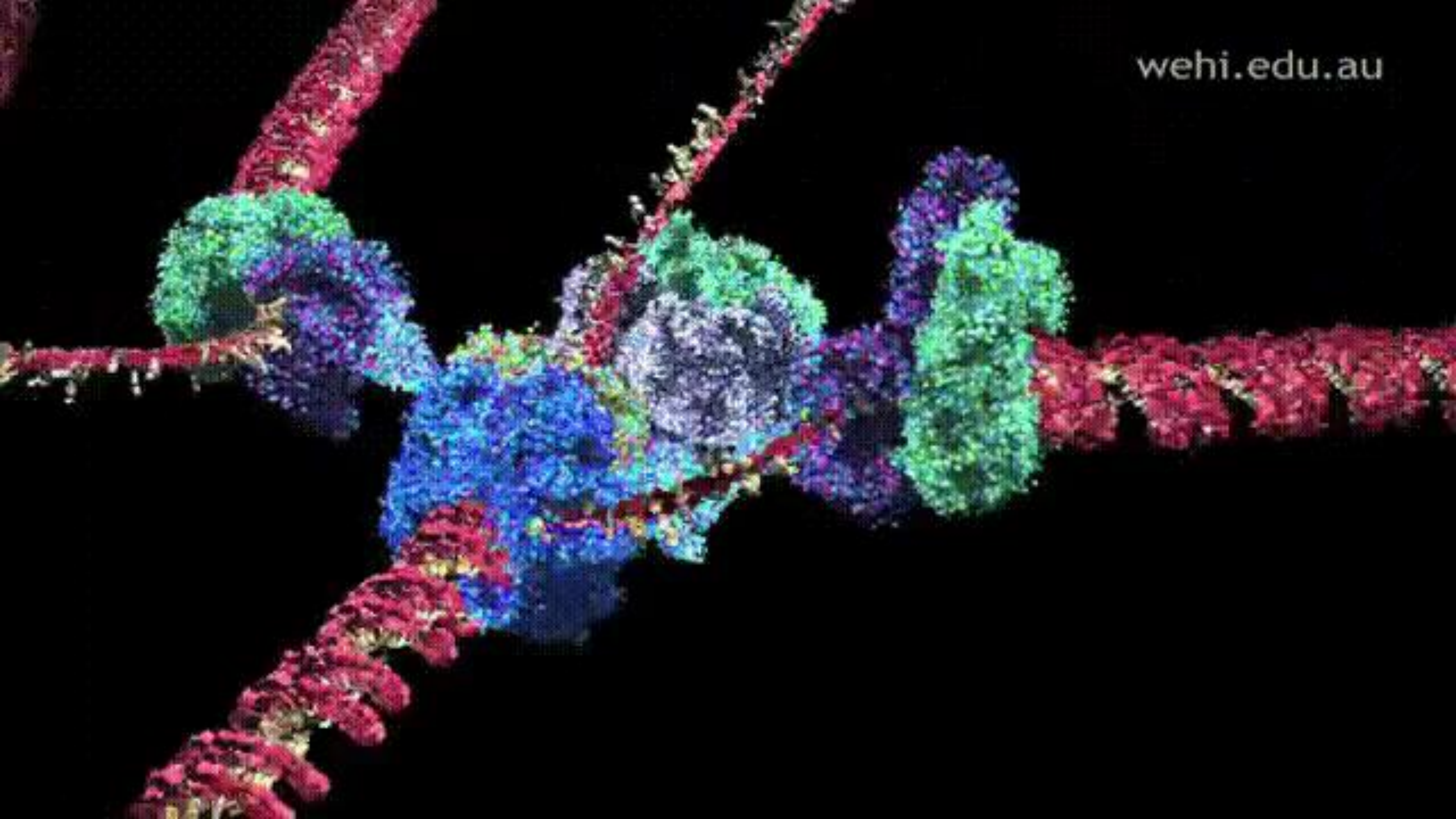
L4 - Quantum Mechanics 4

Quantum mechanics in context

The classical nuclear motion


wehi.edu.au

Quantum nuclear motion

$$\hbar \to 0$$

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

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

↔

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

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

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

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)

Messiah. Quantum Mechanics, 1961 (vol 1, p. 222)

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

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

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

$\lim \hbar \to 0$

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

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

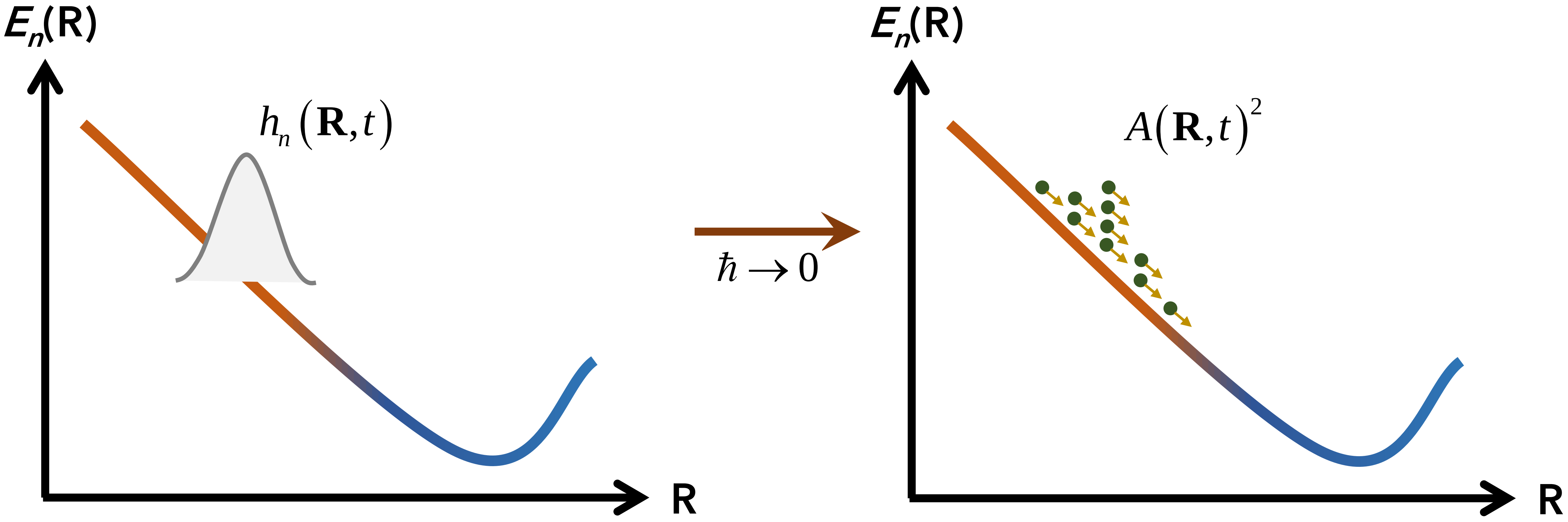
Classical Hamilton-Jacobi equation!

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

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

"In the classical approximation, $h_n(\mathbf{R}, t)$ describes a fluid of non-interacting classical particles of mass **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



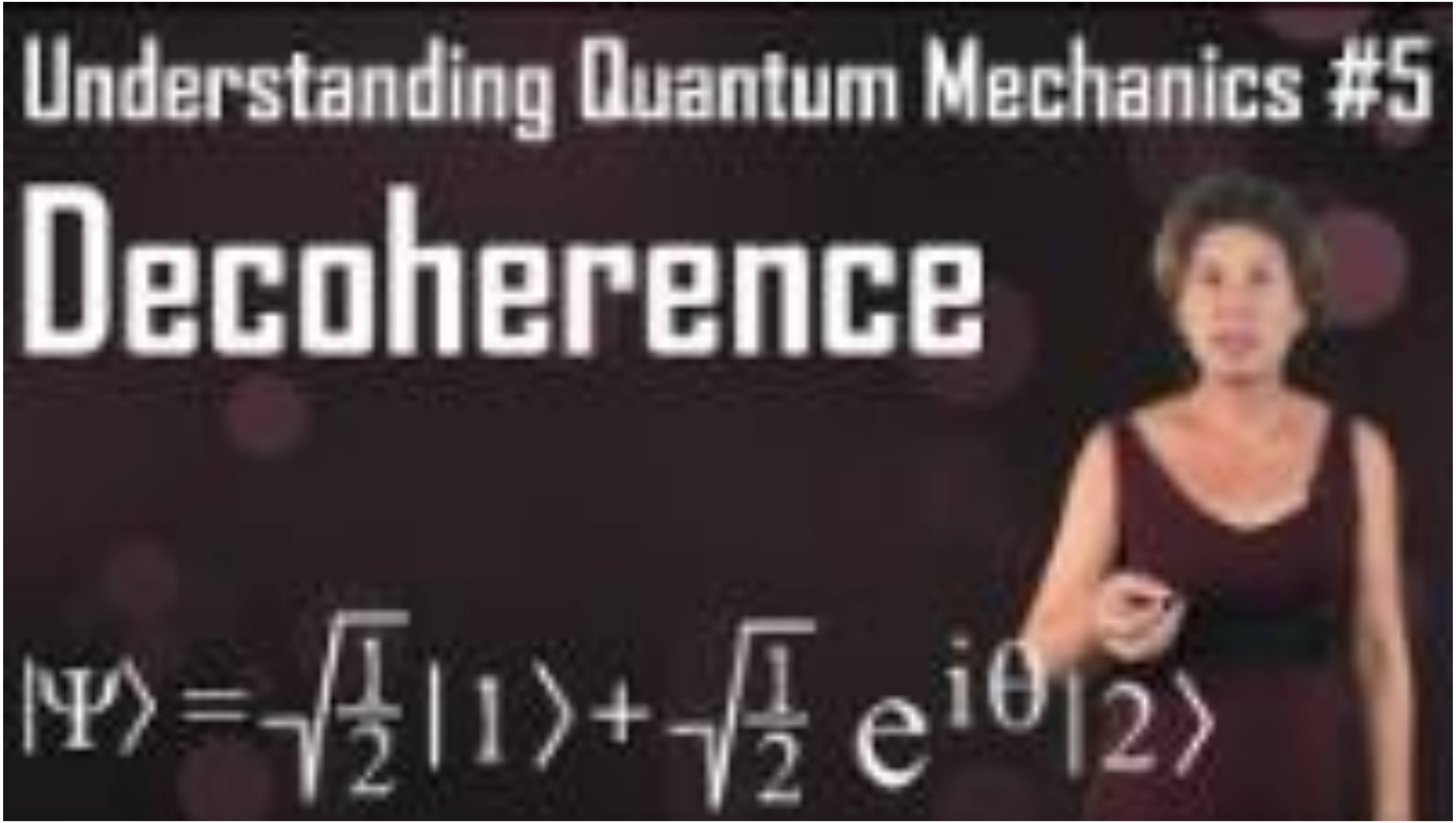
"In the classical approximation, $h_n(\mathbf{R}, t)$ describes a fluid of non-interacting classical particles of mass $\mathbf{M}$ (statistical mixture) and subject to the potential $E_n(\mathbf{R})$. The density and current density at each point of space are at all times respectively equal to the probability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

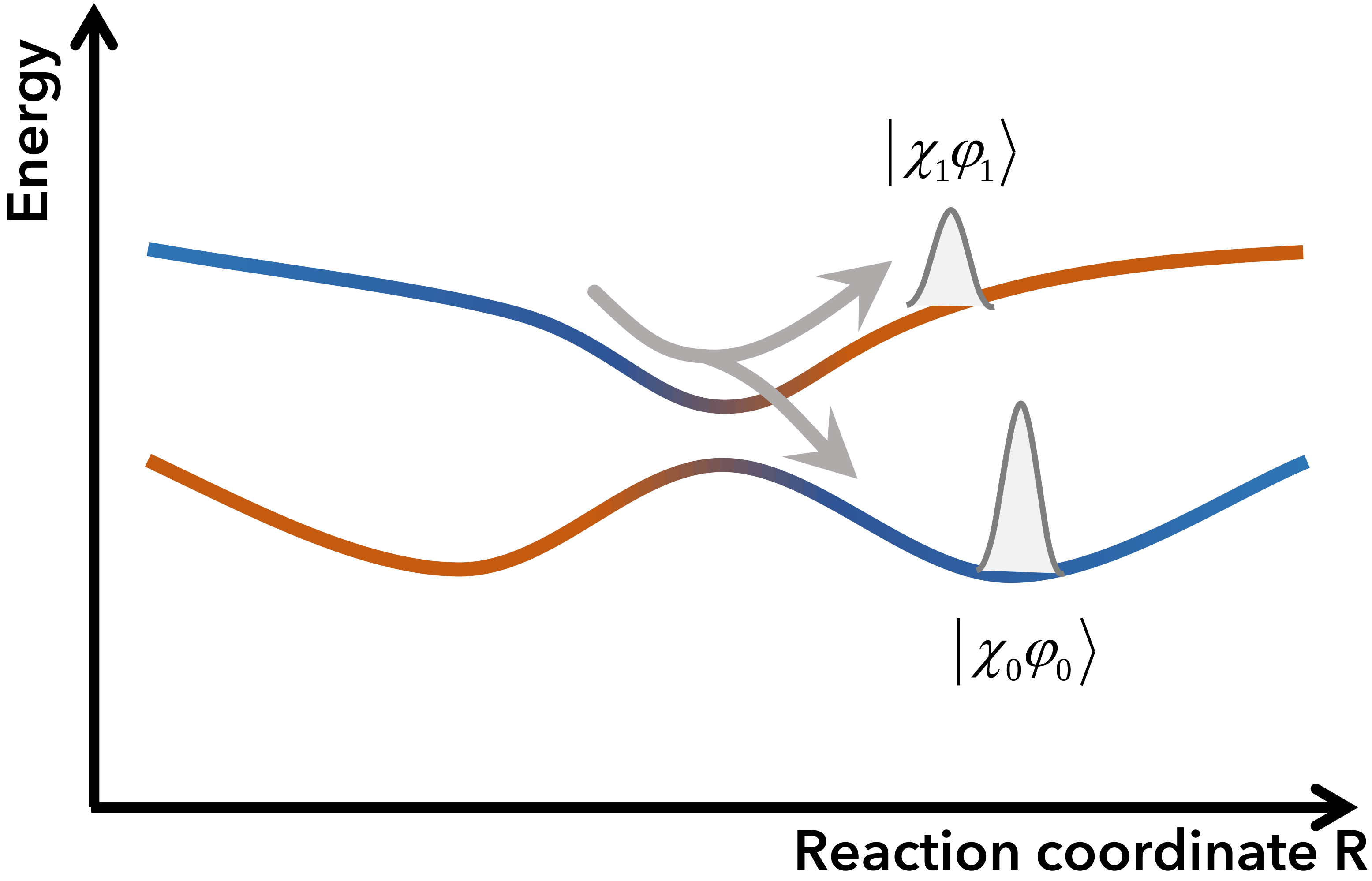
This classical limit of the nuclear Schrödinger equation is the formal reason we can do molecular dynamics of molecules.

