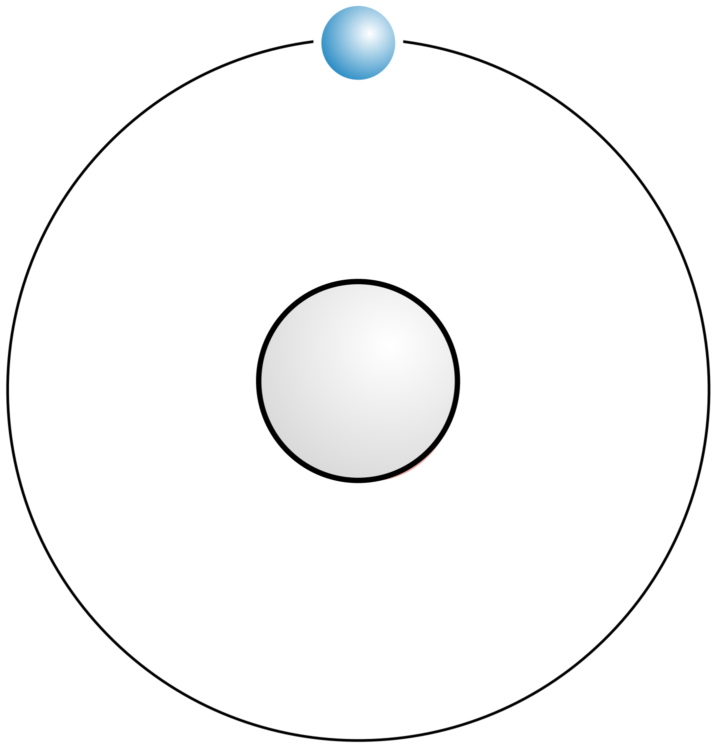
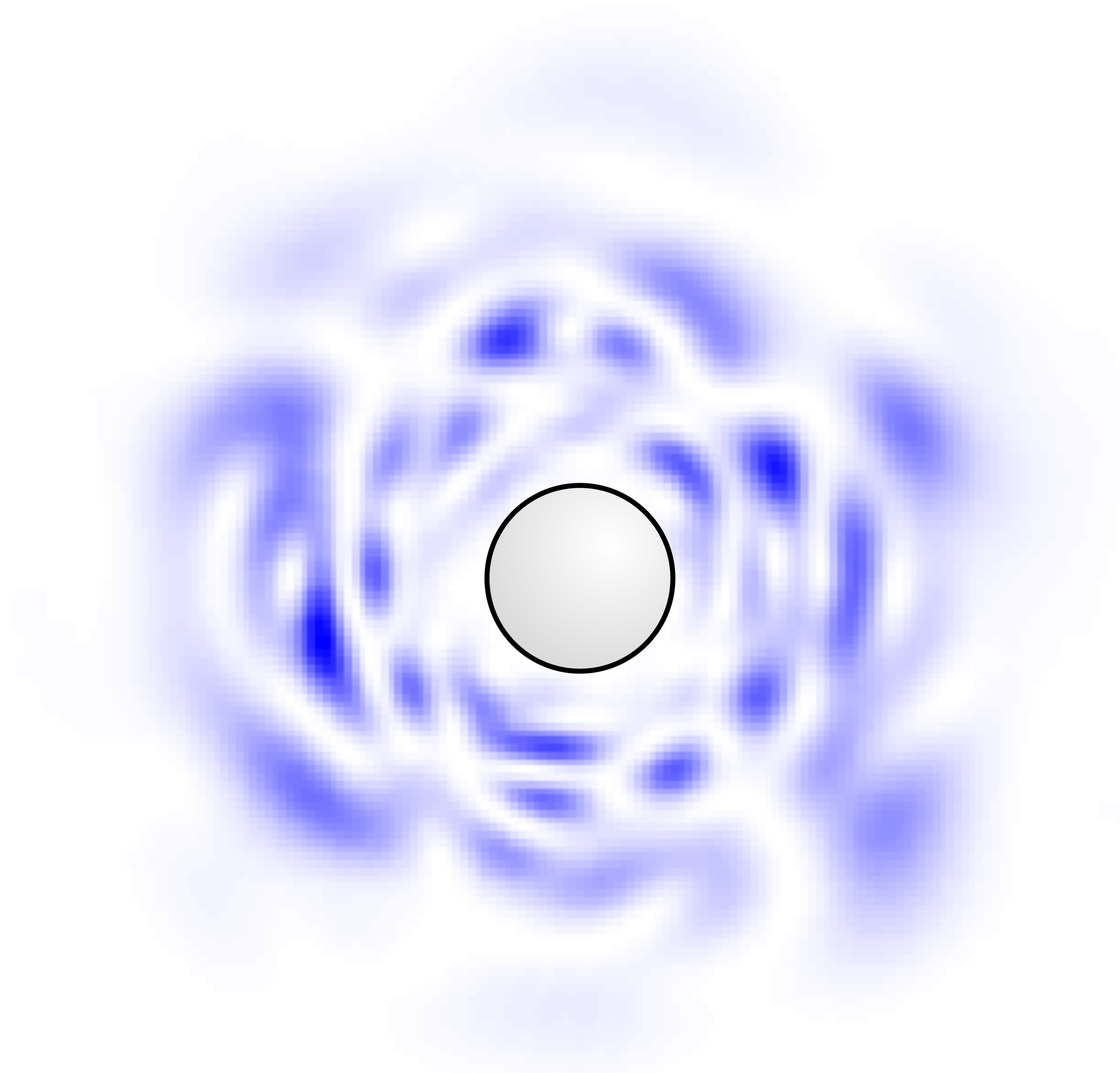
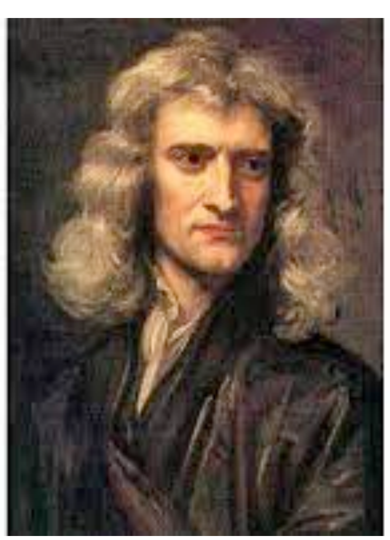
Introduction: Schrödinger's Equations



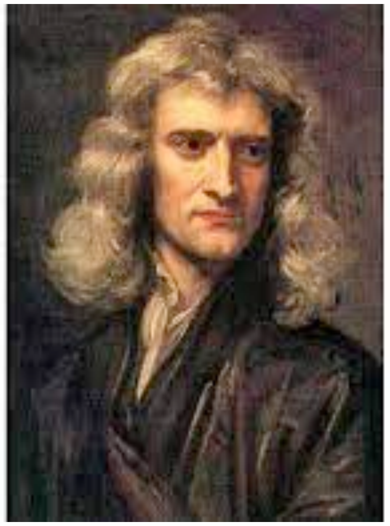
vs.

