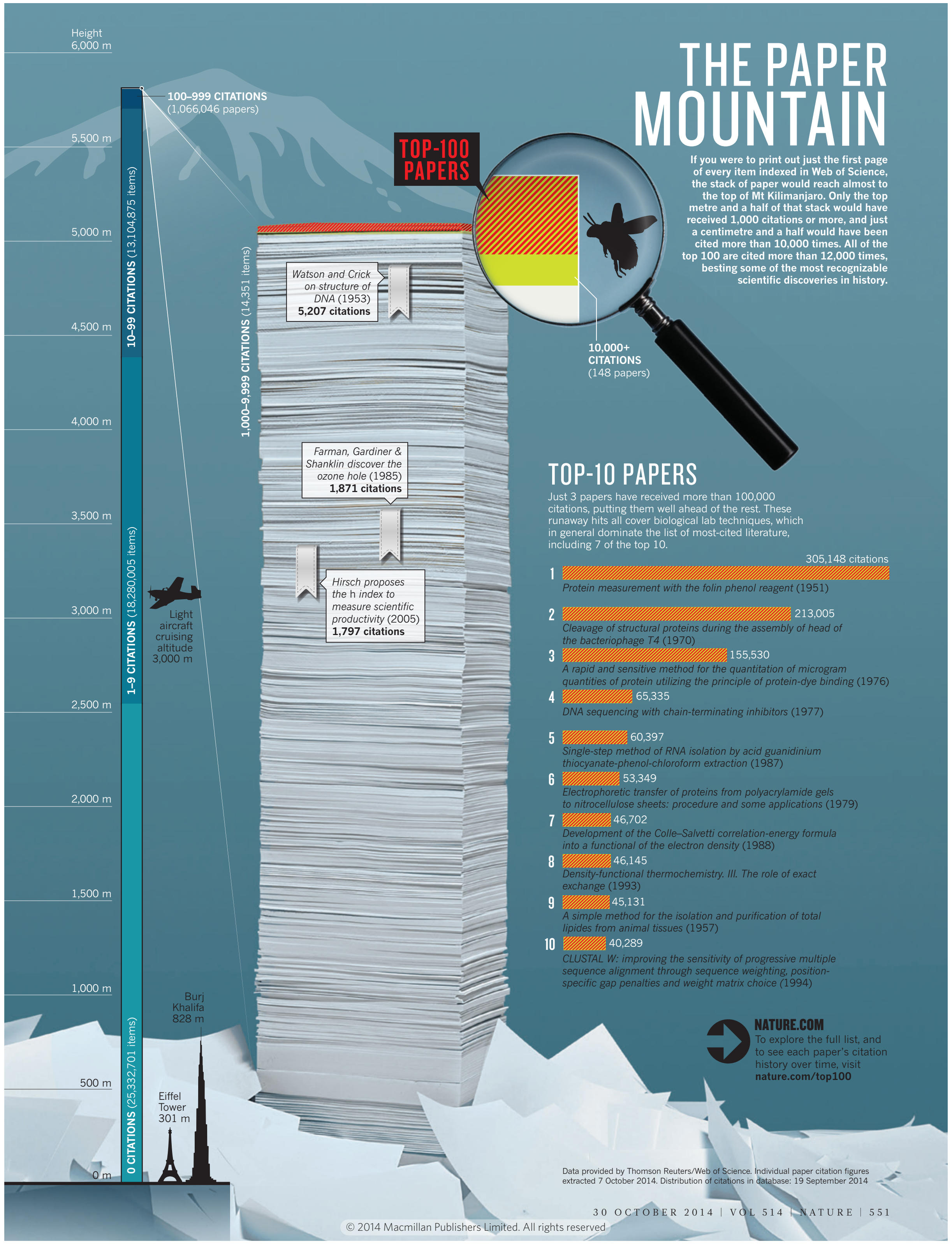
Fundamentals: Schrödinger Equation

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

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

Why this workshop…



Van Noorden *et al.*, *Nature* 514, 550 (2014)

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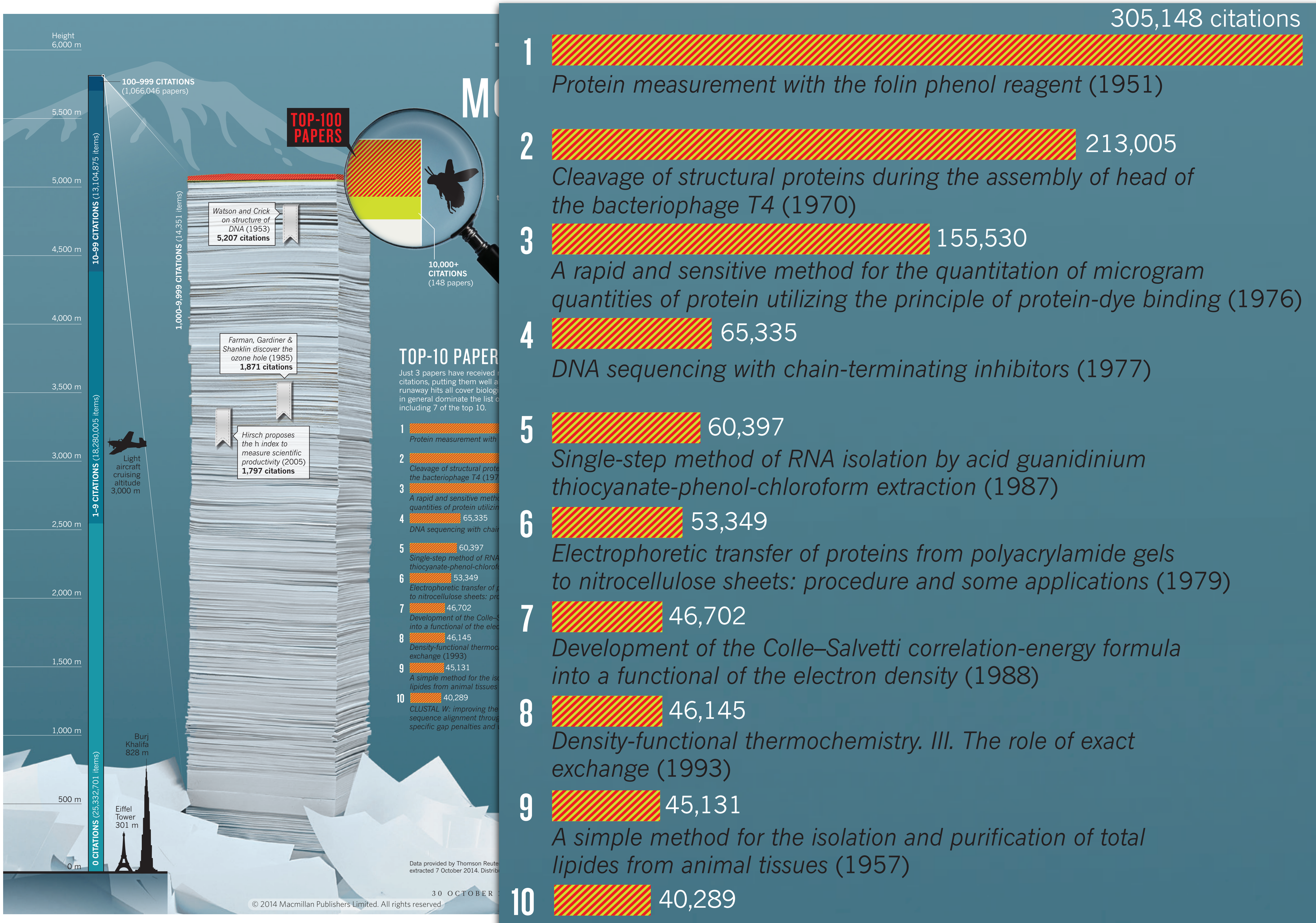

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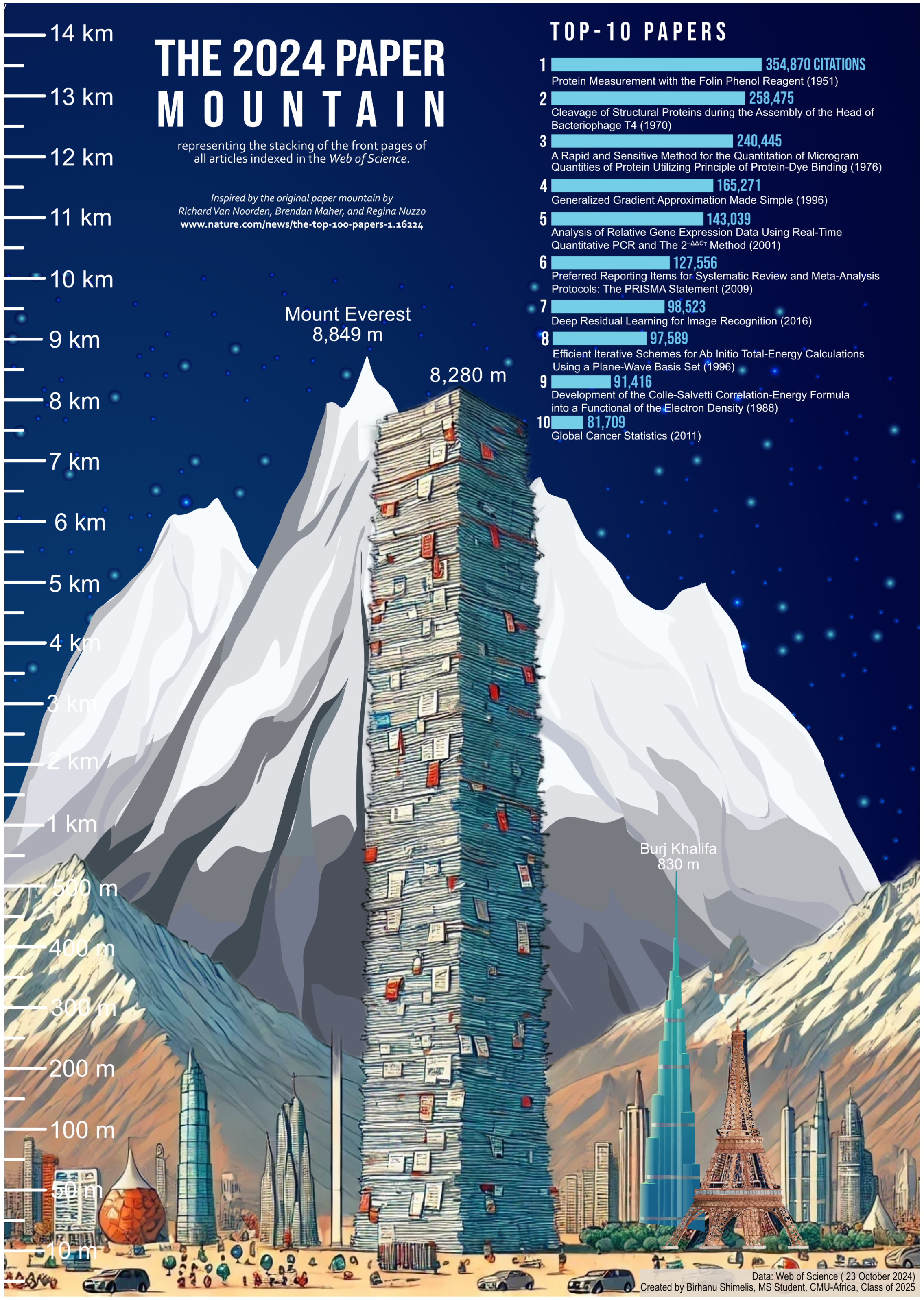