Decoherence & collapse

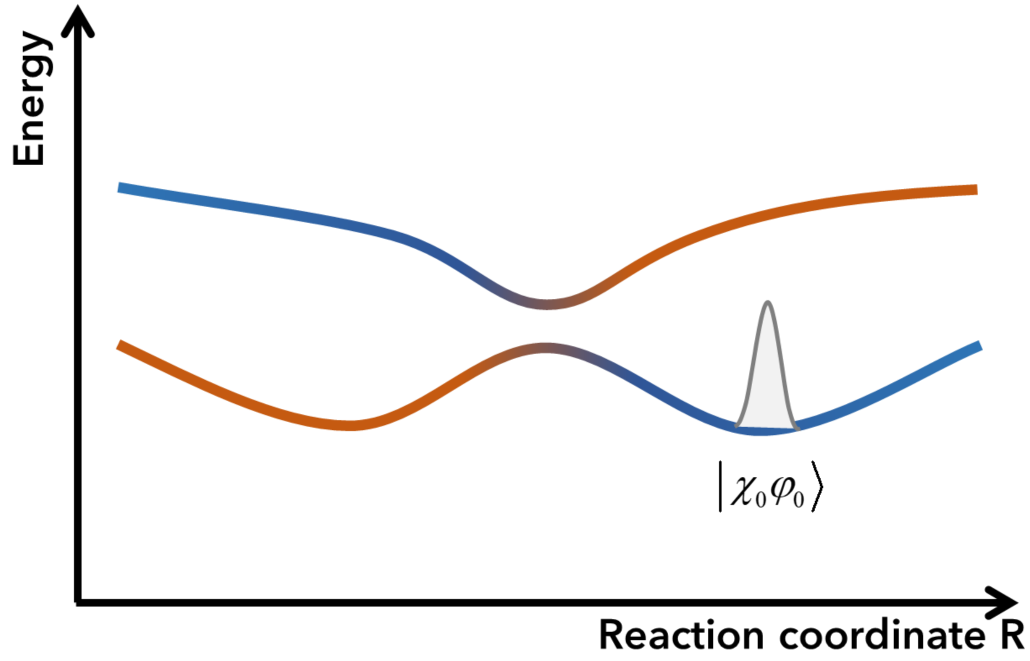
https://youtu.be/igsulul_HAQ

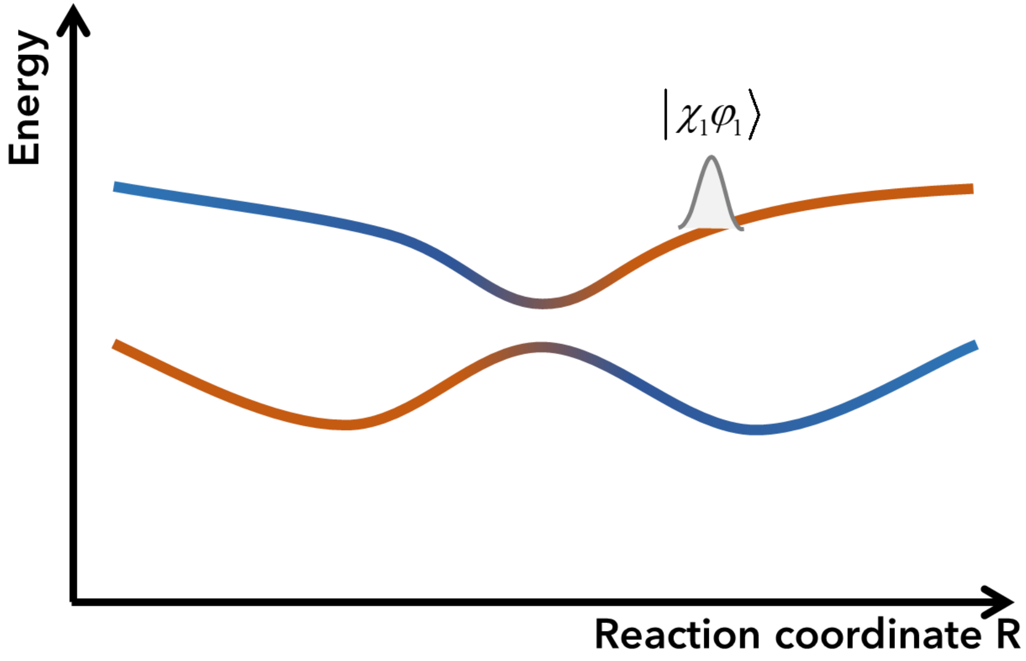


$$|\Psi\rangle = a_0(t)|\chi_0\varphi_0\rangle + a_1(t)|\chi_1\varphi_1\rangle$$



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

Forming the **molecular density matrix** for

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

$\left|\chi_i\right\rangle - nuclei$

$\left|\varphi_i\right\rangle - electrons$

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

$$= \begin{bmatrix} \left|a_0(t)\right|^2 & a_0(t)a_1^*(t) \\ a_1(t)a_0^*(t) & \left|a_1(t)\right|^2 \end{bmatrix}$$

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

Forming the **electronic reduced density** matrix for

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

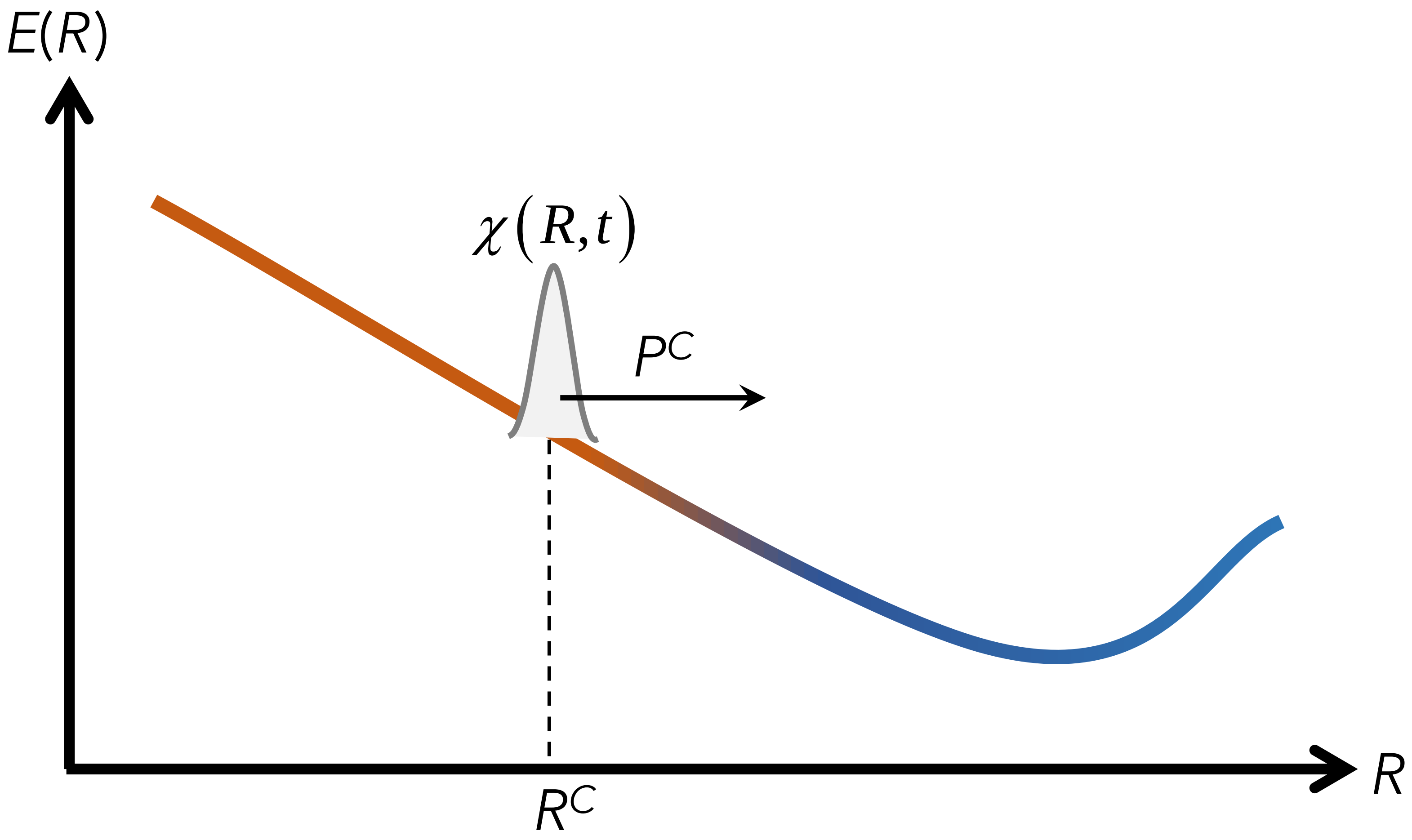
$$\rho_{el} = Tr_{nuclei}\left[\rho_{mol}\right]$$

$$= \begin{bmatrix} \left|\chi_0\left(\mathbf{R},t\right)\right|^2 & \chi_0\left(\mathbf{R},t\right)\chi_1^*\left(\mathbf{R},t\right) \\ \chi_1\left(\mathbf{R},t\right)\chi_0^*\left(\mathbf{R},t\right) & \left|\chi_1\left(\mathbf{R},t\right)\right|^2 \end{bmatrix}$$

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

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

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



Assuming a 1-D Gaussian nuclear wave packet

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

Electronic populations

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

Electronic coherences

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

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

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

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

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

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

The electronic coherence tends to zero with time.
That's called **decoherence**.

Decoherence

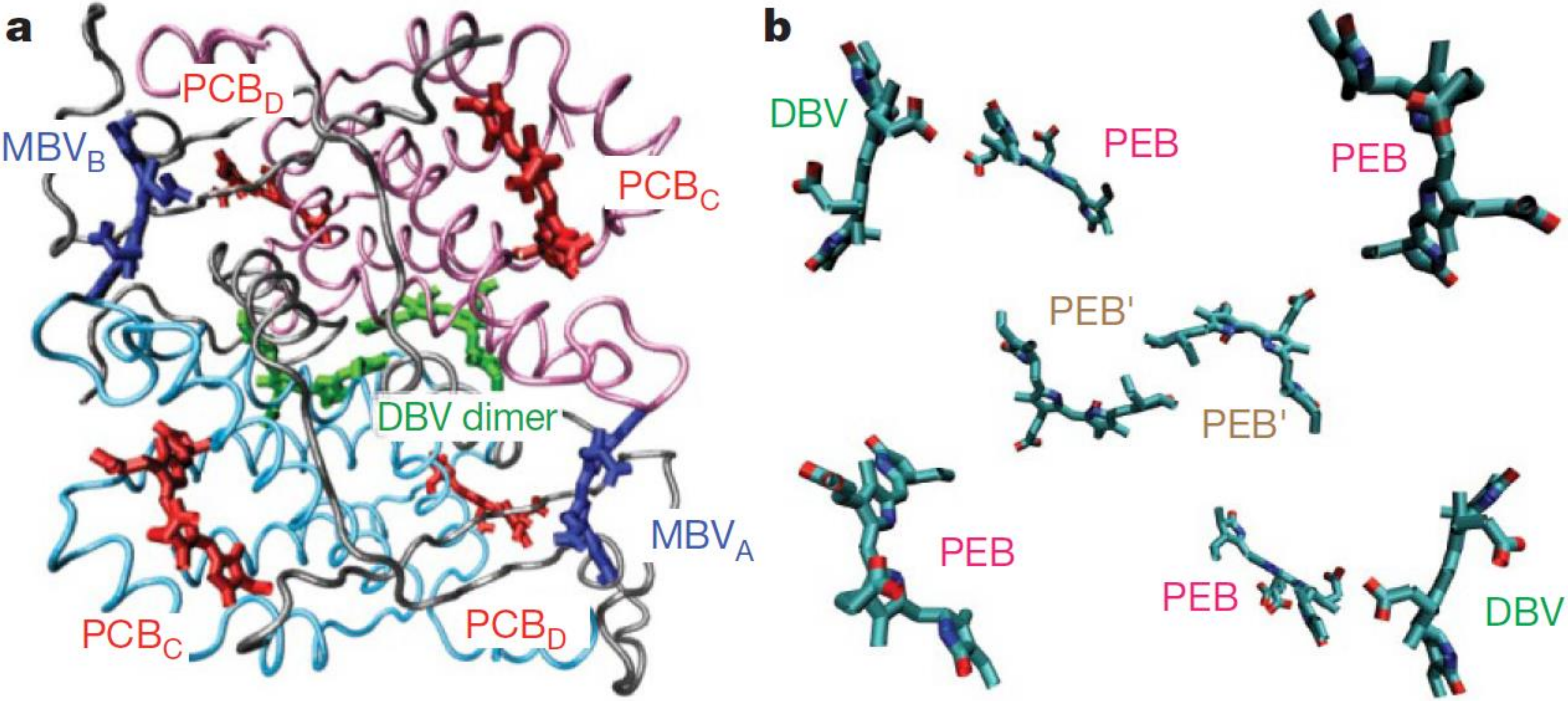
$$\rho(t_\infty) \rightarrow \begin{bmatrix} |\chi_0(R,t_\infty)|^2 & 0 \\ 0 & |\chi_1(R,t_\infty)|^2 \end{bmatrix}$$

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

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

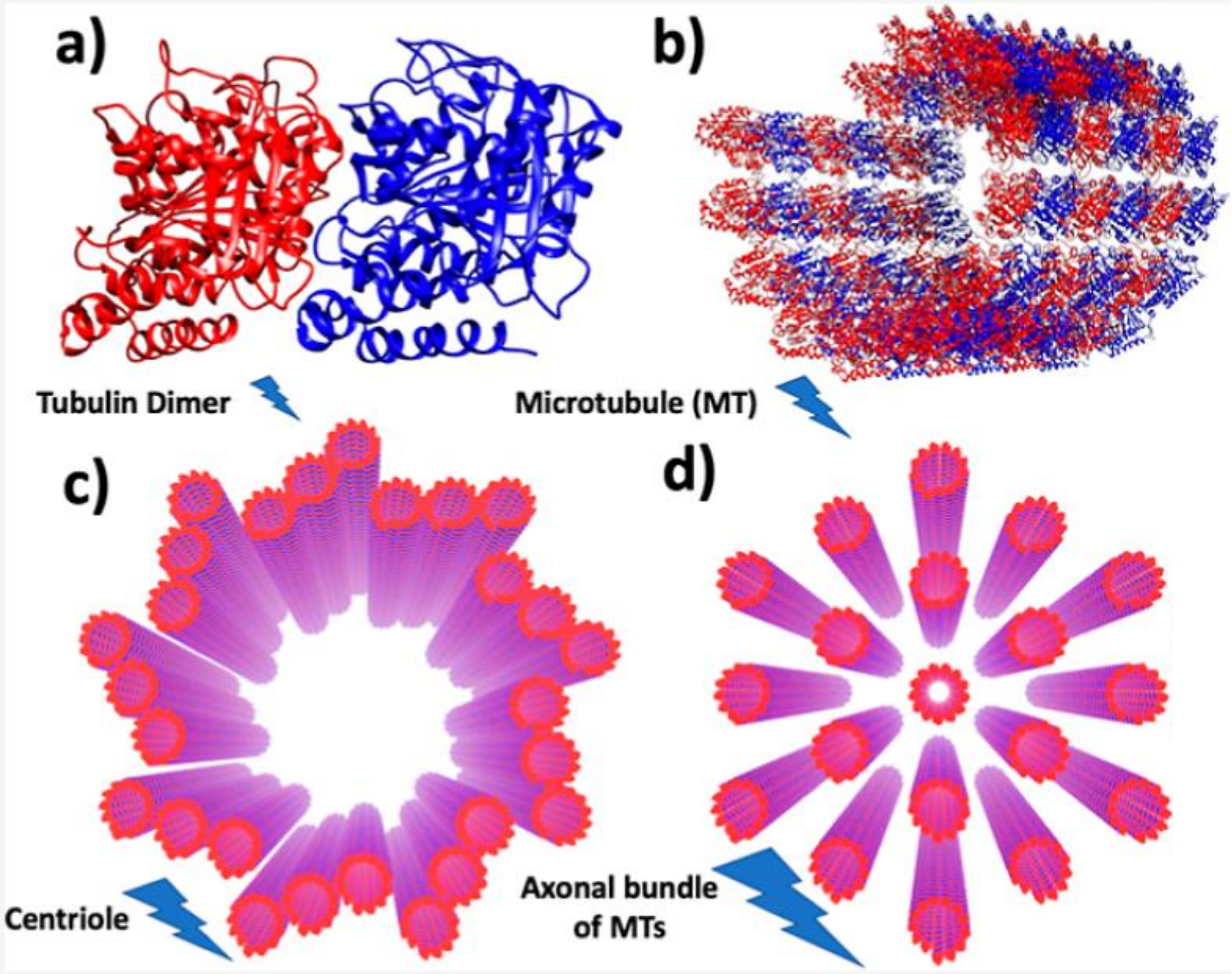
Zurek. *Rev Mod Phys* **2003,** *75*, 715

