THE HYDROGEN ATOM IN 10 MINUTES

Heavy, motionless nucleus around which much lighter particle rotates, subject to a force exclusively depending on their distance.

Schrödinger's equation:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi \qquad \text{where} \quad V(r) = -\frac{e^2}{4\pi\varepsilon_0}\cdot\frac{1}{r}$$

We look for <u>stationary</u> states, eigenstates of the Hamiltonian

$$\mathcal{H}\psi = -\hbar^2/2m\,\nabla^2 + V(r)$$

(Schrödinger equation above is a eigenvalue equation)

Solution: lowest energy state:

$$\psi_{nlm}(r,\theta,\varphi), \quad E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\cdot\frac{1}{n^2} \qquad E_1 = -13.6\,eV$$

The energy depends exclusively on the quantum number n

l and m are related to the orbital angular momentum.

For each n, $l = 0 \ldots n-1$ are allowed; for each l, $m = -l, \ldots, -1, 0, \ldots l$ are allowed.

Since only n determines the energy, for each value of n we have

$$\sum_{l=0}^{n-1}(2l+1) = \underline{\underline{n^2}} \quad \text{independent wavefunctions.}$$

ANGULAR MOMENTUM

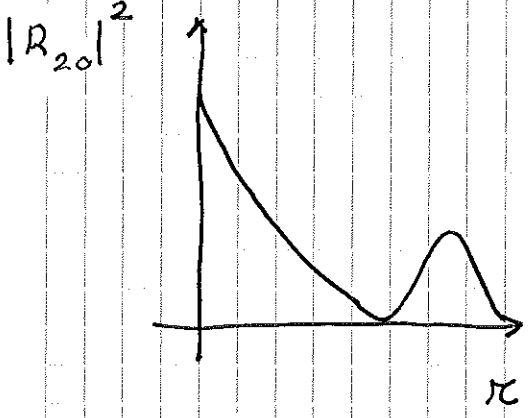
We saw the stationary states of the H atom are labelled by 3 quantum numbers: n, ℓ, m

The principal quantum number, n, determines the energy:

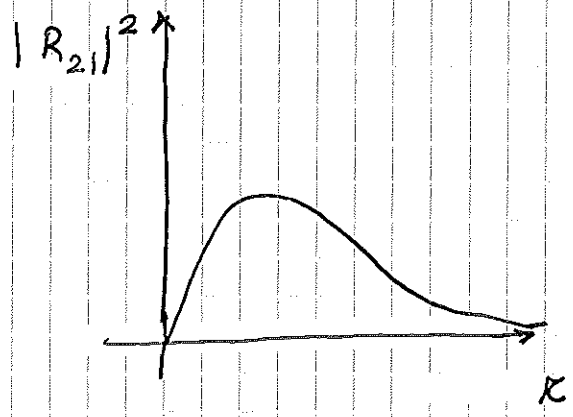
$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \cdot \frac{1}{n^2} \Leftarrow$$

ℓ and m are related to the orbital angular momentum. For each energy E_n, there are n^2 states with the same energy but a different orbital configuration.

E.g. $n = 2$, $\ell = 0$



$n = 2$, $\ell = 1$



$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r) \cdot Y_\ell^m(\theta,\phi)$$

it is unlikely to find particle close to $r \sim 0$, when particle is in a state with angular momentum $\neq 0$ (i.e., $\ell > 0$).

Let us review how the angular momentum operator is defined, and its properties. As we will do many times, let us start from the classical mechanic angular momentum:

$$\vec{L} = \vec{r} \times \vec{p} \qquad (\text{"}\times\text{" is the cross product})$$

This vectorial equation can be split in cartesian components:

$$L_x = y p_z - z p_y$$
$$L_y = z p_x - x p_z$$
$$L_z = x p_y - y p_x$$

The corresponding quantum operator is obtained by replacing the terms in the classical expression with their quantum mechanics version:

$$p_x \to \frac{\hbar}{i}\frac{\partial}{\partial x} \qquad p_y \to \frac{\hbar}{i}\frac{\partial}{\partial y} \qquad p_z \to \frac{\hbar}{i}\frac{\partial}{\partial z}$$

We now have an issue. In classical mechanics, $\vec{L}$ is a vector which I can measure, in all its components. Now, L_x, L_y and L_z are mixtures of position and momentum operators, which I know to be NOT compatible: $[x, p_x] = i\hbar$; better yet: $[x_i, p_j] = i\hbar\delta_{ij}$, using the Kronecker delta: $\delta_{ij} = 1$ if $i=j$; 0 otherwise.

Let us check:

$$[L_x, L_y] = [y p_z - z p_y, z p_x - x p_z] =$$
$$= [y p_z, z p_x] - [y p_z, x p_z] - [z p_y, z p_x] + [z p_y, x p_z]$$
$$= 0 \qquad = 0 \quad \text{(all terms here commute)}$$
$$= [y p_z, z p_x] + [z p_y, x p_z]$$
$$= y p_x [p_z, z] + p_y x [z, p_z] =$$
$$= -i\hbar\, y p_x + i\hbar p_y x = i\hbar(x p_y - y p_x) = i\hbar L_z$$

Similarly, I can find that L_z, L_y, L_x do not commute with each other:

$$[L_x, L_y] = i\hbar L_z \qquad [L_y, L_z] = i\hbar L_x \qquad [L_z, L_x] = i\hbar L_y$$

How about L^2 ?

