# QUANTUM MECHANICS
# Lecture 23

## The hydrogen atom
## The angular momentum

Enrico Iacopini

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D. J. Griffiths: paragraph 4.2 - 4.3

# The hydrogen atom



1. The hydrogen atom consists in a bounded system of an **electron** and a **proton.**
2. Since the proton mass is almost 2000 times the mass of the electron, we can assume the proton at rest, in the origin of the (inertial) reference system.
3. The electron electrostatic potential energy in the proton electric field is given by

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

4. As a consequence, the radial equation reads

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[-\frac{e^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = E\,u$$

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1. We have to see for what energies $E < 0$ (bound states), the radial equation admits square-integrable solutions.
2. Let us divide the radial equation by $E$

$$-\frac{\hbar^2}{2mE}\frac{d^2u}{dr^2} + \frac{\hbar^2}{2mE}\frac{l(l+1)}{r^2}u - \frac{e^2}{4\pi\epsilon_0 E}\frac{1}{r}u = u$$

3. and let us define

$$k = \frac{\sqrt{-2mE}}{\hbar}\ m^{-1}$$

$$a_0 = \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m} \approx 0.529 \times 10^{-10}\, m$$

$$\rho_0 = \frac{2}{a_0 k}$$

where $\rho_0$ is an adimensional variable.

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$$\begin{aligned} \kappa &= \frac{\sqrt{-2mE}}{\hbar}\ m^{-1} \\ a_0 &= \frac{4\pi\epsilon_0}{e^2}\frac{\hbar^2}{m} \approx 0.529 \times 10^{-10}\, m \\ \rho_0 &= \frac{2}{a_0 \kappa} \end{aligned}$$

where $\rho_0$ is an adimensional variable.

# The hydrogen atom



1. We have

$$-\frac{e^2}{4\pi\epsilon_0 E} = -\frac{e^2}{4\pi\epsilon_0\hbar^2}\frac{2m}{E}\frac{\hbar^2}{2m} = \frac{2}{a_0 k^2} = \frac{\rho_0}{k}$$

2. Therefore, the radial equation

$$-\frac{\hbar^2}{2mE}\frac{d^2u}{dr^2} + \frac{\hbar^2}{2mE}\frac{l(l+1)}{r^2}u - \frac{e^2}{4\pi\epsilon_0 E}\frac{1}{r}u - u = 0$$

simplifies in

$$\frac{1}{k^2}\frac{d^2u}{dr^2} - \frac{1}{k^2}\frac{l(l+1)}{r^2}u + \frac{\rho_0}{k}\frac{1}{r}u - u = 0$$

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1. If, instead of $r$, we use now the adimensional variable $\rho = k\,r$, the equation becomes

$$\frac{d^2u}{d\rho^2} - \frac{l(l+1)}{\rho^2}\,u + \frac{\rho_0}{\rho}\,u - u = 0$$

2. or, in other words

$$\frac{d^2u}{d\rho^2} = \left[\frac{l(l+1)}{\rho^2} - \frac{\rho_0}{\rho} + 1\right] u = 0$$

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Square-integrable solutions of the radial equation

$$\frac{d^2u}{d\rho^2} = \left[\frac{l(l+1)}{\rho^2} - \frac{\rho_0}{\rho} + 1\right]$$

do exist if and only if

$$\rho_0 = 2n$$

where $n > 0$ is (any) integer.

# The hydrogen atom



But

$$\rho_0 = \frac{2}{a_0 k} = 2n \quad \Rightarrow \quad k = \frac{1}{a_0\, n}$$

and since

$$k = \frac{\sqrt{-2mE}}{\hbar}$$

we get the following condition on the possible energy eigenvalues

$$\sqrt{-2mE} = \frac{\hbar}{a_0\, n} \quad \Rightarrow \quad E_n = -\frac{\hbar^2}{2ma_0^2}\frac{1}{n^2} \equiv -\frac{\mathcal{E}}{n^2}$$

where

$$\mathcal{E} = \frac{\hbar^2}{2ma_0^2} \approx 13.6\, eV$$

# The hydrogen atom



The corresponding radial solutions are

$$R_{nl}(r) = A_{nl}\, e^{-\frac{r}{na_0}} \left(\frac{2r}{na_0}\right)^l \cdot L^{2l+1}_{n-l-1}\left(\frac{2r}{na_0}\right)$$

$$with \quad A_{nl} = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}$$

The $L^s_r(x)$ are the associated Laguerre polynomials

$$L^p_{q-p}(x) = (-1)^p \frac{d^p}{dx^p} L_q(x)$$

$$L_q(x) = e^x \frac{d^q}{dx^q}(e^{-x}\, x^q) \quad \Rightarrow$$

$$L_0(x) = 1; \qquad L_1(x) = -x + 1;$$

$$L_2(x) = x^2 - 4x + 2; \quad L_3(x) = -x^3 + 9x^2 - 18x + 6$$

...

