



Fundamentals: Schrödinger Equation

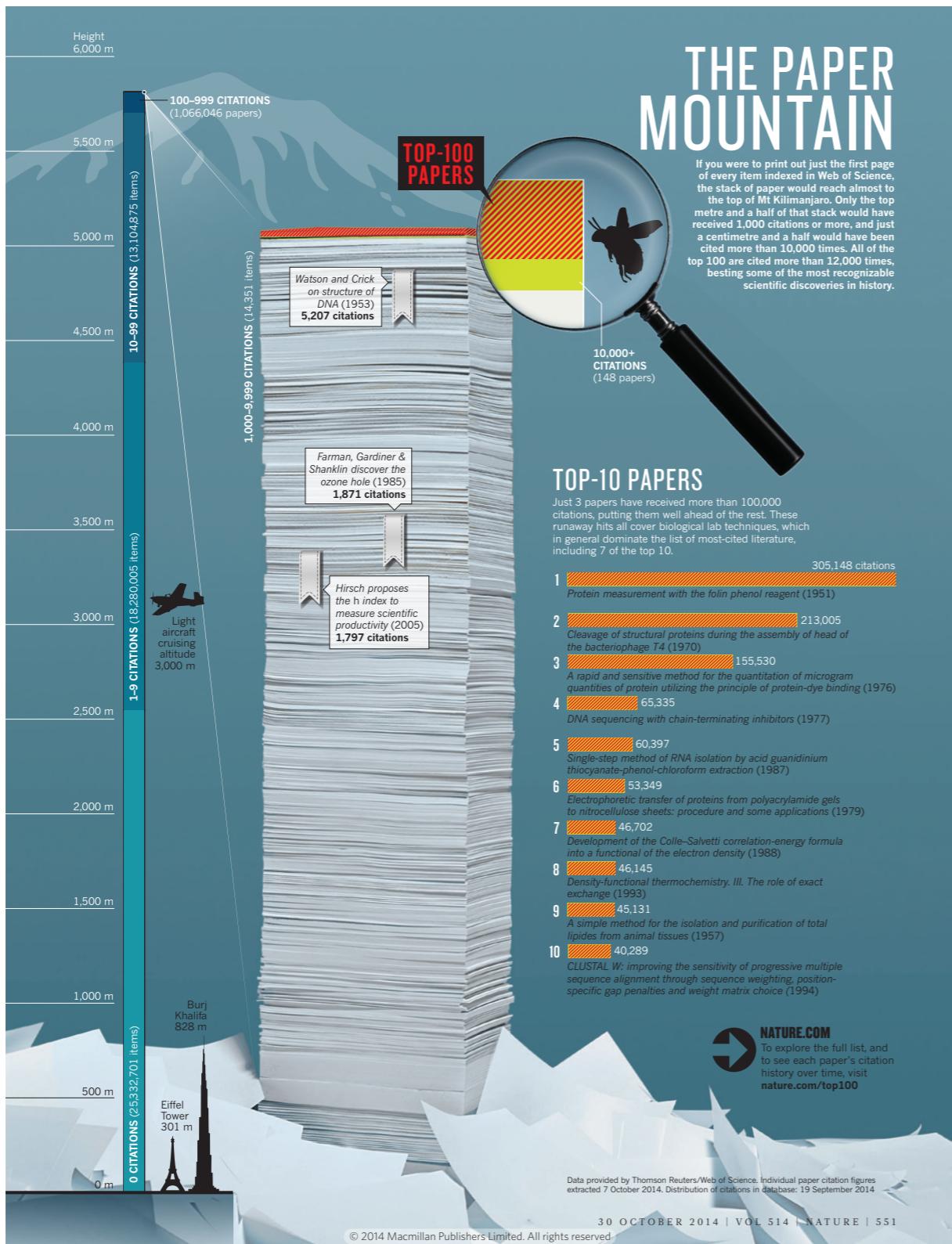
12th Conference of African Materials Research Society
Workshop: Introduction to Computational Materials Science

UniPod · College of Science & Technology
University of Rwanda · December 14, 2024

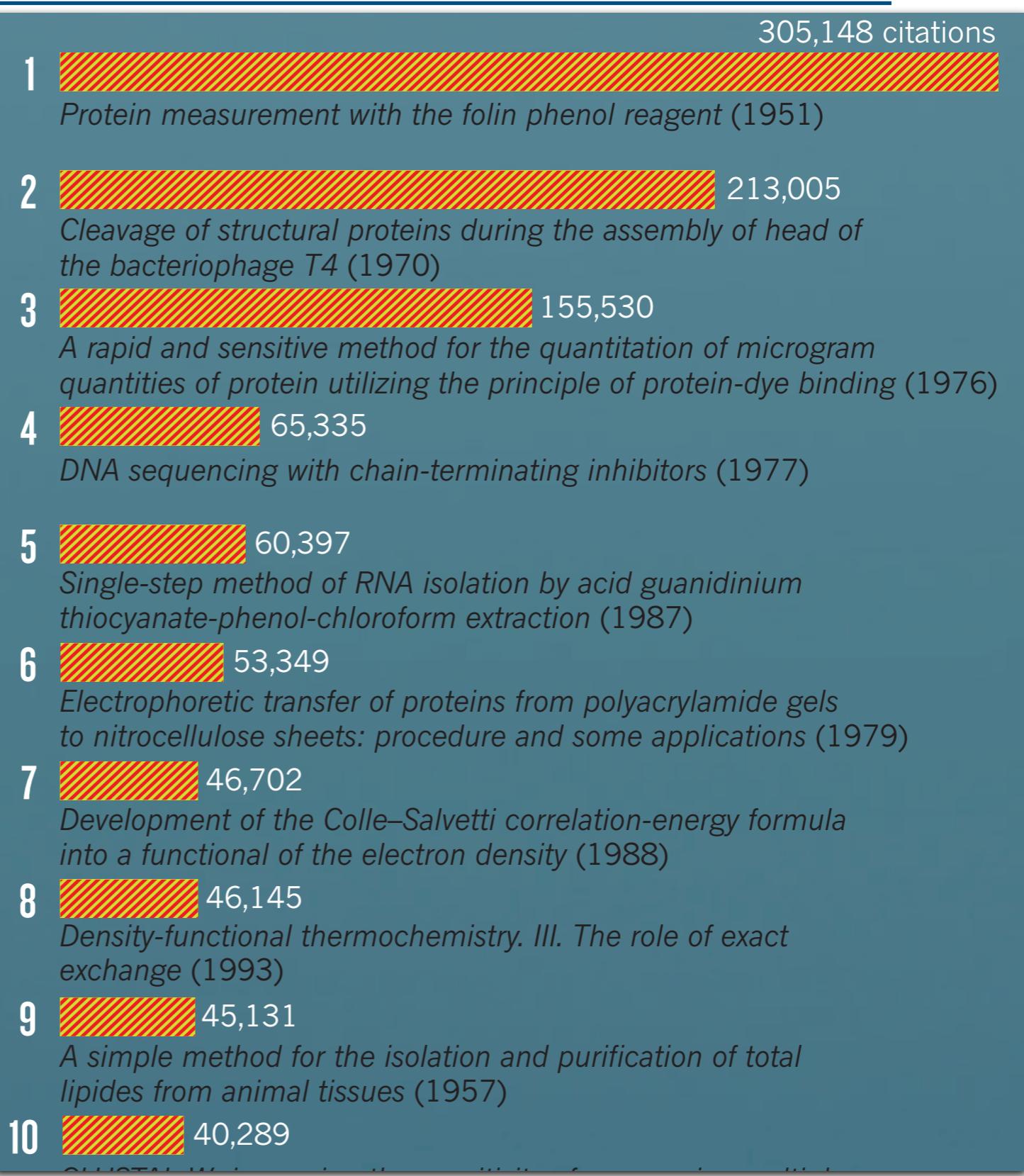
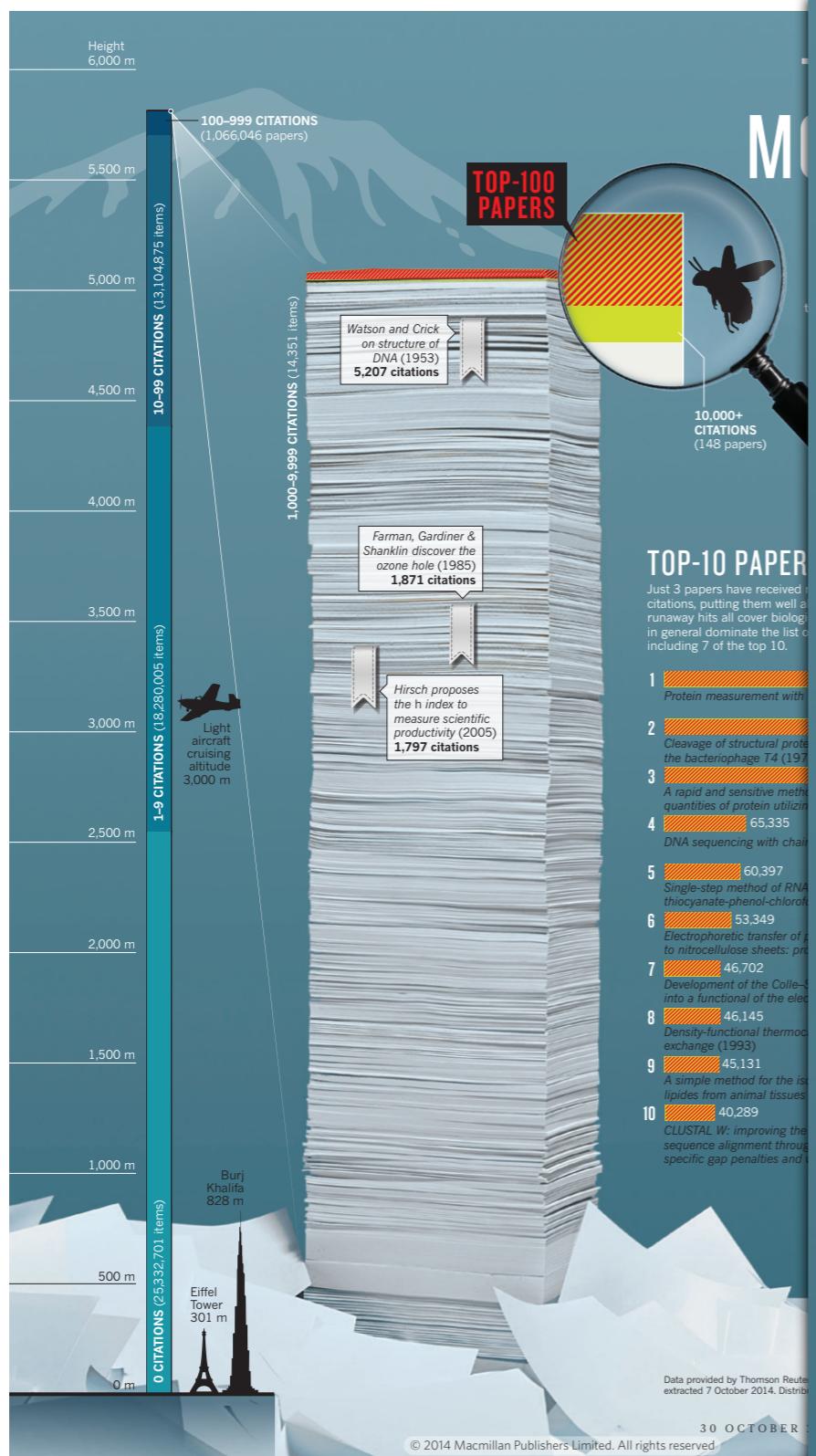