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

$$= 0 + L_y[L_y, L_x] + [L_y, L_x]L_y +$$
$$+ L_z[L_z, L_x] + [L_z, L_x]L_z$$

$$= L_y(-i\hbar L_z) + (-i\hbar L_z)L_y +$$
$$+ L_z(i\hbar L_y) + (i\hbar L_y)L_z = \underline{0}$$

Therefore, I can measure precisely only the total angular momentum L^2 and one of its components (traditionally, we choose L_z). In other words, I can define wavefunctions characterized by a quantum number for L^2 and one for L_z. A bit of an a-posteriori result, but this is the convention we choose to describe H atoms: ℓ is the quantum number corresponding to L^2 and m to L_z. $Y_\ell^m(\theta, \varphi)$ is an eigenstate of both L^2 and L_z, with eigenvalues $\hbar^2\ell(\ell+1)$ for L^2 and $\hbar m$ for L_z.

Now, onto something more "quantum mechanics": the spin. I don't think that picturing spin as the result of our particle rotating around itself is great. In particular, it does not really fit with the idea of semi-integer spins. Let us assume that particles have an intrinsic property, the spin, which behaves a lot like an angular momentum.

I have: $[S^2, \begin{matrix} S_x \\ S_y \\ S_z \end{matrix}] = 0$; $[S_x, S_y] = i\hbar S_z$

$[S_y, S_z] = i\hbar S_x$

$[S_z, S_x] = i\hbar S_y$

$|s,m\rangle$

and, again, I can write states, that are eigenfunctions of S^2 and (conventionally chosen) S_z, with corresponding eigenvalues $\hbar^2 s(s+1)$ and $\hbar m_s$:

$$S^2 |s,m\rangle = \hbar^2 s(s+1) |s,m\rangle$$

$$S_z |s,m\rangle = \hbar m |s,m\rangle$$

in Dirac's notation

Define here also S_+ and S_-

NOTE: eigenvectors are not spherical harmonics: no reason to exclude half-integer values of s and m.

The case of spin-1/2 particles (such as the electron in our H atom):

With a spin-1/2 particle, we don't need many eigenfunctions:

we have only two eigenstates: either the spin is up, or it is down ($S^2 = 3/4\ \hbar^2$ and S_z is either $\hbar/2$ or $-\hbar/2$).

I can write:

$$\chi = a\chi_+ + b\chi_-$$: any spinor χ is a linear combination of the two eigenspinors ($|a|^2+|b|^2=1$: normalization)

where:

$$S_z \chi_+ = \hbar/2\ \chi_+$$

$$S_z \chi_- = -\hbar/2\ \chi_-$$

↑ works well because S has discrete eigenvalues

Let us choose to use a 2D linear representation of spinors:

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

From this simple choice I can derive (simple exercise!) the following:

$$S^2 = \frac{3\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}; \quad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \quad S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}; \quad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

[note: divide S_{xyz} by $\hbar/2$: obtain Pauli matrices]

Here is a rather different way of finding these representations!
The point is that when we wrote the energy of a particle, we started from:

$$E = \frac{p^2}{2m}$$

But what if we consider a relativistic energy? We get:

$$E = \sqrt{(mc^2)^2 + (pc)^2}$$

The corresponding relativistic Schrödinger's equation becomes:

$$i\hbar \frac{\partial \psi}{\partial t} = \left(\sqrt{(mc^2)^2 - \hbar^2 c^2 \nabla^2}\right)\psi$$

what is the square root of the operator on the right side?
The problem disappears if the operator $(mc^2)^2 + (pc)^2$ is a perfect square:

$$\left(\alpha_0 mc^2 + \sum_{j=1}^{3} \alpha_j p_j c\right)^2 = (mc^2)^2 + (pc)^2$$

If I can find $\alpha_0, \alpha_1, \alpha_2, \alpha_3$ such that expression above is true, I am in business.
If I do the math, I find that the above expression is true only if:

$$\alpha_0^2 = \alpha_j^2 = 1 \quad \text{and} \quad \{\alpha_i, \alpha_j\} = \alpha_i \alpha_j + \alpha_j \alpha_i = 0 \quad \text{if } i \neq j$$

These constraints define a <u>Clifford algebra</u>, and yield <u>Dirac's equation</u> of a free particle:

$$\left(\alpha_0 mc^2 + \sum_{j=1}^{3} \alpha_j p_j c\right)\psi = i\hbar \frac{\partial \psi}{\partial t}$$

the $\{\alpha_i, \alpha_j\} = 0$ for $i \neq j$ rule cannot be satisfied by scalar values. I need matrices, and the smallest dimension that works is 4×4. One possible choice is the following:

$$\alpha_0 = \begin{pmatrix} I_2 & O_2 \\ O_2 & -I_2 \end{pmatrix} \qquad \alpha_j = \begin{pmatrix} O_2 & \sigma_j \\ \sigma_j & O_2 \end{pmatrix}$$

where σ_j satisfies commutator

$$[\sigma_i, \sigma_j] = \sigma_i\sigma_j - \sigma_j\sigma_i = 2i\sigma_k$$

2×2 $\begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix}$ 2×2 identity $\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$

We are back to Pauli matrices:

$$\sigma_1 = \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Also note that:

$$S_{\substack{x\\y\\z}} = \frac{\hbar}{2}\sigma_{\substack{x\\y\\z}}$$

S matrices introduced before

You can easily show that $[S_x, S_y] = i\hbar S_z$ work with this definitions

$$[\sigma_x, \sigma_y] = 2i\sigma_z$$

What happens to Dirac equation in matrix form?

$$\begin{pmatrix} mc^2 I_2 & (\vec{\sigma}\cdot\vec{p})c \\ (\vec{\sigma}\cdot\vec{p})c & -mc^2 I_2 \end{pmatrix}$$

is the new Hamiltonian, and it is 4×4

If $\vec{p} = 0$, I find 4 eigenvalues: 2 are $+mc^2$, and 2 are $-mc^2$. The former correspond to an electron-like particle, the other two to an anti-particle. Both of them have two components (guess: spin up and spin down parts).