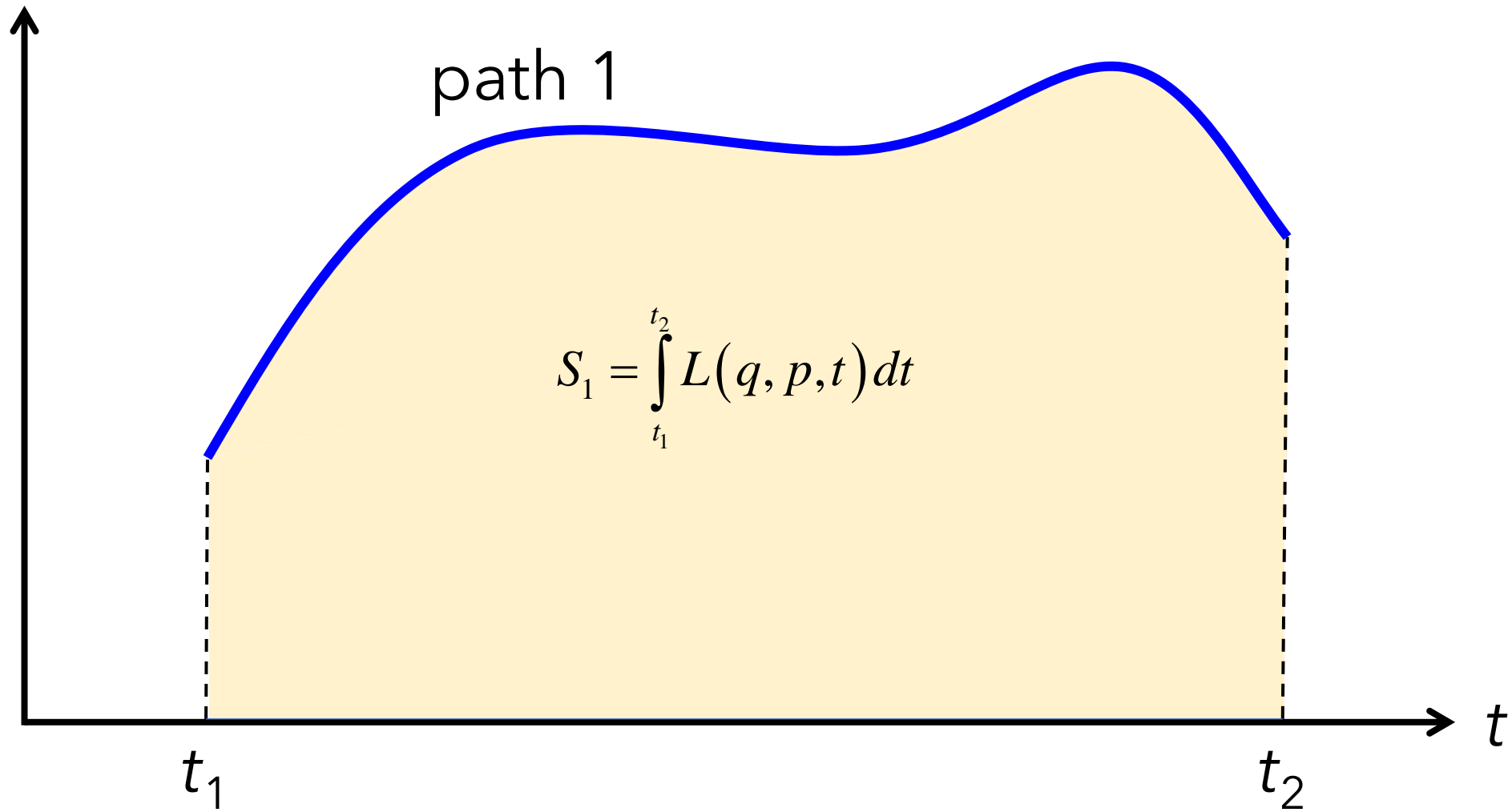
# The **Core Theory** (Frank Wilczek)