Data: Web of Science (3 October 2024) · Created by **Birhanu Shimelis**, M.S. Student, CMU-Africa

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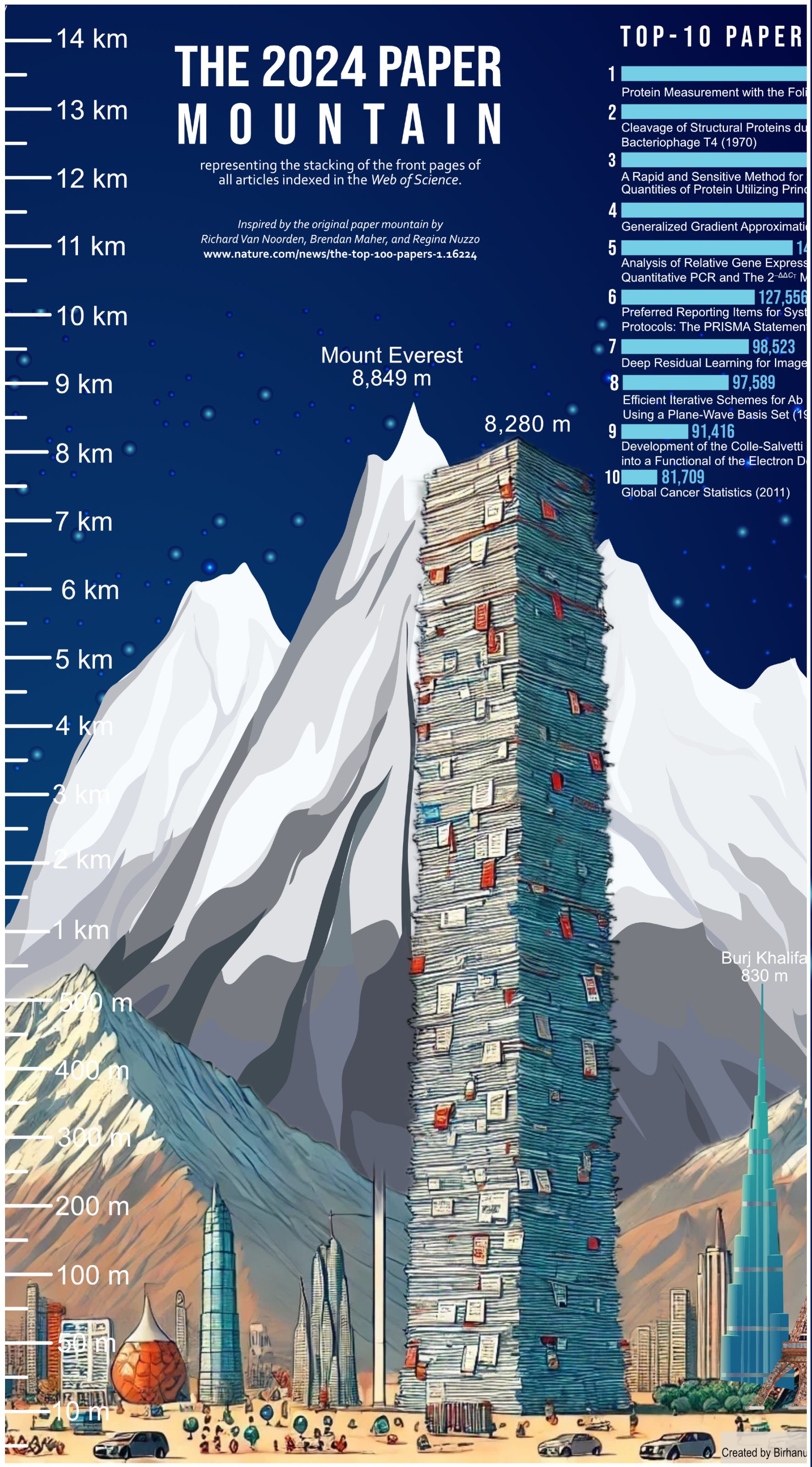