Photosynthetic centers have long-lived coherences



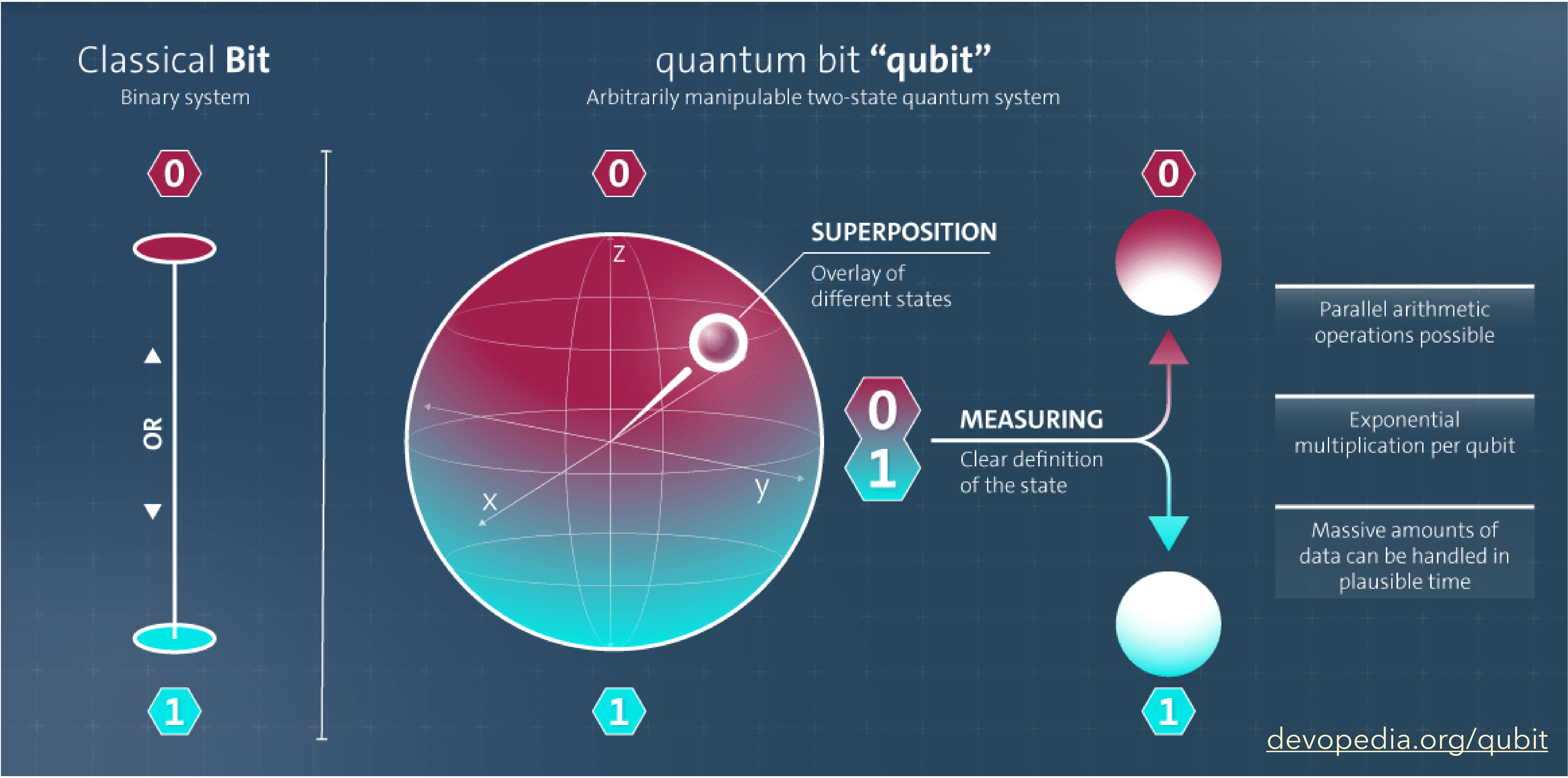
Collini *et al. Nature* **2010**, *463*, 644

Superradiance in Trp protein architectures



Babcock *et al. J Phys Chem B* **2024**, *128*, 4035

Long-lived coherences are the heart of quantum computing



Decoherence

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

Decoherence time

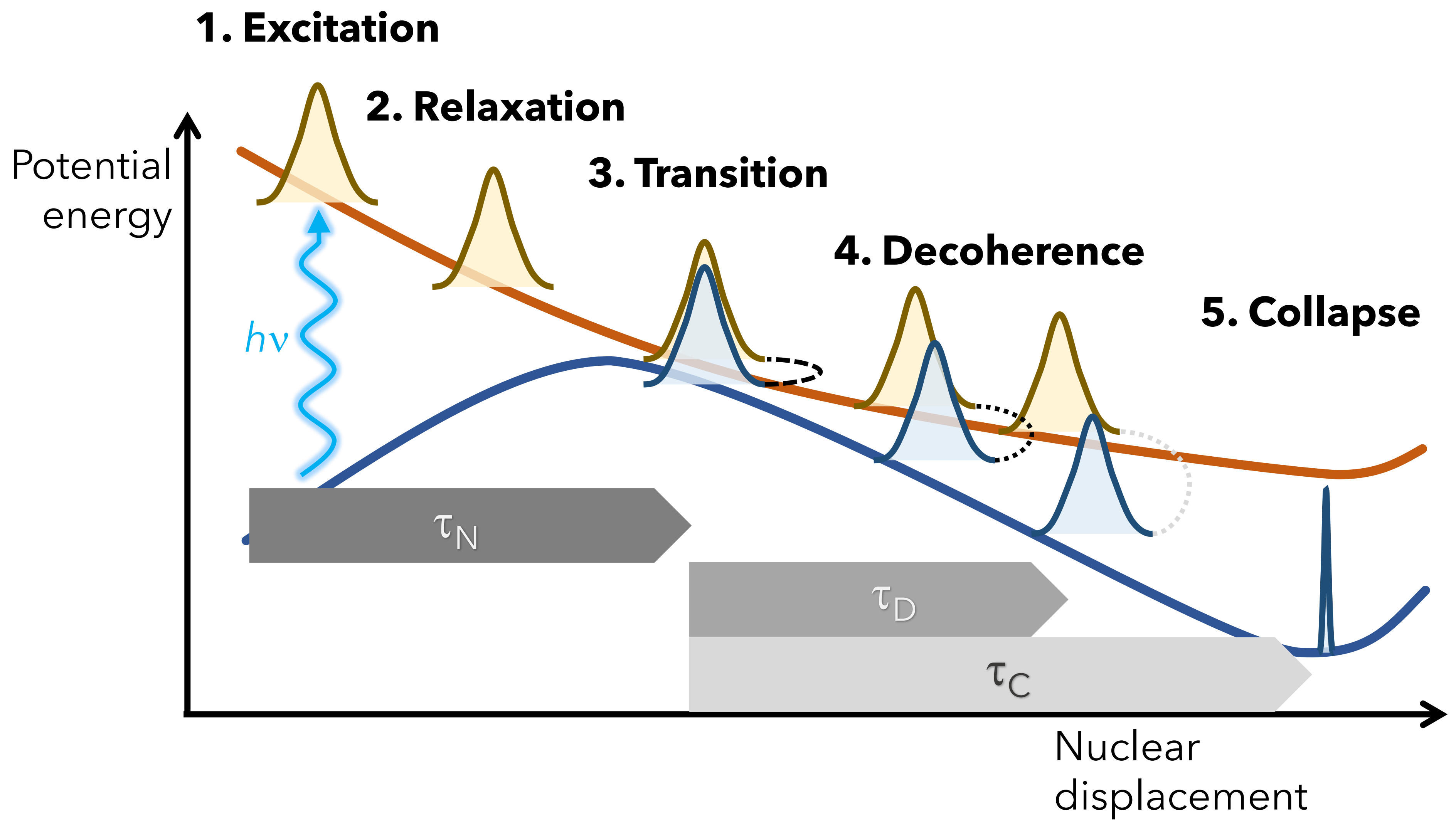
$$\tau_D = \frac{1}{|v_k^C - v_l^C|}\sqrt{\frac{2}{\alpha}}$$