The Core Theory encompasses

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

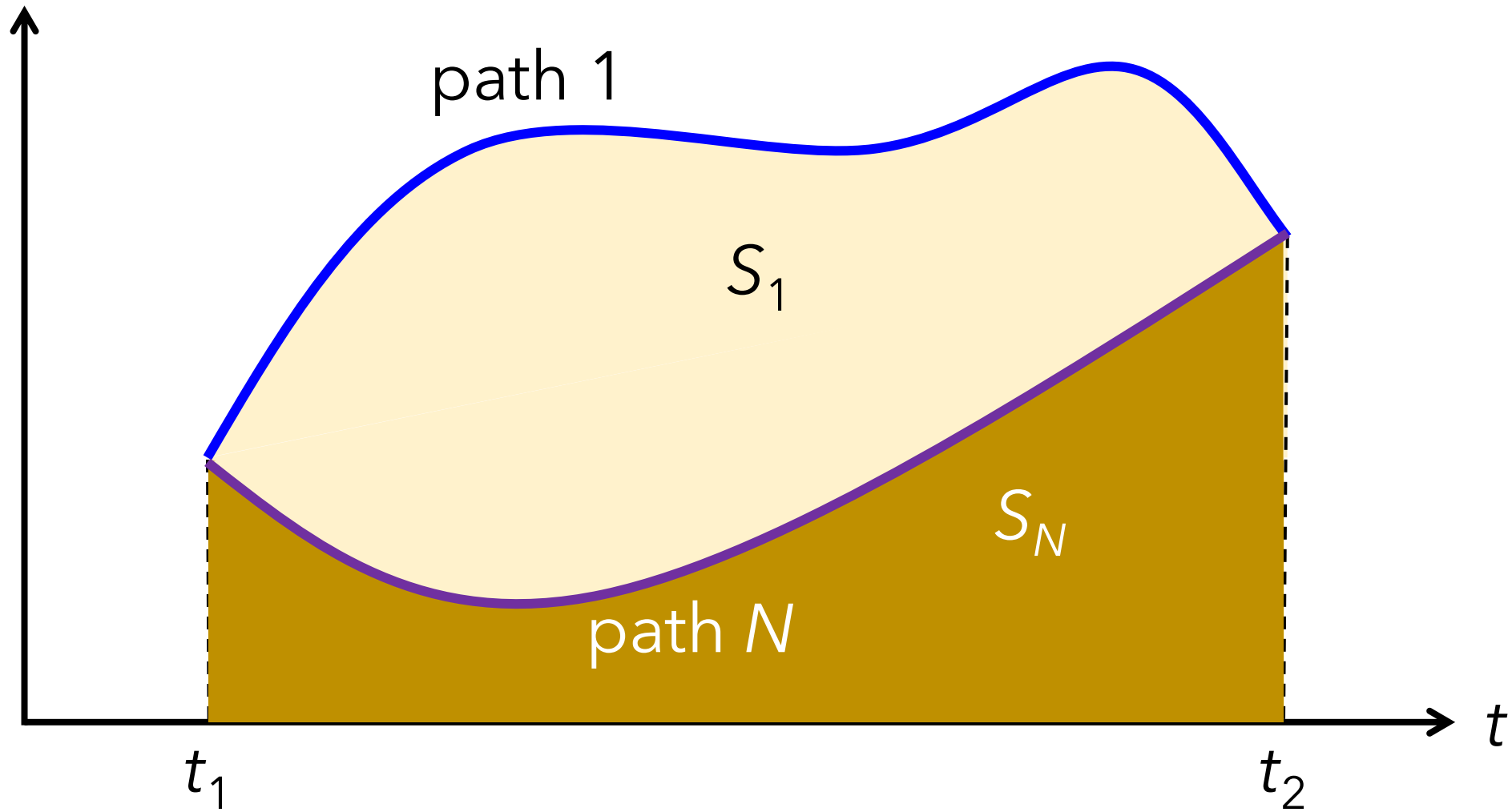
We can express the Core Theory in the language of path integrals