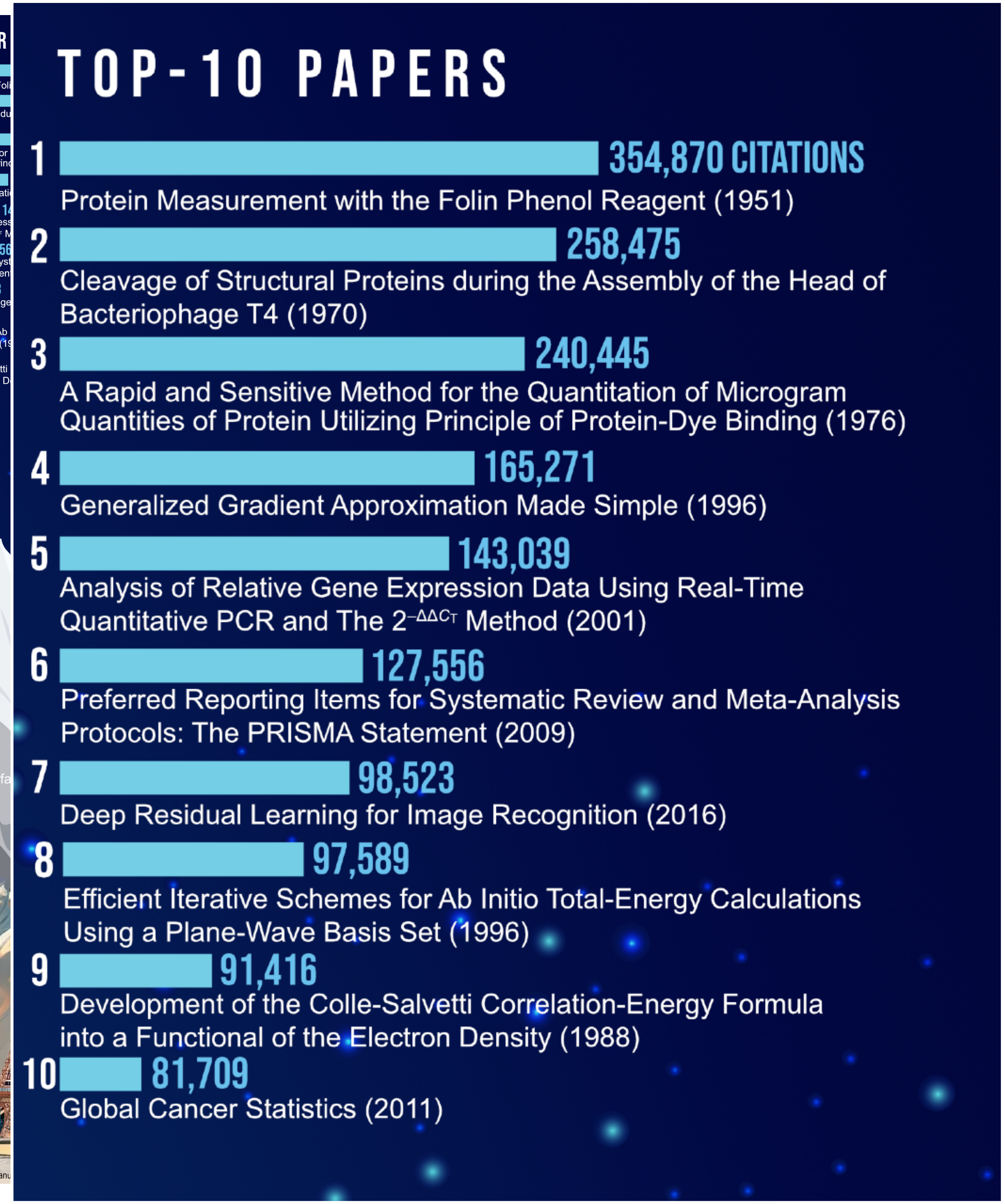

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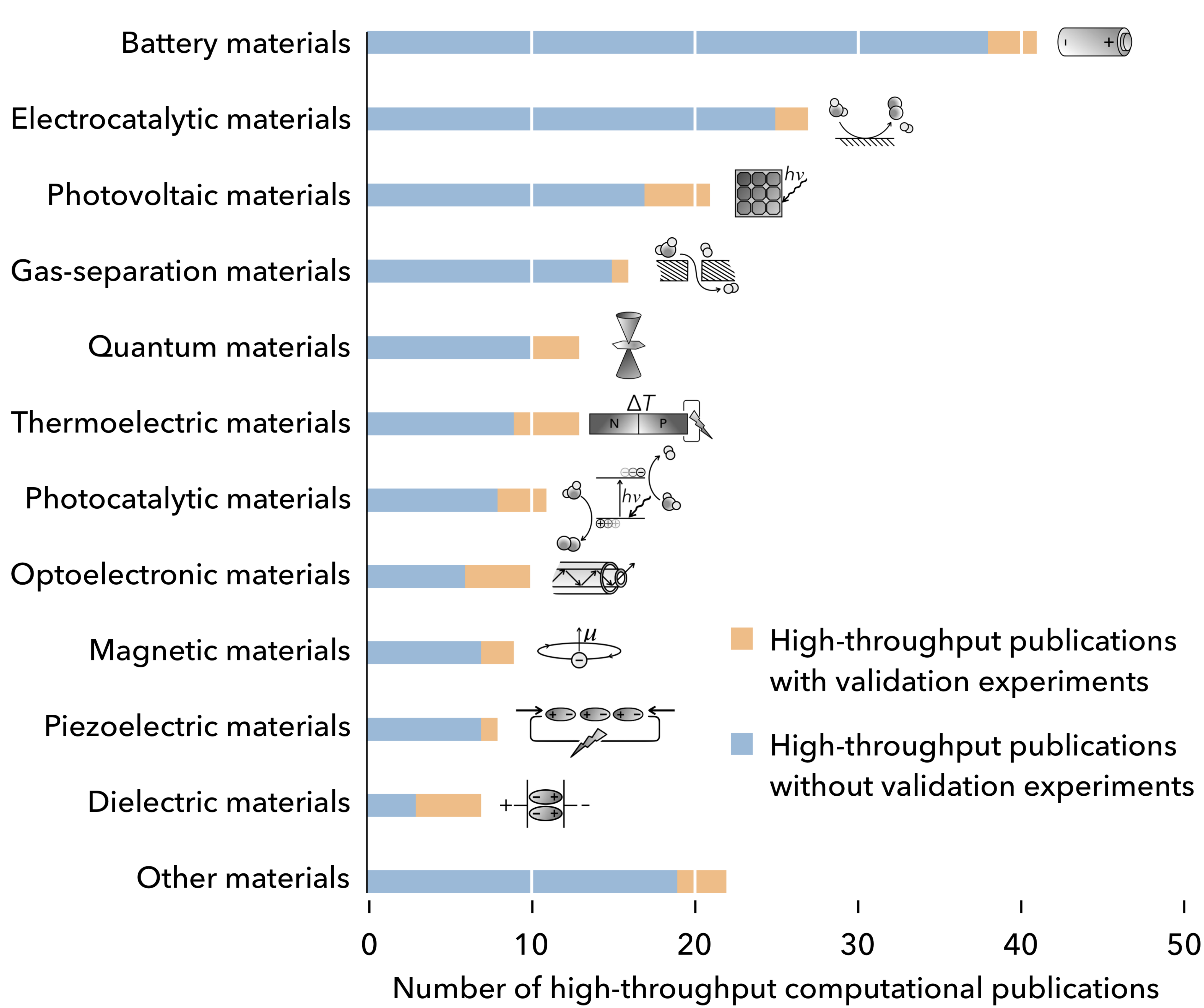
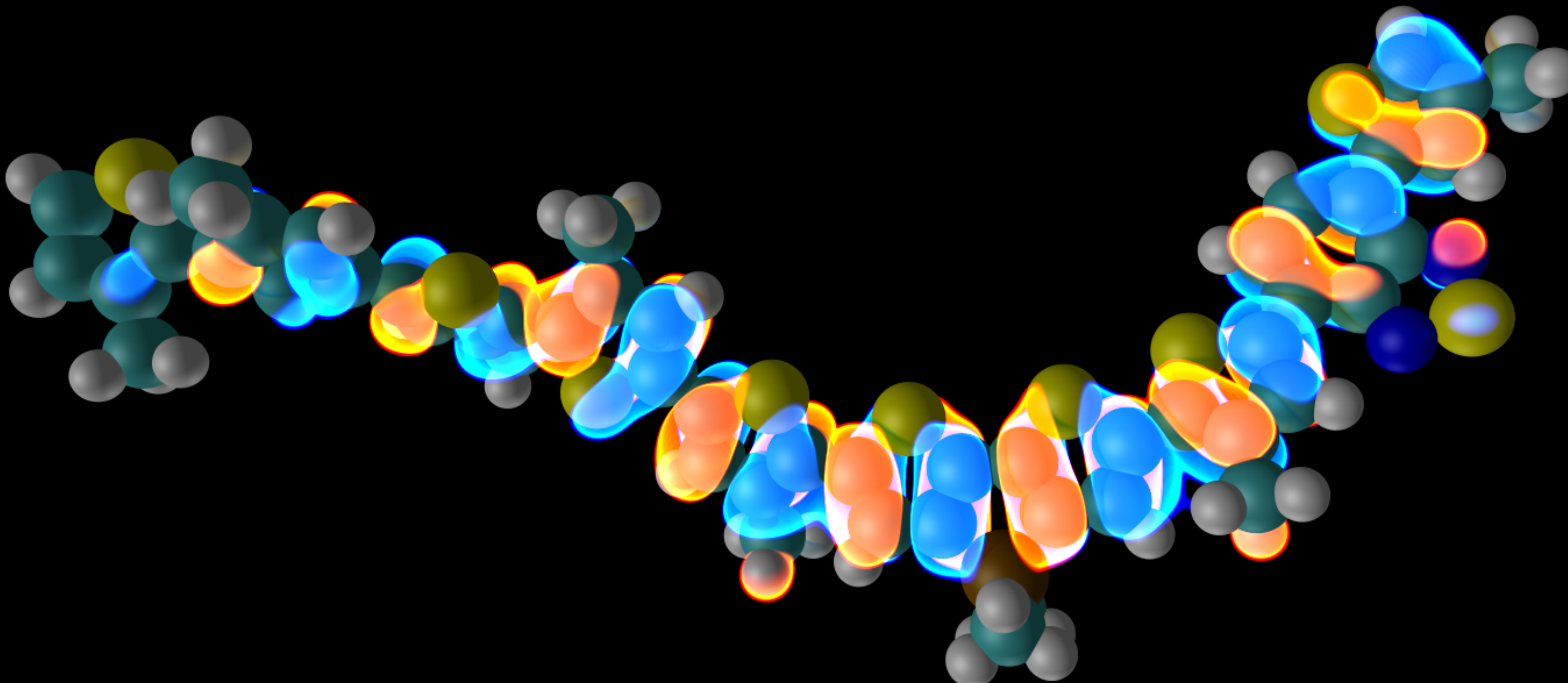
Towards materials discovery for technology

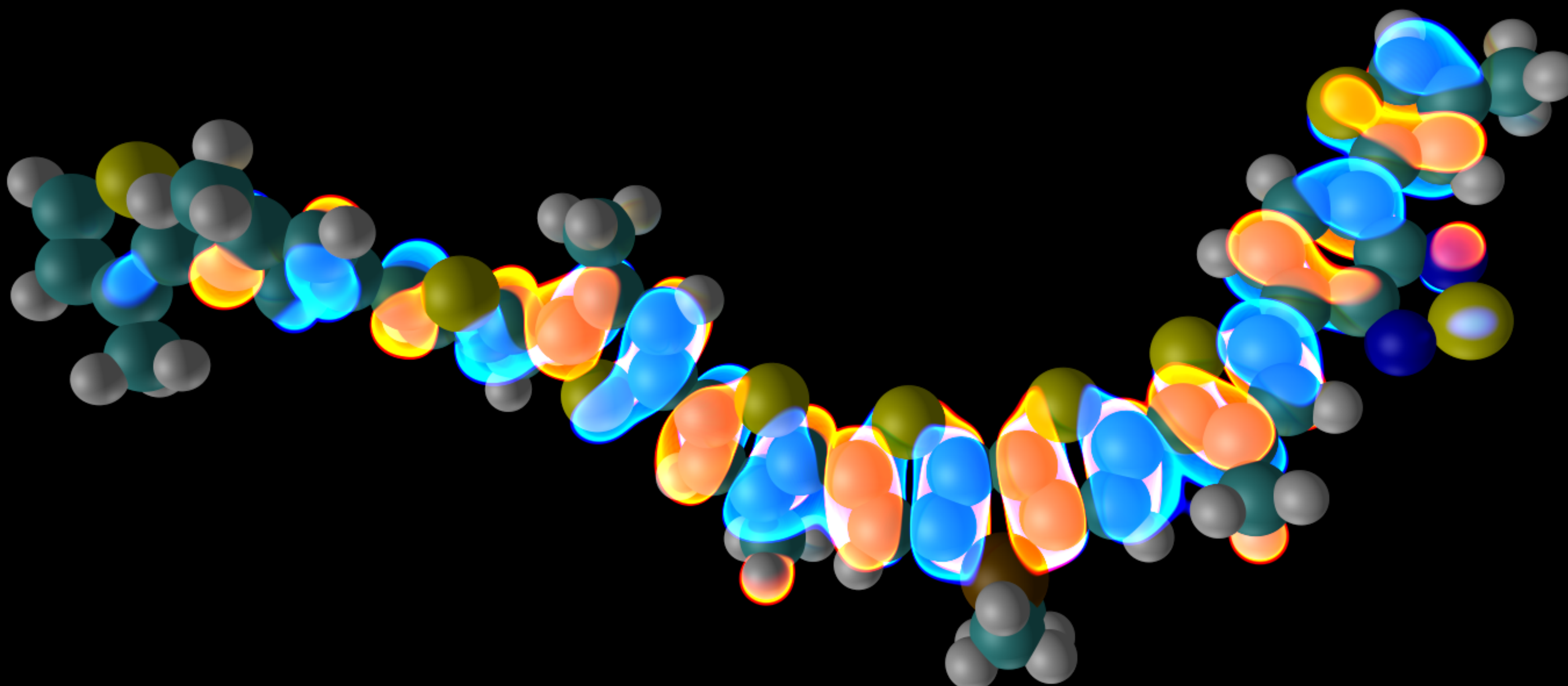


Xiong *et al.*, *Energy Environmental Science* **14**, 2335-2348 (2021)

