Physical foundations

The continuity equation

The Schrödinger equation for a one-electron system reads:

$$i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r},t)=\left(-\frac{\hbar^2}{2m}\Delta+V(\boldsymbol{r})\right)\psi(\boldsymbol{r},t)$$

By means of the wave function $\psi(\boldsymbol{r},t)$, i.e. a solution of the Schrödinger equation, we define the expressions:

$$\rho:=\psi^*\psi \tag{1}$$

and

$$\boldsymbol{j}:=\frac{\hbar}{2m\mathrm{i}}\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right) \tag{2}$$

Using the Schrödinger equation we get:

$$\frac{\partial\rho}{\partial t}+\operatorname{div}\boldsymbol{j}=0\,. \tag{3}$$

Equation (3) has the mathematical structure of a continuity equation. $\rho(\boldsymbol{r},t)$ and $\boldsymbol{j}(\boldsymbol{r},t)$, taken together, describe the system exhaustively, and are thus equivalent to the wave function $\psi(\boldsymbol{r},t)$.

Multiplication of the equations (1), (2) and (3) with the elementary charge e:

$$\rho_e:=e\psi^*\psi$$

$$\boldsymbol{j}_e:=\frac{e\hbar}{2m\mathrm{i}}\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right)$$

$$\frac{\partial\rho_e}{\partial t}+\operatorname{div}\boldsymbol{j}_e=0 \tag{4}$$

ρ_e is a charge density and $\boldsymbol{j}_e$ an electric current density. Equation (4) can be read as a continuity equation of the electric charge.

Multiplication of the equations (1), (2) and (3) with the electron mass m:

$$\rho_m:=m\psi^*\psi$$

$$\boldsymbol{j}_m:=\frac{\hbar}{2\mathrm{i}}\left(\psi^*\nabla\psi-\psi\nabla\psi^*\right)$$

$$\frac{\partial\rho_m}{\partial t}+\operatorname{div}\boldsymbol{j}_m=0 \tag{5}$$

ρ_m is a mass density and $\boldsymbol{j}_m$ a mass current density. Equation (4) can be read as a continuity equation of the mass.

The description of the electronic states by means of the functions $\rho(\boldsymbol{r},t)$ and $\boldsymbol{j}(\boldsymbol{r},t)$ suggests the following interpretation:

The electron consist of a kind of substance or „stuff“ that is distributed in space and that can flow. Since in the following we often have to refer to this „substance“, we give it a name: *Electronium* . In this interpretation, the electron consists of electronium in the same way as a sea consists of water or a coin of metal.

ρ_e = charge density $\mathbf{j}_e$ = electric current density ρ_m = mass density $\mathbf{j}_m$ = mass current density	} of the electronium

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Stationary and non-stationary states

For the Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r},t)=\left(-\frac{\hbar^2}{2m}\Delta+V(\boldsymbol{r})\right)\psi(\boldsymbol{r},t)$$

we try the solution:

$$\psi_k(\boldsymbol{r},t)=u_k(\boldsymbol{r})e^{-\frac{i}{\hbar}E_k t} \tag{1}$$

Inserting into the Schrödinger equation we get:

$$E_k u_k(\boldsymbol{r})=\left(-\frac{\hbar^2}{2m}\Delta+V(\boldsymbol{r})\right)u_k(\boldsymbol{r}) \tag{2}$$

This equation is of the type of an eigenvalue equation. Its solutions $u_k(\boldsymbol{r})$ form a complete set of functions. To every function $u_k(\boldsymbol{r})$ corresponds a well-defined *eigenvalue* E_k of the energy. Those states which are described by the particular solutions (1) of the Schrödinger equation, are called *eigenstates* of the energy.

