Why Are Atoms Stable?

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• from Thomson's pudding to Rutherford's planet

Through a series of work on cathode rays, Thomson discovered electrons in 1897. Because atoms are charge neutral, he proposed a pudding model for atoms – the positive charge distributes uniformly inside the atoms and the negatively charged electrons are placed in appropriate equilibrium positions. Take hydrogen atom as a simple example (shown in Figure 1). Upon perturbations, the electron oscillates and emits light of the same frequency. However, Thomson's pudding model seems to predict a unique emission frequency while the observed spectrum for the hydrogen atom is rather complicated.
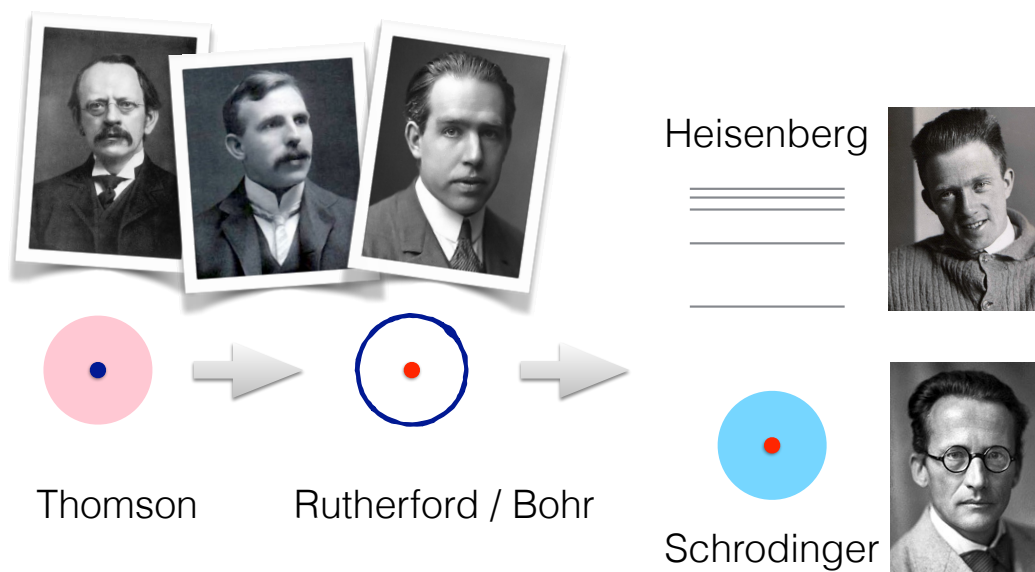

Figure 1: Evolution of atomic models for the hydrogen atom. The red color denotes the positive charge while the blue denotes the negative charge.

But, this is not the knell for the pudding model. The famous gold foil experiment shows that the incident alpha particles (much heavier than elec-

trons) occasionally bounce back. These experimental evidences motivated Rutherford to propose the planet model in 1909 – positive charge forms tiny nucleus at the centre of the atom and electrons move around it like planets. But, Rutherford's model violates Maxwell equations. Because electrons are moving in orbits, the acceleration is not zero and will radiate electromagnetic waves. We thus run into this famous puzzle: *Moving charge means radiation of light and thus jeopardizes the stability of atoms.*

• Bohr's model for hydrogen atom

The first cure to Rutherford's planet model is proposed by Bohr in 1913. As a young scientist, he was bold and courageous the make the following statements without solid derivations:

1. Electrons in an atom can stay in stationary states of constant energy without radiating.

2. An atom emits (absorbs) radiation of definite frequency when an electron transfers from one stationary state to another.

Hum, what a great approach to cure the stability problem – Bohr just assumed that it cannot happen! The true value of Bohr's model is not that it provides a reasonable explanation for the stability of atoms. Instead, it is the first model with quantitative predictions for the observed spectrum.

