

## Key concepts of quantum mechanics

The fundamental constituents of materials are electrons and atomic nuclei. These objects (in particular electrons) are so small and light that we cannot use the laws of classical mechanics, such as Newton's equation, to describe their motion. Instead the behaviour of these particles is governed by the laws of quantum mechanics.

In quantum mechanics, the state of a particle (we will mostly talk about electrons) is described by its **wavefunction**  $\psi(\mathbf{r}, t)$ . The physical meaning of the wavefunction is as follows:  $|\psi(\mathbf{r}, t)|^2 dV$  is the **probability that an electron can be found in the volume element  $dV$  at position  $\mathbf{r}$  at time  $t$** . **Note that this means that we cannot say with absolute certainty where an electron is located at a specific time  $t$**  (this gives rise to the famous Heisenberg uncertainty relation). **But the electron has to be somewhere and as a consequence the wavefunction must be normalized**, i.e.

$$\int_{\text{all space volume}} dV |\psi(\mathbf{r}, t)|^2 = 1, \quad \text{电子 - 定在某处} \quad (1)$$

when we integrate over all of space.

To calculate  $\psi$ , we have to solve the Schrödinger equation. We will mostly be studying its time-independent version

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r}) \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r}), \quad (2)$$

where  $\hbar = 1.05 \times 10^{-34} \text{ m}^2\text{kg/s}$  is the **reduced Planck constant**,  $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$  denotes the **Laplacian operator** and  $m = 9.1 \times 10^{-31} \text{ kg}$  is the electron mass. Moreover,  **$V(\mathbf{r})$  is the potential energy of the electron - in a material this arises from the interaction with the positively charged nuclei and the other electrons**. Finally,  $\epsilon$  is the energy of the electron.

An alternative way to write the Schrödinger equation is

$$\hat{H} \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r}), \quad \text{+ attracted - repulsed} \quad (3)$$

where we introduced the Hamiltonian operator

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \quad \text{potential energy, } E_p \quad (4)$$

In this form, the Schrödinger equation resembles a matrix eigenvalue problem where  $\psi$  is the **eigenvector** and  $\epsilon$  the **eigenvalue**.

The **Hamiltonian operator** can be used to calculate the total energy through the so-called **expectation value** defined as

$$\hat{H} \quad \int dV \psi^*(\mathbf{r}) \hat{H} \psi(\mathbf{r}) = \epsilon, \quad (5)$$

where the Schrödinger equation and the normalization of the wavefunction was used.

Note that the first term in the Hamiltonian describes the kinetic energy of the electron. In classical mechanics, the kinetic energy is given by  $mv^2/2 = p^2/(2m)$ , where  $v$  is the velocity and  $p = mv$  the momentum. The transition from classical to quantum mechanics is achieved by replacing the momentum by  $-i\hbar\nabla$ .

### 0.1 Electron in free space

Let us now solve the **Schrödinger equation for an electron in free space**, ie a situation where there are **no nuclei or other electrons around**. In that case, the potential that enters the Schrödinger equation (SE) vanishes  **$V(\mathbf{r}) = 0$**  and we have to solve

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r}). \quad (6)$$

#### Equation 2

-  $\hbar$ , reduced Planck's constant

$$= \text{Planck's constant} / 2\pi$$

$6.63 \times 10^{-34} \text{ Js}$

-  $\nabla^2$ , Laplacian operator 拉普拉斯算子

a differential operator that represent the divergence of the gradient of a function.

#### Equation 4

$$-\frac{\hbar^2}{2m} \nabla^2 = \frac{1}{2} mv^2 = \frac{1}{2} \frac{\vec{p}^2}{m}$$

$$-\hbar^2 \nabla^2 = \vec{p}^2$$

$$i\hbar \nabla = \frac{\hbar \nabla}{i} = \vec{p} \quad \text{momentum}$$

#### Equation 5 (for a given wave function, $\psi(\mathbf{r})$ )

$$\hat{H} \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r}) \quad \text{Matrix eigenvalue} \quad A v = \lambda v$$