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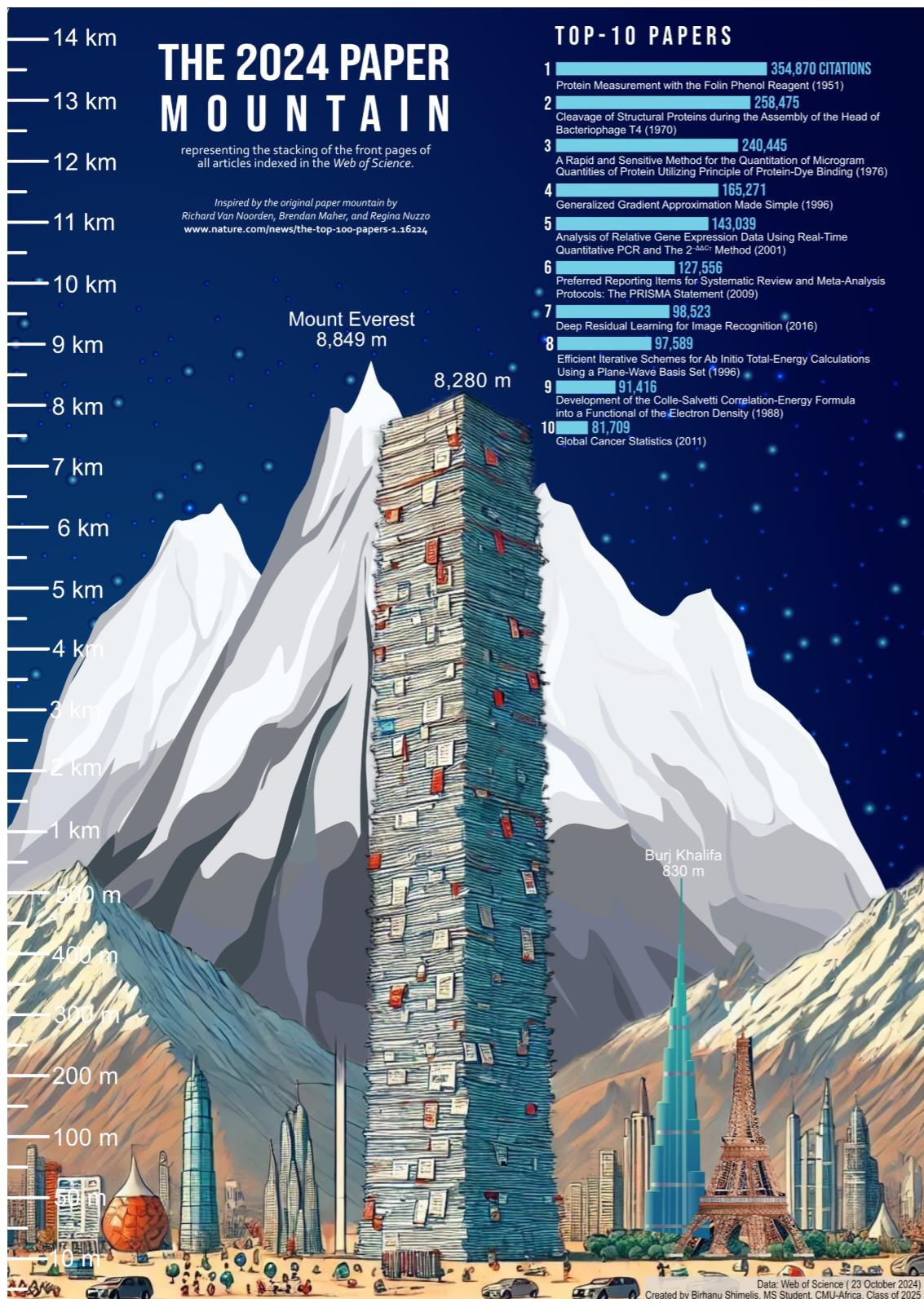
Why this workshop...