First of all, we need to find these stationary states in atoms. Let us start from the simplest hydrogen atom. Bohr proposed that the angular momentum of the circulating electron is quantized in units of $\hbar$,

$$L = n\hbar, \qquad n = 1, 2, 3, \cdots . \tag{1}$$

Suppose the electron moves in circular orbit and still respects Newton's second law and Maxwell equations,

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}. \tag{2}$$

Combined with the quantization rule $L = mvr = n\hbar$, it is straightforward to solve for the radii of the stationary states,

$$r_n = \left(\frac{h^2 \epsilon_0}{\pi m e^2} \right) n^2 = a_0 n^2, \tag{3}$$

where $a_0 \approx 0.053$ nm is the radius of the hydrogen atom in the ground state ($n = 1$). The energy for each stationary state can be computed as well,

$$E_n = -\left(\frac{me^4}{8h^2\epsilon_0^2}\right)\frac{1}{n^2} \approx -\frac{13.6 \text{ eV}}{n^2}. \tag{4}$$

Bohr's second postulate is about the frequency of radiating emission when the electron moves from stationary state m (with higher energy) to stationary state n (with lower energy),

$$\omega_{mn} = \frac{E_m - E_n}{\hbar}. \tag{5}$$

Similarly, the absorption frequency from state n to state m is the same. It is quite remarkable that the predicted frequencies agree with the observed spectrum for the hydrogen atom rather well.

• de Broglie wave

The quantization of angular momentum seems to pop out from nowhere in Bohr's model. In 1924, de Broglie proposed that all matters have wave-like behavior, satisfying the same relations for photons proposed by Einstein,

$$\lambda = \frac{h}{p}, \qquad f = \frac{E}{h}. \tag{6}$$

The math is simple but the physical implications are deep – profound enough to win de Broglie a Noble Prize. If one imagines these stationary states are standing waves around the circular orbits, it requires that the circumference is integer multiples of the wave length,

$$2\pi r = n\lambda \quad \rightarrow \quad L = n\hbar. \tag{7}$$

But, this is not the moment to celebrate yet. Do matter waves share the same dynamics as ordinary waves? To simplify the algebra, let us focus on the one dimensional case. We know the general solution for the travelling waves in one dimension is

$$u(x,t) = f(x - vt) + g(x + vt), \tag{8}$$

where $f(x - vt)$ and $g(x + vt)$ corresponds to right-moving and let-moving waves respectively. A standing wave composed of equal amplitude for the right-moving and the left-moving components takes the simple form,

$$u(x,t) = A\sin(kx)\cos(\omega t). \tag{9}$$

As can be seen in Figure 2, the standing wave still gives rise to oscillatory motions and thus cannot account for the stability of atoms.

• Heisenberg's matrices

Heisenberg thought about these magic orbits for the stationary states and eventually came to the conclusion that it is meaningless to talk about "trajectories" of an electron in atoms because no one is able to measure their existence ever. Instead, one should focus on observables like ω_{mn} constructed from these stationary states. At the end of the day, he came to the bizarre conclusion that all physical quantities should be represented by matrices. For instance, the position of the electron x is a matrix and the momentum of the electron p is also a matrix. Because they are matrices, their products depend on the orders,

$$xp - px = i\hbar \neq 0. \tag{10}$$

Heisenberg's matrix approach is probably too abstract for most freshman students. So, I shall stop here with a brief comment that his approach is completely equivalent to Schrödinger's approach in the following sections.

• emergence of probability description

Heisenberg was wise to abandon searching for the magic orbits. It turns out that the stability of atoms find its natural explanation by the probability interpretation of the de Broglie waves. Suppose the matter wave is described by the wave function $\psi(x, t)$. In quantum world, we no longer know where the electron is and requires a probability distribution,

$$P(x, t) = |\psi(x, t)|^2. \tag{11}$$

Because the probability adds up to unity, the wave function satisfies the integral constraint,

$$\int |\psi(x, t)|^2 \, dx = 1, \tag{12}$$

often referred as the normalization condition. Note that the charge density of the electron is related to the probability density,