Collapse

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

Collapse time

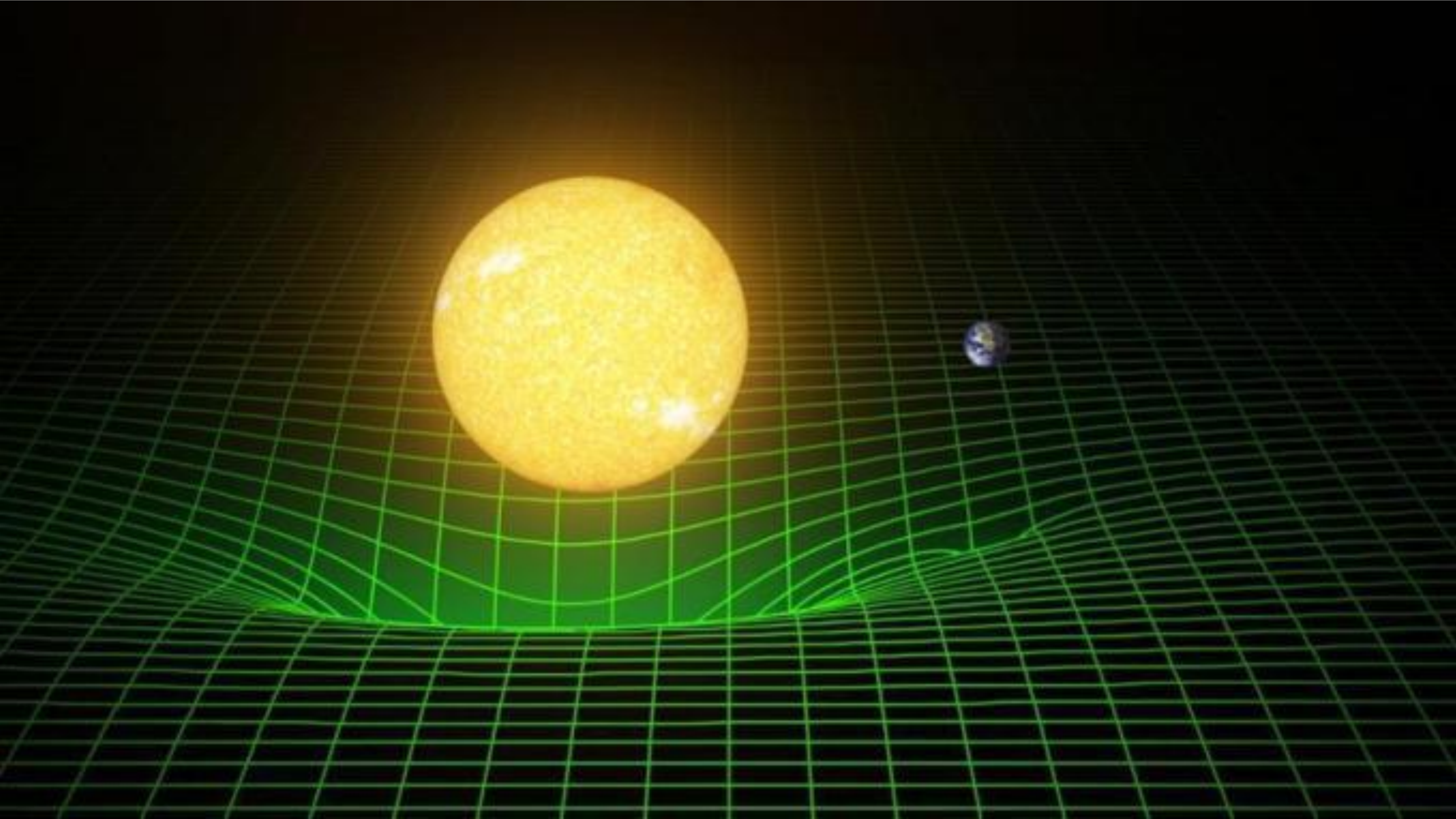
$$\tau_C = ?$$


1. Excitation
2. Relaxation
3. Transition
4. Decoherence
5. Collapse
Potential energy
hν
τN
τD
τC
Nuclear displacement

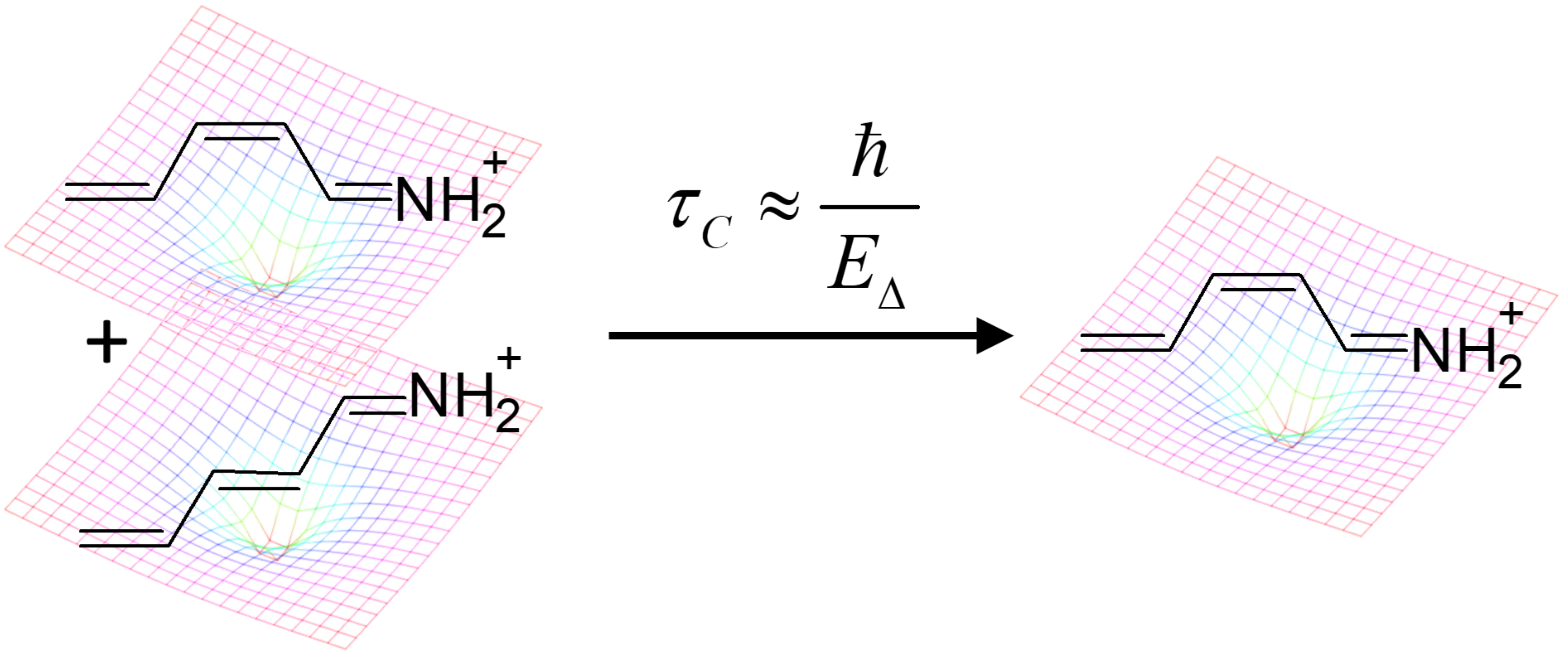
Interpretations of quantum mechanics

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



Diósi-Penrose model

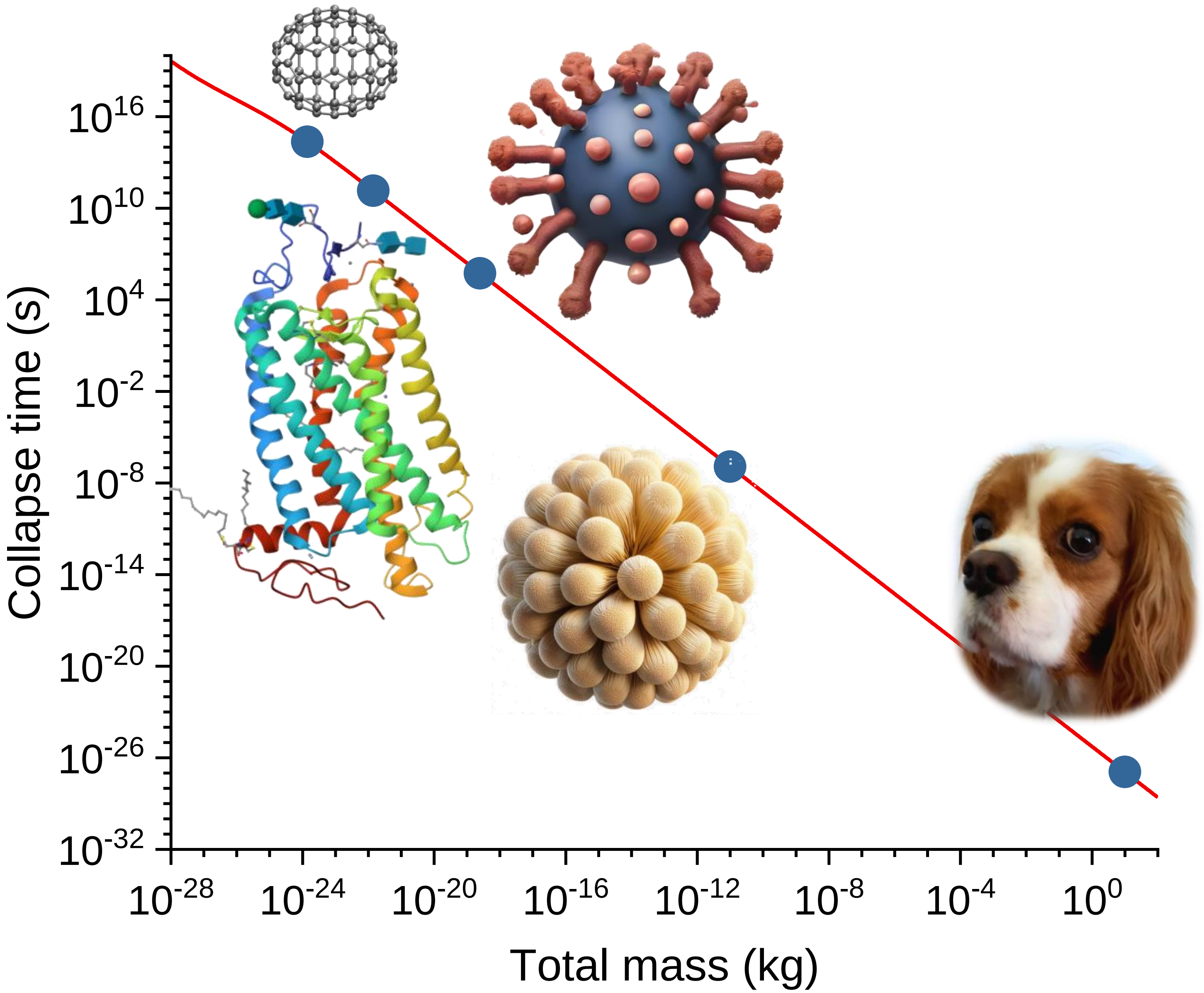


$$\tau_C = \frac{\hbar}{4\pi G\left[\int d\mathbf{r}d\mathbf{r}'\frac{\left(\mu_A(\mathbf{r}')-\mu_B(\mathbf{r}')\right)\left(\mu_A(\mathbf{r})-\mu_B(\mathbf{r})\right)}{\left|\mathbf{r}-\mathbf{r}'\right|}\right]}$$

Diósi. *AVS Quantum Science* **2022,** *4*, 015605

Tomaz; Souza Mattos; Barbatti. *PCCP* **2024**, *26*, 20785

Diósi-Penrose collapse time



Tomaz; Souza Mattos; Barbatti. *PCCP* **2024**, *26*, 20785

The most complex place in the universe

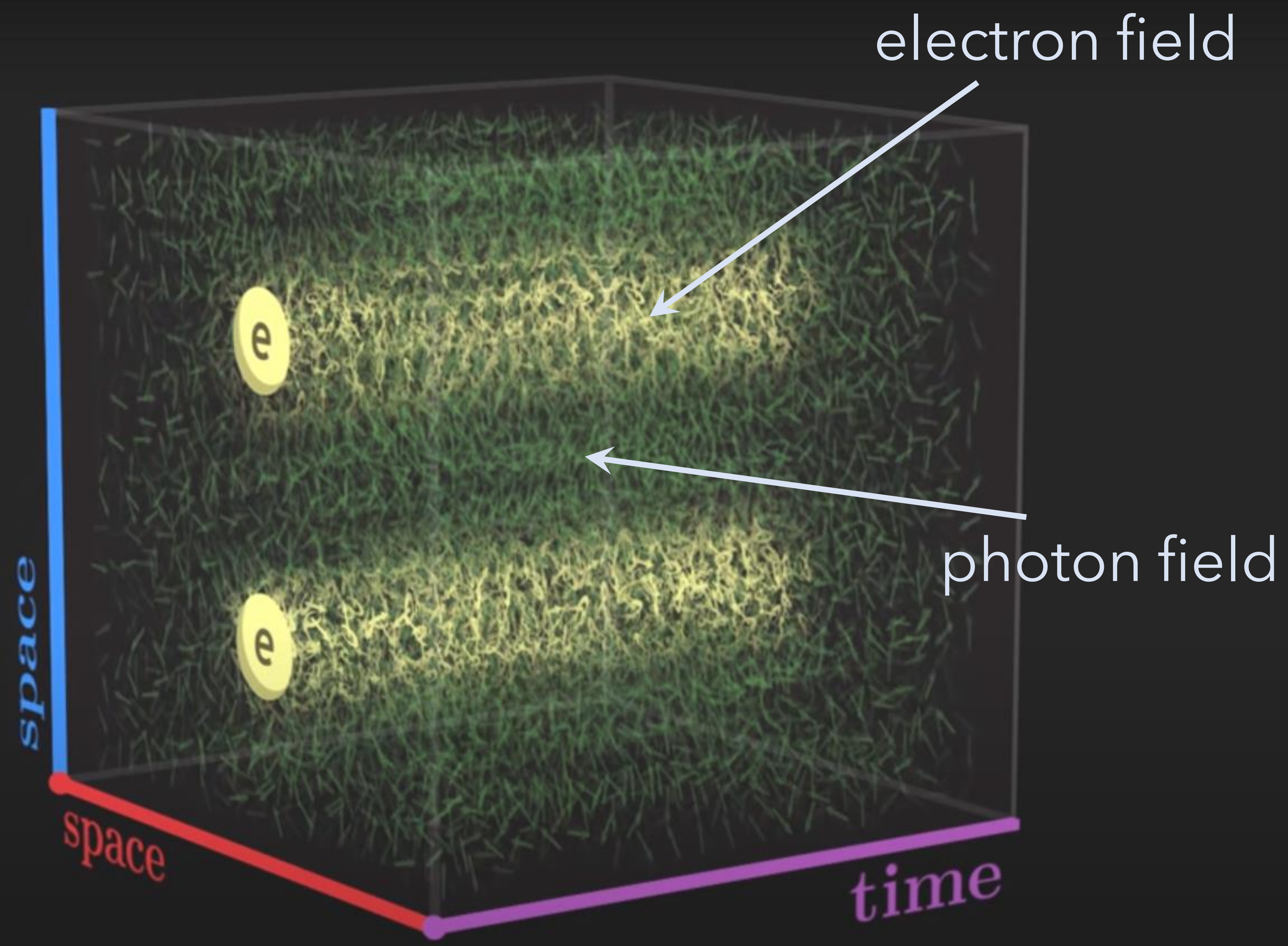
youtu.be/Unl1jXFnzgo

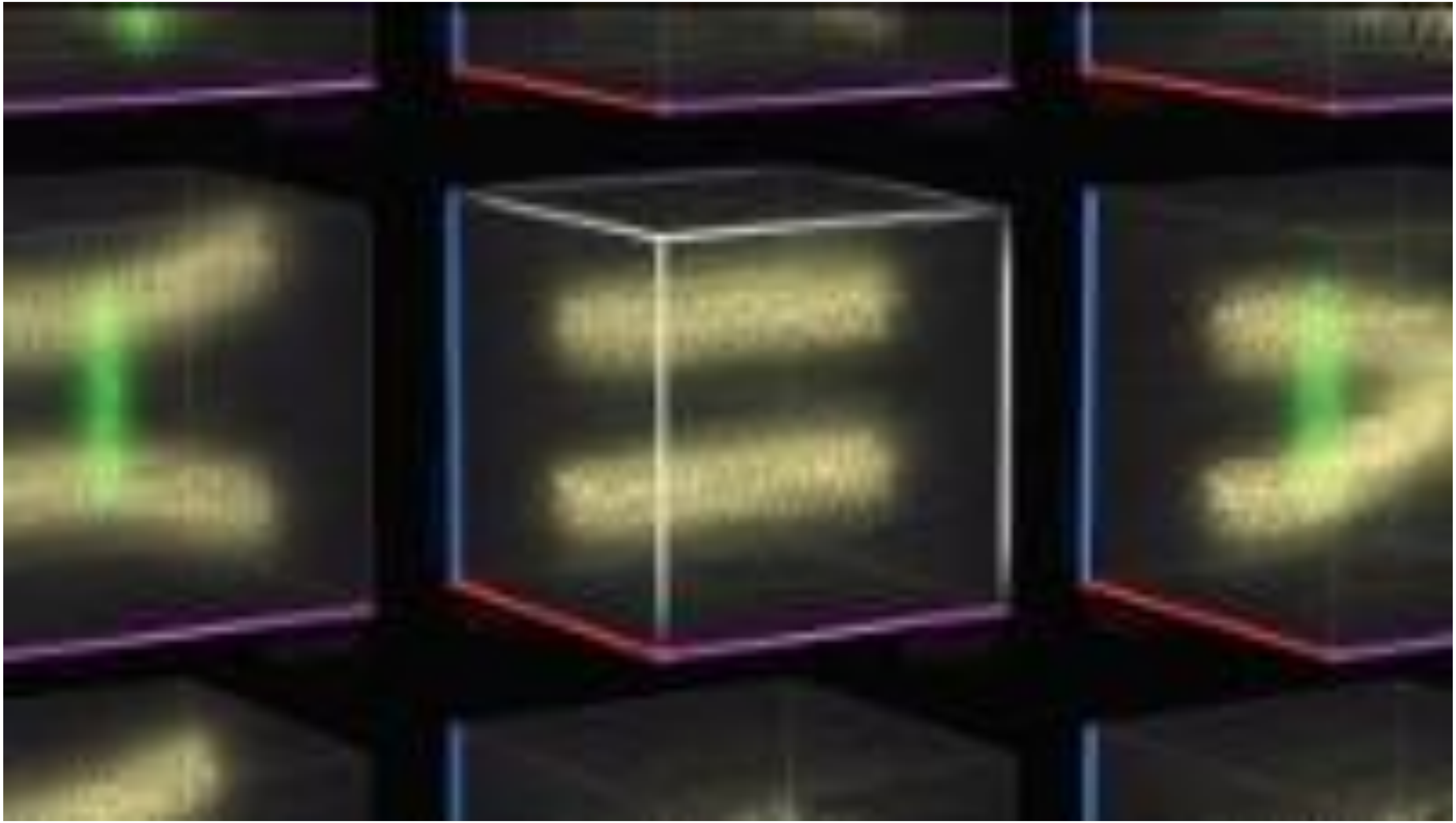

u
Up quark
d
Down quark
c
Charm quark
s
Strange quark
t
Top quark
γ
Photon
g
Gluon
b
Bottom quark
graviton
H
Higgs boson
τ
Tau
W
W boson
Z
Z boson
Tau neutrino
μ
Muon
Muon neutrino
e
Electron
Electron neutrino