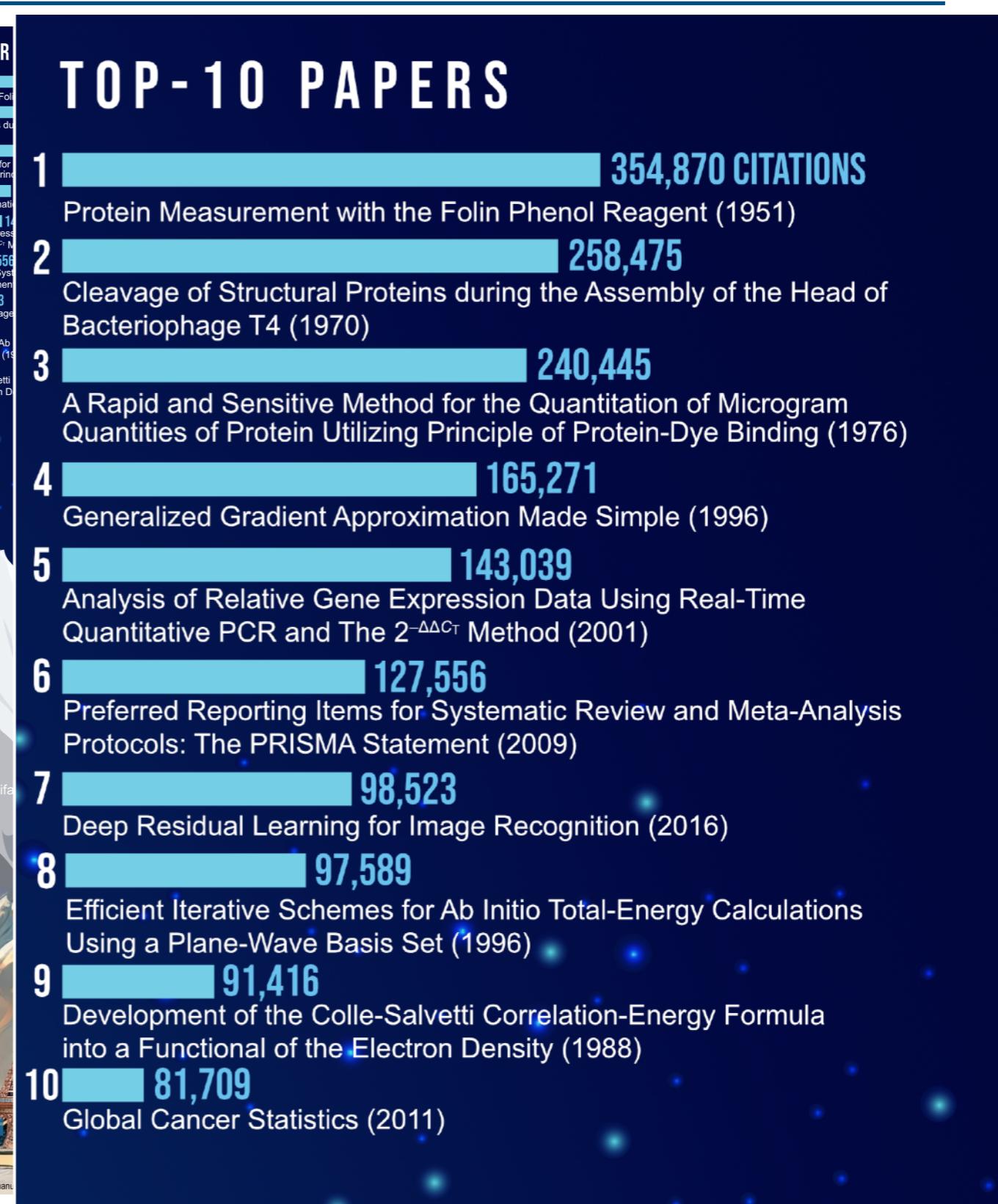
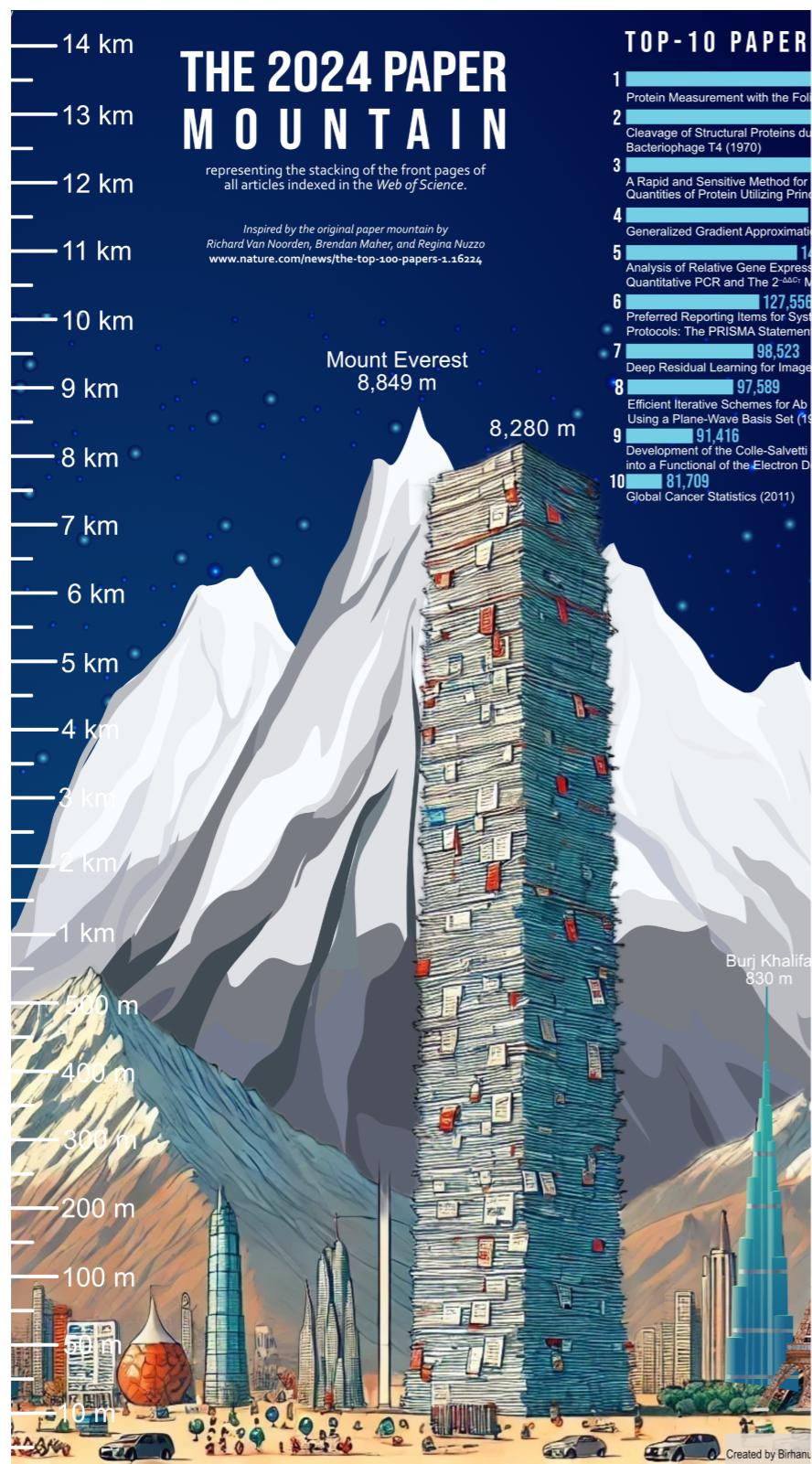
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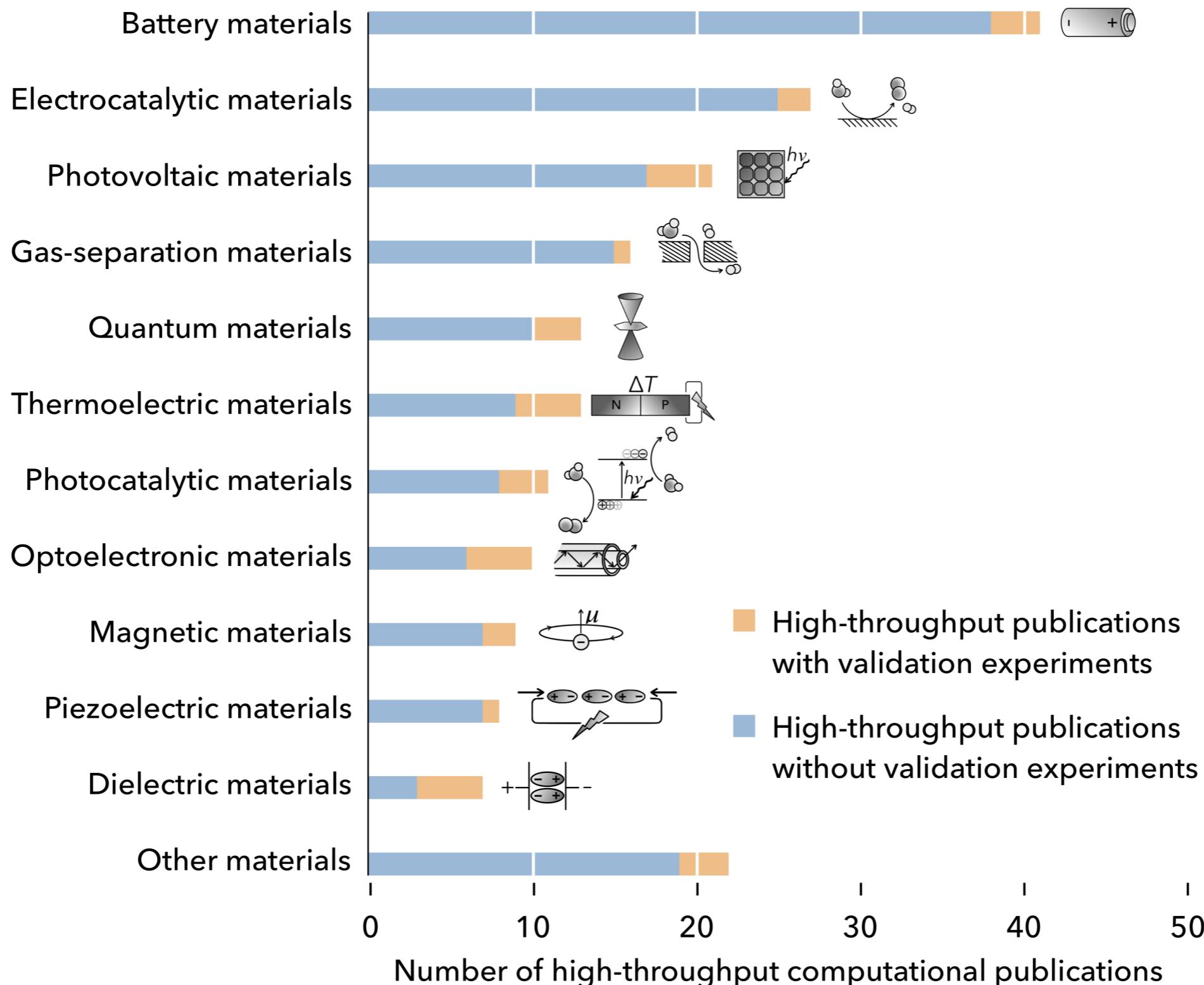
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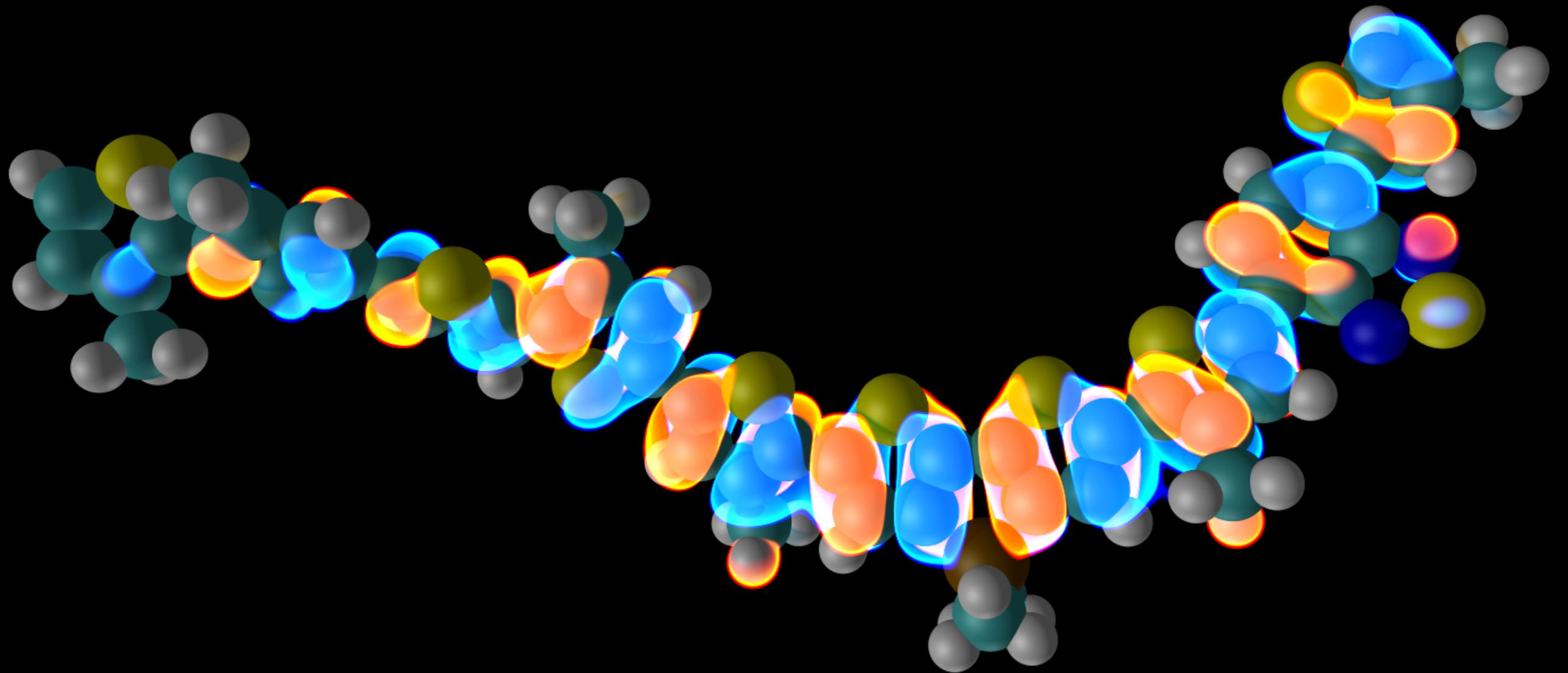
Why this workshop...