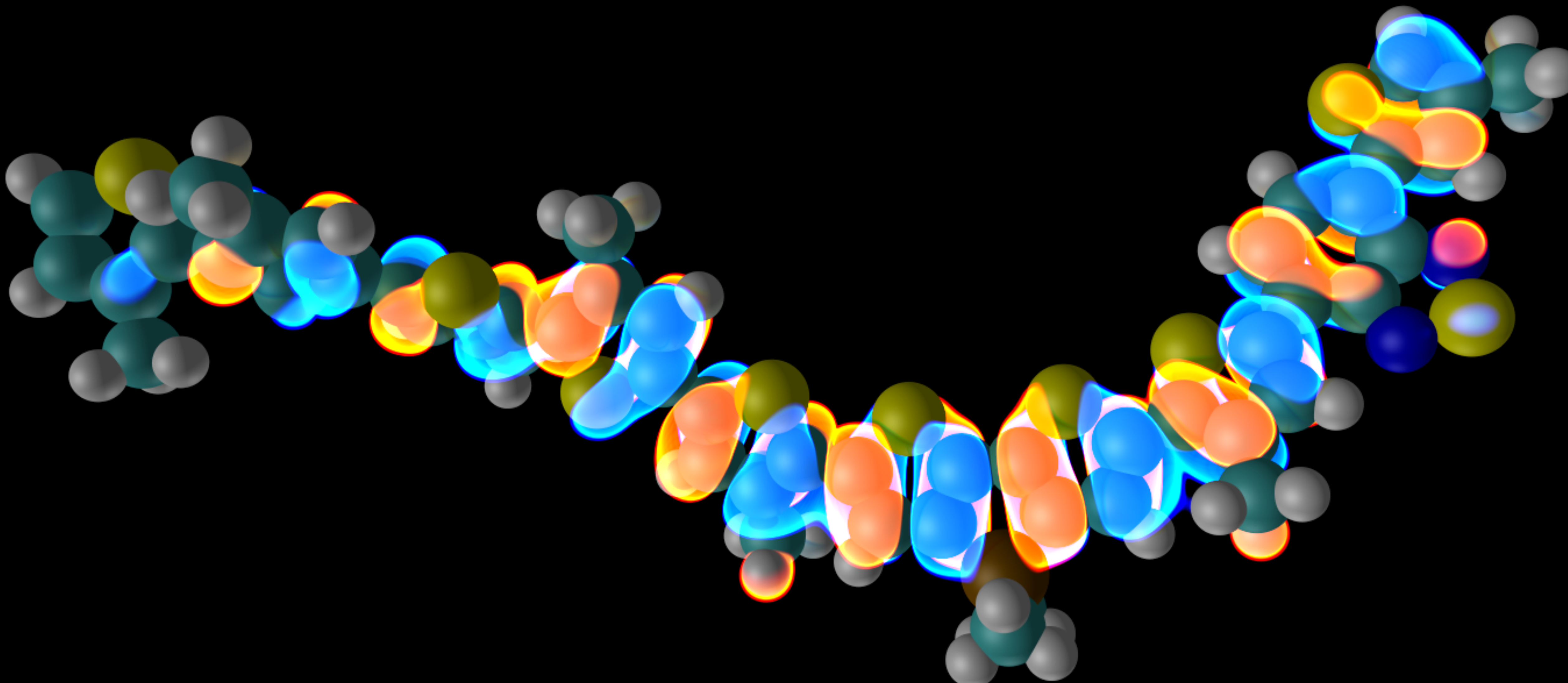
Why quantum mechanics to simulate materials



material = nuclei + electrons

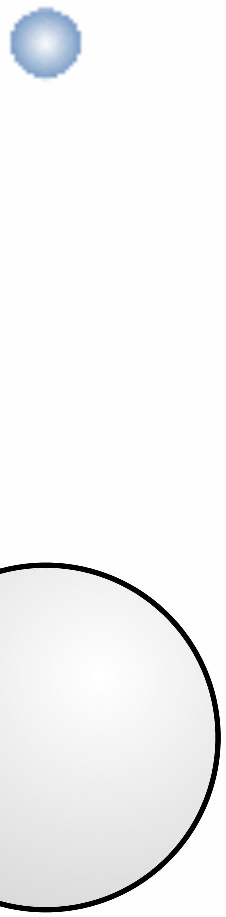


$$\text{material} = \underbrace{\text{nuclei}}_{+} + \underbrace{\text{electrons}}_{-}$$

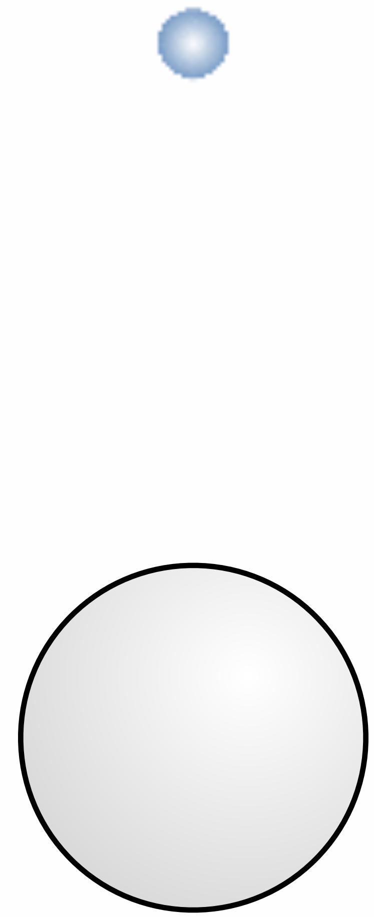


material = nuclei + $\underbrace{\textbf{electrons}}_{\textbf{‘glue’}}$

Classical mechanics vs. quantum mechanics



Newton's law



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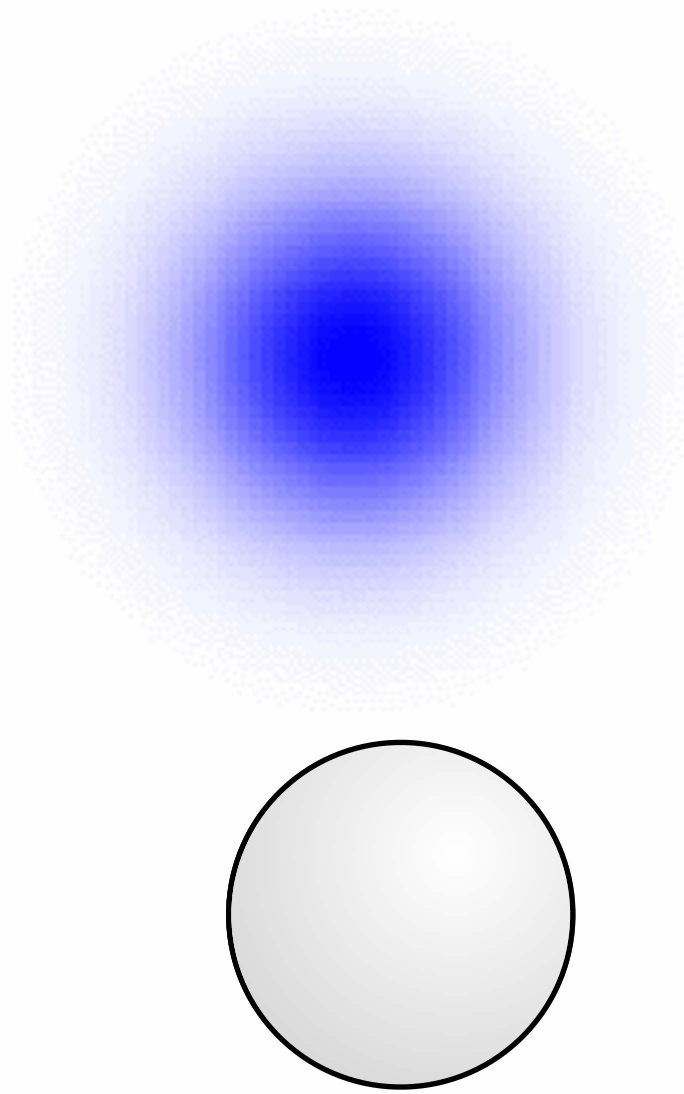
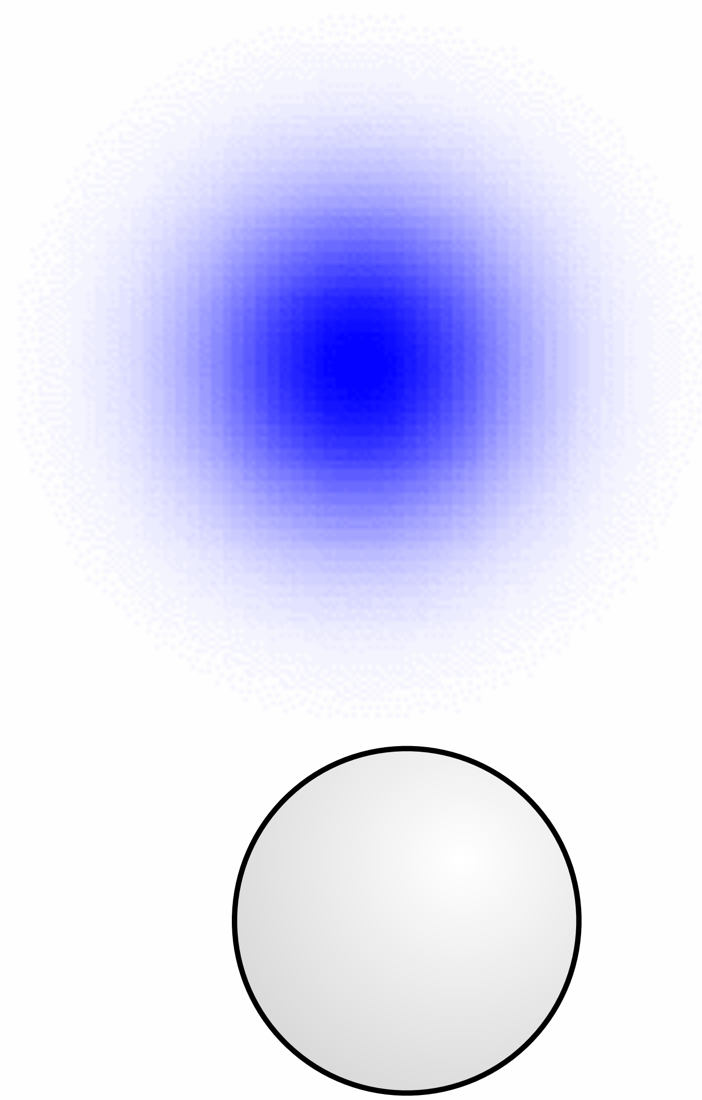
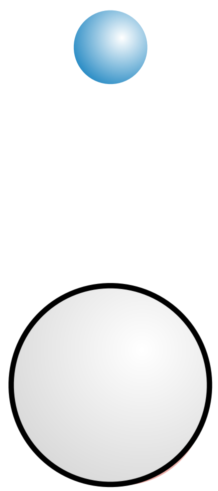


