Comments about our 3d eigenenergies & functions

① E depends on ℓ via centripetal potential but not m as orientation of motion doesn't matter if potential is isotropic. m ranges: $-\ell \le m \le \ell$ so this yields a $2\ell+1$ degeneracy

② Typically, we label the lowest energy state with a given value of ℓ one: eg 1p is the lowest energy $\ell=1$ state. The next lowest state is labelled two: 2p etc.

③ The H-atom is an exception! Note principal quantum number $n = n_r + \ell + 1$ determines the energy so there is an additional degeneracy — un related to isotropic: trade n_r for ℓ eg the following are degenerate: values of (n_r, ℓ): $(2,0)$, $(1,1)$, $(0,2) \rightarrow n=3$

$$\underset{3s}{(2,0)}, \quad \underset{3p}{(1,1)}, \quad \underset{3d}{(0,2)}$$

Thus the First (lowest) d state is "3d" an instead of labelling with $(n_r + 1)$ we label with n.

The total degeneracy of the $n=3$ states is then
$3s = 1$, $3p = 3$, $3d = 5$ $= 1+3+5 = 9 = n^2$
$\underset{2\ell+1}{\uparrow}$

④ Notice the <u>level spacing</u> : For SHO it is uniform, for infinite Square well the spacing <u>increases</u> with energy for H-atom the spacing <u>decreases</u> with energy The spacing can be related to the classical frequency. For SHO the frequency does not depend on the amplitude (total energy). For square well — more energy means more speed which means higher frequency. For H-atom more energy means larger semi-major axis (orbit size) which means longer Period (lower frequency)

Note: not all transitions are equally likely — $\Delta\ell = \pm 1$ is often likely. "Forbidden" transitions do occur. More on this in future.

⑤ level spacing is what we can measure ∵ in a transition ΔE is the energy of that the photon carries away & $\Delta E = hf$ ← can measure f

⑥ in the H-atom the ΔE is largly determined by the final state - sets of transitions with the same final state are named for FDP

to $n=1 \to$ Lyman → in UV ∴ hard to measure

to $n=2 \to$ Balmer ← famous red & blue-green lines in visible

to $n=3 \to$ Paschen ← mostly in IR

to $n=4 \to$ Pfund

the smallest ΔE (longest λ) in a sequence is labelled α: $n=3 \to n=2$ $B\alpha$
$n=4 \to n=2$ $B\beta$ etc

⑦ Notice for small r: $R \propto r^l$ so the only wavefunctions with non-zero amplitude at $r=0$ are $\underline{s}$ ← zero angular momentum ∴ pure radial oscillations. In fact for an s wave function the maximum probability density $=|\psi|^2$ occurs at origin. This should make sense as a radially collapsing wave should get concentrated as $r \to 0$ due to reduced area.

Remark: books often plot $u = r/R$ which makes it look like $r=0$ is an unlikely place to be

Remark 2: In fact electrons have no problem moving thru the nucleus — in the case of high Z atoms with muon having replaced electron — muon may spend most of its time inside nucleus with no effect other than Electrostatic potential.

⑧ Notice with SHO & square well can plot a stack of wave functions on same plot as $\langle r \rangle$ increases slowly (if at all) with energy — Not so with H-atom where $r \sim n^2$ so range of R varies hugely with energy.

Intro to spin

Classically an extended object (eg CH_4 molecule) can have translation KE & rotational KE. Rotational KE depends on moments of inertia & spin rates — it is complex mathematically requiring things like Euler angles. We can of course translate that classical mechanics to QM, we will need addition coordinates to describe orientation; it becomes quite complex but its no too bad with symmetric molecules where $KE = \frac{L^2}{2I}$

There is of course degeneracy as if (in this symmetric case) ~~it won't matter~~ the orientation of the spin will not matter. $\longrightarrow |\ell m\rangle$ states: function of those orientation coordinates. In many cases we don't care about those internal coordinates an we can proceed just knowing $|\ell m\rangle$ are orthonormal.