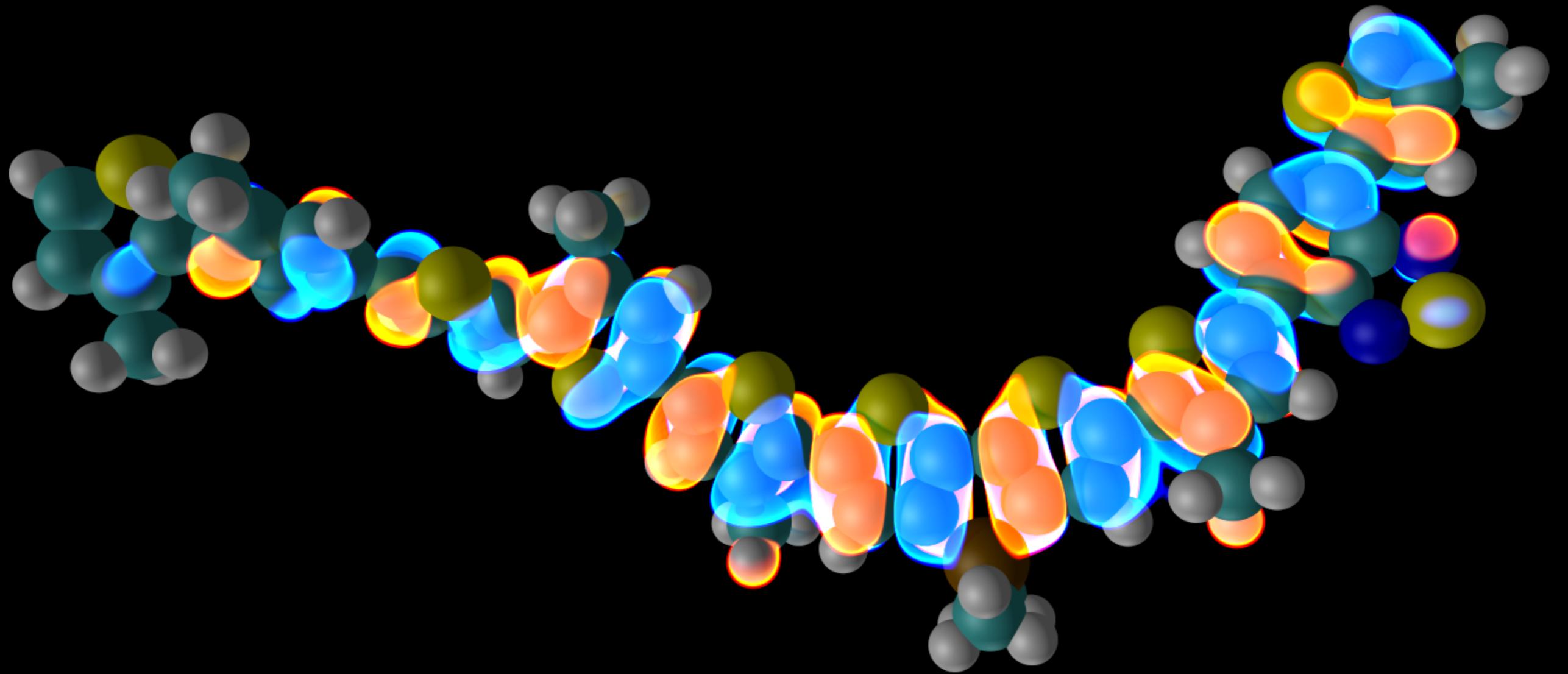
Towards materials discovery for technology



Why quantum mechanics to simulate materials

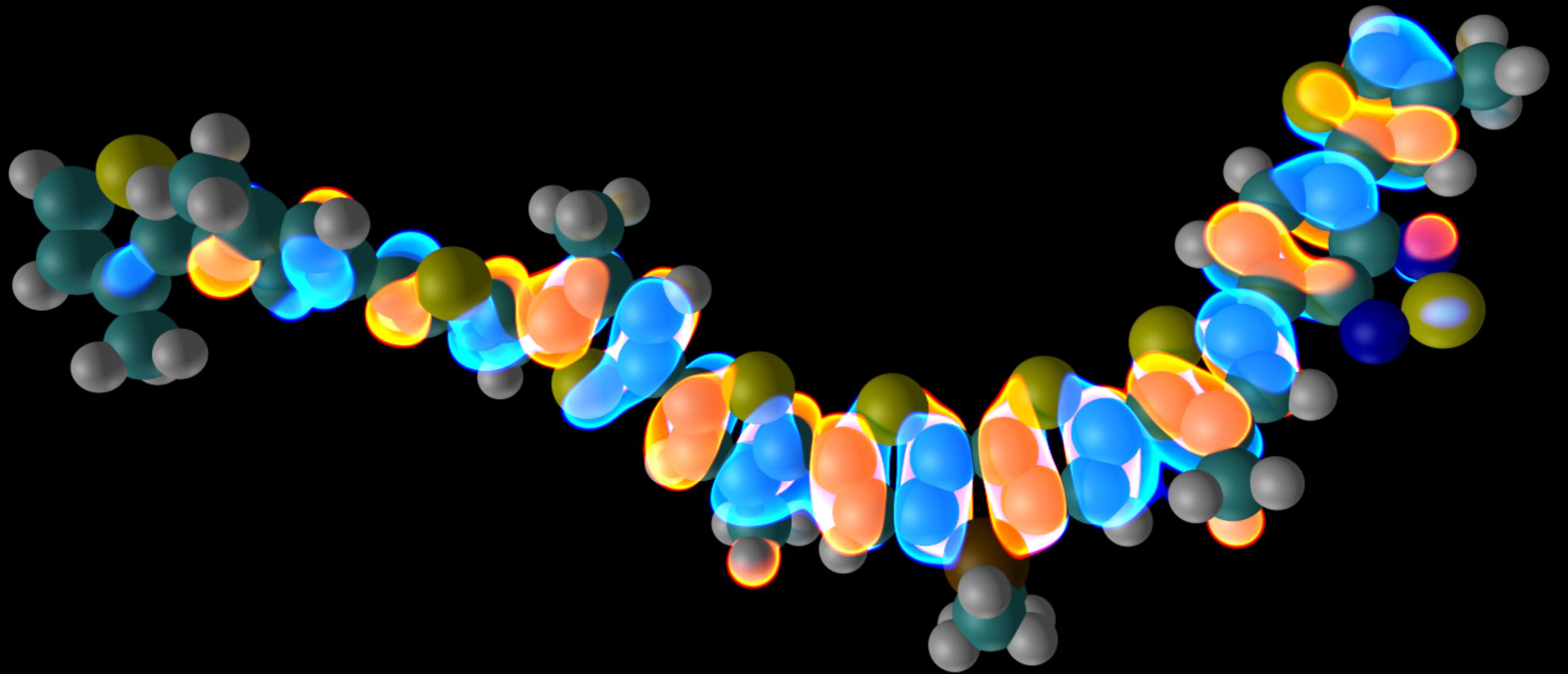


material = nuclei + electrons



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$$\begin{array}{c} \{} \\ \{} \\ + \quad - \end{array}$$

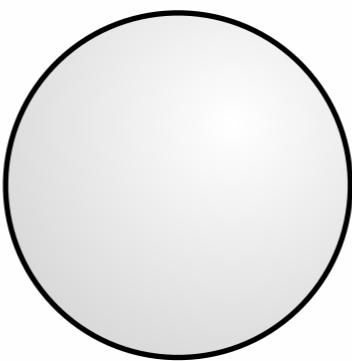


material = nuclei + electrons

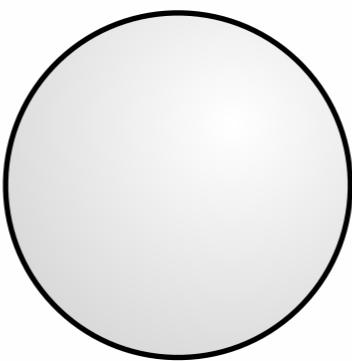


'glue'

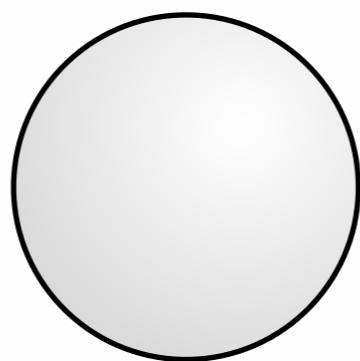
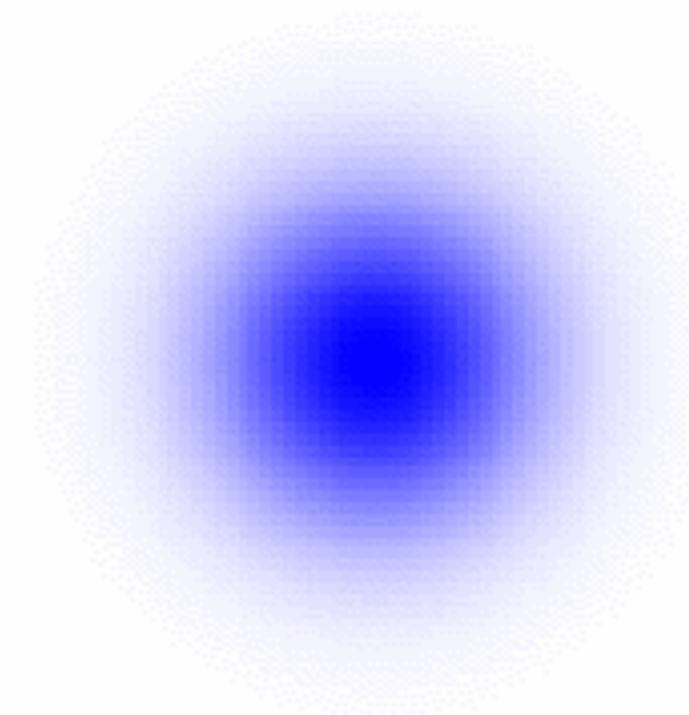
Classical mechanics vs. quantum mechanics



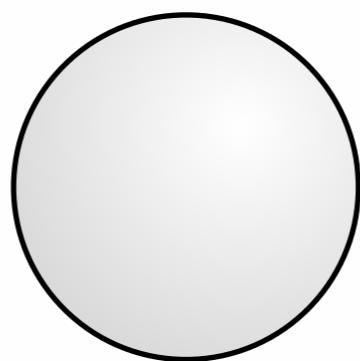
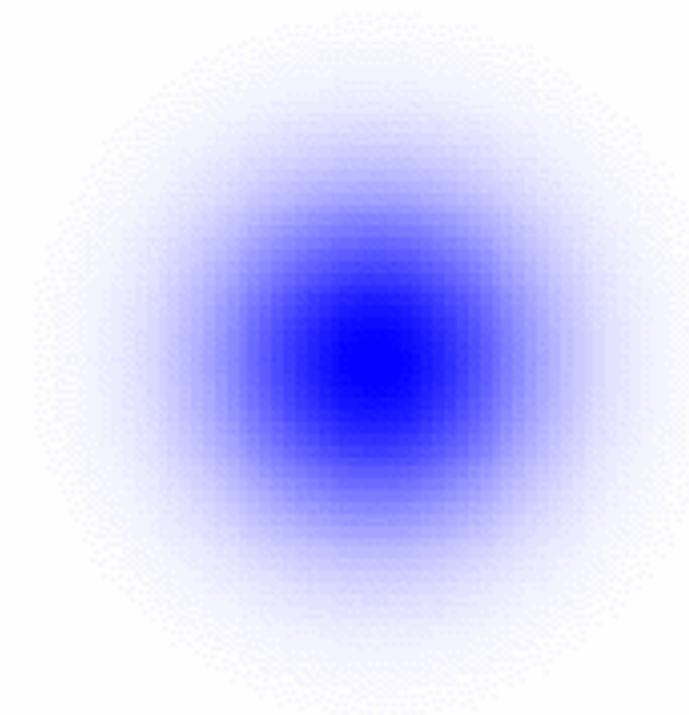
Newton's law