$$L = T - V$$

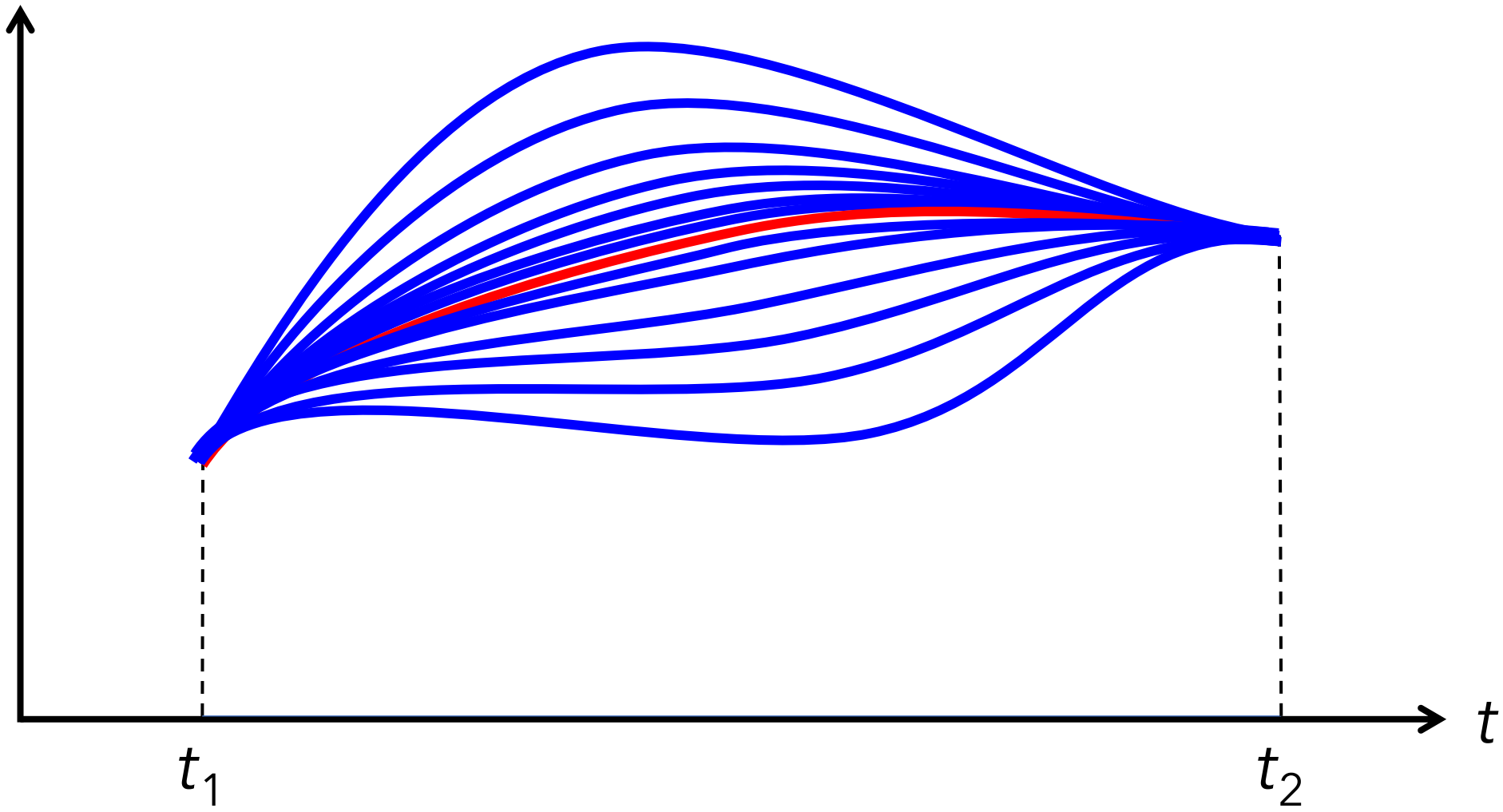


S is the Action

$$L = T - V$$



$$L = T - V$$





# Path integral formulation of quantum mechanics

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

Which interactions go into  $S$   
to fully describe a molecule?