(On the other hand you might want to know the doppler shift of those rotations, Its in CH_4 but in the case we are about to consider we absolutely cannot measure those orientation coordinates so there is exactly ~~two~~ zero reason to work out those functions)

There is one important difference between rotating CH_4 and a rotating electron: we can't make the electron spin faster: ℓ is fixed [we will call it $s = \frac{1}{2}$] $\rightarrow$ its maybe not quite as simple as that — if you plug in reasonable values for I you find ΔE for changing s would be comparable to mc^2 — a faster spin (and higher mass) version of electron would be given a new name. [Nevertheless there is no such candidate particle]. In the case of a proton we call higher spin versions Δ

In any case either because of SG experiments or facts I say electron can exist in just two states
$$|s\,m_s\rangle = |\tfrac{1}{2}\,\tfrac{1}{2}\rangle = \uparrow \qquad \& \qquad |s\,m_s\rangle = |\tfrac{1}{2}\,\tfrac{-1}{2}\rangle = \downarrow$$

Since we cannot measure any internal coordinates the plan is to never express these states as functions of those internal coordinates — just get by with orthonormality of those states.

Remark: It turns out that an alternative explanation of spin exists: it is just a required consequence of relativity. This alternative point of view shows that the electron is the way it is because it cannot be any other way. Nevertheless electron spin is angular momentum that can be exchanged for other types of angular moment that has macroscopic measurable effects — eg Einstein - de Haas effect

Plan: work with the functions: $\uparrow \ \downarrow$ as basis vectors - no need to ever express them as functions.

$$S^2\,|s\,m_s\rangle = \hbar^2\, s(s+1)\,|s\,m_s\rangle \longrightarrow S^2\uparrow = \hbar^2\tfrac{3}{4}\uparrow \quad \& \quad S^2\downarrow = \hbar^2\tfrac{3}{4}\downarrow$$

$$S_z\,|s\,m_s\rangle = \hbar\, m_s\, |s\,m_s\rangle \longrightarrow S_z\uparrow = \tfrac{\hbar}{2}\uparrow \quad \& \quad S_z\downarrow = -\tfrac{\hbar}{2}\downarrow$$

$$S_+\,|s\,m_s\rangle = \hbar\sqrt{s(s+1) - m(m+1)}\ |s\,m_s+1\rangle \qquad S_+\uparrow = 0 \quad S_+\downarrow = \hbar\uparrow$$

$$S_- \qquad\qquad\qquad - \qquad\qquad - \qquad\qquad S_-\uparrow = \hbar\downarrow \quad S_-\downarrow = 0$$

$$\left.\begin{array}{l} S_+ = S_x + iS_y \\ S_- = S_x - iS_y \end{array}\right\} \quad \begin{array}{l} S_x = \tfrac{1}{2}(S_+ + S_-) \\ S_y = \tfrac{1}{2i}(S_+ - S_-) \end{array}$$

$$\Rightarrow S_x = \tfrac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S_y = \tfrac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad S_z = \tfrac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$S^2 = S_x^2 + S_y^2 + S_z^2 = \hbar^2\tfrac{3}{4}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad S_+ = \hbar\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad S_- = \hbar\begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

Note: In textbook $\uparrow = \chi_+ \qquad \downarrow = \chi_-$

Note: Classically relate magnetic dipole moment $= IA$ to spin
$$\bar{\mu} = \frac{q}{2m}\,\vec{S}$$
"gyromagnetic ratio"
in fact turns out $2\times$ this classical value.

E'

E'

5 10 15 20

0 2 4 6 8 ℓ

E^l

20 40 60 80 100

1 2 3 4 5 ℓ

n E'

4
3
2

1

-0.5 -0.4 -0.3 -0.2 -0.1

s p d f g l

5 10 15 20 25

0 1 2 3 4 5

E^l

50 100 150 200

0.2 0.4 0.6 0.8 1 r^l

$\ell = 0$

50 100 150 200

0.2 0.4 0.6 0.8 1

$\ell = 1$

50 100 150 200

0.2 0.4 0.6 0.8 1

$\ell = 2$

5 10 15 20 25

0 1 2 3 4 5