Newton's law

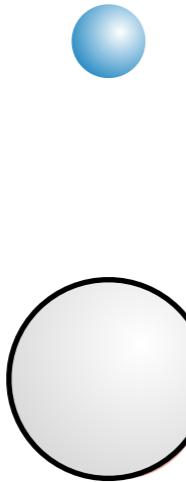


Schrödinger's equation



Schrödinger's equation

Classical mechanics vs. quantum mechanics

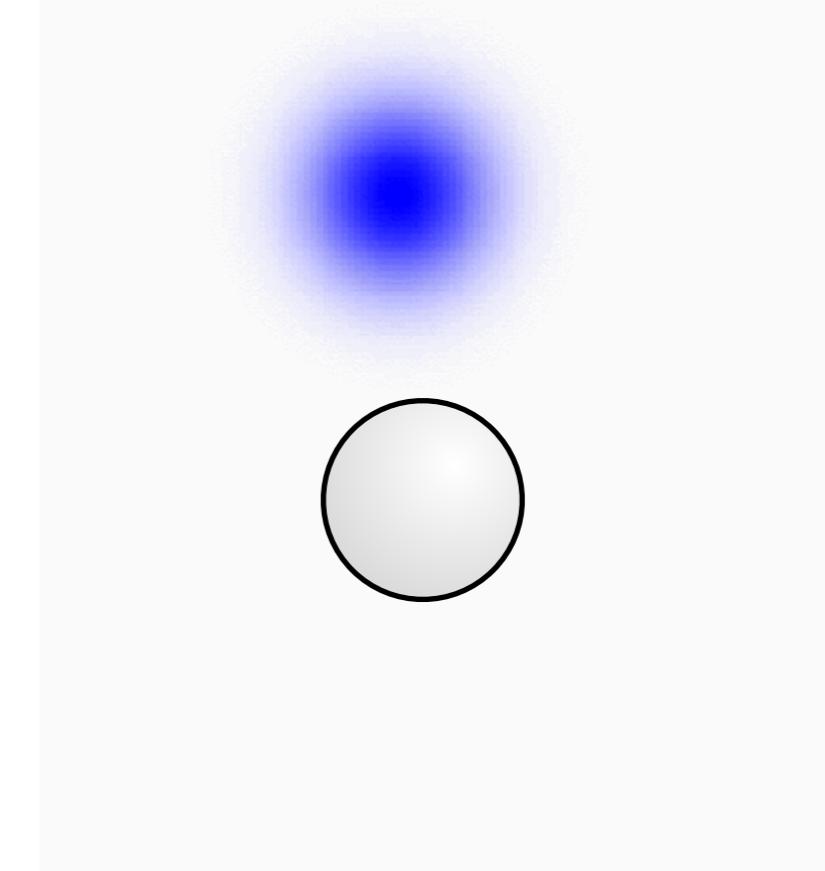


In classical mechanics,
electrons are points

Classical mechanics vs. quantum mechanics

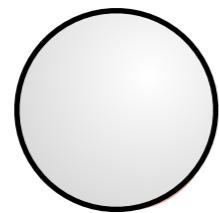


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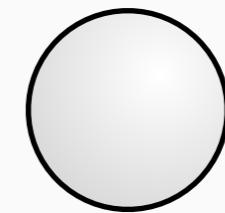


In quantum mechanics,
electrons are clouds

Classical mechanics vs. quantum mechanics



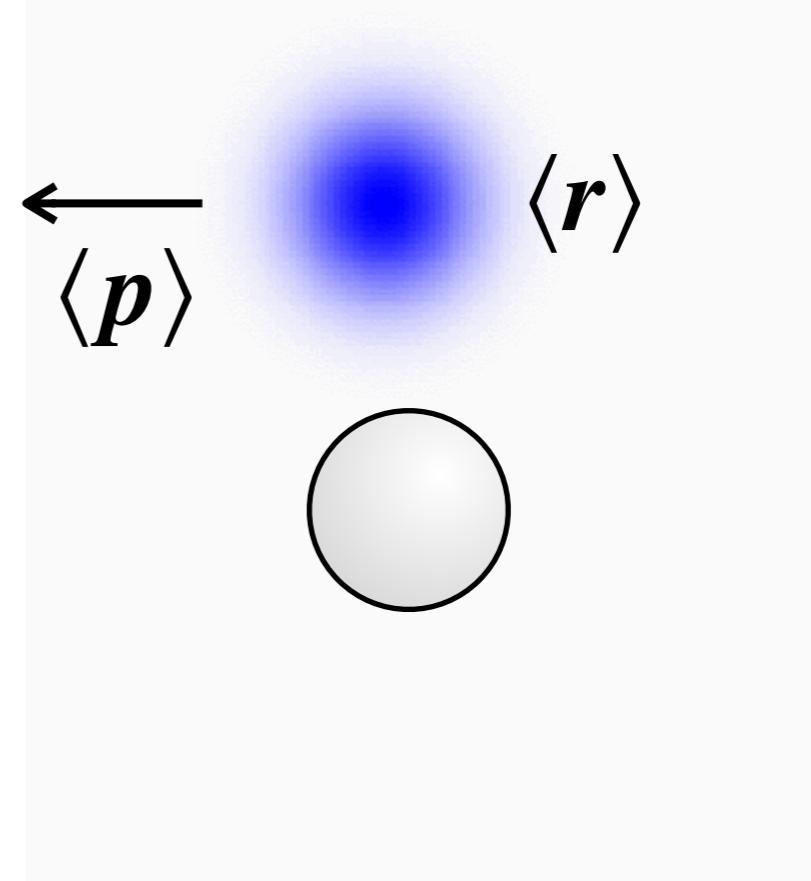
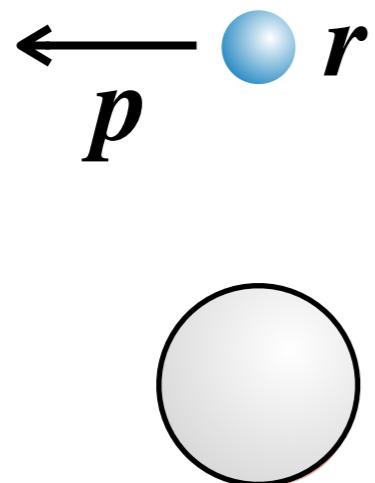
In classical mechanics,
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In quantum mechanics,
electrons are clouds

In both classical mechanics and quantum mechanics,
electrons have a mass m ...

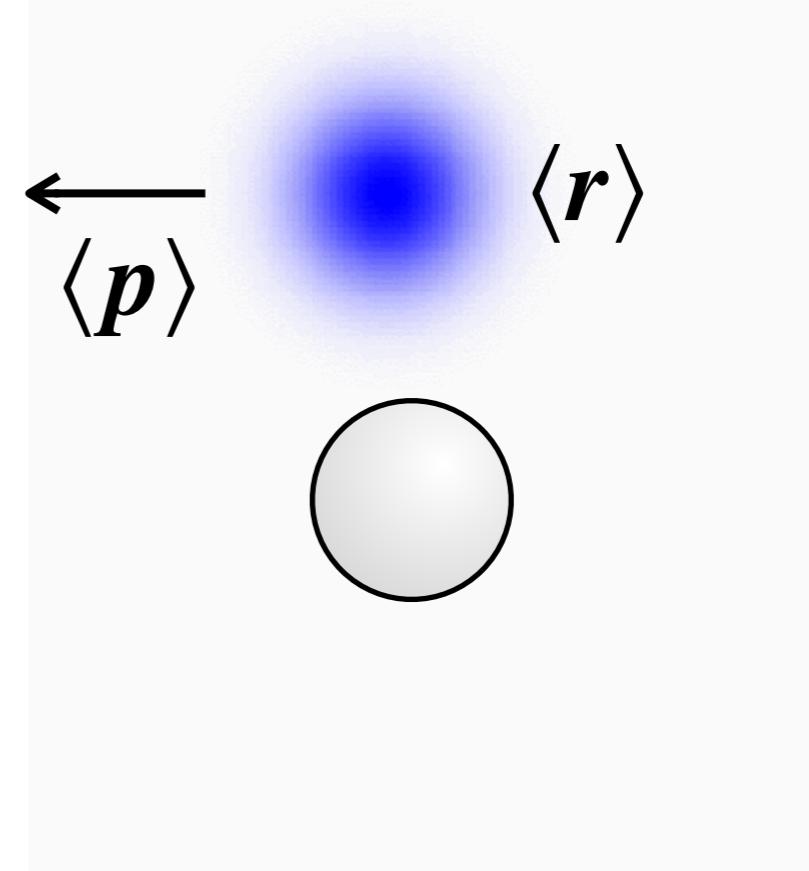
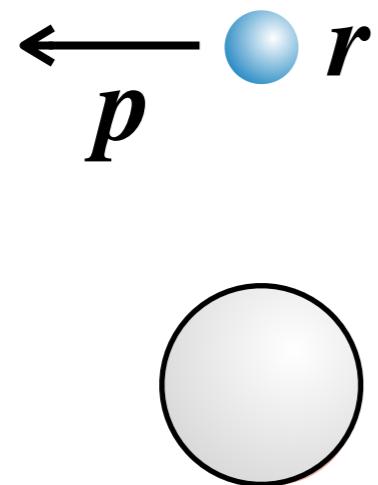
Classical vs. quantum mechanics



... but in classical mechanics, the
position p and **momentum r**
are precisely known...

... while in quantum mechanics,
only the their averages
 $\langle p \rangle$ and $\langle r \rangle$ are known.