Schrödinger's equation



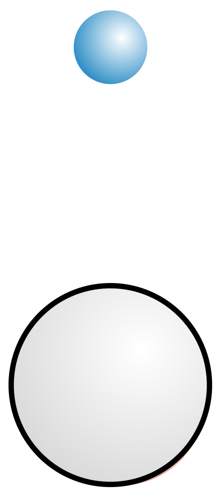
Schrödinger's equation

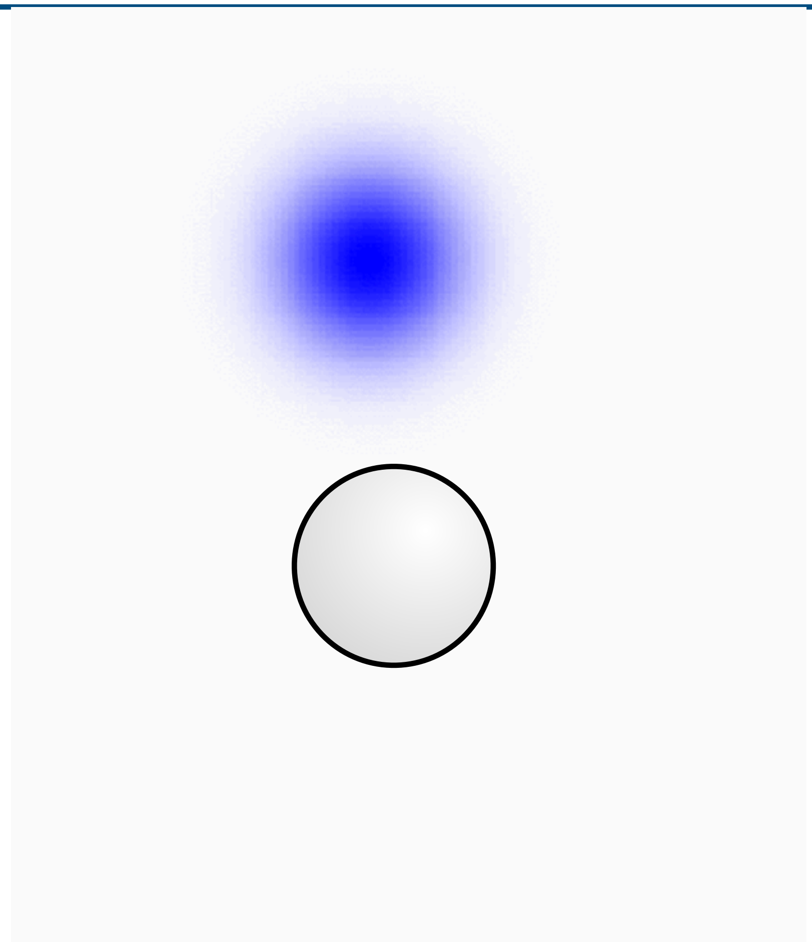
Classical mechanics vs. quantum mechanics



In classical mechanics,
electrons are points

Classical mechanics vs. quantum mechanics

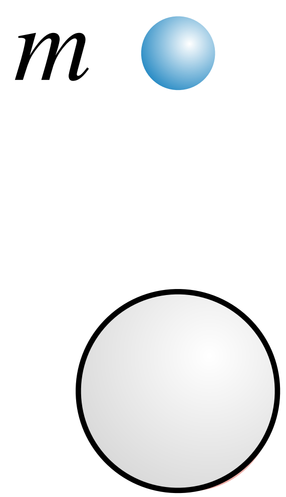


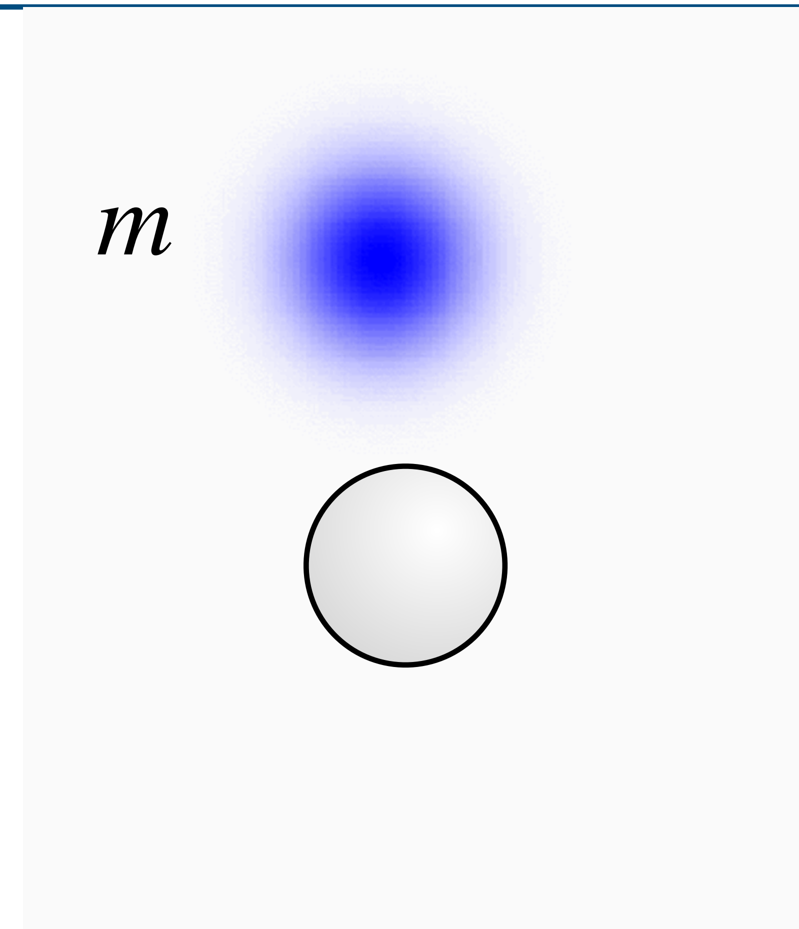


In classical mechanics, **electrons** are points

In quantum mechanics, **electrons** are clouds

Classical mechanics vs. quantum mechanics





In classical mechanics,
electrons are points

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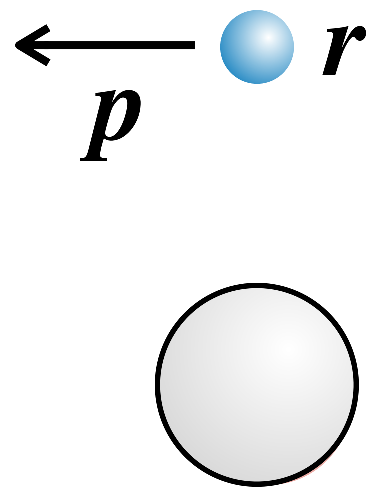
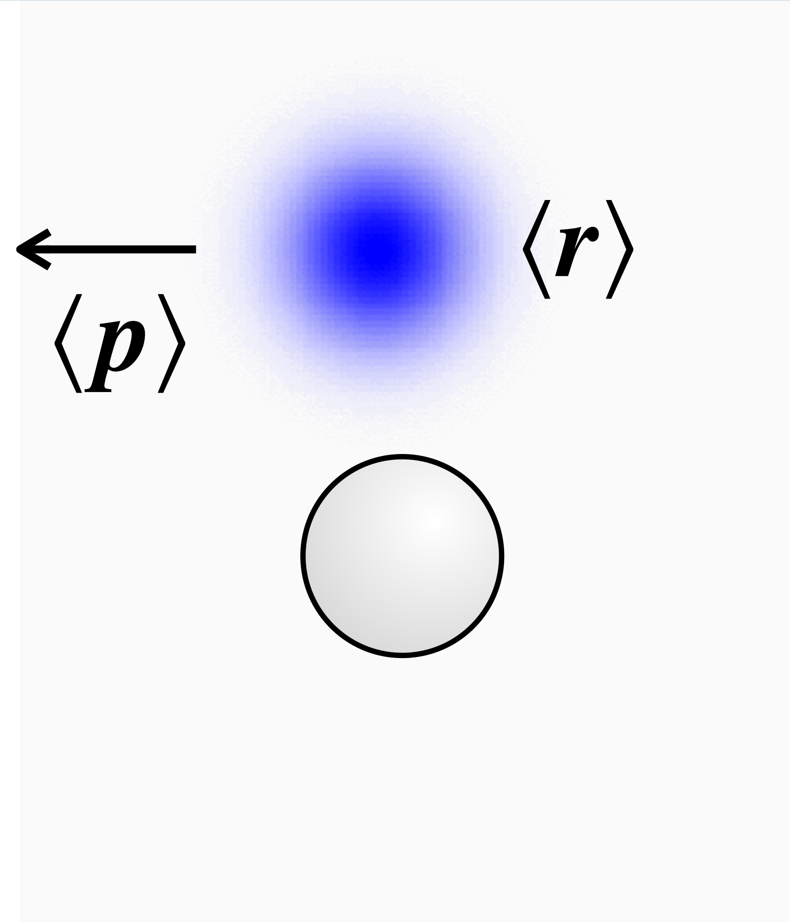
In both classical mechanics and classical mechanics,
electrons have a mass m…