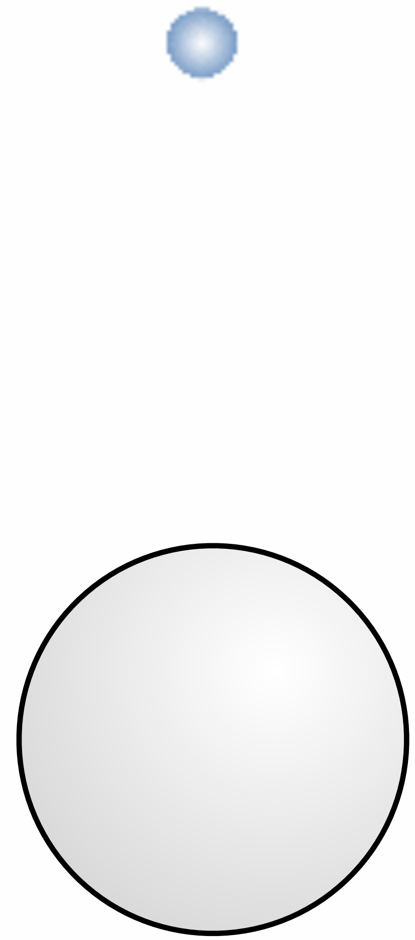




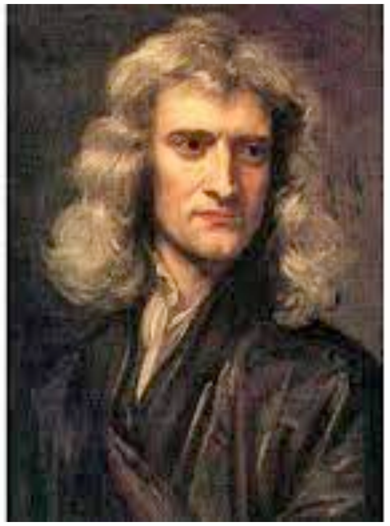
Isaac Newton
(1643–1727)

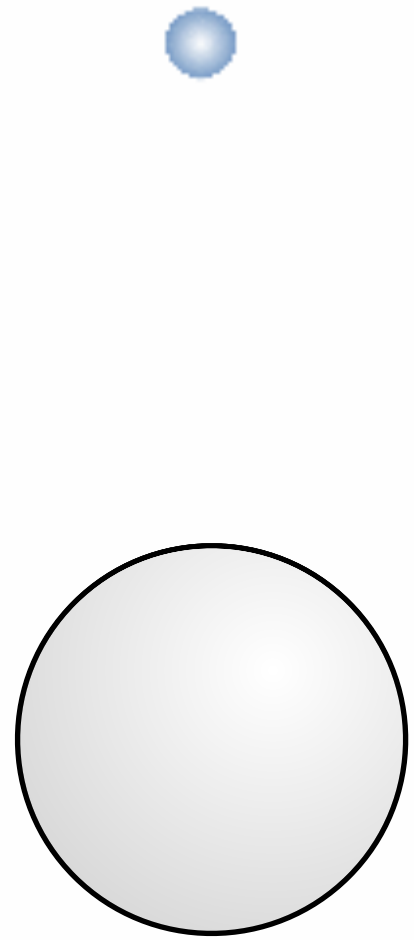
Erwin Schrödinger
(1887–1961)