量子力学中, state's expectation value 由 inner product (内积) of state & operator

$$\text{expectation value formula. } \langle \hat{O} \rangle = \int \psi^*(x) \hat{O} \psi(x) dx \quad (\text{in 2D})$$

$$\hat{H} \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r}) \implies \int \psi^*(\mathbf{r}) \hat{H} \psi(\mathbf{r}) dV = \int \psi^*(\mathbf{r}) \epsilon \psi(\mathbf{r}) dV \quad (\text{in 3D})$$

$$E_{\text{avg}} = \int \psi^*(\mathbf{r}) \hat{H} \psi(\mathbf{r}) dV$$

$$\epsilon = \epsilon \int \psi^*(\mathbf{r}) \psi(\mathbf{r}) dV$$

$$\epsilon = E_{\text{avg}} = \int \psi^*(\mathbf{r}) \hat{H} \psi(\mathbf{r}) dV$$

The partial differential equation can be solved by the separation of variables techniques. In this approach the wavefunction is written as

$$\psi(\mathbf{r}) \Rightarrow \psi(x, y, z) = f(x)g(y)q(z), \quad (7)$$

with  $f$ ,  $g$  and  $q$  being functions to be determined. Inserting this ansatz into the SE yields

$$\frac{1}{f(x)} \frac{\partial^2 f(x)}{\partial x^2} + \frac{1}{g(y)} \frac{\partial^2 g(y)}{\partial y^2} + \frac{1}{q(z)} \frac{\partial^2 q(z)}{\partial z^2} = \boxed{-\frac{2m\epsilon}{\hbar^2}} \text{ constant} \quad (8)$$

Note that the first term on the left hand side only depends on  $x$ , the second only on  $y$  and the third only on  $z$ , but the right hand side is a constant. Thus we must conclude that each term on the left hand side is also a constant. For example, the first term can be written as

$$\text{constant} + \frac{1}{f(x)} \frac{\partial^2 f(x)}{\partial x^2} = -\frac{2m\epsilon_x}{\hbar^2}, \quad (9)$$

where we introduced the constant  $\epsilon_x$ . Similar expressions can be derived for the second and third terms. The equation for  $f(x)$ , however, is easy to solve. The solutions can be written as plane waves, i.e.

$$f(x) = A_x e^{ik_x x}, \quad (10)$$

where  $A_x$  and  $k_x$  are constants. Note that  $k_x$  can be interpreted as the  $x$ -component of a wave vector. Inserting this solution into the equation for  $f(x)$  yields

$$-k_x^2 f(x) = -\frac{2m\epsilon_x}{\hbar^2} f(x), \quad (11)$$

which provides a relationship between  $k_x$  and  $\epsilon_x$ .

The total energy  $\epsilon$  can then be written as

$$\epsilon = \epsilon_x + \epsilon_y + \epsilon_z = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 \mathbf{k}^2}{2m}. \quad (12)$$

We find that the energy of the electron in free space is proportional to the magnitude of its wavevector squared.

The full wavefunction is given by

$$\psi(\mathbf{r}) = A e^{i\mathbf{k} \cdot \mathbf{r}} \quad (13)$$

with  $A = A_x A_y A_z$  being a constant that is determined by the normalization condition.

## 0.2 Electron in a hydrogen atom

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An electron in a hydrogen atom feels the electrostatic attraction of the positively charged nucleus (a single proton in the case of a hydrogen atom) which gives rise to the potential energy

$$V(\mathbf{r}) = -\frac{e^2}{4\pi\epsilon_0 r}, \quad (14)$$

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where  $\epsilon_0$  is the permittivity of free space and  $r$  denotes the distance of the electron from the nucleus.

The corresponding SE can be solved analytically, but it is quite complicated. We will therefore only describe the results. The state with the lowest energy, often called the ground state, is denoted by  $1s$  and has an energy

$$\epsilon_{1s} = -\frac{m}{2\hbar^2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \approx -13.6 \text{ eV}. \quad (15)$$

Note that  $1 \text{ eV} \approx 1.6 \times 10^{-19} \text{ J}$ . The corresponding wave function is

$$\psi_{1s}(\mathbf{r}) = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}, \quad (16)$$

where we introduced the Bohr radius  $a_0 = 4\pi\epsilon_0 \hbar^2 / (me^2) = 0.5291 \times 10^{-10} \text{ m}$ , which reflects the size of the hydrogen atom.