Classical vs. quantum mechanics

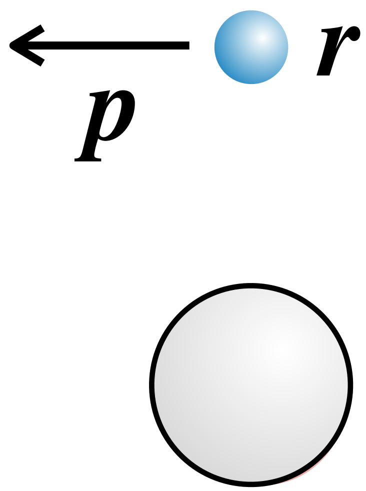


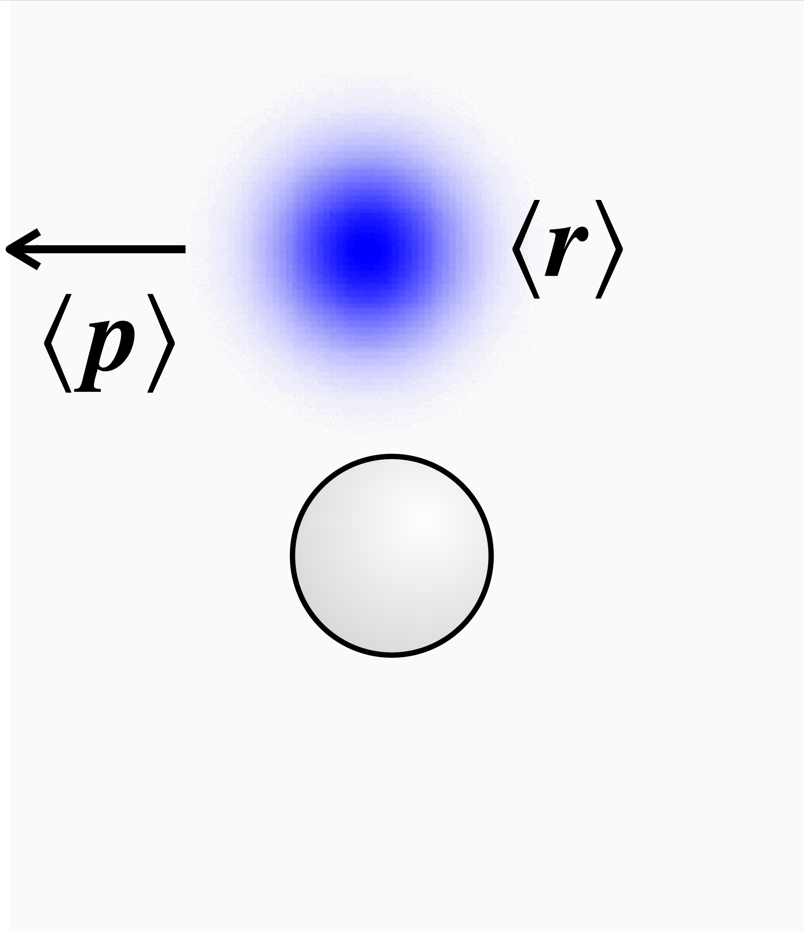
… but in classical mechanics, the **position** $\boldsymbol{p}$ and **momentum** $\boldsymbol{r}$ are precisely known…



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

Classical vs. quantum mechanics (cont'd)

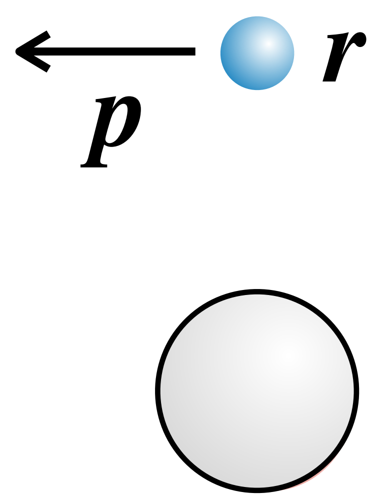


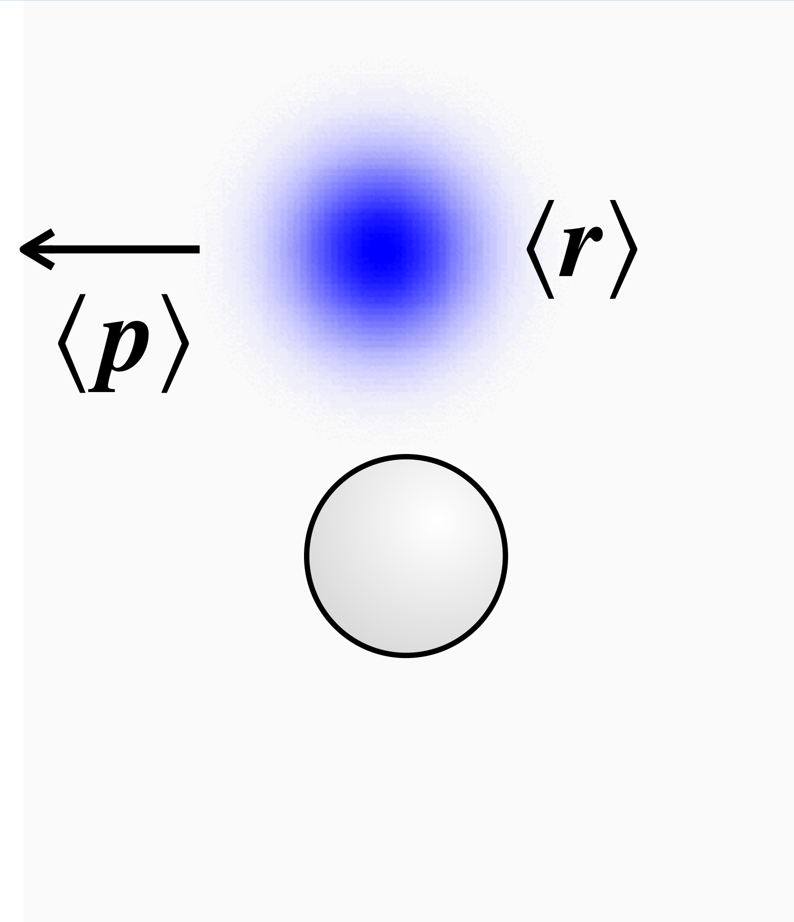


In classical mechanics, $\boldsymbol{p}$ and $\boldsymbol{r}$ completely define the electron state and electron energy E

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

Classical vs. quantum mechanics (cont'd)





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

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

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

$$\underbrace{\psi}_{\text{wave function}} \longmapsto E$$

Wave function of an electron

Definition | wave function

The wave function $\psi(\boldsymbol{r})$ 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: $\rho(\boldsymbol{r}) = |\psi(\boldsymbol{r})|^2$.

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

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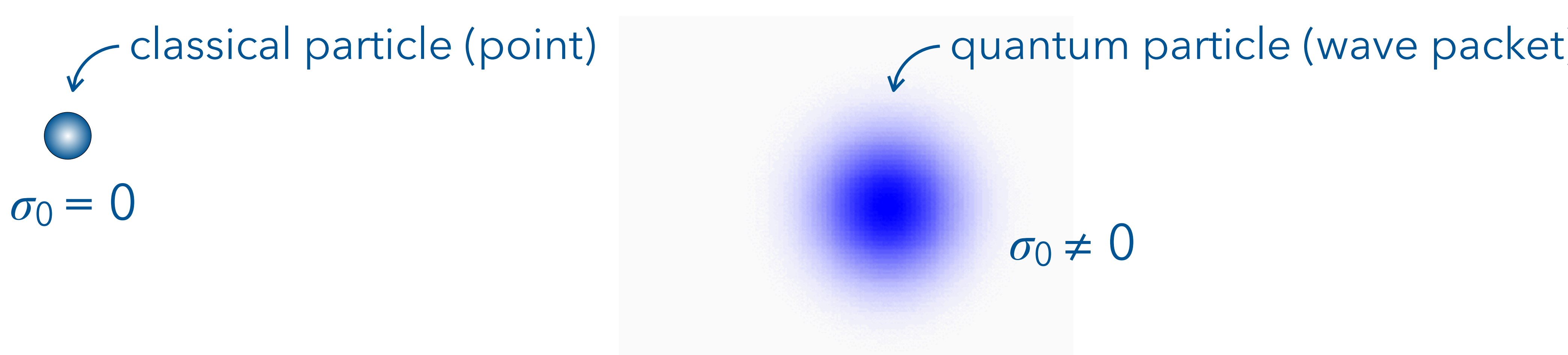
- **Example.** A wave packet is a type of wave function describing an electron around an average location $\mathbf{r}_0$ with a given spread σ_0.