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

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

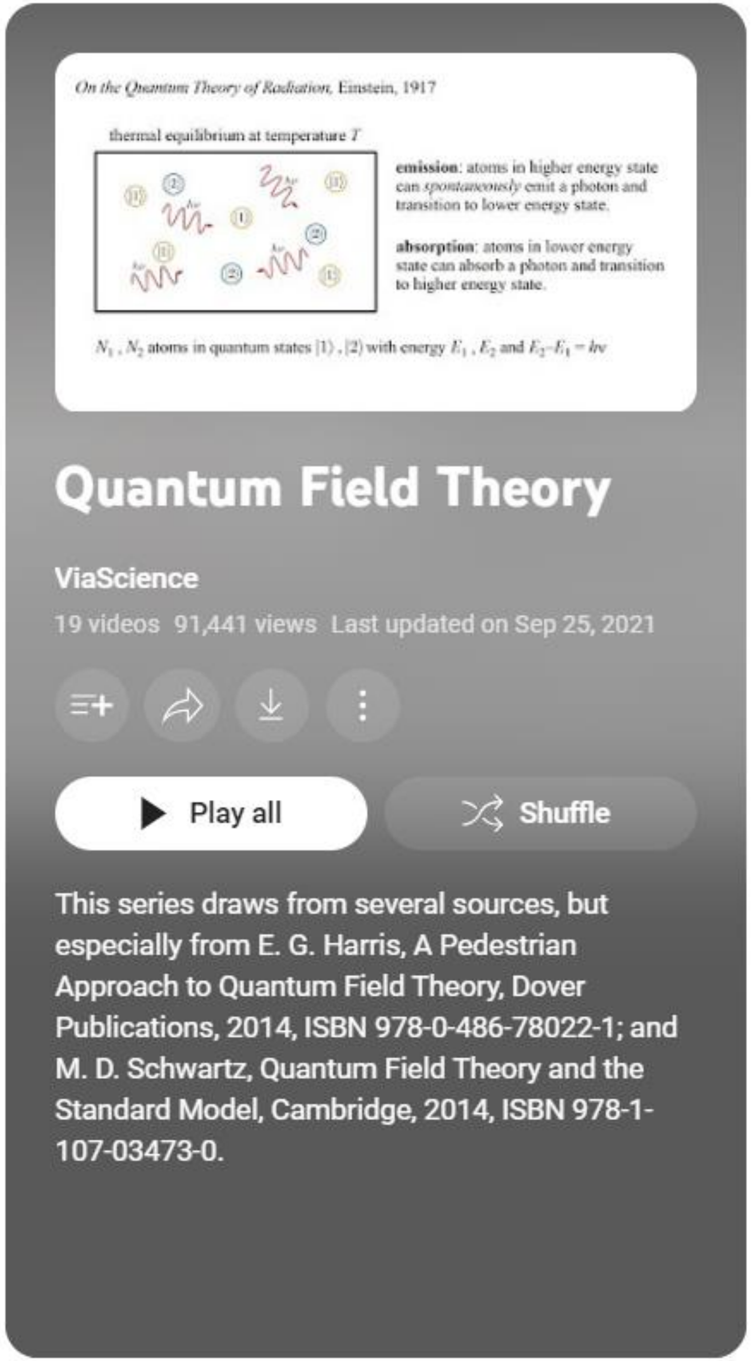
(second quantization)


electron field
photon field
e
e
space
space
time

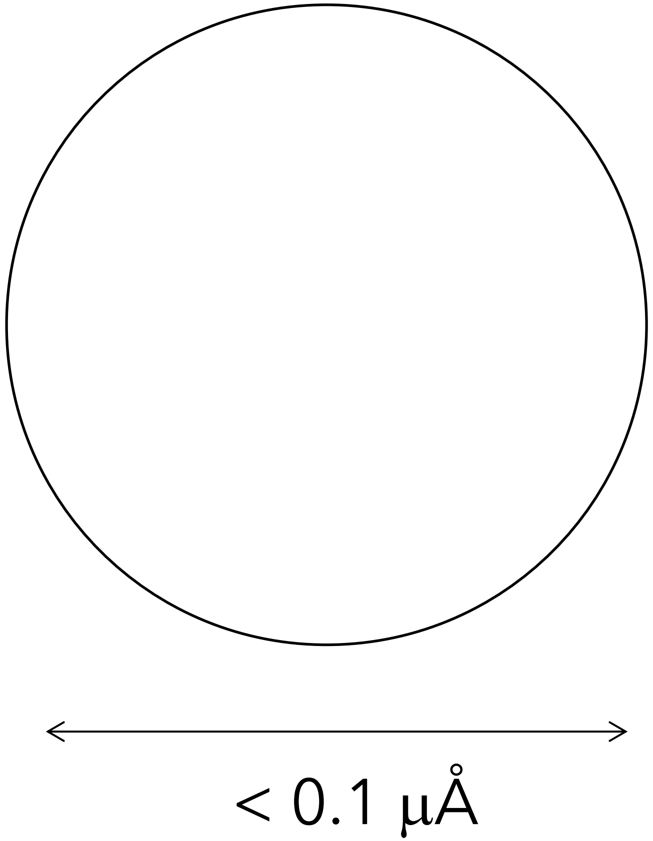


tinyurl.com/sciclickqft

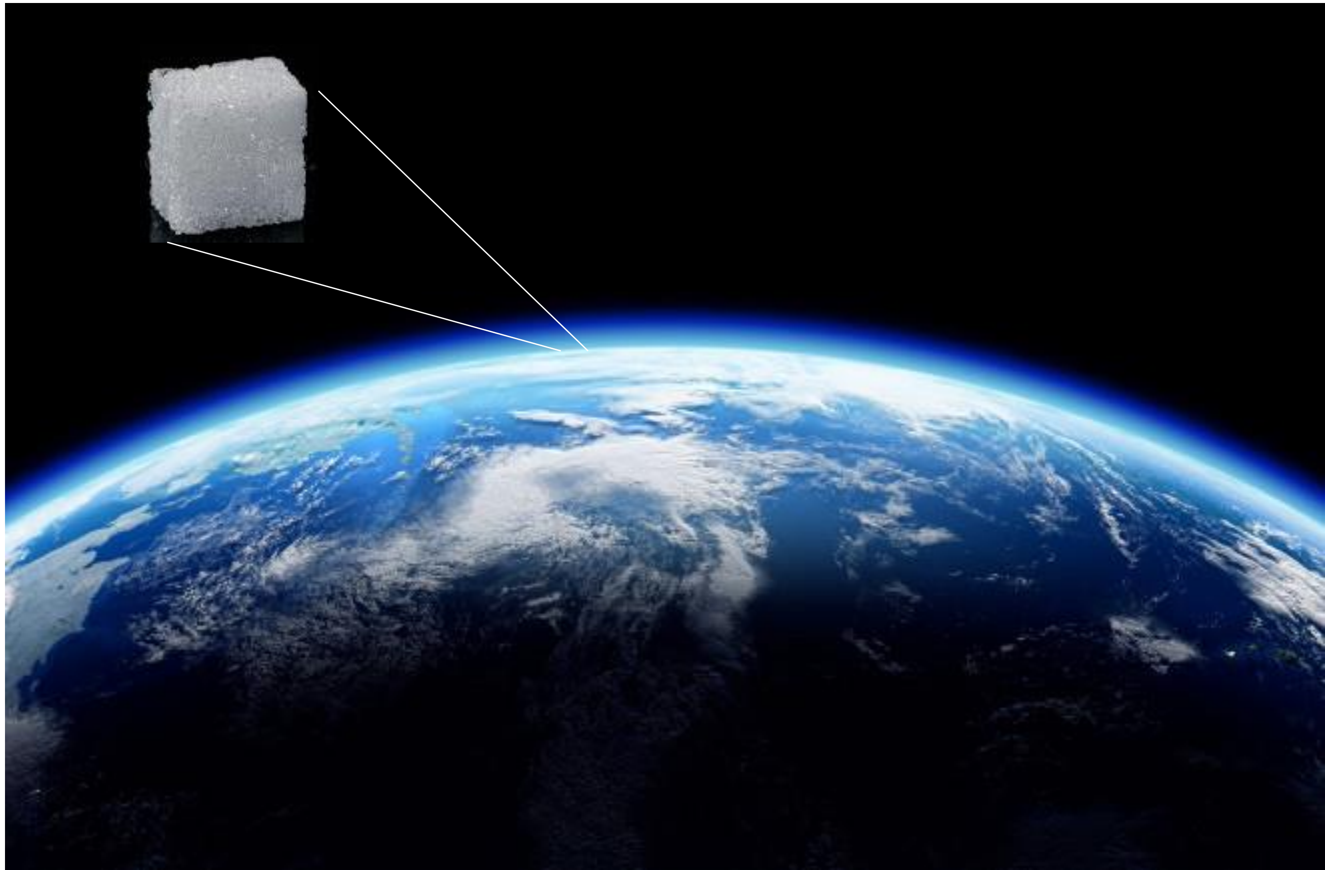
Course on quantum field theory
ViaScience, tinyurl.com/viasciQFT



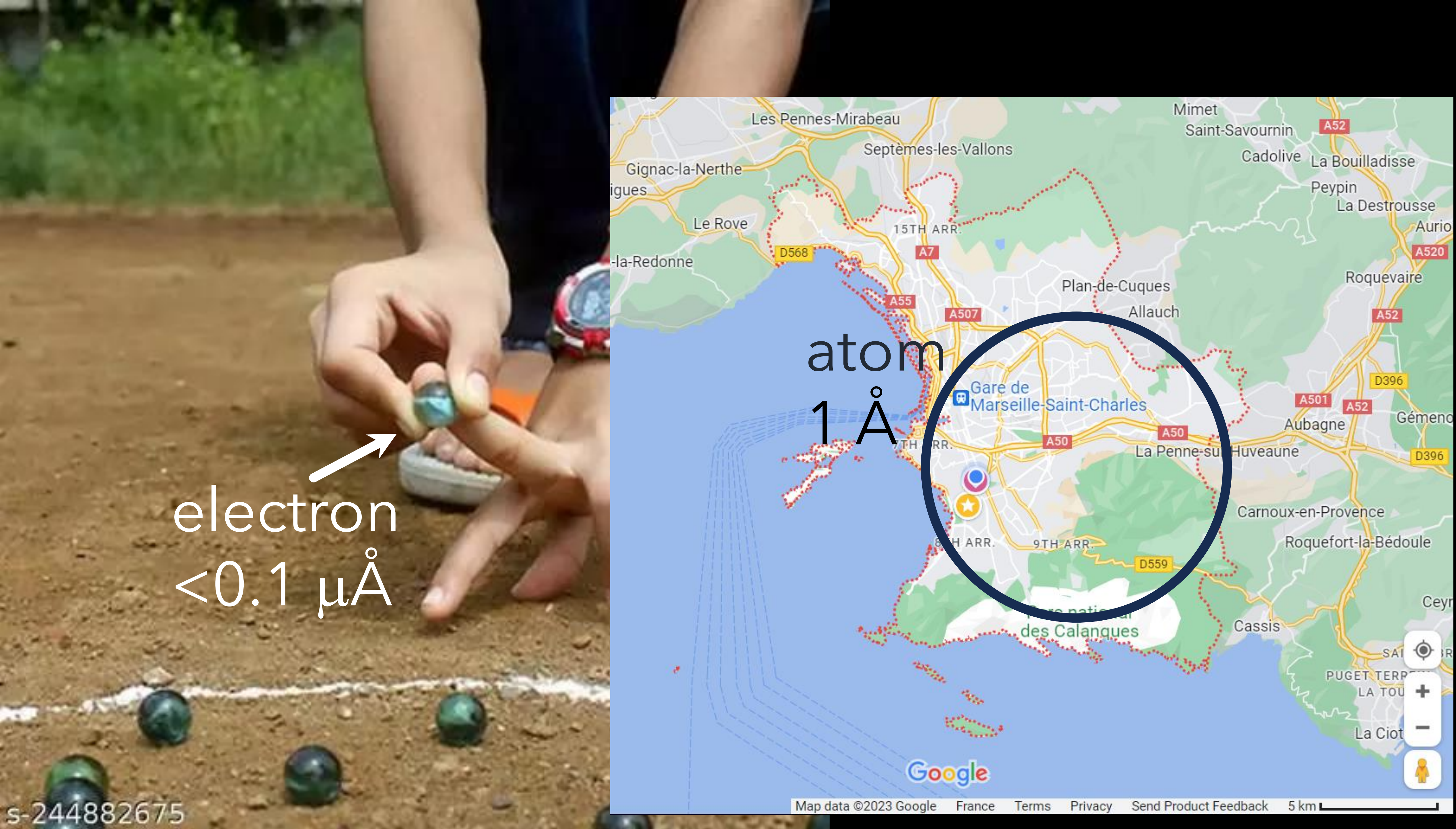
electron



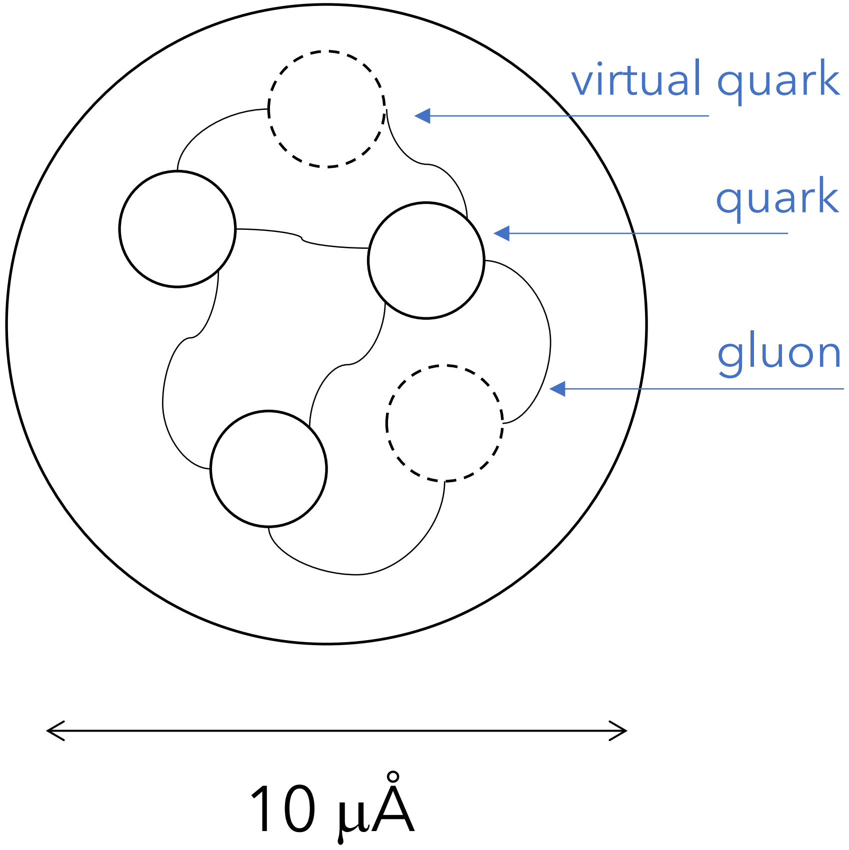
lifetime 6.6×10^{28} years
mass 1
charge -1
spin 1/2