# 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)

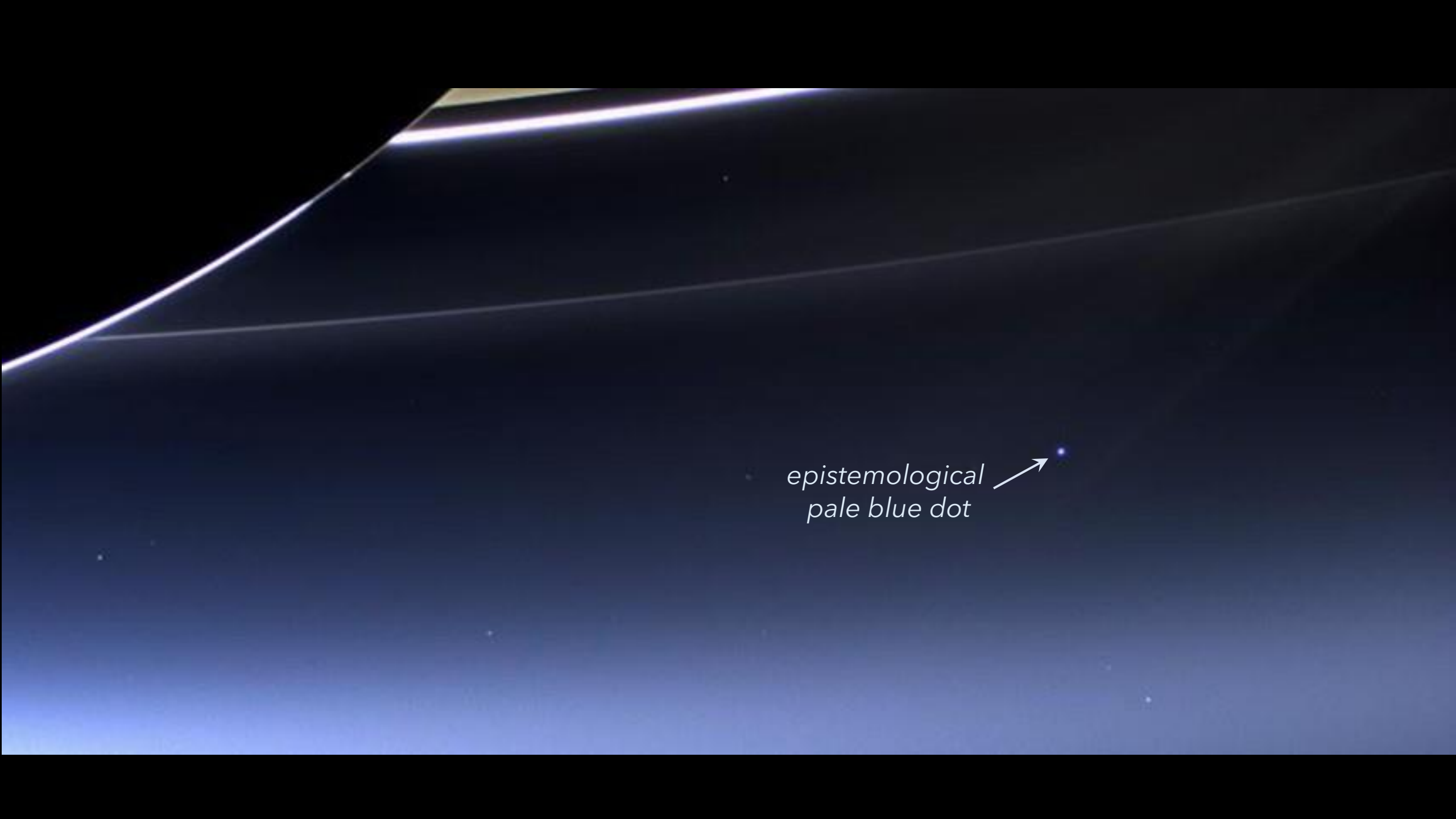
$$W = \int_{k < \Lambda} [Dg][DA][D\psi][D\Phi] \exp \left\{ i \int d^4x \sqrt{-g} \times \right.$$

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

quantum chemistry  
& molecular physics

"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."