Wave function of an electron (cont'd)

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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

$$K = \int \psi^*(\boldsymbol{r})\left(-\frac{\hbar^2}{2m_\mathrm{e}}\nabla^2\psi(\boldsymbol{r})\right)d\boldsymbol{r} = -\frac{\hbar^2}{2m_\mathrm{e}}\int \psi^*(\boldsymbol{r})\,\nabla^2\psi(\boldsymbol{r})d\boldsymbol{r}$$

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

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

complex conjugate: $(a+ib)*=a-ib$

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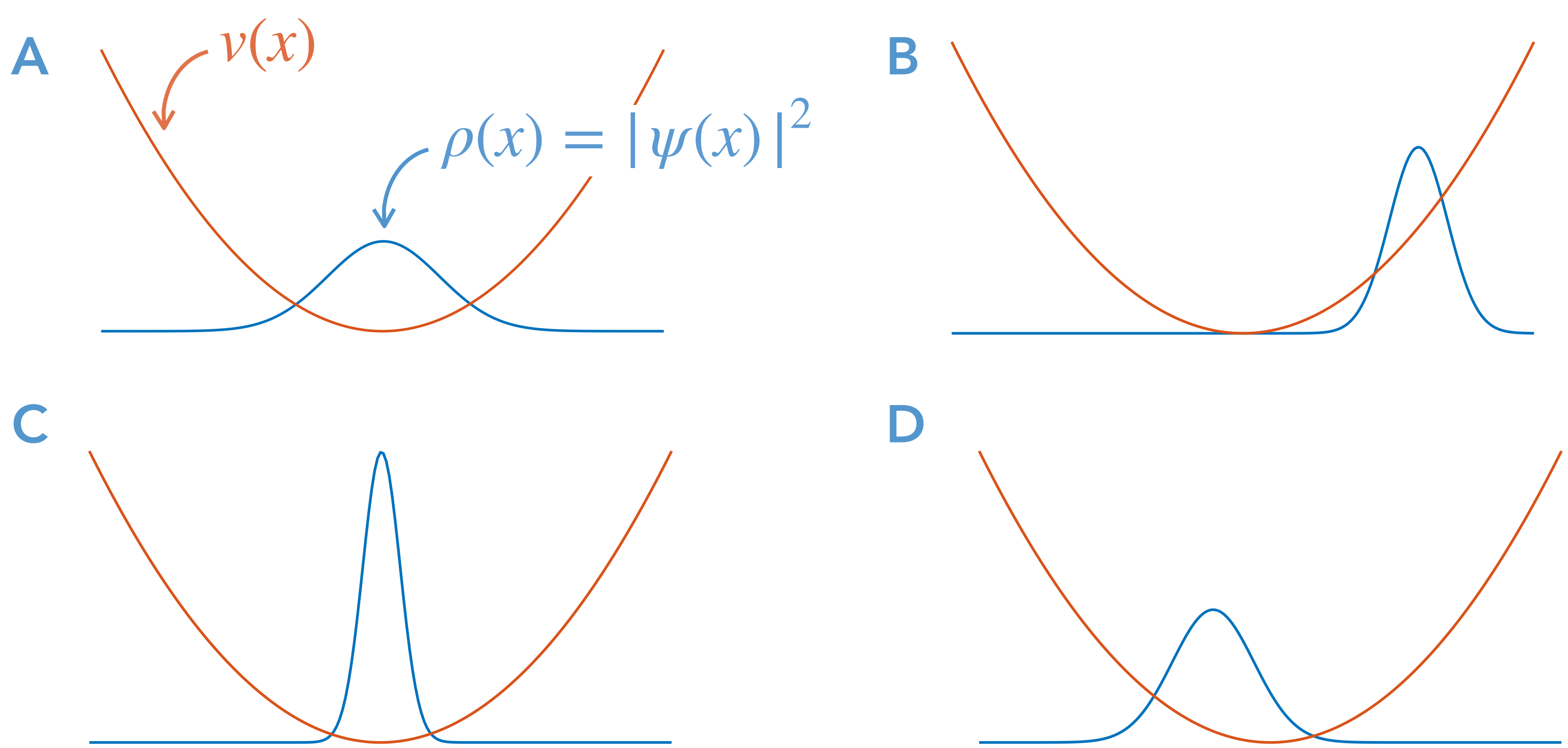
- **Problem.** Find the order of K and U for the 4 cases below:



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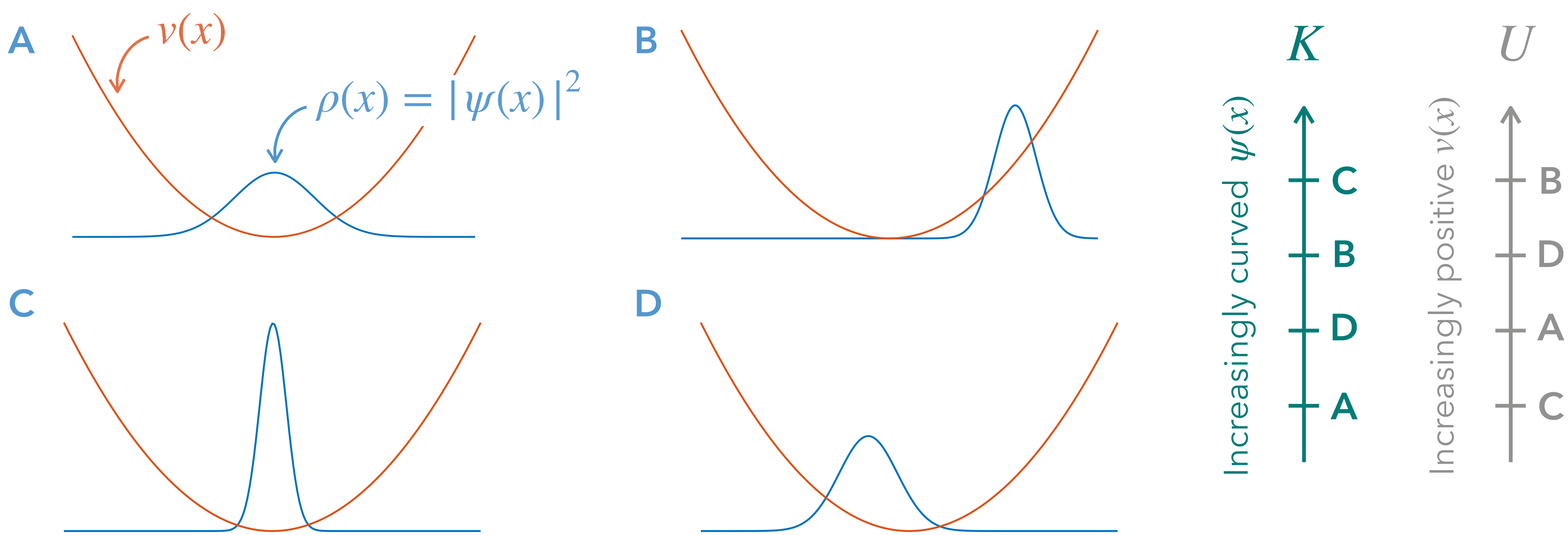

Energy of an electron

- 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

$$E = \int \psi^*(\boldsymbol{r})\left(-\frac{\hbar^2}{2m_{\mathrm{e}}}\nabla^2\psi(\boldsymbol{r}) + v(\boldsymbol{r})\psi(\boldsymbol{r})\right)d\boldsymbol{r}$$

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

^ denotes an operator

$$\hat{H} \equiv -\frac{\hbar^2}{2m_e}\nabla^2 + v(\boldsymbol{r})$$

Hamiltonian

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

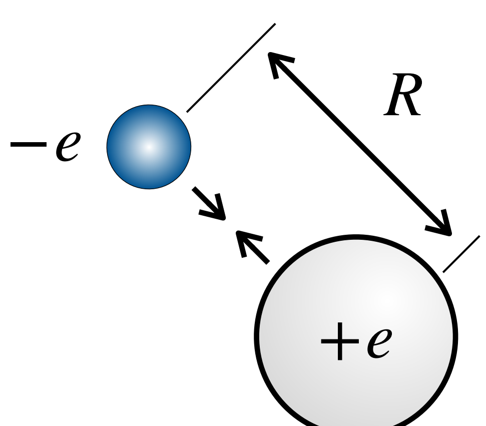
An operator is an instruction to perform a certain calculation on an object (here, a wave function)

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



$$\hat{H} \equiv -\frac{\hbar^2}{2m_e}\nabla^2 + v(\boldsymbol{r})$$

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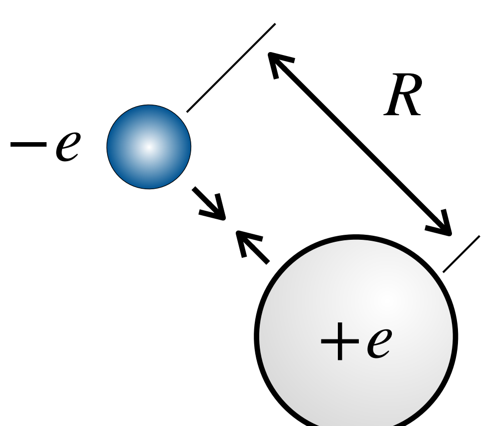

$$\hat{H} \equiv -\frac{\hbar^2}{2m_e}\nabla^2 + v(\boldsymbol{r}) \longrightarrow \hat{H} \equiv -\nabla^2 + v(\boldsymbol{r})$$

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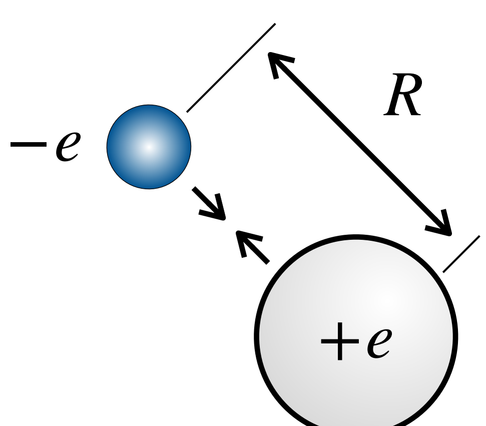


$$\hat{H} \equiv -\frac{\hbar^2}{2m_e}\nabla^2 + v(\boldsymbol{r}) \longrightarrow \hat{H} \equiv -\nabla^2 + v(\boldsymbol{r})$$