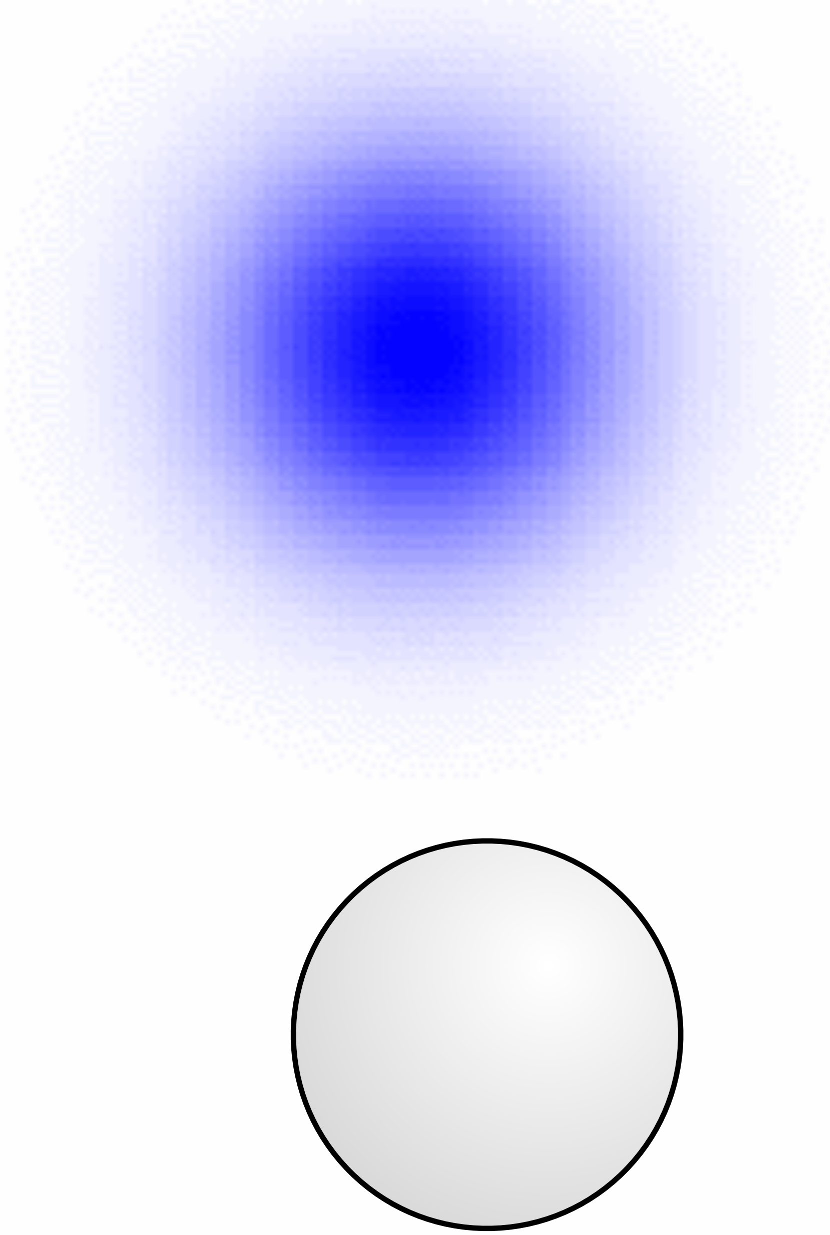


hydrogen atom

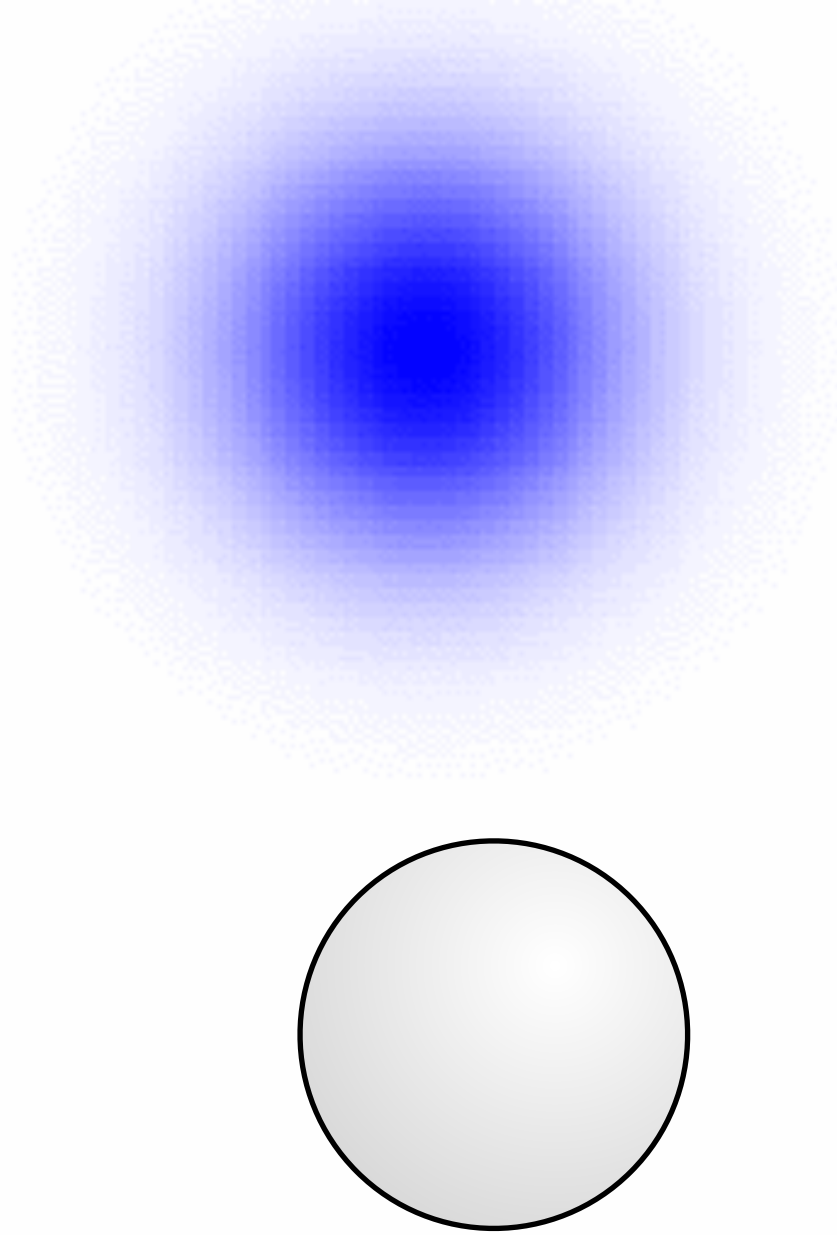




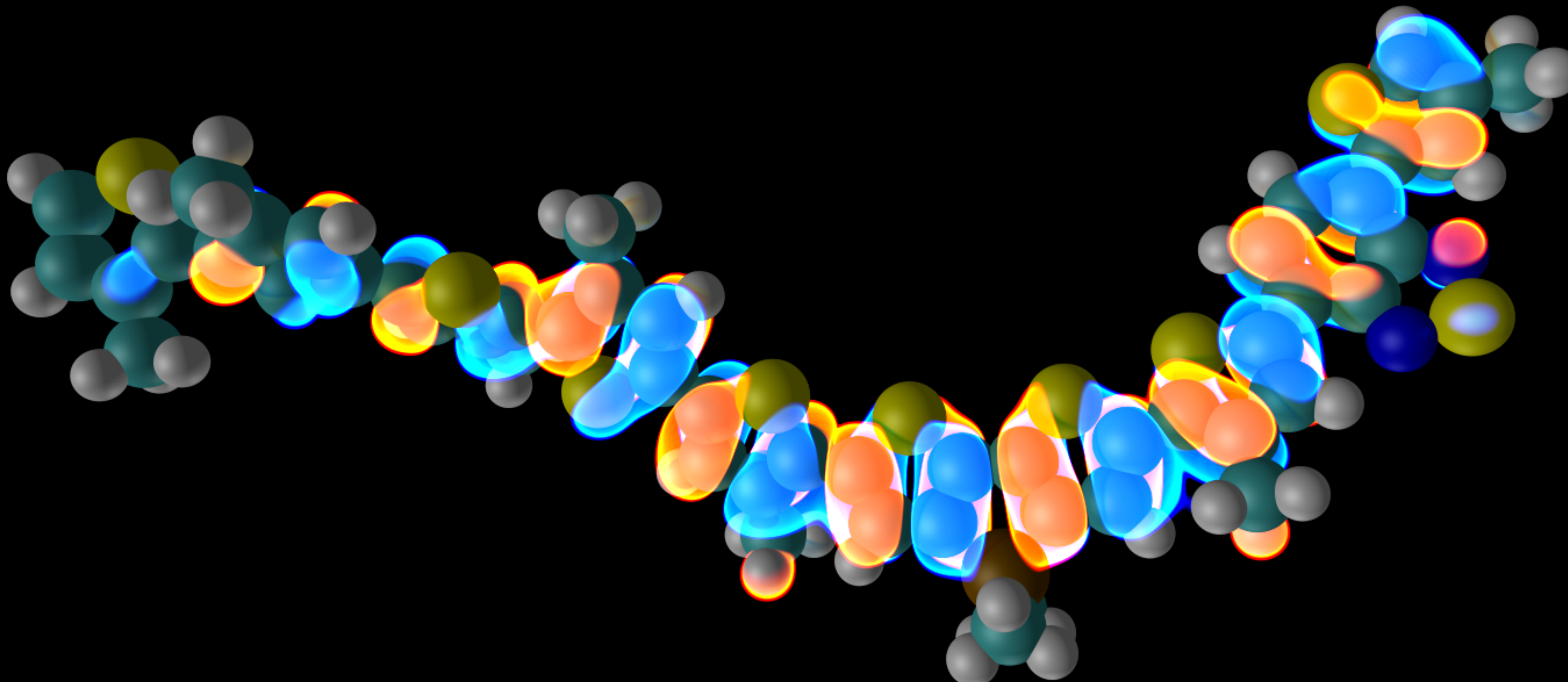
hydrogen atom



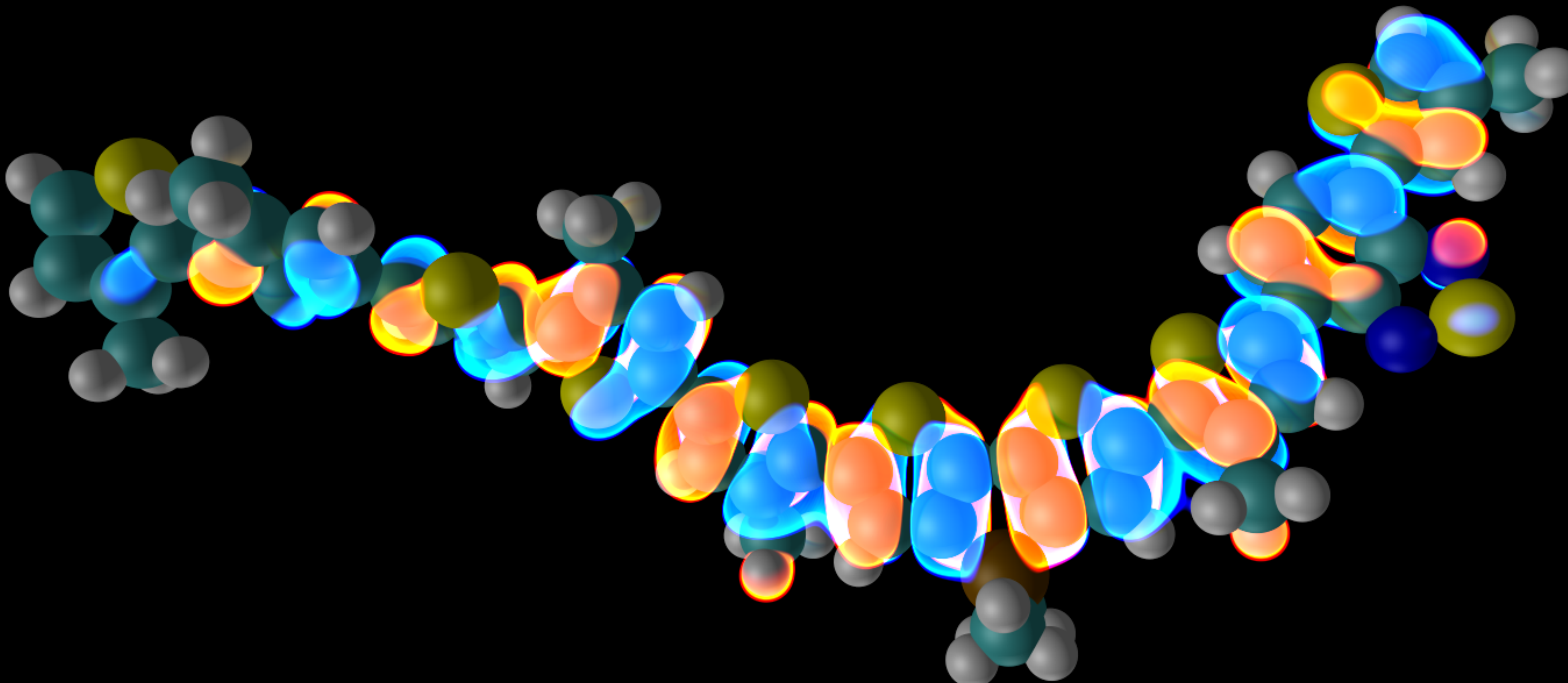
hydrogen atom



hydrogen atom

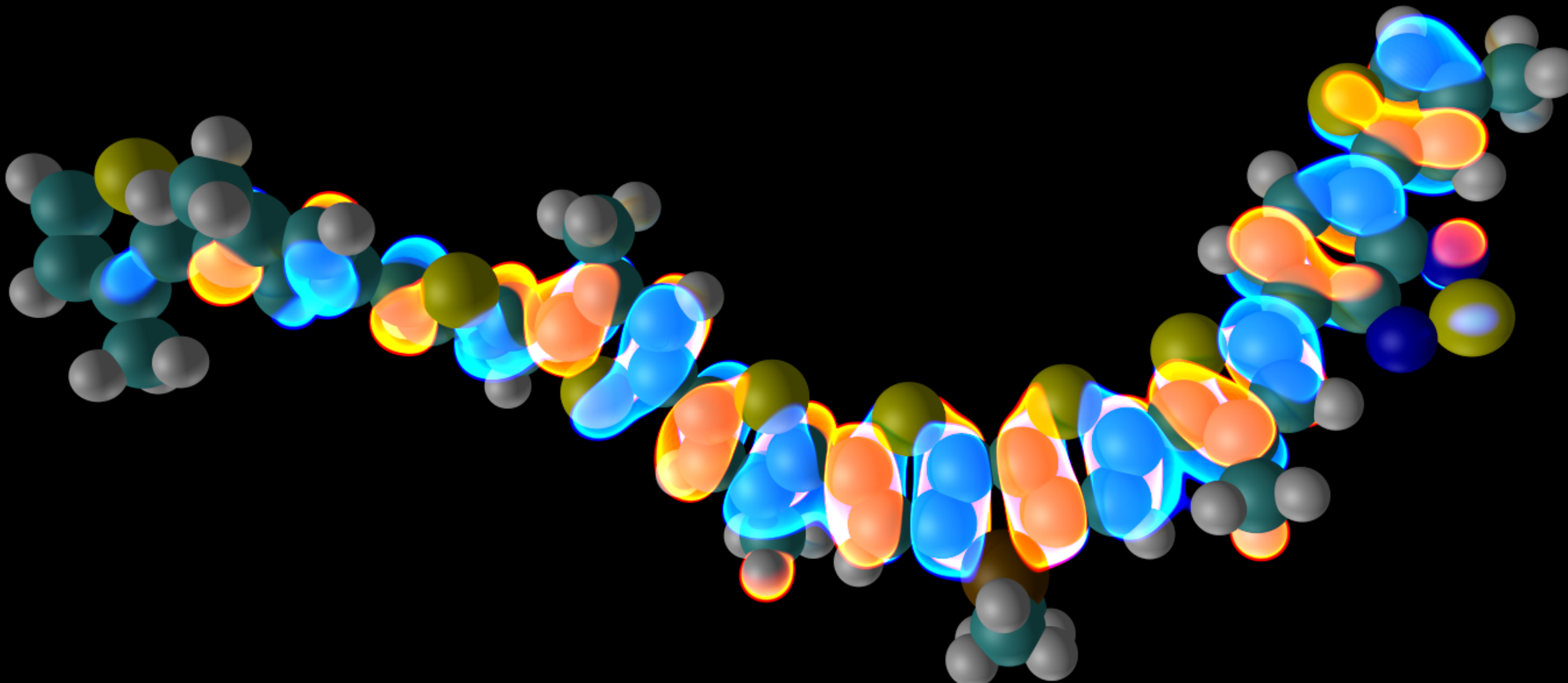


material = nuclei + electrons

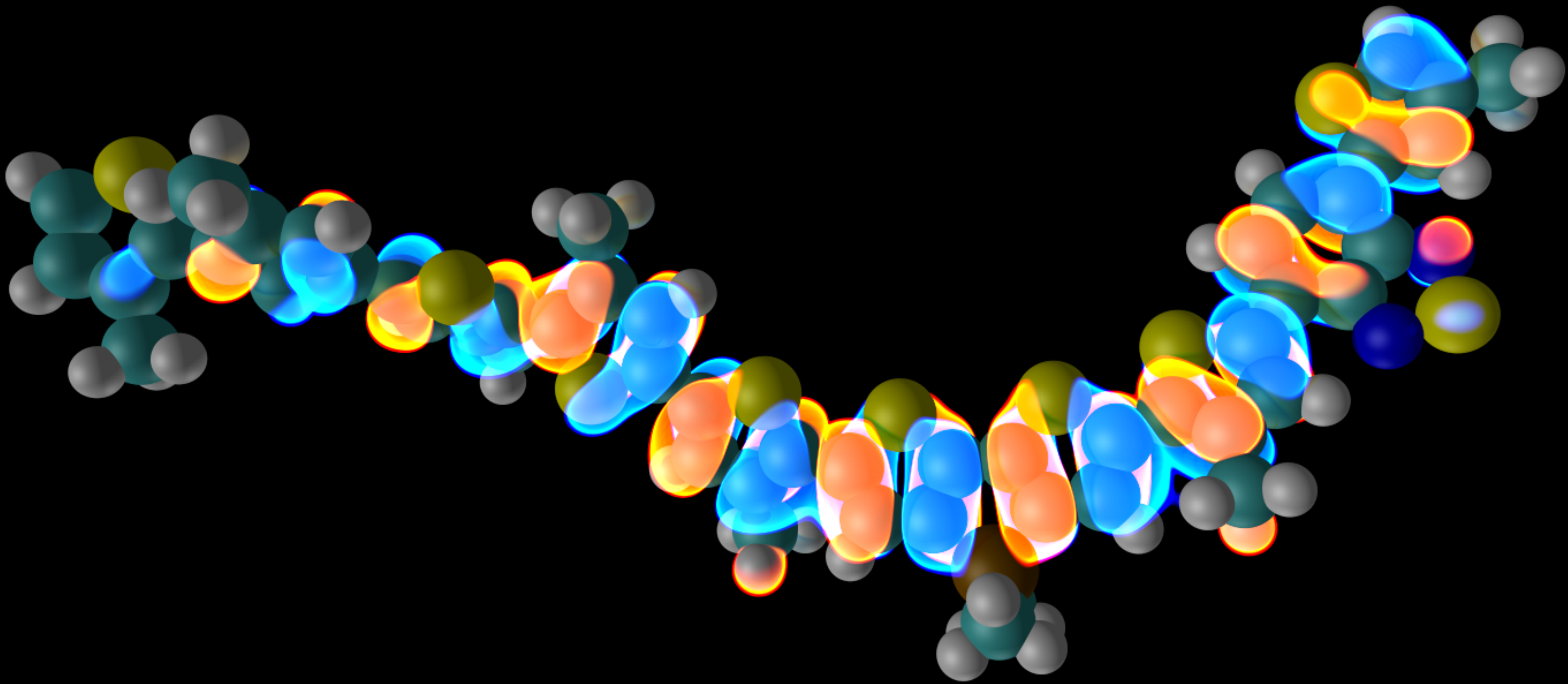


material = nuclei + electrons

$$\underbrace{\text{nuclei}}_{+} \qquad \underbrace{\text{electrons}}_{-}$$

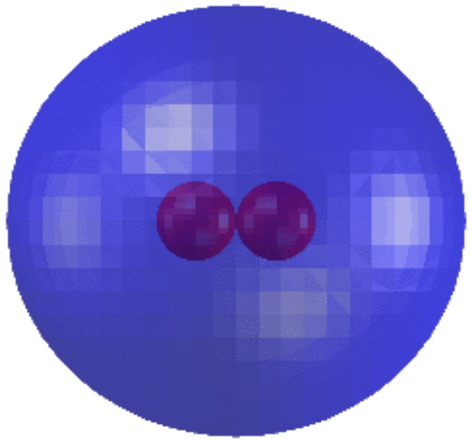


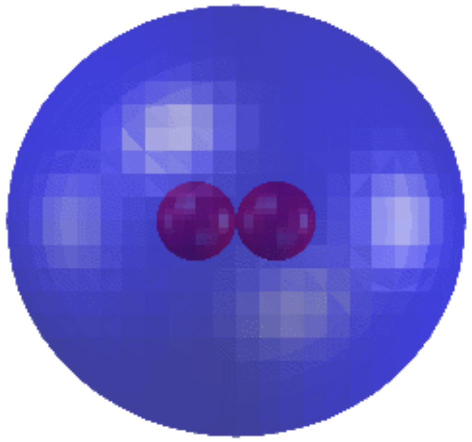
$$\textbf{material} = \textbf{nuclei} + \underbrace{\textbf{electrons}}_{\textbf{‘glue’}}$$