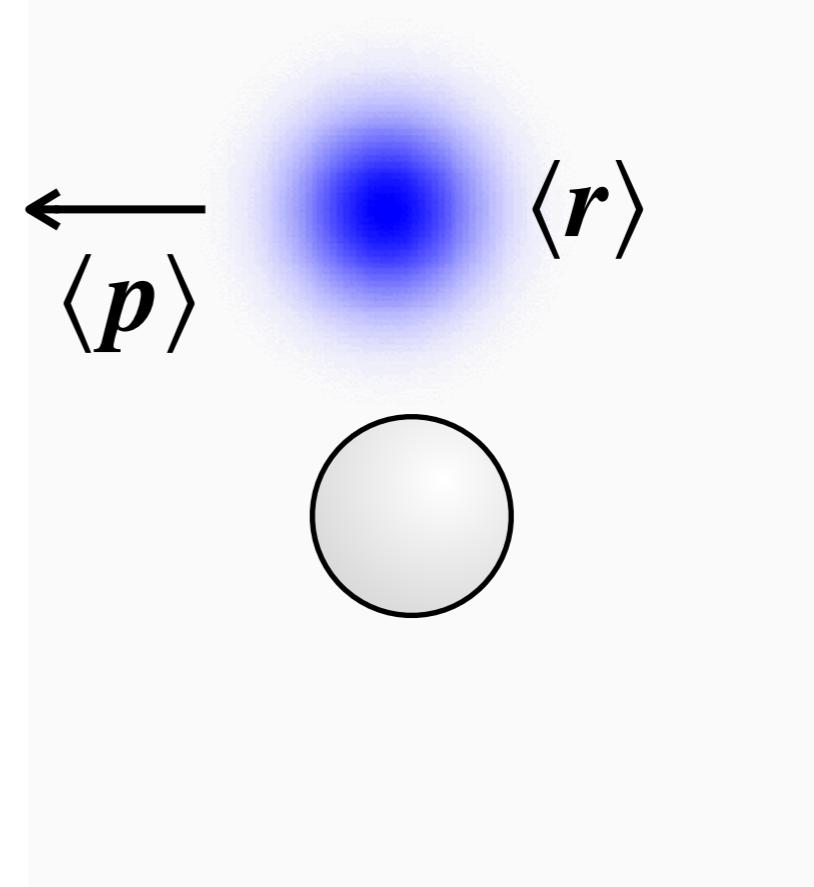
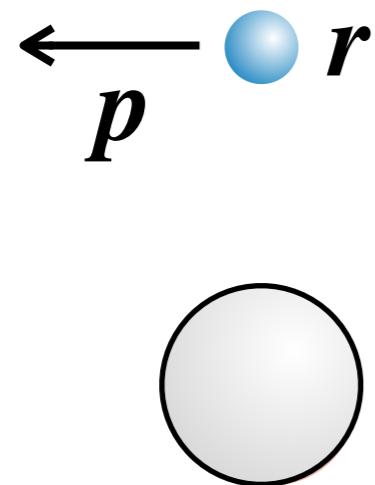
Classical vs. quantum mechanics (cont'd)



In classical mechanics, p and r completely define the electron state and electron energy E

$$(r, p) \longmapsto E$$

Classical vs. quantum mechanics (cont'd)



In classical mechanics, \mathbf{p} and \mathbf{r} completely define the electron state and electron energy E

$$(\mathbf{r}, \mathbf{p}) \longmapsto E$$

In quantum mechanics, $\langle \mathbf{p} \rangle$ and $\langle \mathbf{r} \rangle$ do not completely define the electron state and electron energy E

$$\psi \longmapsto E$$



wave function

Wave function of an electron

Definition | wave function

The wave function $\psi(\mathbf{r})$ of an electron is a function of the space variable \mathbf{r} describing the state of the electron. Its values are complex. Its square modulus gives the probability density: $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$.

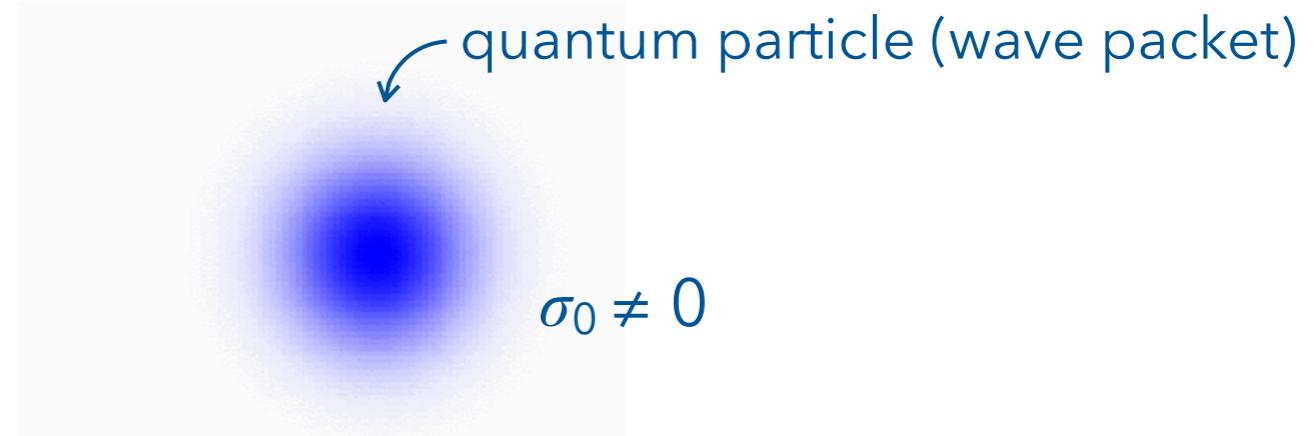
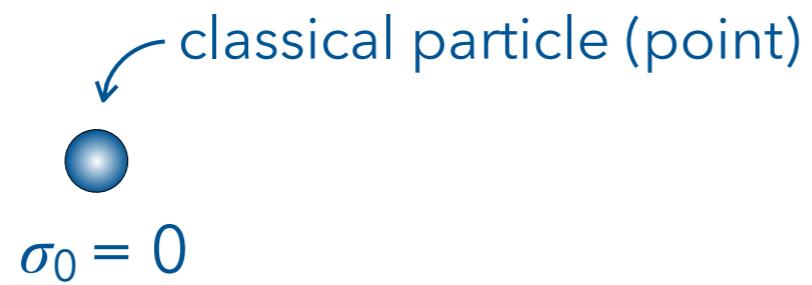
- ▶ **Note.** The total probability $\int \rho(\mathbf{r}) d\mathbf{r}$ is always equal to 100%. This important property is known as the **normalization condition**.

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- ▶ **Note.** The total probability $\int \rho(\mathbf{r}) d\mathbf{r}$ is always equal to 100%. This important property is known as the **normalization condition**.
- ▶ **Example.** A wave packet is a type of wave function describing an electron around an average location \mathbf{r}_0 with a given spread σ_0 .



Wave function of an electron (cont'd)

Definition | wave function

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- ▶ **Problem.** In one dimension ($d = 1$), the wave packet reads

$$\psi(x) = \frac{1}{(2\pi\sigma_0^2)^{\frac{1}{4}}} \exp\left(-\frac{(x - x_0)^2}{4\sigma_0^2}\right) \exp(ik_0x)$$

Complete the notebook [0_Example_of_Wave_Function.ipynb](#) to plot the real part, imaginary part, and probability of the wave packet for $x_0 = 0$, $k_0 = 1$, $\sigma_0 = 5$ units. Verify that the normalization condition is fulfilled.

How to find the state and energy of an electron

Energy of an electron

- The **kinetic energy** and potential energy can be expressed as

$$K = \int \psi^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) \right) d\mathbf{r} = -\frac{\hbar^2}{2m_e} \int \psi^*(\mathbf{r}) \nabla^2 \psi(\mathbf{r}) d\mathbf{r}$$

$$U = \int \psi^*(\mathbf{r}) v(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = \int v(\mathbf{r}) \psi^*(\mathbf{r}) \psi(\mathbf{r}) d\mathbf{r} = \int v(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}$$

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Energy of an electron

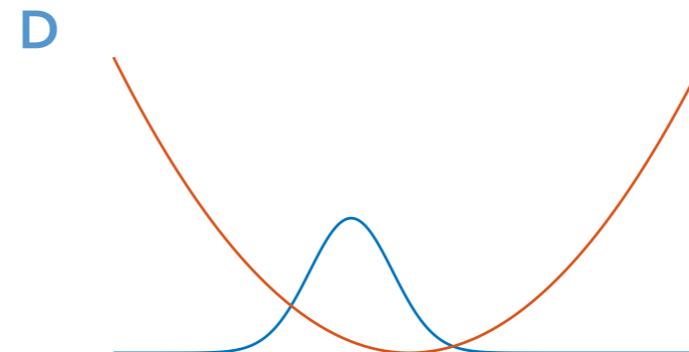
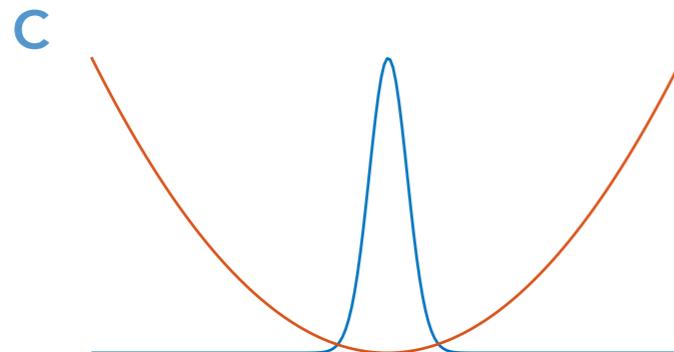
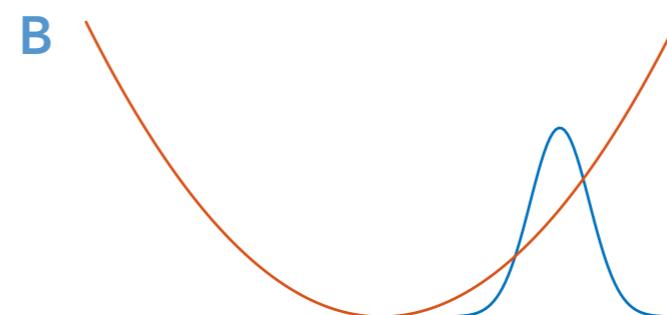
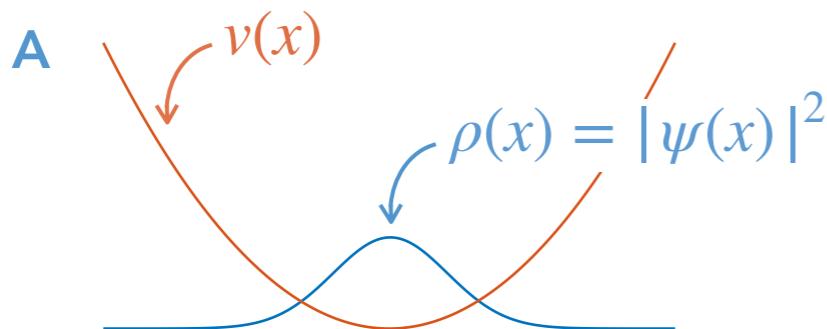
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- Problem.** Find the order of K and U for the 4 cases below:



Energy of an electron

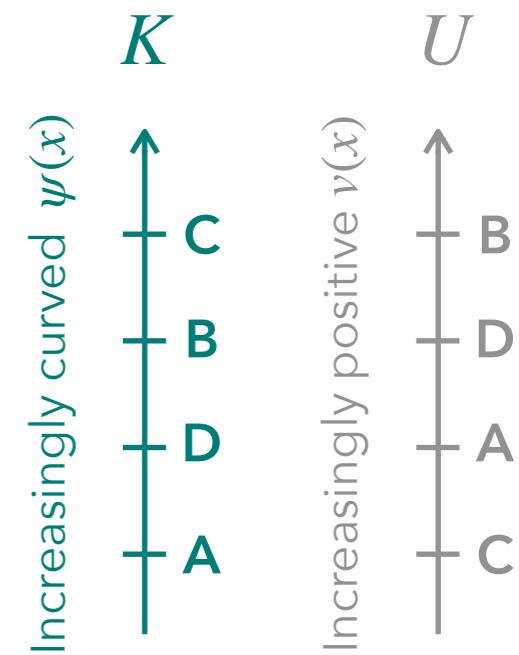
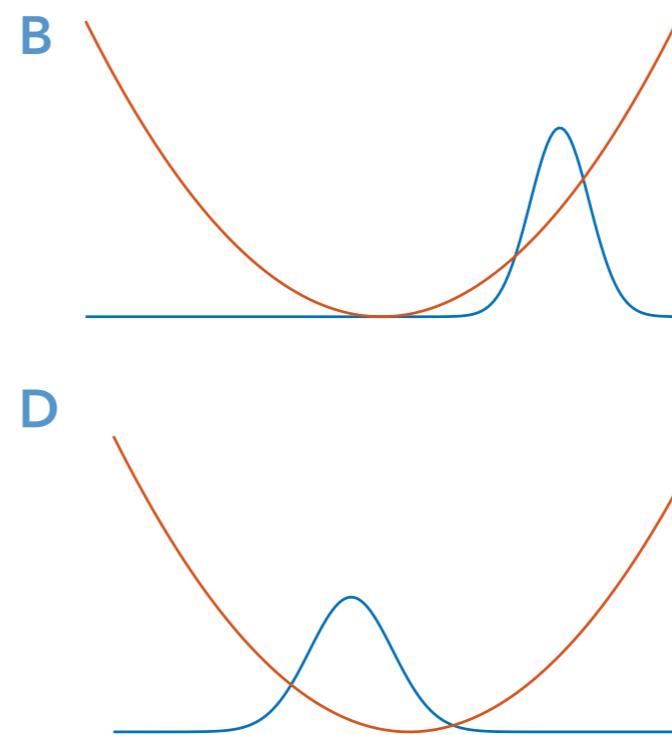
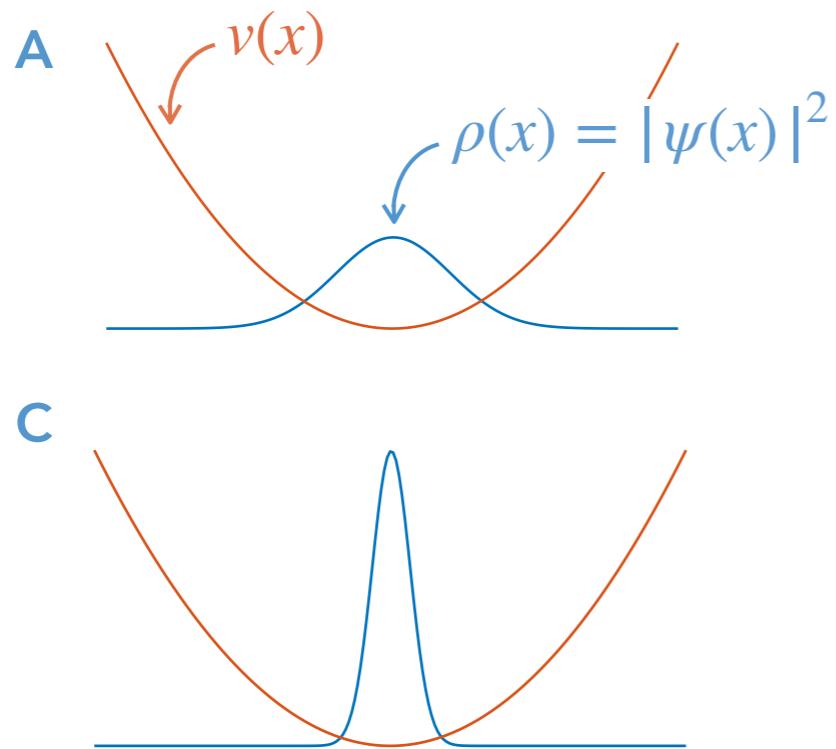
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Energy of an electron

- Consequently, the **total energy** of an electron is a competition a driving force to spread out and driving force to concentrate around the minimum of the potential

$$E = \int \psi^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) + v(\mathbf{r}) \psi(\mathbf{r}) \right) d\mathbf{r}$$

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- In quantum mechanics, we often use **simplifying notations**

$\hat{}$ denotes an operator
 $\hat{H} \equiv -\frac{\hbar^2}{2m_e} \nabla^2 + v(\mathbf{r})$
Hamiltonian

$$\langle f | g \rangle \equiv \int f^*(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}$$

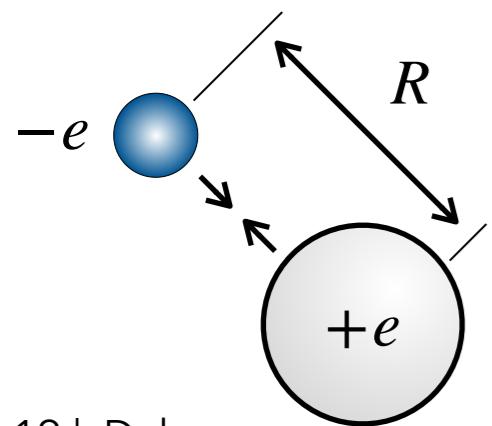
An operator is an instruction to perform a certain calculation on an object (here, a wave function)

Rydberg atomic units

- In quantum mechanics, it is convenient to work in **atomic units**

Quantity	Symbol	Atomic Units	S.I. Units
Energy	Ry	1 a.u. (of energy)	2.18×10^{-18} J (= 13.6 eV)
electron charge	e	$\sqrt{2}$ a.u. (of charge)	1.60×10^{-19} C
electron mass	m	$\frac{1}{2}$ a.u. (of mass)	9.11×10^{-31} kg
Bohr radius	a_0	1 a.u. (of length)	0.529×10^{-10} m
permittivity of free space	ϵ_0	$\frac{1}{4\pi}$ a.u.	8.85×10^{-12} C ² .N ⁻¹ .m ⁻²
Planck's constant	\hbar	1 a.u.	1.054×10^{-34} J.s

- Example.** In Rydberg atomic units, we get



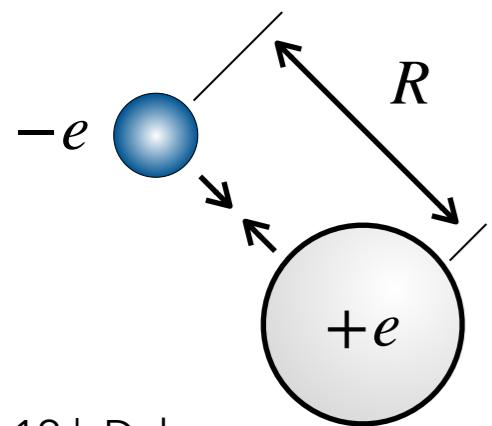
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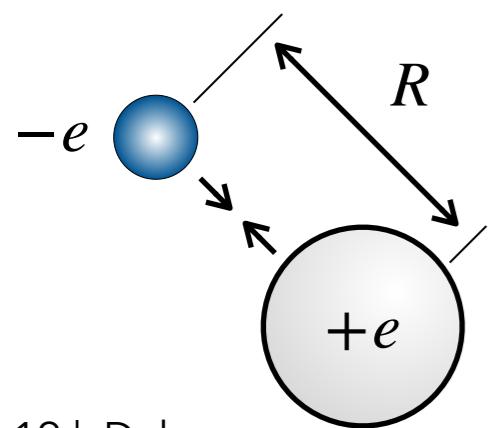
$$\hat{H} \equiv -\frac{\hbar^2}{2m_e} \nabla^2 + v(\mathbf{r}) \quad \longrightarrow \quad \hat{H} \equiv -\nabla^2 + v(\mathbf{r})$$
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$$\hat{H} \equiv -\frac{\hbar^2}{2m_e} \nabla^2 + v(\mathbf{r}) \quad \longrightarrow \quad \hat{H} \equiv -\nabla^2 + v(\mathbf{r})$$
$$-\frac{e^2}{4\pi\epsilon_0 R} \quad \longrightarrow \quad -\frac{2}{R}$$

How to compute the equilibrium state and energy of an electron

Equilibrium states

- ▶ In quantum mechanics, the equilibrium states of an electron can be found by solving an eigenvalue problem

Definition | (time-independent) Schrödinger equation

The equilibrium states ψ of an electron for a system described by the Hamiltonian \hat{H} can be determined by solving