Each solution of the Schrödinger equation can be written as a linear combination of the *eigenfunctions* $\psi_k(\boldsymbol{r},t)$:

$$\psi(\boldsymbol{r},t)=\sum_k a_k\psi_k(\boldsymbol{r},t)=\sum_k a_k u_k(\boldsymbol{r})e^{-\frac{i}{\hbar}E_k t}. \tag{3}$$

Sometimes, the eigenvalues of several solutions of the eigenvalue equation (2) are identical. The corresponding states are called *degenerate*.

The particular solutions $\psi_k(\boldsymbol{r},t)$ of the Schrödinger equation have the peculiarity that the electronium density ρ is time-independent:

$$\rho_k=\psi_k^{*}\psi_k=u_k^{*}(\boldsymbol{r})e^{+\frac{i}{\hbar}E_k t}\cdot u_k(\boldsymbol{r})e^{-\frac{i}{\hbar}E_k t}=u_k^{*}(\boldsymbol{r})\cdot u_k(\boldsymbol{r})$$

The same holds true for the current density $\boldsymbol{j}$, which is for $\psi_k(\boldsymbol{r},t)$ time-independent as well. That is why one says that the eigenstates of the energy are *stationary*. A linear combination (3) of eigenfunctions is, in general, not time-independent. The corresponding state is not stationary.

Only sometimes, such a linear combination is time-independent: if the $\psi_k(\boldsymbol{r},t)$ correspond to degenerate states. In this case we have

$$\psi(\boldsymbol{r},t)=\sum_m a_m u_m(\boldsymbol{r})e^{-\frac{i}{\hbar}E_m t}=\sum_m a_m u_m(\boldsymbol{r})e^{-\frac{i}{\hbar}Et}=e^{-\frac{i}{\hbar}Et}\sum_m a_m u_m(\boldsymbol{r})$$

Therewith the density becomes:

$$\rho=\psi^{*}\psi=e^{+\frac{i}{\hbar}Et}\sum_m a_m u_m^{*}(\boldsymbol{r})\cdot e^{-\frac{i}{\hbar}Et}\sum_n a_n u_n(\boldsymbol{r})=\sum_m a_m u_m^{*}(\boldsymbol{r})\cdot\sum_n a_n u_n(\boldsymbol{r})$$

Thus, the electronium density is time-independent. The same holds true for the current density

$$\left.\begin{aligned}\psi_k(\mathbf{r},t) &= u_k(\mathbf{r})e^{-\frac{i}{\hbar}E_k t} && \triangleright \text{ eigenstate of the energy}\\ \psi(\mathbf{r},t) &= \sum_{\substack{k,\text{ sum of}\\ \text{degenerate states}}} a_k u_k(\mathbf{r})e^{-\frac{i}{\hbar}E_k t} && \triangleright \text{ sum of degenerate states}\end{aligned}\right\} \quad \left\{\begin{aligned}&\rho \text{ and } \mathbf{j} \text{ time-independent}\\ &\text{stationary state}\end{aligned}\right.$$

$$\psi(\mathbf{r},t) = \sum_{\substack{k,\text{ sum of}\\ \text{non-degenerate states}}} a_k u_k(\mathbf{r})e^{-\frac{i}{\hbar}E_k t} \quad \triangleright \text{ sum of non-degenerate states} \left\{\begin{aligned}&\rho \text{ and } \mathbf{j} \text{ time-dependent}\\ &\text{non-stationary state}\end{aligned}\right.$$

Physical foundations

Angular momentum and magnetic moment

In states with $m \neq 0$ the current density $\boldsymbol{j}$ is unequal zero. A mass and a charge current is associated with the electronium current around the nucleus.

To the mass current corresponds an angular momentum. This can be calculated from the mass current. The result is the same as that from the quantum-mechanical eigenvalue equation:

$l_z = m\,\hbar$.