Savitsky, Quanta Magazine, **2023**


electron
<0.1 µÅ
atom
1 Å
s-244882675
Les Pennes-Mirabeau
Septèmes-les-Vallons
Mimet
Saint-Savournin
Cadolive
La Bouilladisse
Peypin
La Destrousse
Gignac-la-Nerthe
Le Rove
-la-Redonne
15TH ARR.
Plan-de-Cuques
Allauch
Roquevaire
Gare de
Marseille-Saint-Charles
Aubagne
La Penne-su Huveaune
Carnoux-en-Provence
Roquefort-la-Bédoule
9TH ARR.
des Calanques
Cassis
La Ciot
D568
A7
A55
A507
A50
A52
A520
A501
D396
D559
Google
Map data ©2023 Google
France
Terms
Privacy
Send Product Feedback
5 km

proton/neutron

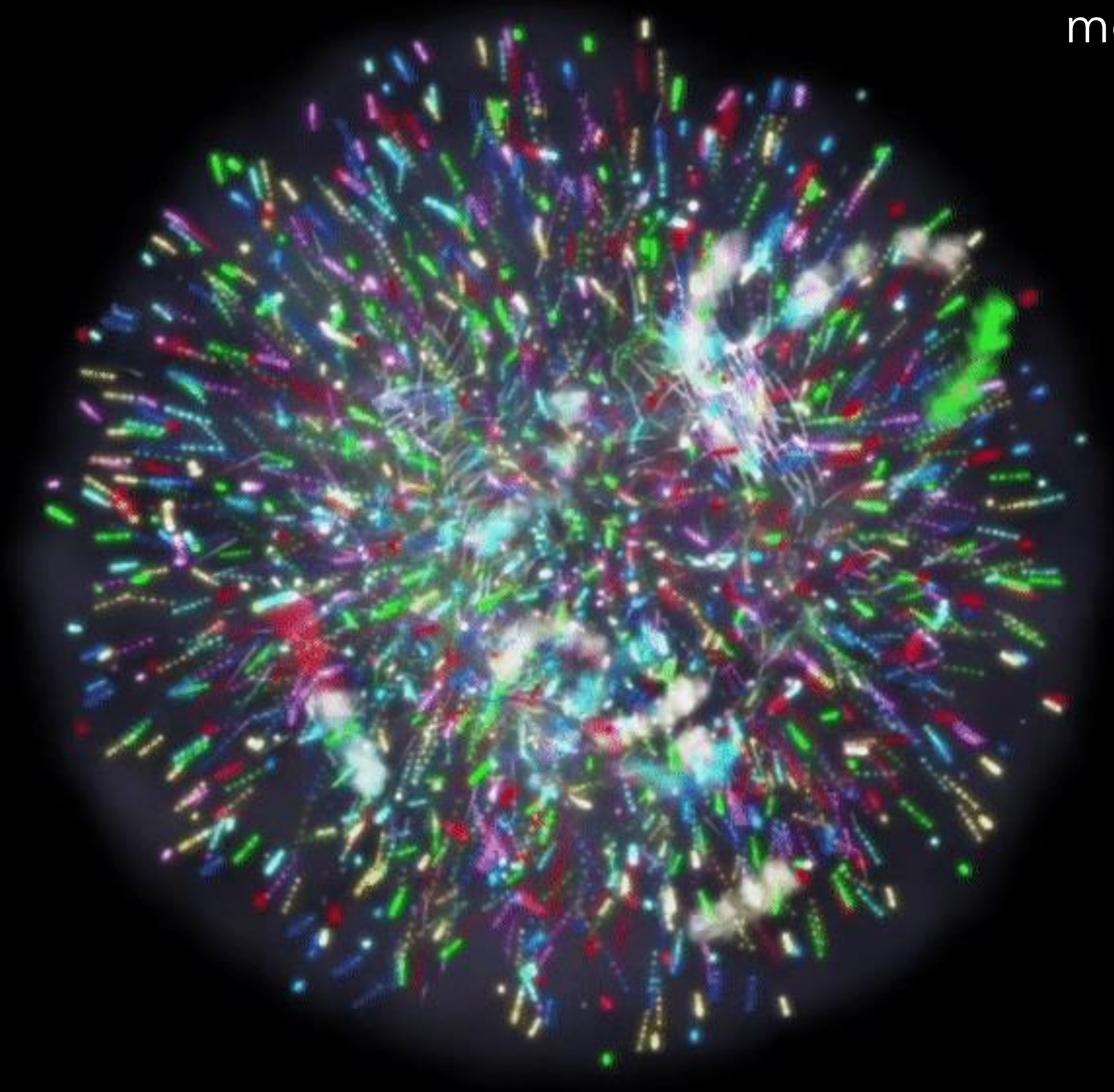


lifetime 10^{34} years
mass 1836
charge 1 (proton) / 0 (neutron)
spin 1/2

High-momentum quarks

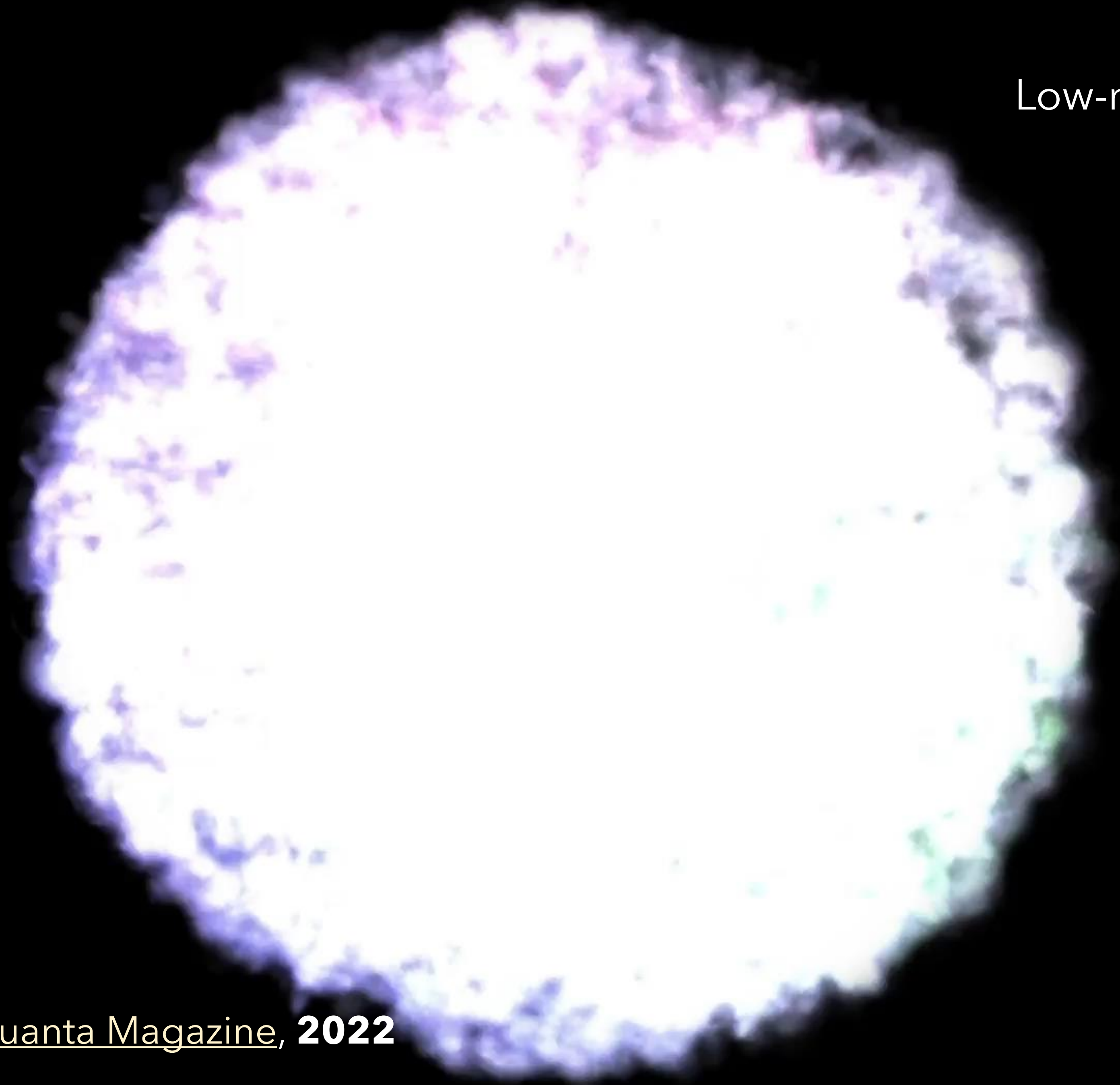
Wood and Shreman, Quanta Magazine, **2022**

medium-momentum quarks

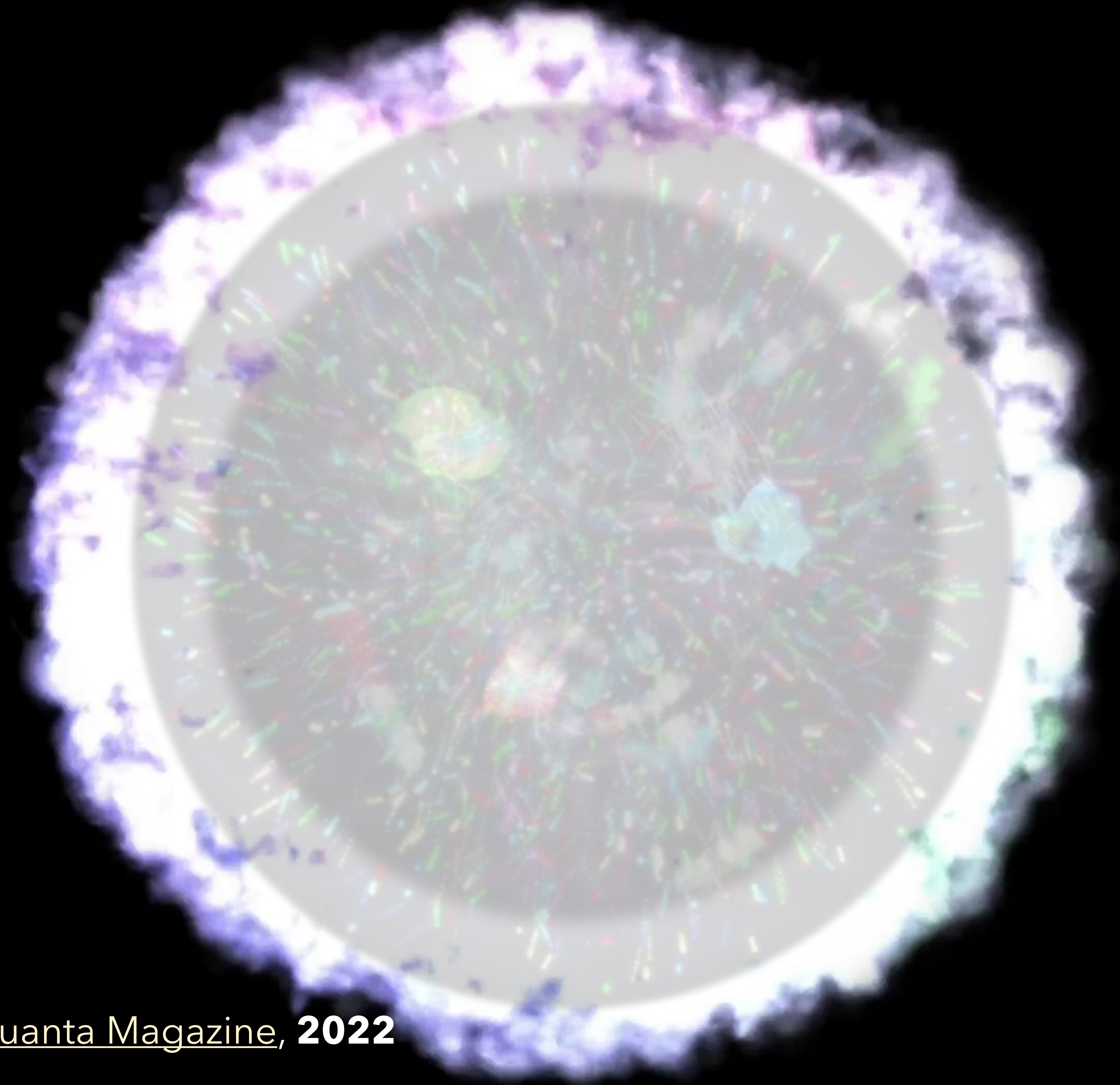


Wood and Shreman, Quanta Magazine, **2022**

Low-momentum quarks

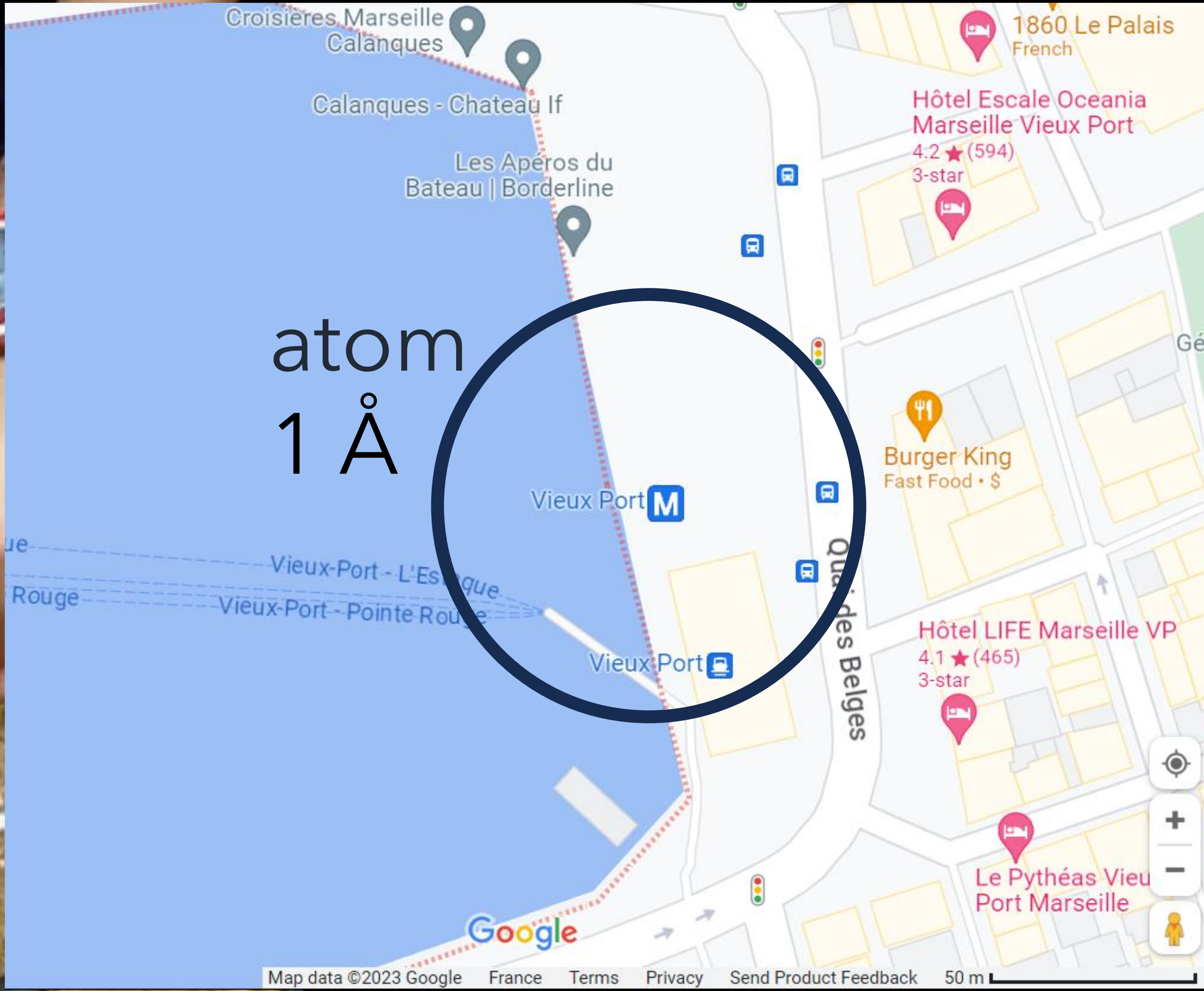


Wood and Shreman, Quanta Magazine, **2022**

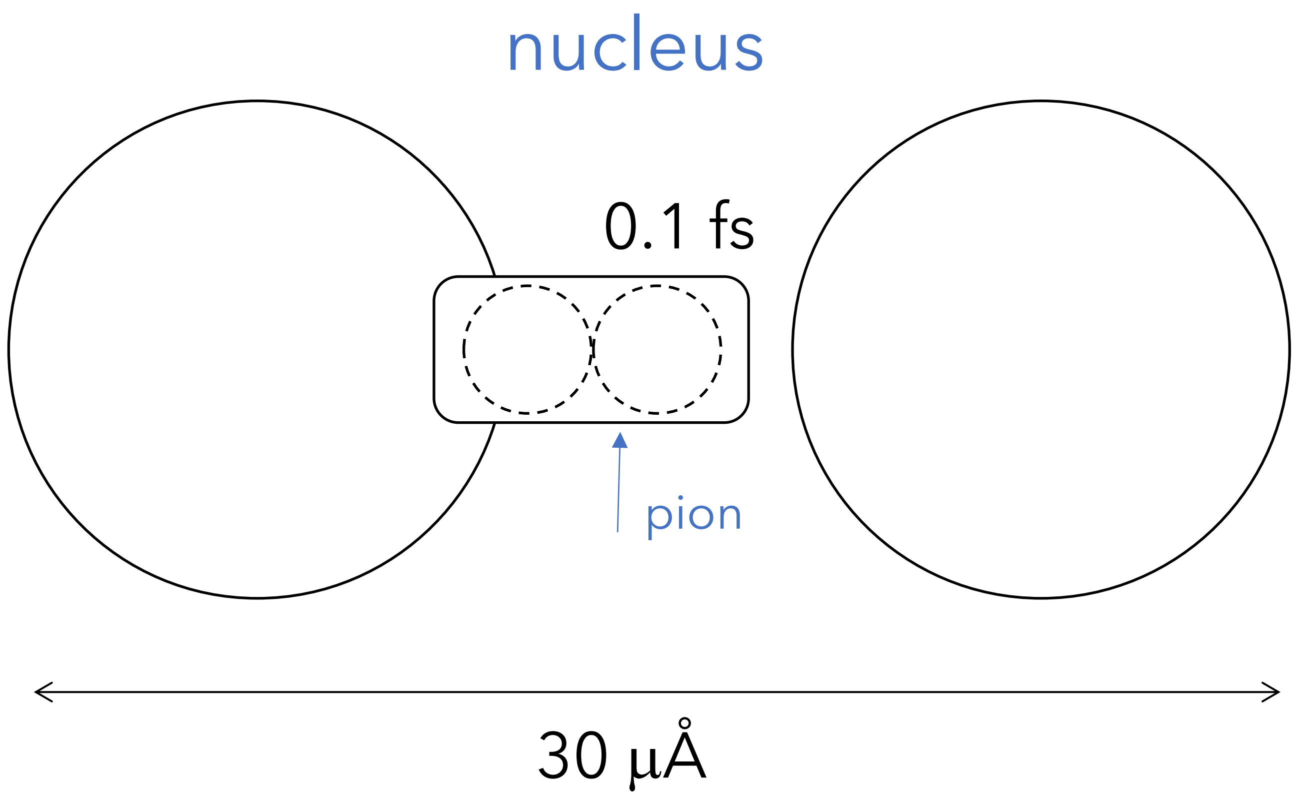


Wood and Shreman, Quanta Magazine, **2022**

proton
10 µÅ



atom
1 Å


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.