$$-\frac{e^2}{4\pi\varepsilon_0 R^2} \longrightarrow -\frac{2}{R^2}$$

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

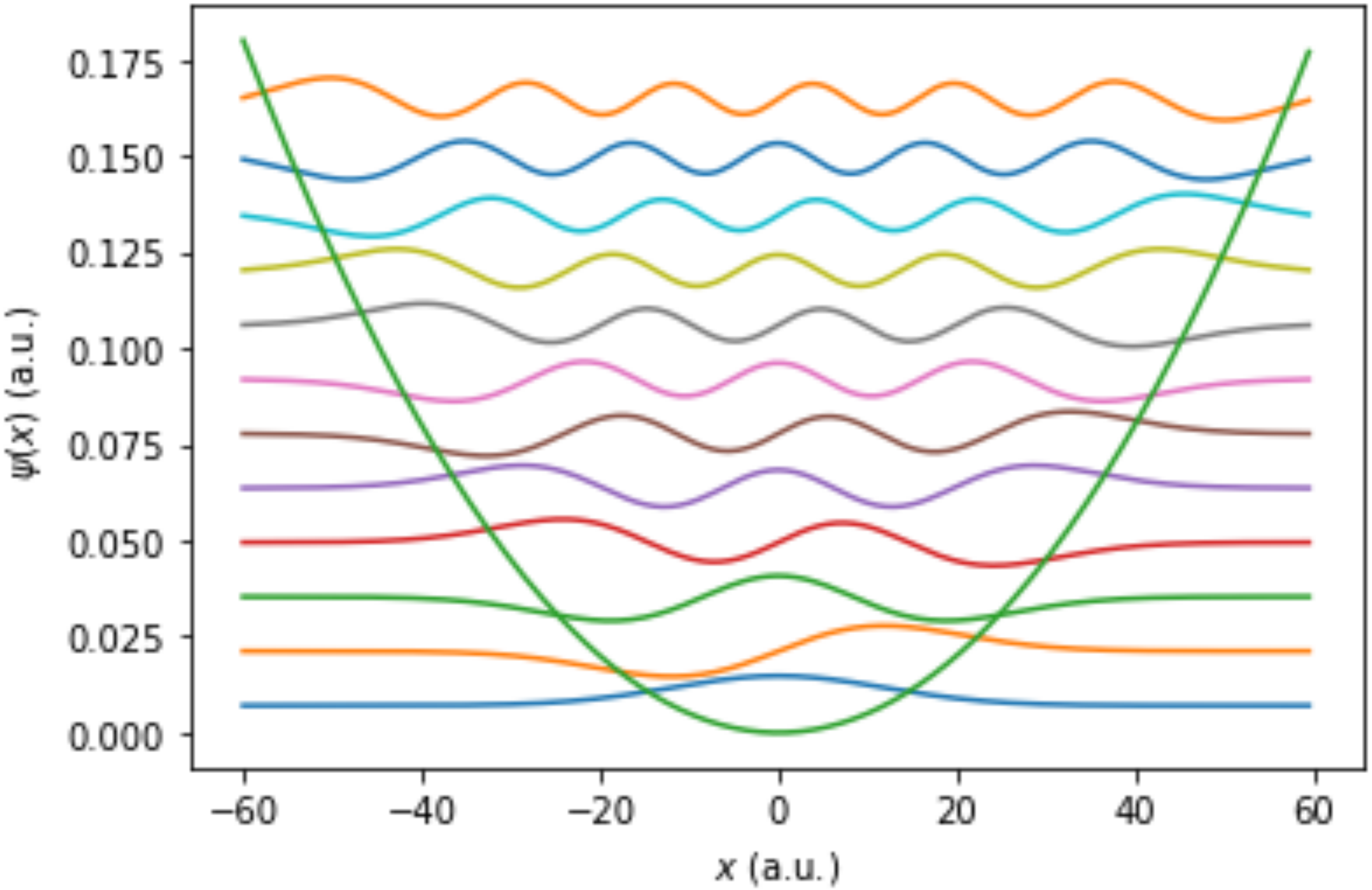
$$\hat{H}\psi = E\psi$$

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**

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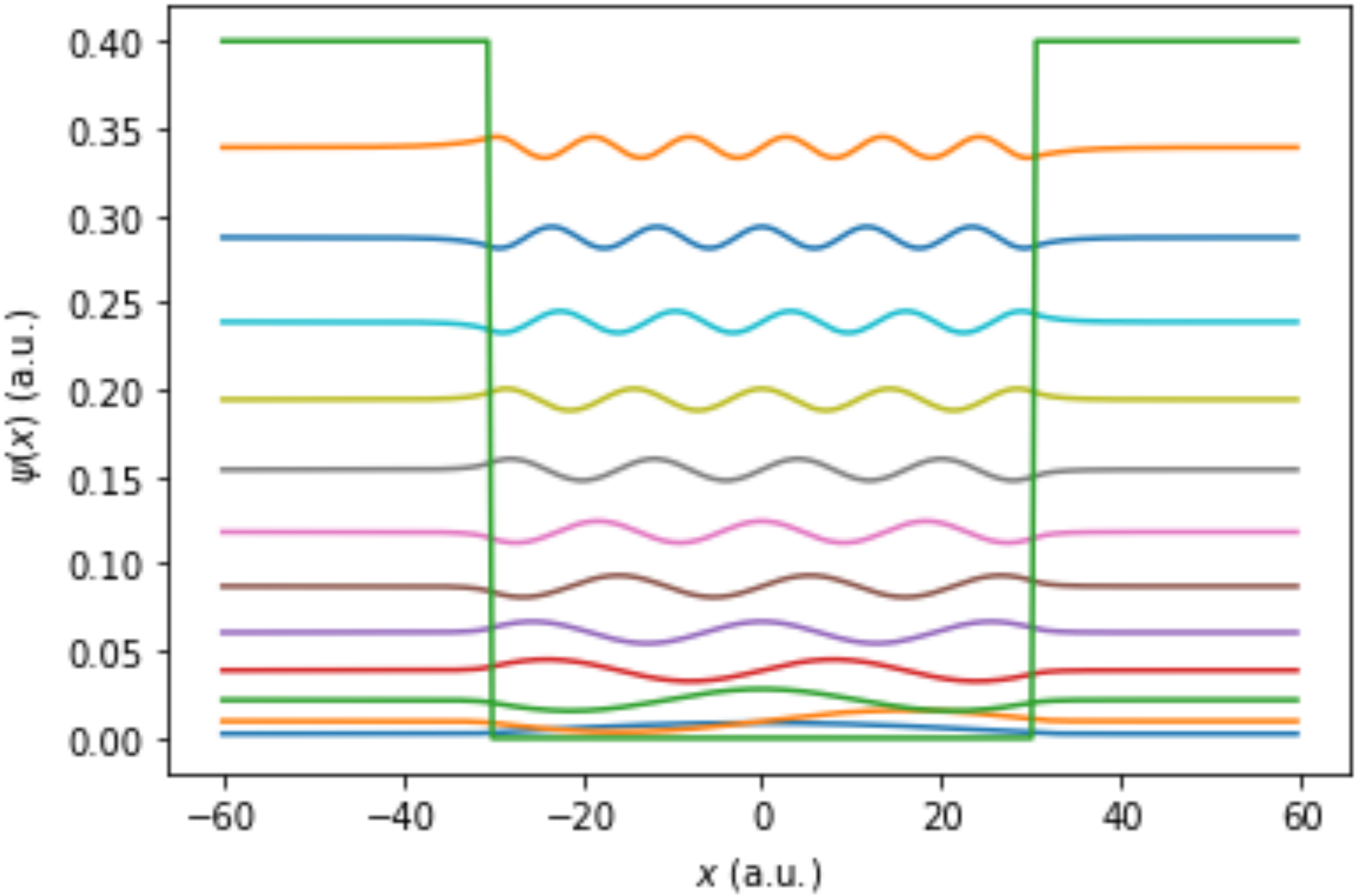

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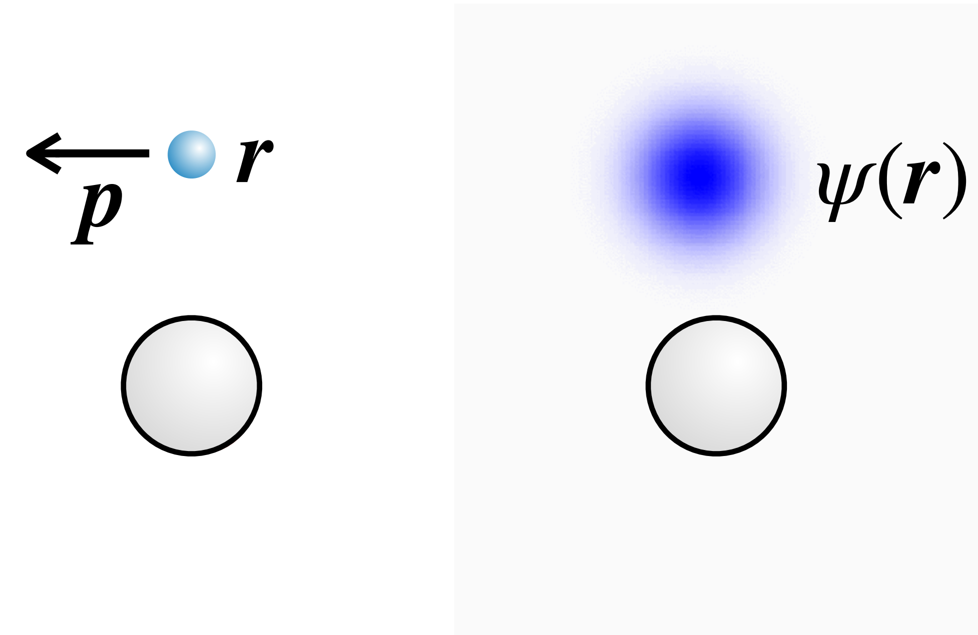
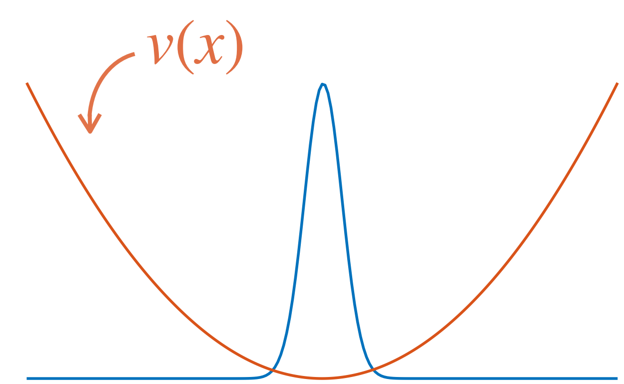
Summary

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



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

$$E = \int \psi^*(\boldsymbol{r}) \left(-\frac{\hbar^2}{2m_\mathrm{e}} \nabla^2 \psi(\boldsymbol{r}) + v(\boldsymbol{r})\psi(\boldsymbol{r}) \right) d\boldsymbol{r} = (\psi \,|\, \underset{\substack{\uparrow \\ \text{Hamiltonian}}}{\hat{H}} \psi)$$



… which can be determined by solving

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