Schrödinger’s equation

$$H\Psi = E\Psi$$





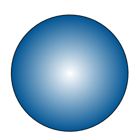
Fundamentals

Classical vs. quantum

- **Classical mechanics** and **quantum mechanics** differ in how they describe **electrons**

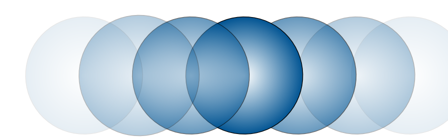
In classical mechanics, **electrons** are points

m_e



In quantum mechanics, **electrons** are clouds

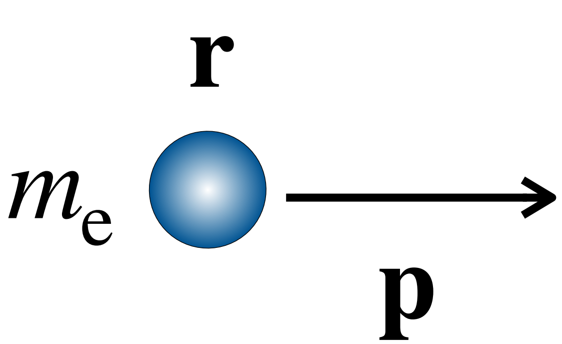
m_e



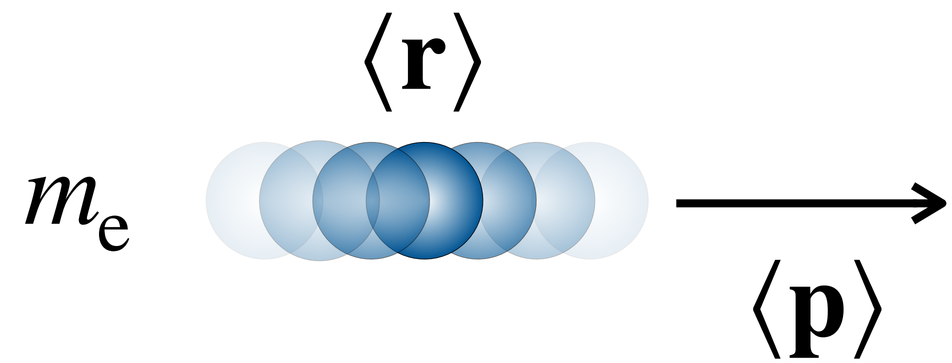
Classical vs. quantum

- **Classical mechanics** and **quantum mechanics** differ in how they describe **electrons**

In classical mechanics, the position and momentum are precisely known



In quantum mechanics, only their averages are known



In classical mechanics, the position and momentum tell everything about the **electron**

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

In quantum mechanics, what defines the state of the **electron** is the **wave function**

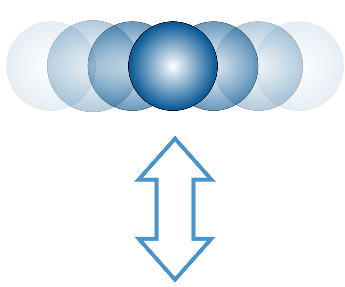
$$\psi(\mathbf{r})$$

Wave function

- In quantum mechanics, an **electron** is described by a **wave function**, which encodes all information about its state

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, i.e., $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$.