# The hydrogen atom



1. The full set of the normalized wave functions solving the time-independent Scrödinger equation for the energy $E_n = -\frac{\mathcal{E}}{n^2}$ are the following

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi) =$$

$$= A_{nl} \cdot e^{-\frac{r}{na_0}} \cdot \left(\frac{2r}{na_0}\right)^l \cdot L_{n-l-1}^{2l+1}\left(\frac{2r}{na_0}\right) \cdot Y_l^m(\theta,\phi)$$

2. The radial scale length of the hydrogen atom is clearly given by $a_0 \approx 0.529 \times 10^{-10}\, m$ which is known as the ***Bohr radius***.

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1. A part from the ground level ($n = 1$, $l = 0$), **all the other energy levels of the hydrogen atom are degenerate**, because, for any given energy $E_n$, all the azimuthal quantum numbers $l$ from 0 to $n - 1$ are possible, and, for any given $l$, all the magnetic quantum numbers $m$ from $-l$ to $+l$ are also possible.

2. It is easy to see that the degeneracy of the level $n$ is

$$N = \sum_{l=0}^{n-1} (2l + 1) = 2\frac{n(n-1)}{2} + n = n^2$$

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# The hydrogen spectrum



Transitions from different energy levels may occur due to the interaction with the e.m. field, through the emission/absorption of a photon having an energy equal to the difference between the energy levels involved.

In case of photon emission, f.i., we have

$$E_\gamma = E_i - E_f = -\mathcal{E}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = \mathcal{E}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where, as we have already said,

$$\mathcal{E} = \frac{\hbar^2}{2ma_0^2} \approx 13.6\, eV$$

# The hydrogen spectrum



Since $E_\gamma = h\nu$ and $\lambda\nu = c$, in terms of the radiation wavelenght $\lambda$, the hydrogen spectrum is such that

$$\frac{1}{\lambda} = \frac{E_\gamma}{hc} = \frac{\mathcal{E}}{hc}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \equiv R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

where $R$ is the **Rydberg constant**, given by

$$R = \frac{\mathcal{E}}{h\,c} \approx 1.097 \times 10^7\, m^{-1}$$

# The hydrogen spectrum



1. The previous formula was discovered empirically in the $XIX^{th}$ century and the great achievement of $QM$ was to justify and calculate $R$ from fundamental constants.
2. Transitions to the ground state ($n_f = 1$) are in the $UV$ and are known as Lyman series.
3. Transitions to the first excited state ($n_f = 2$) fall in the visible and constitute the Balmer series.
4. Transitions to ($n_f = 3$) are in the infrared (Paschen series).

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# The angular momentum



1. As we have just seen, the stationary states of the hydrogen atom are labeled with three quantum numbers: $n$, $l$, $m$.

2. The principal quantum number $n$ is the only one directly related to the energy.
   But what about $l$ and $m$ ?
   Which is their meaning ?

3. As we will show now, these two quantum numbers are related to the angular momentum.

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# The angular momentum



1. In classical mechanics, when the potential energy is central, together with the **total energy** also the **angular momentum** is conserved.
2. It is not surprising that, also in $QM$, angular momentum plays a significant role.
3. Classically, the angular momentum of a point-like particle of momentum $\vec{p}$, evaluated with respect to the origin, reads

$$\vec{L} \equiv \vec{r} \times \vec{p}$$

which, in terms of components, becomes

$$L_x = y\,p_z - z\,p_y; \quad L_y = z\,p_x - x\,p_z; \quad L_z = x\,p_y - y\,p_x$$

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# The angular momentum



1. The corresponding quantum operators are obtained using the usual prescription

$$p_x \to -i\hbar\frac{\partial}{\partial x};\quad p_y \to -i\hbar\frac{\partial}{\partial y};\quad p_z \to -i\hbar\frac{\partial}{\partial z};$$

2. One of the most important properties of the components $L_x$, $L_y$, $L_z$ of the angular momentum is that they **do not commute one with the other.**

3. We have in fact that

$$\begin{aligned}[L_x, L_y] &= i\hbar L_z \\ [L_y, L_z] &= i\hbar L_x \\ [L_z, L_x] &= i\hbar L_y\end{aligned}$$

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# The angular momentum



1. This means that the three components of the angular momentum are **incompatible observables**: they cannot be measured simultaneously and, therefore, they do not admit simultaneous eigenfunctions.

2. In other words, **it does not exixt a physical state which is a determinate state for two of them** (a part the case where all the eigenvalues are zero ...).

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# The angular momentum



However, the modulus square of the angular momentum operator

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

**does** commute with each of the three components

$$[L^2, L_x] = 0; \quad [L^2, L_y] = 0; \quad [L^2, L_z] = 0$$

# The angular momentum



Let us consider, f.i., the commutator $[L^2, L_x]$. We have

$$[L^2, L_x] = [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x] =$$

$$= [L_y^2, L_x] + [L_z^2, L_x] =$$

$$= L_y[L_y, L_x] + [L_y, L_x]L_y + \\ + L_z[L_z, L_x] + [L_z, L_x]L_z =$$

$$= L_y(-i\hbar\, L_z) + (-i\hbar\, L_z)L_y + \\ + L_z(i\hbar\, L_y) + (i\hbar\, L_y)L_z = 0$$

# The angular momentum



Concerning the angular momentum, **the maximum we can do** is, therefore, to look for simultaneous eigenfunctions $f$ of $L^2$ and, for instance, of $L_z$ :

$$L^2 f = \lambda f \quad and \quad L_z f = \mu f$$