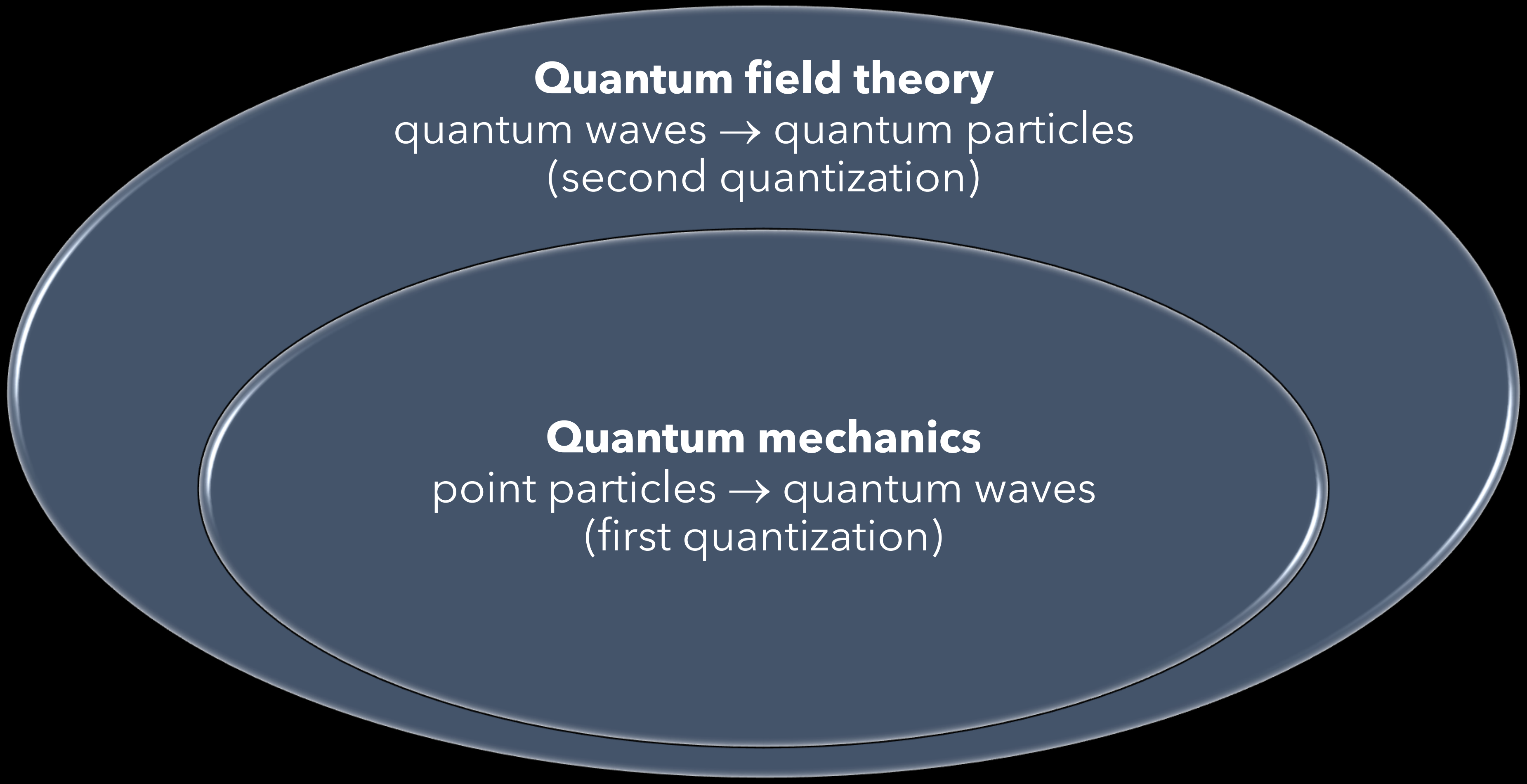
Quantum mechanics: point particles → quantum waves

(first quantization)

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

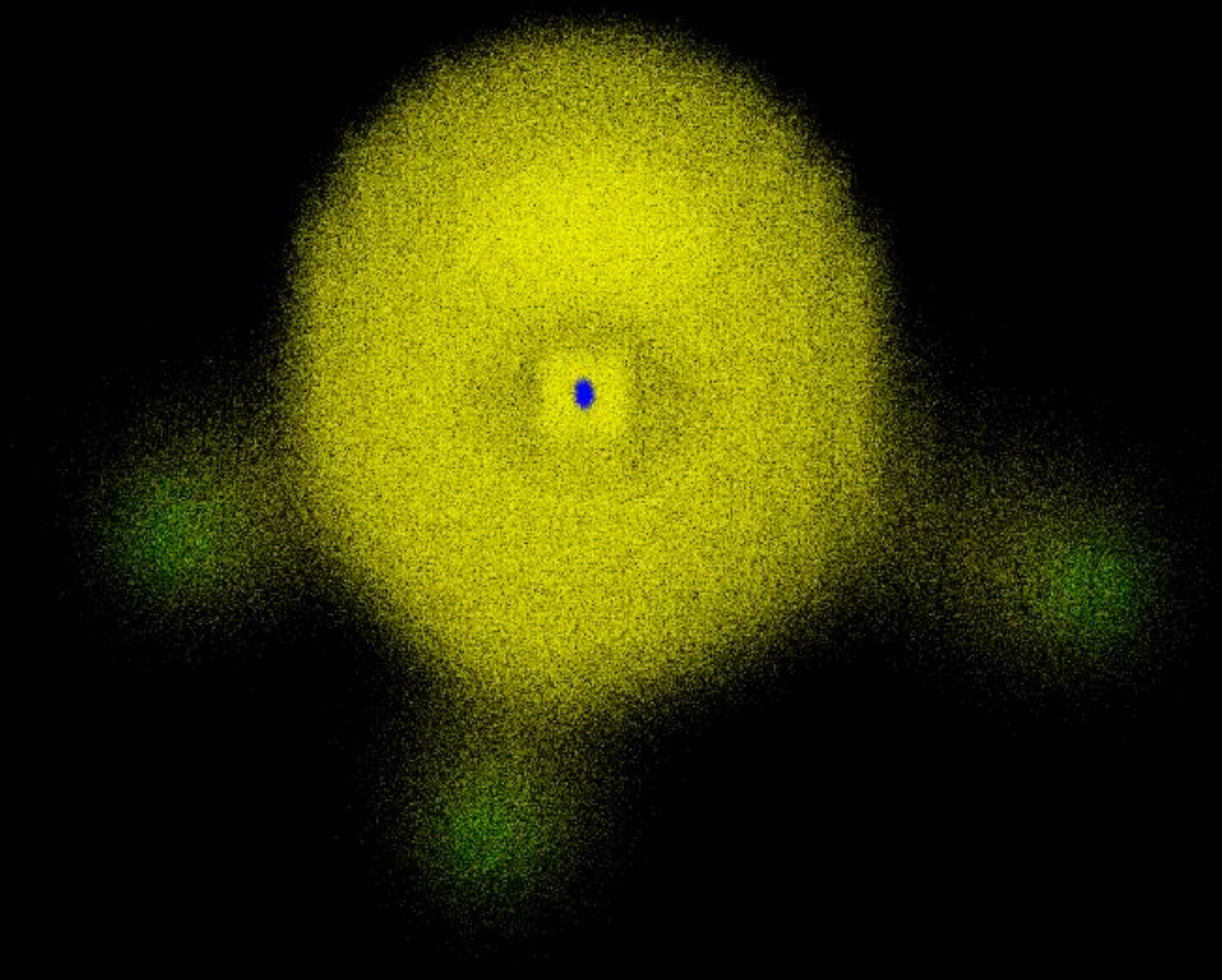
$$H\left(\mathbf{R},\mathbf{r}\right)\Psi^k\left(\mathbf{R},\mathbf{r}\right)=i\hbar\frac{\partial\Psi^k\left(\mathbf{R},\mathbf{r}\right)}{\partial t}$$

Quantum theory



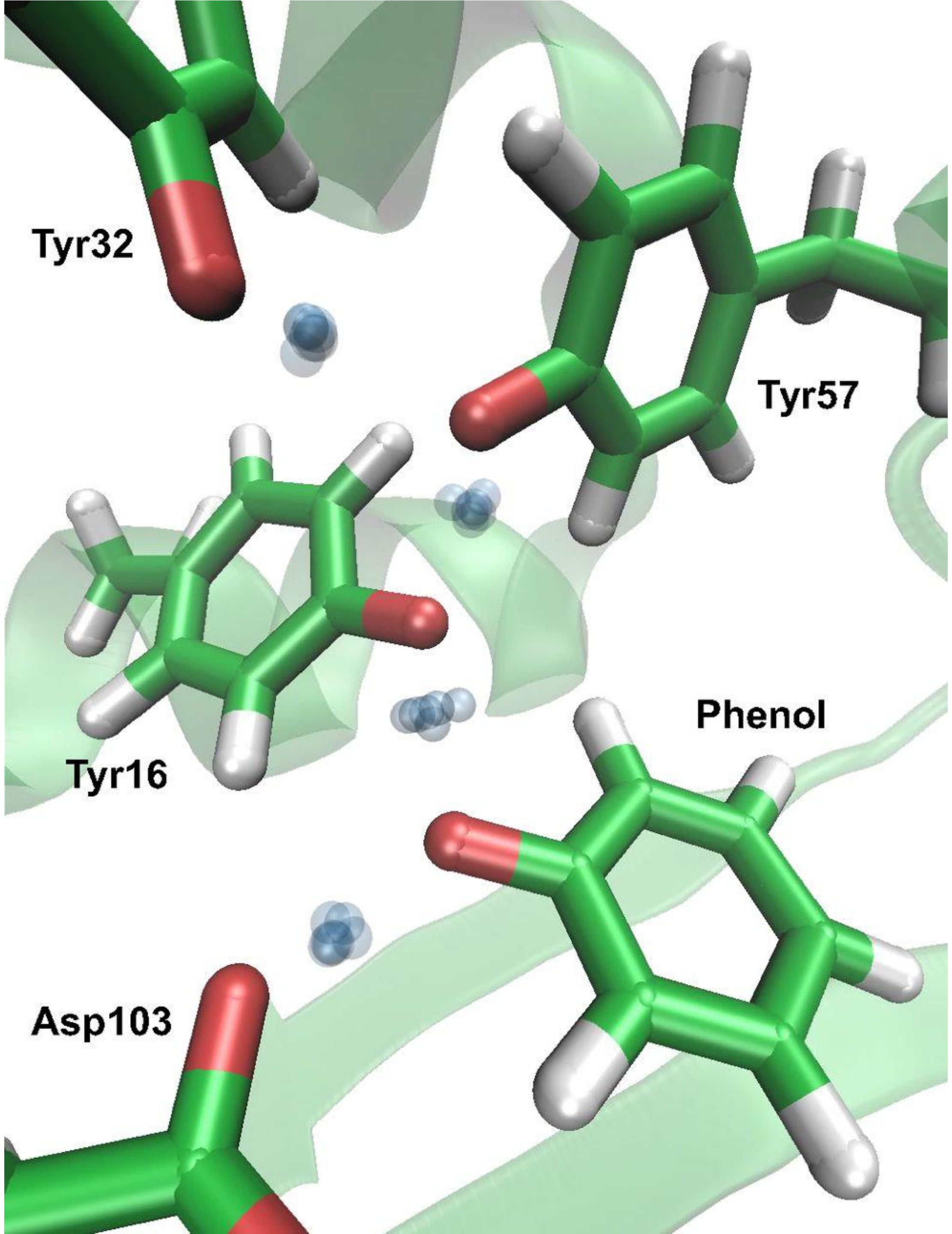
Delocalization predicted by quantum mechanics is central to describing molecules.