$$\rho(x, t) = -eP(x, t) = -e|\psi(x, t)|^2. \tag{13}$$

To explain the existence of these stationary states, one looks for a time-dependent wave function $\psi(x, t)$ with a static probability density $P = P(x)$.
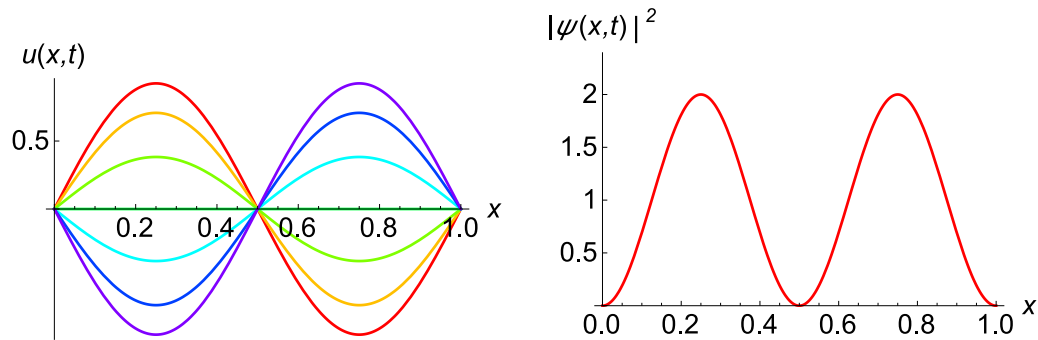
Figure 2: Standing wave (left panel) and stationary state (right panel) with wave number $k = 2\pi/L$ inside a box of unit length $L = 1$.

• Schrödinger's stationary waves

Schrödingier found the wave equation to describe the dynamics of matter waves. We will learn more about the technical details of the Schrödingier equation in later lectures. For comparison, consider the matter wave confined in a 1D box of length L. Unlike the ordinary standing waves, the wave function for a stationary state turns out to be

$$\psi(x,t) = \sqrt{\frac{2}{L}} \sin(kx)\, e^{-i\omega t}, \tag{14}$$

where the wave number k and the angular frequency ω are related,

$$E = \frac{p^2}{2m} \quad \rightarrow \quad \hbar\omega = \frac{\hbar^2 k^2}{2m}. \tag{15}$$

Try to convince yourself that the prefactor $\sqrt{2/L}$ ensures that the resultant probability adds up to unity. Note that the dynamics of the stationary state solely shows up in the complex phase and thus disappears when evaluating the probability density (shown in Figure 2),

$$|\psi(x,t)|^2 = \frac{2}{L} \sin^2(kx) \quad \rightarrow \quad P(x) = \frac{2}{L} \sin^2(kx). \tag{16}$$

This is the key to solve the long-standing puzzle. For an electron in the stationary state, its dynamics is captured by the time-dependent wave function. The kinetic energy of the electron is not zero, $E = \hbar\omega = \hbar^2 k^2/2m$. However, the probability density does not depends on time and the resultant charge density is stationary – no radiation! We learn from this inspiring example that an electron can carry non-zero kinetic energy without moving around.

The stability of atoms is explained by the dynamical complex phase $e^{-i\omega t}$ in the stationary states – puzzle solved by the Schrödinger equation.

When will the time dependence becomes observable in experimental measurements? The dynamical complex phase also explains Bohr's second postulate. Consider the superposition of two stationary states,

$$\psi = \frac{1}{\sqrt{2}}\,\phi_1(x)e^{-i\omega_1 t} + \frac{1}{\sqrt{2}}\,\phi_2(x)e^{-i\omega_2 t}. \tag{17}$$

In general, the functions $\phi_i(x) = |\phi_i(x)|e^{i\theta_i}$ are complex. The probability density contains a static part and an oscillatory part,

$$P(x,t) = \frac{1}{2}\,|\phi_1(x)|^2 + \frac{1}{2}\,|\phi_2(x)|^2 + |\phi_1(x)|\,|\phi_2(x)|\cos(\omega_{21}t - \theta_{21}), \tag{18}$$

where $\theta_{21} = \theta_2(x) - \theta_1(x)$. It is quite remarkable that the oscillatory frequency is nothing but the difference of the frequencies,

$$\omega_{21} = \omega_2 - \omega_1. \tag{19}$$

Therefore, the superposition of two stationary states generates oscillatory charge density with non-zero frequency ω_{21} and thus radiations of the same frequency as postulated by Bohr. It is worth emphasizing that, due to the peculiar quantum dynamics, the frequency of the emitted (or absorbed) radiation is neither ω_1 nor ω_2 but the difference of them.

Happy

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