S. M. Carroll. The Big Picture



*epistemological  
pale blue dot*



## To know more:

### Decoherence

- Sabine Hossenfeld, [youtu.be/igsulul\\_HAQ](https://youtu.be/igsulul_HAQ)
- Phillip Ball, [Aeon Magazine](#), **2017**

### Many worlds interpretation

- Brassard; Raymond-Robichaud. *Entropy* **2019**, 21
- PBS Space Time, [youtu.be/z-syaCoqkZA](https://youtu.be/z-syaCoqkZA)

### Pilot wave

- PBS Space Time, [youtu.be/RIXdsyctD50](https://youtu.be/RIXdsyctD50)

### Objective collapse

- Bassi *et al.* *Rev Mod Phys* **2013**, 85, 471
- PBS Space Time, [youtu.be/FP6iyVJ70OU](https://youtu.be/FP6iyVJ70OU)

### QBism

- Mermin. *Nature* **2014**, 507, 421
- Corin S. Powell, [Aeon Magazine](#), **2017**

Papers available for download at:

[amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX](https://amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX) (Ask me for the password)

### Classical nuclear motion

- Messiah. *Quantum Mechanics*, **1961** (v 1, p. 222)
- Tully. *Faraday Discuss* **1998**, 110, 407

### Inside the proton

- Wood and Shreman, [Quanta Magazine](#), **2022**
- Quanta Magazine, [youtu.be/Unl1jXFnzgo](https://youtu.be/Unl1jXFnzgo)

### Nuclear delocalization

- Clary *et al.* *Acc Chem Res* **2000**, 33, 441
- Hammes-Schiffer. *Philos Trans R Soc A* **2022**, 380, 20200377
- Barbatti, [Aeon magazine](#), **2023**

### Quantum field theory

- Science click, [tinyurl.com/sciclickqft](https://tinyurl.com/sciclickqft)
- ViaScience, [tinyurl.com/viasciQFT](https://tinyurl.com/viasciQFT) (full course)

### Poetic naturalism and core theory

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

# **Demonstration of the classical limit of the Nuclear Schrödinger Equation**



$$-\frac{\hbar^2}{2\mathbf{M}} \nabla^2 \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] + E_n(\mathbf{R}) \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] \\ -i\hbar \partial_t \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] = 0$$

Now, we make a lot of algebraic manipulation

$$-\frac{\hbar^2}{2\mathbf{M}} \nabla^2 \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] + E_n(\mathbf{R}) \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] - i\hbar \partial_t \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] = 0$$

$$\begin{aligned} \nabla^2 \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] &= \nabla \cdot \nabla \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] \\ &= \nabla \cdot \left[ \nabla A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) + A(\mathbf{R}, t) \nabla \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] \\ &= \nabla \cdot \left[ \nabla A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) + \frac{i}{\hbar} A(\mathbf{R}, t) \nabla S(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] \end{aligned}$$

$$\begin{aligned}
\nabla^2 \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] &= \nabla \cdot \left[ \nabla A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] + \nabla \cdot \left[ \frac{i}{\hbar} A(\mathbf{R}, t) \nabla S(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] \\
&= \left[ \nabla^2 A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) + \nabla A(\mathbf{R}, t) \cdot \nabla \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] \\
&+ \left[ \frac{i}{\hbar} \nabla A(\mathbf{R}, t) \cdot \nabla S(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) + \frac{i}{\hbar} A(\mathbf{R}, t) \nabla^2 S(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) + \frac{i}{\hbar} A(\mathbf{R}, t) \nabla S(\mathbf{R}, t) \cdot \nabla \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] \\
&= \nabla^2 A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) + \frac{2i}{\hbar} \nabla A(\mathbf{R}, t) \cdot \nabla S(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \\
&+ \frac{i}{\hbar} A(\mathbf{R}, t) \nabla^2 S(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) - \frac{1}{\hbar^2} A(\mathbf{R}, t) (\nabla S(\mathbf{R}, t))^2 \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right)
\end{aligned}$$

$$-\frac{\hbar^2}{2\mathbf{M}} \nabla^2 \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] + E_n(\mathbf{R}) \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] - i\hbar \partial_t \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] = 0$$

$$\begin{aligned} \partial_t \left[ A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \right] &= \partial_t A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) + A(\mathbf{R}, t) \partial_t \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \\ &= \partial_t A(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) + \frac{i}{\hbar} A(\mathbf{R}, t) \partial_t S(\mathbf{R}, t) \exp\left(\frac{i}{\hbar} S(\mathbf{R}, t)\right) \end{aligned}$$