$\psi(\mathbf{r})$

A **wave function** $\psi(\mathbf{r})$ is a function of space whose values are complex and which defines the state of an electron

Probability density

$$\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2 = [\mathrm{Re}(\psi(\mathbf{r}))]^2 + [\mathrm{Im}(\psi(\mathbf{r}))]^2$$

$$\int |\psi(\mathbf{r})|^2 d\mathbf{r} = 1$$

Normalization condition

Average energy of a wave function

- In quantum mechanics, only the average of the total energy $\langle E \rangle$ of the wave function is known

- This average energy is also called the expectation value of the total energy

Definition | Expectation value of the total energy

The **expectation value of the total energy** of an electron is the average value of the total energy over experimental trials for a given state of that electron. If $\psi(\mathbf{r})$ is the wave function of the electron, this value is

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

Complex conjugate

$\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$

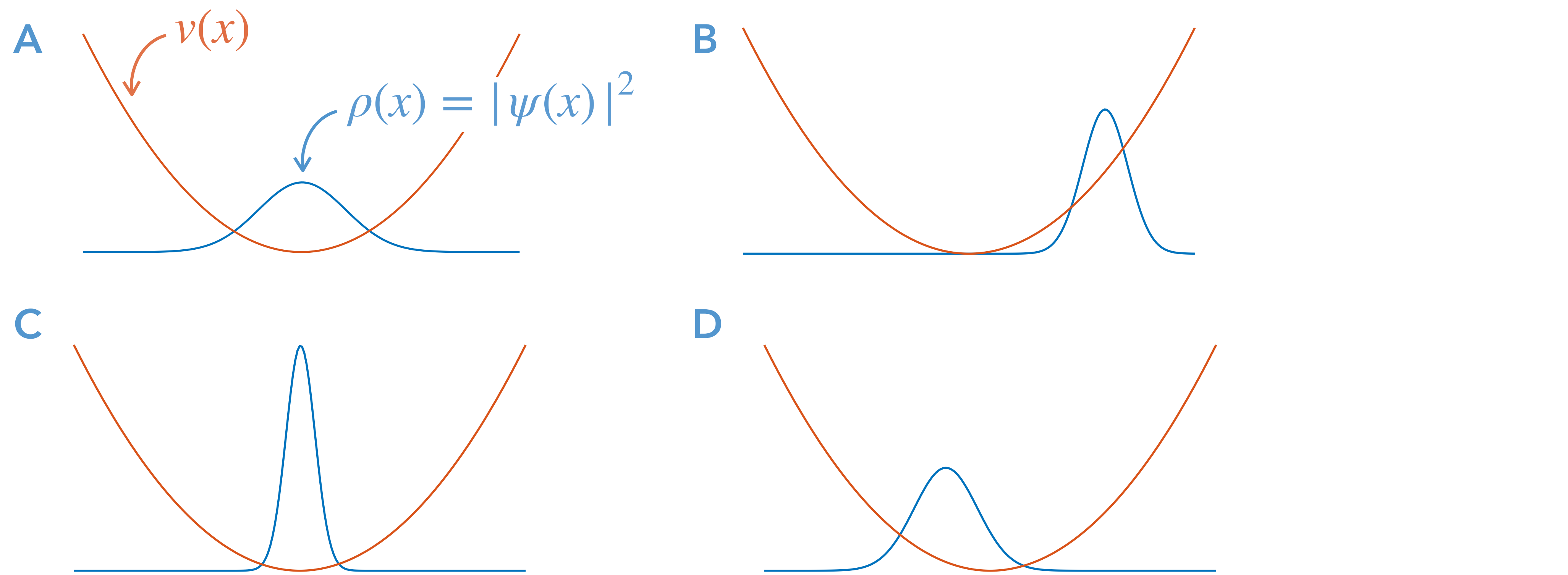
Understanding each term of the total energy

- The total energy can be split into **kinetic** and **potential** parts

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

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

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



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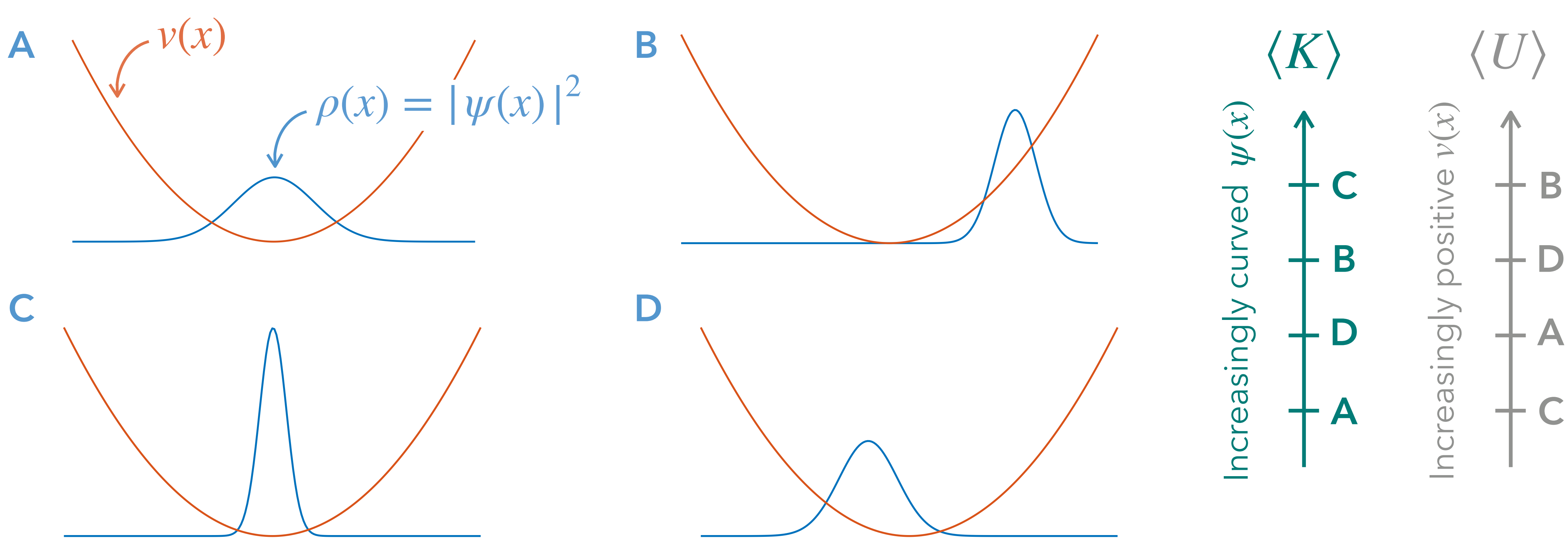
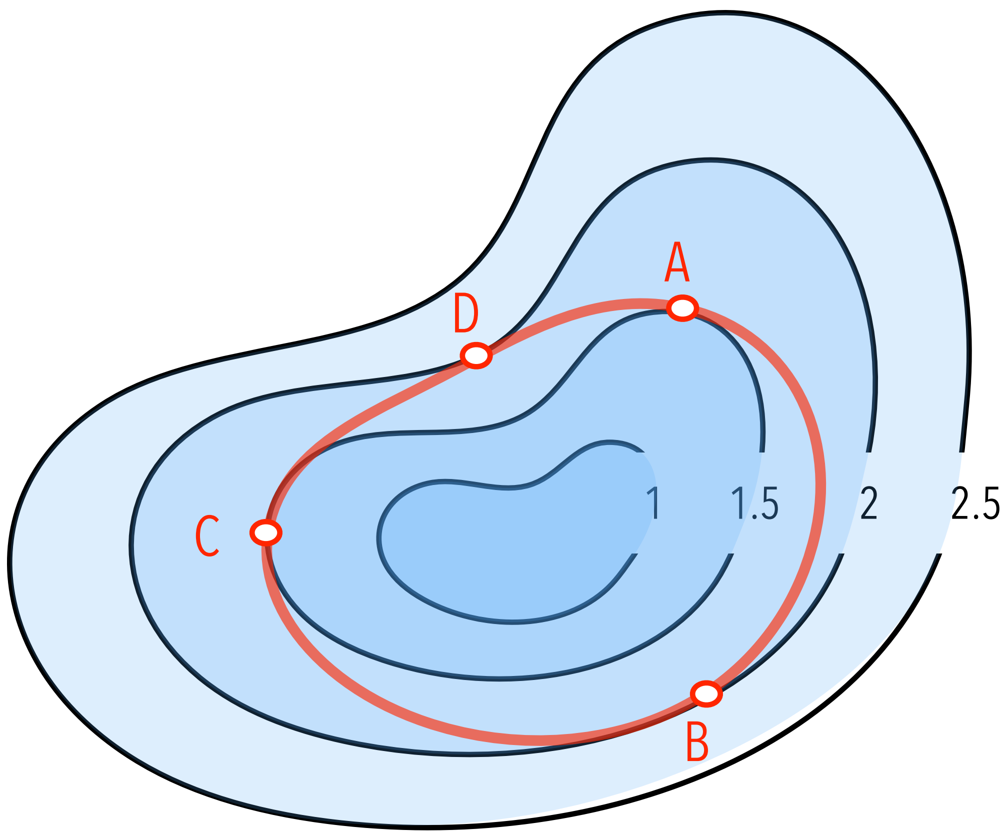