The charge current respresents a circular electric current, corresponding to a magnetic moment. The magnetic moment can be calculated from the distribution of the current density. The result is the same as that from the quantum-mechanical calculation:

$$\mu_z = -\frac{e\hbar m}{2m_0}$$

(m_0 = electron mass)

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Transitions

The wave-function of non-stationary states can be described as a linear combination of the wave-functions of the eigenstates:

$$\psi(\boldsymbol{r},t) = \sum_k a_k \psi_k(\boldsymbol{r},t) .$$

We consider the simplest case, i.e. the linear combination of only two summands:

$$\psi(\boldsymbol{r},t) = c_\mathrm{A}\psi_\mathrm{A}(\boldsymbol{r},t) + c_\mathrm{B}\psi_\mathrm{B}(\boldsymbol{r},t) \qquad (1)$$

with

$$\psi_\mathrm{A}(\boldsymbol{r},t) = u_\mathrm{A}(\boldsymbol{r}) e^{-\frac{i}{\hbar}E_\mathrm{A}t} \text{ and } \psi_\mathrm{B}(\boldsymbol{r},t) = u_\mathrm{B}(\boldsymbol{r}) e^{-\frac{i}{\hbar}E_\mathrm{B}t}$$

We assume $E_\mathrm{A} > E_\mathrm{B}$.

For the charge density we find an expression of the form:

$$\rho(\boldsymbol{r},t) = C_0(\boldsymbol{r}) + C_1(\boldsymbol{r})\cos(\omega t) + C_2(\boldsymbol{r})\sin(\omega t) \qquad (2)$$

At every location $\boldsymbol{r}$, the expression consists of a time-independent and a harmonic contribution. The same holds true for the electric current density.

In general, an oscillating charge and current distribution causes the emission of an electromagnetic wave. Thereby the atom loses energy. That means that the atom cannot remain in its original state (1). Little by little it goes into a state of lower energy: The weighting factor c_A of $\psi_\mathrm{A}(\boldsymbol{r},t)$ decreases steadily, the weighting factor c_B of $\psi_\mathrm{B}(\boldsymbol{r},t)$ increases, until c_A is equal to zero and c_B is one.

Thus, for a non-stationary state the weighting factors are time-dependent:

$$\psi(\boldsymbol{r},t) = c_\mathrm{A}(t)\psi_\mathrm{A}(\boldsymbol{r},t) + c_\mathrm{B}(t)\psi_\mathrm{B}(\boldsymbol{r},t) .$$

That means that also the quantities C_0, C_1 and C_2 in equation (2) are time-dependent. However, this time-dependence is in general much slower than the harmonic time dependence of equation (2).

If at the beginning $c_\mathrm{A} = 1$ und $c_\mathrm{B} = 0$, the atom is in a stationary state. The transition to state B cannot begin without external help. Indeed, the atom remains for a while in this excited state. However, the equilibrium is precarious. A small perturbation is sufficient to iniciate the transition. Such perturbations are collisions with other atoms, or fluctuations of the ground state of the electromagnetic field.

The rate of change of the weighting factors c_A and c_B depends on how strong the radiation is that the atom emits, and this depends on the distribution in space and the time rate of change of the charge and current density. After a little practice, it is easy to see from an animation of the function $\rho(\boldsymbol{r},t)$, if the transition proceeds quickly, slowly or not at all.

If the secondary quantum number l of the involved states differs by 1, i. e. if Δl is equal to ±1, then the charge oscillation has dipole character and the atom emits strongly – just a a macroscopic dipole antenna. The transition is fast.

If Δl is equal to 0 or ±2, the oscillation has quadrupole character and the atom radiates much more weakly – like a macroscopic quadrupole antenna (i. e. two dipole antennas which are side by side and oscillate in opposite directions).

If for both involved states $l = 0$, the oscillation has spherical symmetry and the atom does not emit at all – just as a macroscopic spherical charge distribtion cannot emit an electromagnetic wave.

If the magnetic quantum number m of the involved states differs by 1, i. e. if $\Delta m = \pm 1$, then one perceives a rotational movement in the animation. The atom emits a circularly polarized wave. For $\Delta m = 0$ the radiation is linearly polarized.