The four states with the second lowest energy are denoted  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$  and have an energy  $\epsilon_{2s} = \epsilon_{1s}/2^2 \approx -3.4 \text{ eV}$ . Then, there are the states  $3s$ ,  $3p_x$ ,  $3p_y$ ,  $3p_z$ ,  $3d_{xy}$ ,  $3d_{xz}$ ,  $3d_{yz}$ ,  $3d_{z^2}$  and  $3d_{x^2-y^2}$  which all have an energy  $\epsilon_{3s} = \epsilon_{1s}/3^2 \approx -1.5 \text{ eV}$ . In general, the energy of a state  $ns$  is given by  $\epsilon_{ns} = \epsilon_{1s}/n^2$ .

$$\nabla^2 \Rightarrow \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

$$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x, y, z) = \epsilon \psi(x, y, z)$$

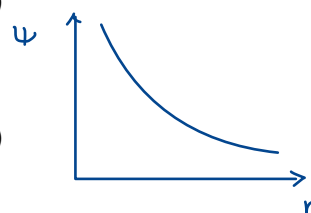
$$\leftarrow -\frac{\hbar^2}{2m} \left( \frac{\partial^2 f(x)}{\partial x^2} + \frac{\partial^2 g(y)}{\partial y^2} + \frac{\partial^2 q(z)}{\partial z^2} \right) = \epsilon f(x) g(y) q(z)$$

Equation 10

a plane wave refers a solution of the free particle Schrödinger equation. (describe the particle without any external force/potential).

Equation 12

$$\text{Equ 11} \Rightarrow k_x^2 f(x) = \frac{2m\epsilon_x}{\hbar^2} f(x) \Rightarrow \epsilon_x = k_x^2 \frac{\hbar^2}{2m}$$



### 0.3 Multi-electron atoms

All atoms other than the hydrogen atom have more than 1 electron in their neutral state. The total number of electrons in the neutral state is equal to the number of protons in the nucleus and denoted by  $Z$ . The potential that the nucleus creates is then given by

$$V(\mathbf{r}) = -\frac{Ze^2}{4\pi\epsilon_0 r}. \quad (17)$$

In the simplest approximation, we neglect the interaction among the electrons. Then, the solutions of the multi-electron atom are related to those of the hydrogen atom, but the Bohr radius  $a_0$  must be replaced by  $a_0/Z$ . The states can still be labelled in the same way and the energies are given by

$$\epsilon_{ns}(Z) = \frac{Z^2}{n^2} \epsilon_{1s}(Z=1). \quad (18)$$

Similarly, the 1s wavefunction is given by

$$\psi_{1s}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi a_0^3}} e^{-Zr/a_0}. \quad (19)$$

To understand the electronic structure of multi-electron atoms, we also have to take the Pauli principle into account which states that only two electrons can be placed into each orbital (one electron with the spin pointing up, the other with spin pointing down - note that the concept of spin will be discussed later in the course).

Knowing the energy levels and the Pauli principle, we can construct the electronic structure of any atom. For example, the hydrogen atom has one electron in the 1s state, the helium atom has 2 electrons in the 1s state. Now that the 1s state is filled, the next atom, Li, has 2 electrons in the 1s state and 1 electron in the 2s state. Next, Be has a full 1s state and 2 electrons in the 2s state which is now also full. This is why in B, there are 2 electrons in 1s, 2 electrons in 2s and 1 electron in one of the 2p states. This procedure is known as the Aufbau principle.

You might ask, though, why we are first putting electrons into the 2s state and not into the 2p states even though they have the same energies according to our analysis above. It turns out that the energy of the 2s state is lower than that of the 2p states if electron-electron interactions are taken into account. However, this is not trivial: to calculate the potential energy due to the other electrons we need to know their distribution in space. To determine their distribution in space, we must calculate their wavefunction by solving the SE. This leads to a self-consistent problem which is solved by density-functional theory.