Finding the minimum of the total energy



Equilibrium states

- Using the Lagrange multiplier method, we get the following important result

Definition | time-independent Schrödinger equation

The equilibrium states ψ of an electron for a system described by the Hamiltonian H can be determined by solving the eigenvalue problem

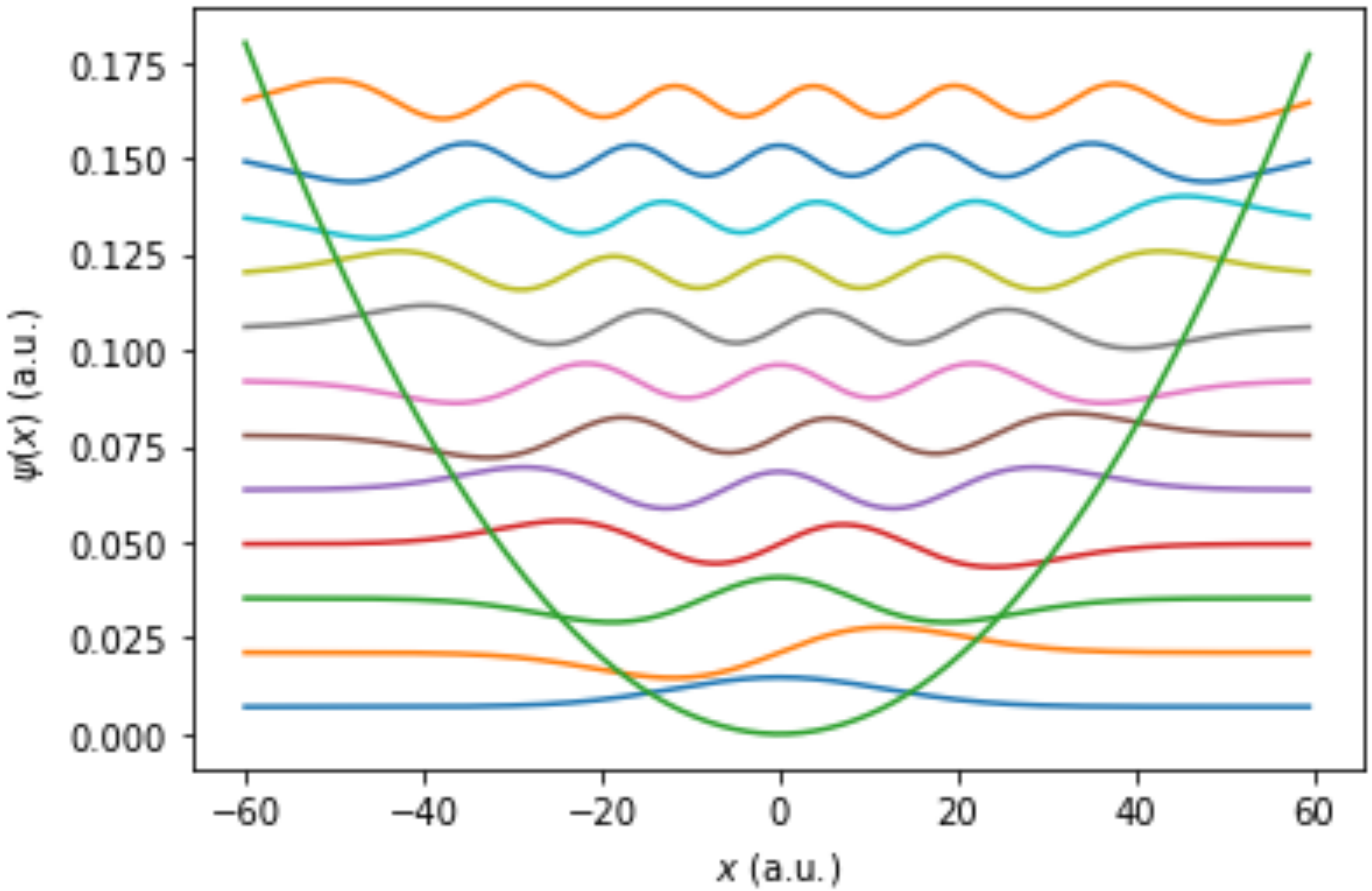
$$H\psi = \mathscr{E}\psi$$

This eigenvalue problem is referred to as the time-independent Schrödinger equation

- **Simulation.** In MATLAB, eigenvalue problems can be solved with `[V,D]=eigs(H,N,'sm')`. Using `electronic_states`, plot the equilibrium states of an electron in a well.