$$-\frac{\hbar^2}{2\mathbf{M}} \left[ \nabla^2 A(\mathbf{R}, t) + \frac{2i}{\hbar} \nabla A(\mathbf{R}, t) \cdot \nabla S(\mathbf{R}, t) + \frac{i}{\hbar} A(\mathbf{R}, t) \nabla^2 S(\mathbf{R}, t) - \frac{1}{\hbar^2} A(\mathbf{R}, t) (\nabla S(\mathbf{R}, t))^2 \right] \\ + E_n(\mathbf{R}) A(\mathbf{R}, t) - i\hbar \partial_t A(\mathbf{R}, t) + A(\mathbf{R}, t) \partial_t S(\mathbf{R}, t) = 0$$

Separate real and imaginary terms

$$-\frac{\hbar^2}{2\mathbf{M}} \left[ \nabla^2 A(\mathbf{R}, t) + \frac{2i}{\hbar} \nabla A(\mathbf{R}, t) \cdot \nabla S(\mathbf{R}, t) + \frac{i}{\hbar} A(\mathbf{R}, t) \nabla^2 S(\mathbf{R}, t) - \frac{1}{\hbar^2} A(\mathbf{R}, t) (\nabla S(\mathbf{R}, t))^2 \right] \\ + E_n(\mathbf{R}) A(\mathbf{R}, t) - i\hbar \partial_t A(\mathbf{R}, t) + A(\mathbf{R}, t) \partial_t S(\mathbf{R}, t) = 0$$

$$\partial_t S(\mathbf{R}, t) + \frac{1}{2\mathbf{M}} (\nabla S(\mathbf{R}, t))^2 + E_n(\mathbf{R}) - \frac{\hbar^2}{2\mathbf{M}} \frac{\nabla^2 A(\mathbf{R}, t)}{A(\mathbf{R}, t)} = 0$$

$$\partial_t A(\mathbf{R}, t) + \frac{1}{\mathbf{M}} \left[ \nabla A(\mathbf{R}, t) \cdot \nabla S(\mathbf{R}, t) + \frac{1}{2} A(\mathbf{R}, t) \nabla^2 S(\mathbf{R}, t) \right] = 0$$

Multiply the second equation by  $2A$

$$2A(\mathbf{R},t)\partial_t A(\mathbf{R},t) + \frac{2A(\mathbf{R},t)}{\mathbf{M}} \left[ \nabla A(\mathbf{R},t) \cdot \nabla S(\mathbf{R},t) + \frac{1}{2} A(\mathbf{R},t) \nabla^2 S(\mathbf{R},t) \right] = 0$$

$$\partial_t A(\mathbf{R},t)^2 + \frac{1}{\mathbf{M}} \left[ \nabla A^2(\mathbf{R},t) \cdot \nabla S(\mathbf{R},t) + A(\mathbf{R},t)^2 \nabla^2 S(\mathbf{R},t) \right] = 0$$

$$\partial_t A(\mathbf{R},t)^2 + \frac{1}{\mathbf{M}} \nabla \cdot \left[ A^2(\mathbf{R},t) \nabla S(\mathbf{R},t) \right] = 0$$

Classical limit

$$\partial_t S(\mathbf{R}, t) + \frac{1}{2\mathbf{M}} (\nabla S(\mathbf{R}, t))^2 + E_n(\mathbf{R}) - \frac{\hbar^2}{2\mathbf{M}} \frac{\nabla^2 A(\mathbf{R}, t)}{A(\mathbf{R}, t)} = 0$$

$\lim \hbar \rightarrow 0$

$$\partial_t S(\mathbf{R}, t) + \frac{1}{2\mathbf{M}} (\nabla S(\mathbf{R}, t))^2 + E_n(\mathbf{R}) = 0$$

$$T_{nuc} = \frac{1}{2\mathbf{M}} (\nabla S(\mathbf{R}, t))^2$$

$$H = T_{nuc} + E_n(\mathbf{R})$$

$$\partial_t S + H(\mathbf{R}, \nabla S, t) = 0$$

That's the Hamilton-Jacobi equation!