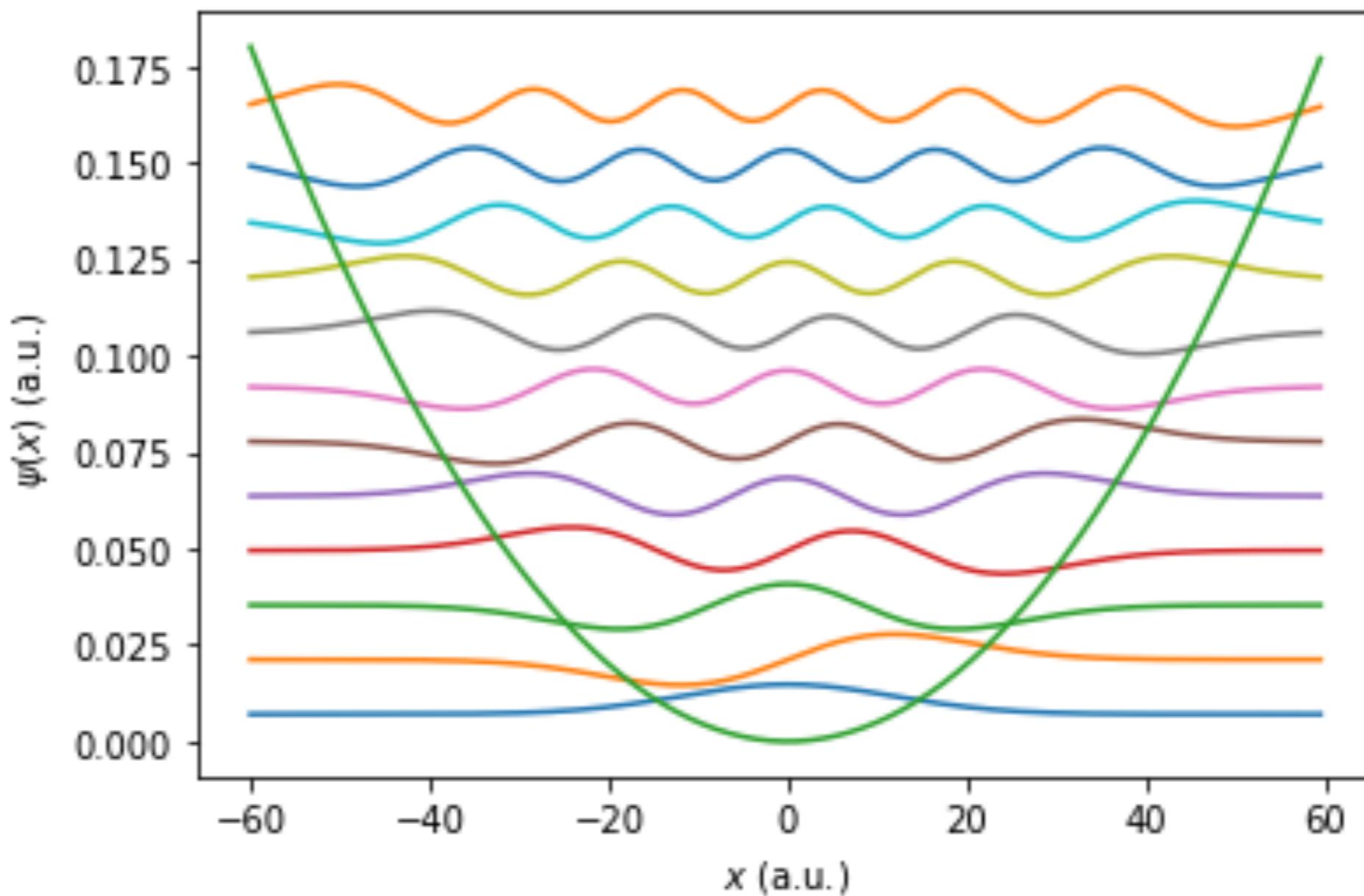
$$\hat{H}\psi = E\psi$$

There exist in general an infinity of possible states separated by gaps along the energy scale (the energy quantization).

- ▶ **Problem.** To see the energy quantization, complete [0_Energy_of_Electron.ipynb](#) and plot the equilibrium states of an electron in different types of wells.

Equilibrium states (cont'd)

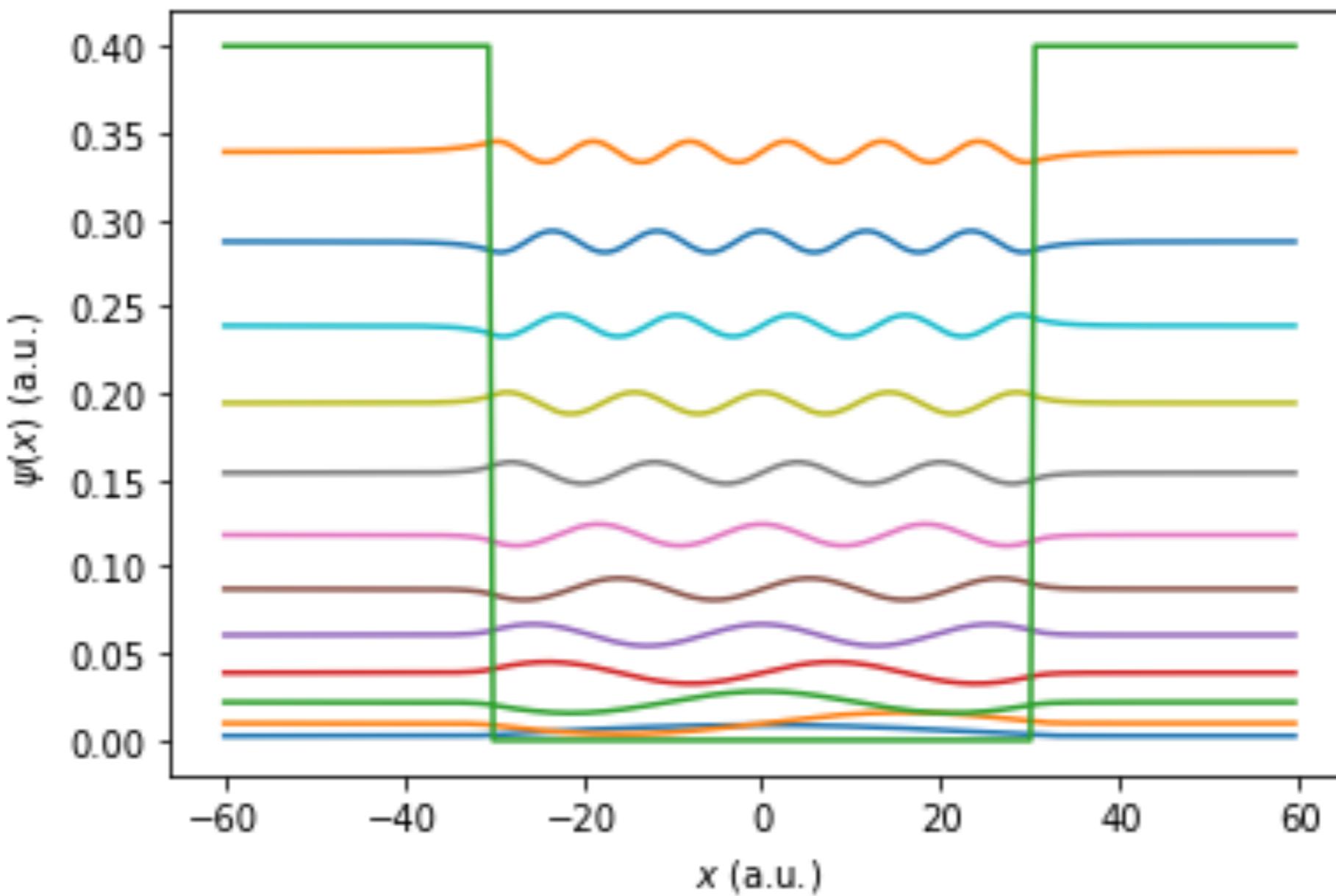
- ▶ **Answer.** We obtain a series of quantum states, whose spacing depends on the shape of the well



- ▶ More examples osscar-quantum-mechanics.materialscloud.io

Equilibrium states (cont'd)

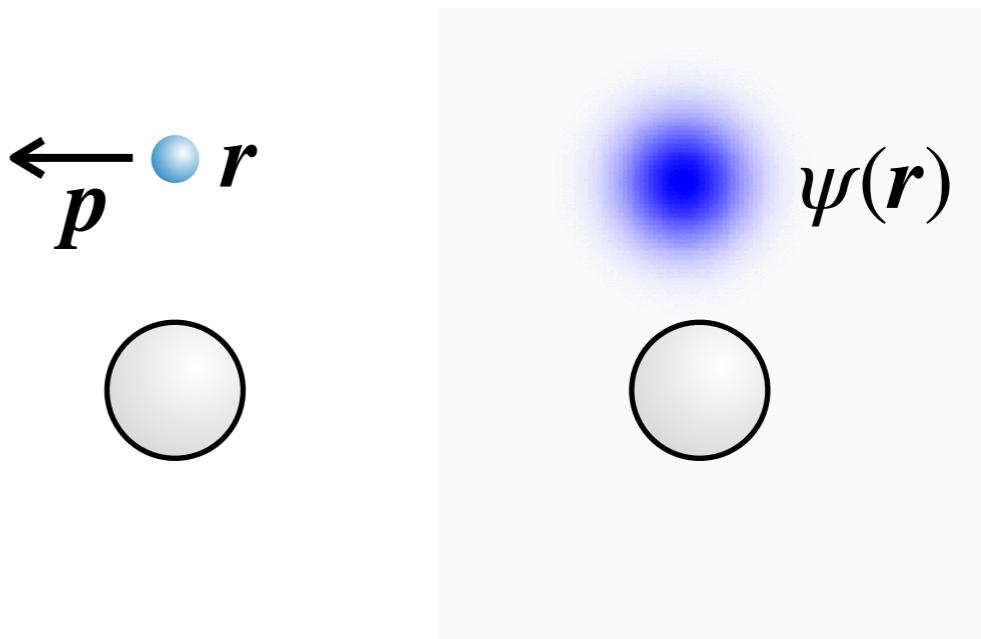
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Summary

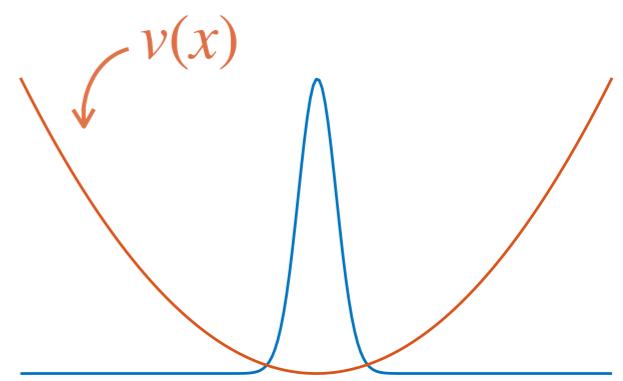
- In classical mechanics, the state of an electron is given by (\mathbf{r}, \mathbf{p}) while in quantum mechanics, it is given by a **wave function $\psi(\mathbf{r})$**



- The **total energy** of an electron wave function is a balancing act...

$$E = \int \psi^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) + v(\mathbf{r}) \psi(\mathbf{r}) \right) d\mathbf{r} = (\psi | \hat{H} \psi)$$

↑
Hamiltonian



... which can be determined by solving

$$\hat{H}\psi = E\psi$$