Equilibrium states (cont'd)

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



Equilibrium states (cont'd)

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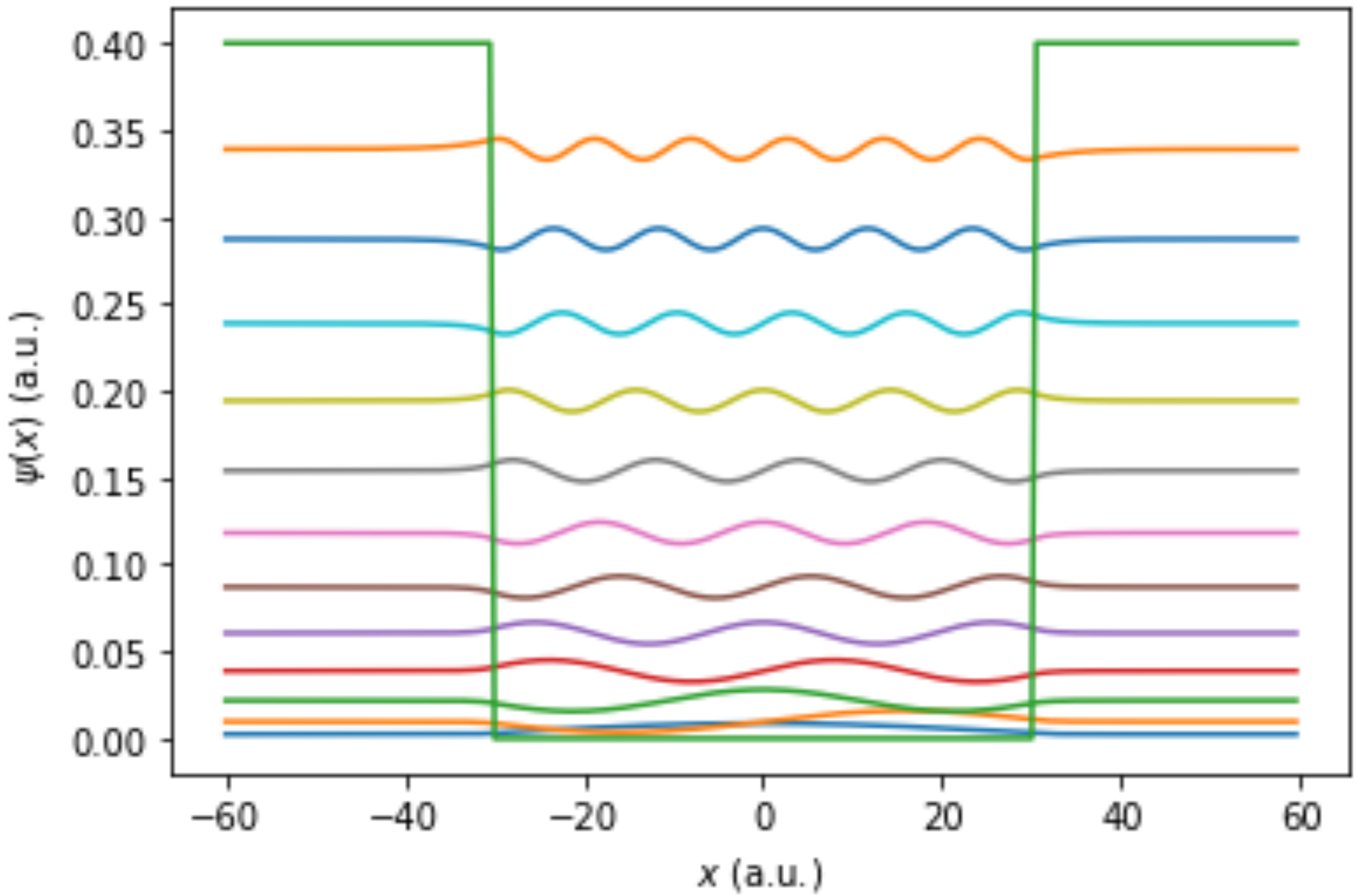

Equilibrium states (cont'd)

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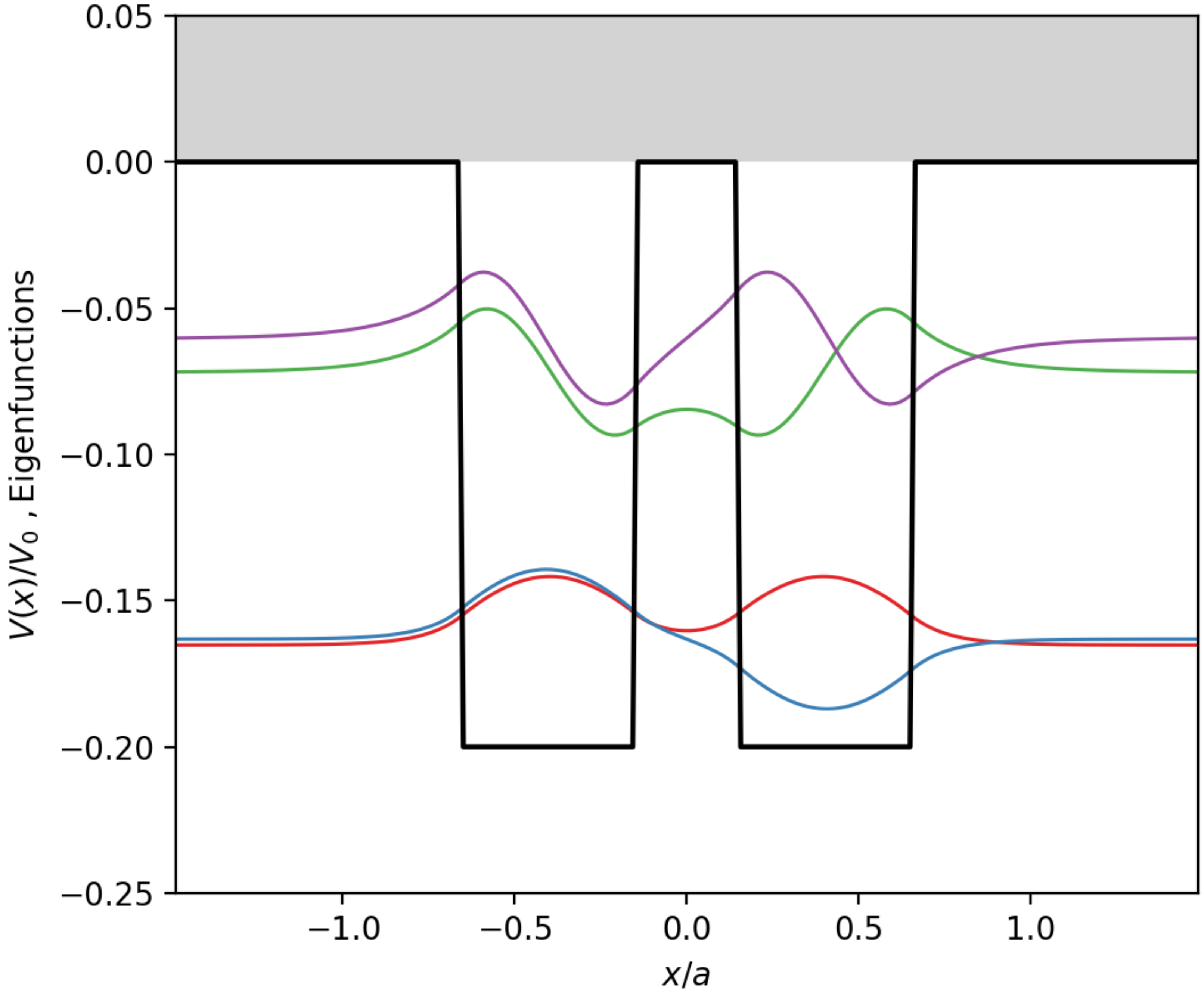

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