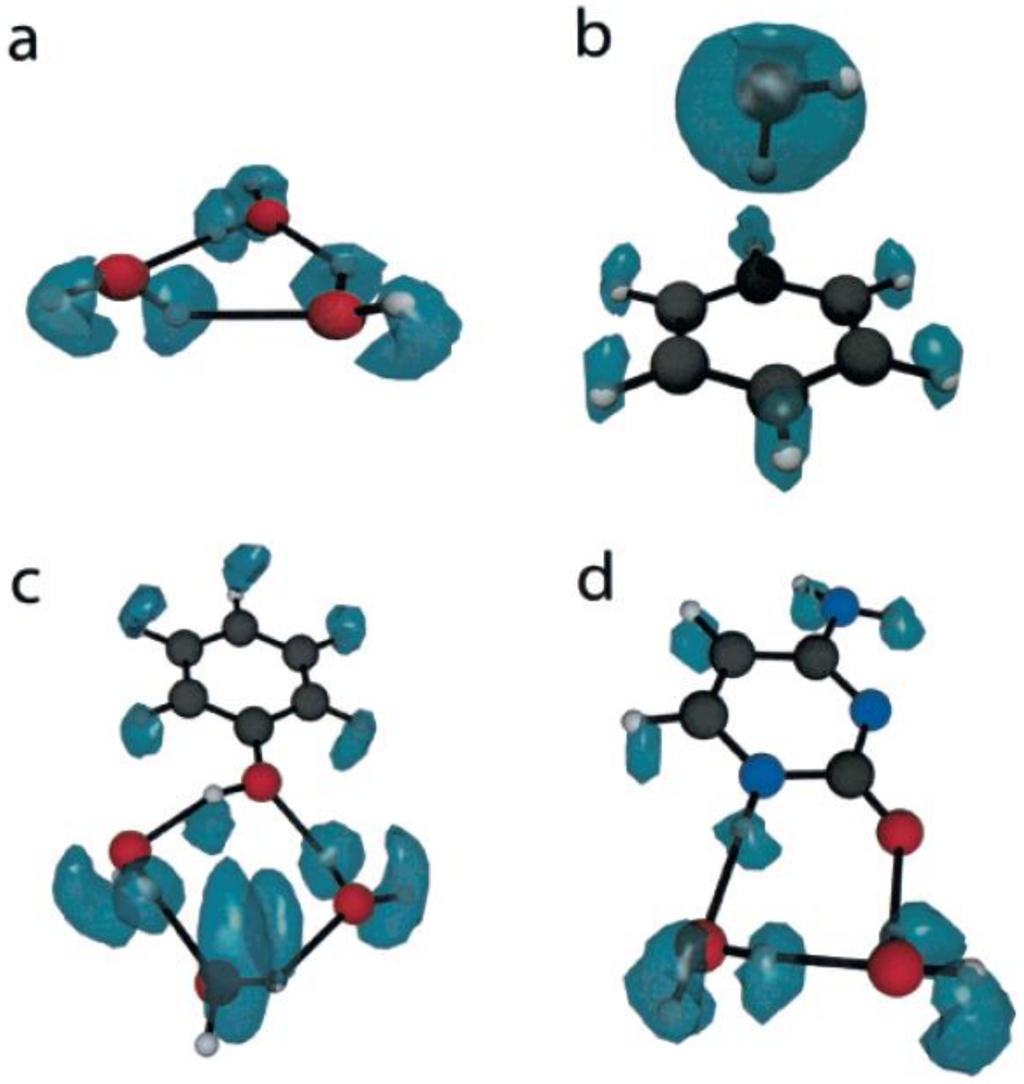
It affects both **electrons** and **nuclei**.



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





Clary *et al. Acc Chem Res* **2000,** *33*, 441

Nuclear–Electronic Orbital methods

BO molecular wave function

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

NEO molecular wave function

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

Hammes-Schiffer. *J Chem Phys* **2021,** *155*, 030901

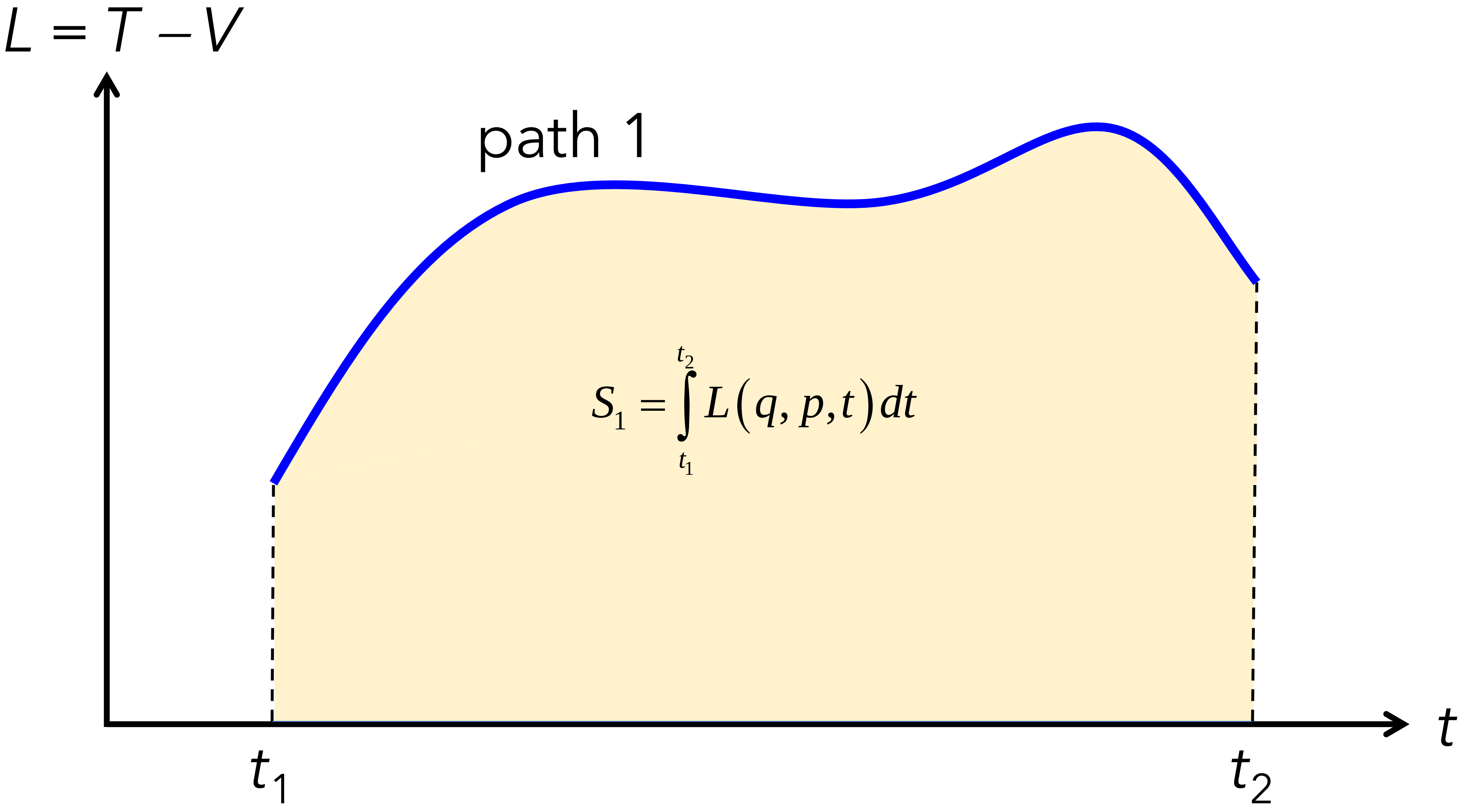
Framing molecules in the Core Theory

The Core Theory (Frank Wilczek)

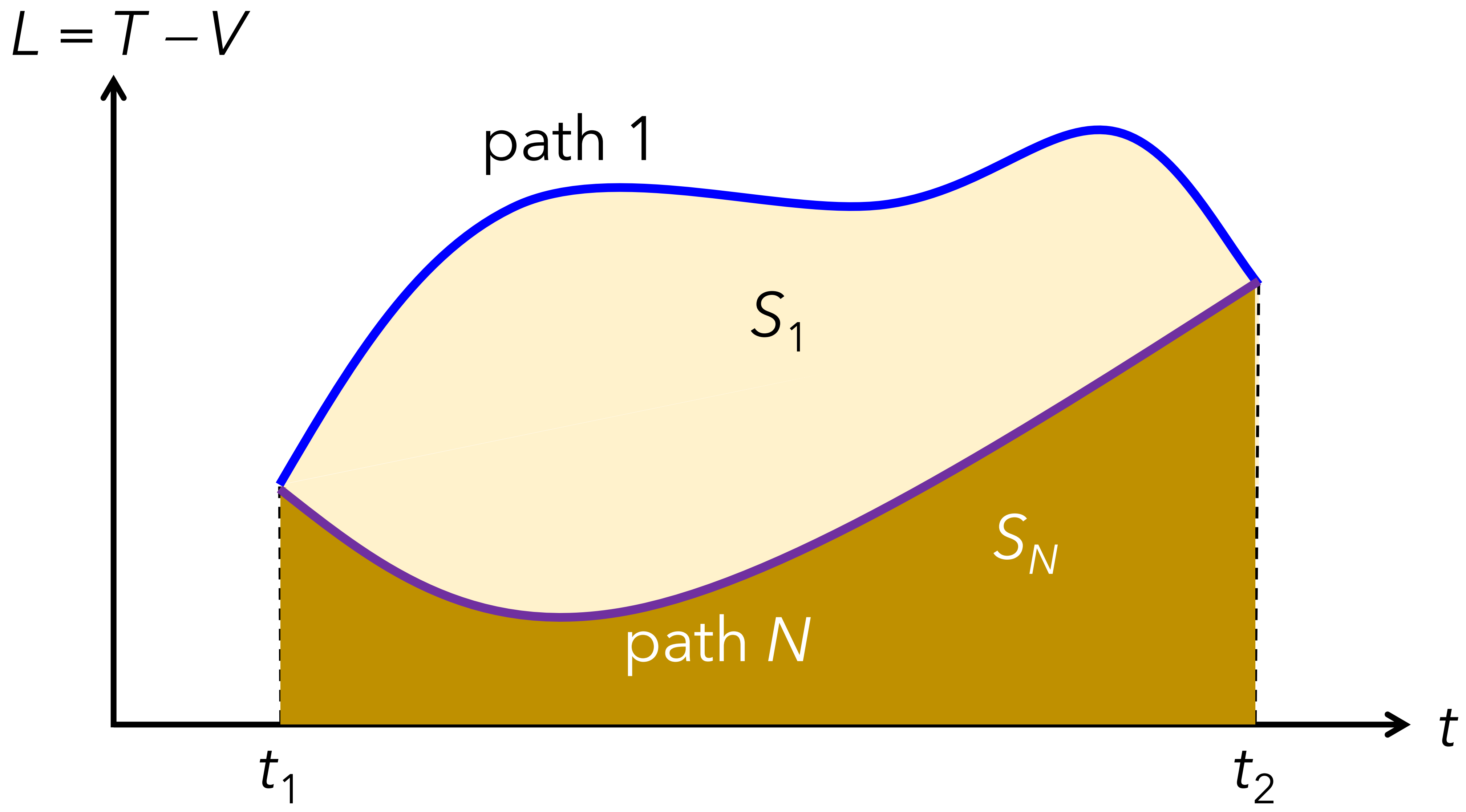
The Core Theory encompasses

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

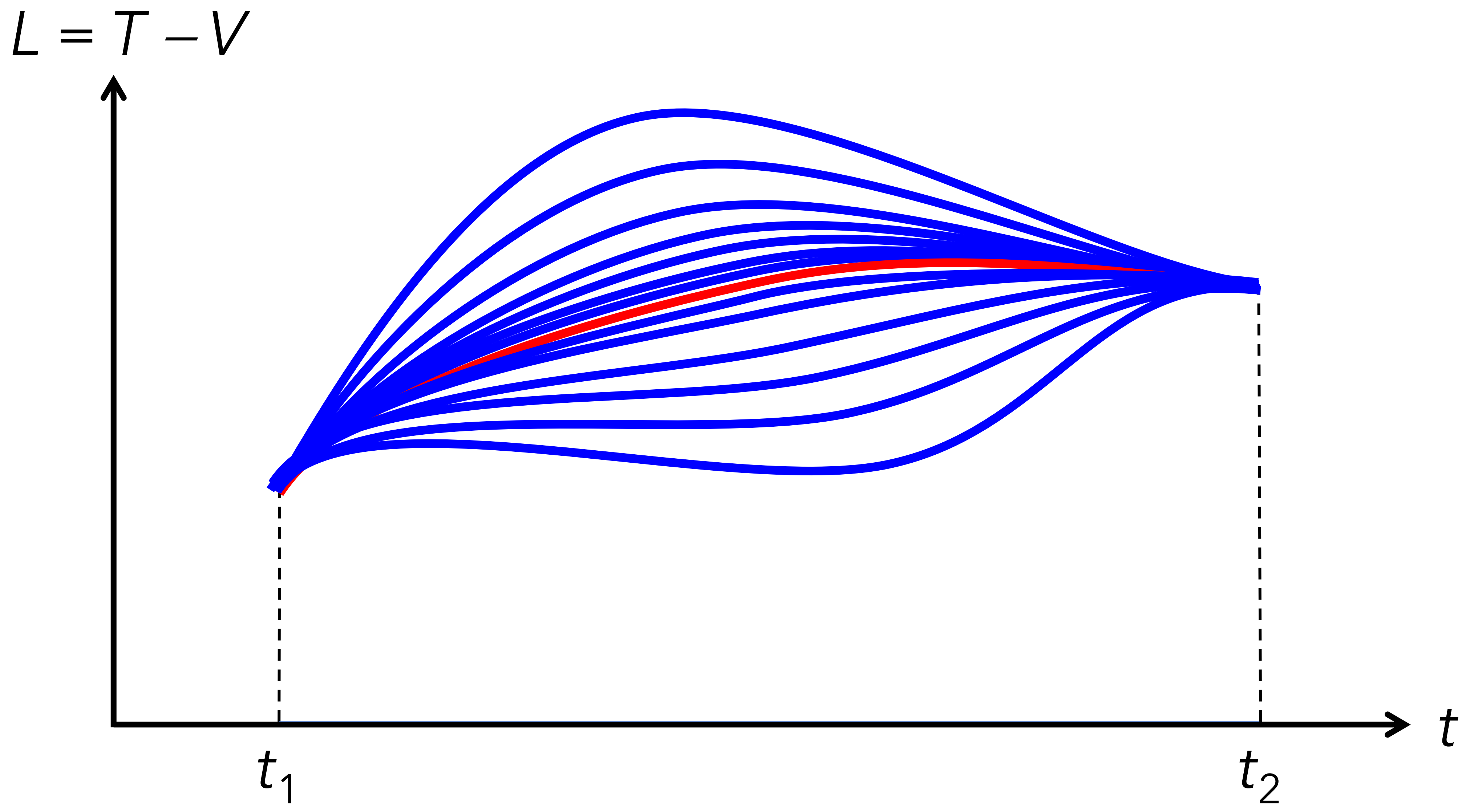
We can express the Core Theory in the language of path integrals



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.“

S. M. Carroll. The Big Picture


epistemological
pale blue dot

To know more:

Decoherence
- Sabine Hossenfeld, 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

Pilot wave
- PBS Space Time, youtu.be/RlXdsyctD50

Objective collapse
- Bassi *et al. Rev Mod Phys* **2013,** *85*, 471
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QBism
- Mermin. *Nature* **2014,** *507*, 421
- Corin S. Powell, Aeon Magazine, **2017**

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

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

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

Papers available for download at:
amubox.univ-amu.fr/s/xXAiMZrDPb9RMRX (Ask me for the password)

Demonstration of the classical limit of the Nuclear Schrödinger Equation

Messiah. Quantum Mechanics, 1961 (vol 1, p. 222)

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

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

Now, we make a lot of algebraic manipulation

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

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

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

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

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

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

$$+\frac{i}{\hbar}A(\mathbf{R},t)\nabla^2 S(\mathbf{R},t)\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)-\frac{1}{\hbar^2}A(\mathbf{R},t)\left(\nabla S(\mathbf{R},t)\right)^2\exp\left(\frac{i}{\hbar}S(\mathbf{R},t)\right)$$

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

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

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

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

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

$$+E_n(\mathbf{R})A(\mathbf{R},t)-i\hbar\partial_t A(\mathbf{R},t)+A(\mathbf{R},t)\partial_t S(\mathbf{R},t)=0$$

Separate real and imaginary terms

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

$$+E_n(\mathbf{R})A(\mathbf{R},t)-i\hbar\partial_t A(\mathbf{R},t)+A(\mathbf{R},t)\partial_t S(\mathbf{R},t)=0$$

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

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

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

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

$$\lim \hbar \to 0$$

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

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

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

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

That's the Hamilton-Jacobi equation!