Chapter 2 - The Hydrogen Atom

In this chapter, we look at aspects of the H-atom wavefunction and how it determines the atomic behavior in different circumstances.

The Hamiltonian

$$H = \frac{p^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0 r}$$

Convert to spherical coordinates

$$H\psi = -\frac{\hbar^2}{2m_e}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{L^2}{2m_e r^2}\psi - \frac{e^2}{4\pi\varepsilon_0 r}\psi$$

The angular momentum operator $L^2\psi = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$

The three operators, H, L^2, L_z, commute with each other. This implies can find <u>simultaneous</u> eigenstate of <u>all</u> three

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

$$H\psi_{n\ell m} = E_{n\ell}\,\psi_{n\ell m}\ , \quad L^2\psi_{n\ell m} = \hbar^2\ell(\ell+1)\psi_{n\ell m}\ , \quad L_z\psi_{n\ell m} = \hbar m\,\psi_{n\ell m}$$

Don't blindly use formulas from one book in the equations of another. Can have different phases in definition.

The $Y_{\ell m}(\theta,\phi)$ come whenever the potential is spherically symmetric. They are normalized over surface of unit sphere.

$$\int_0^{\pi}\int_0^{2\pi} Y^*_{\ell m}(\theta,\phi)\, Y_{\ell' m'}(\theta,\phi)\, d\phi\, \sin\theta\, d\theta = \delta_{\ell\ell'}\,\delta_{mm'}$$

$$Y_{\ell m} = \overset{\text{const}}{(\ \ )}\ \underbrace{P_\ell^m(\cos\theta)}_{\text{associated Legendre function}}\, e^{im\phi}$$

Look at the $Y_{\ell m}$ and discuss generic properties.

As $|m|$ increases, less probability near $\cos\theta \sim \pm 1$!

Number of nodal planes

The $Y_{\ell m}$ are eigenstates of the parity operator

$$P\,Y_{\ell m}(\theta,\phi) = Y_{\ell m}(\pi-\theta, \phi+\pi) = (-1)^\ell\, Y_{\ell m}(\theta,\phi)$$

Show?

The radial part of Ψ satisfies

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR_{n\ell}(r)}{dr}\right)\right] + \underbrace{\left(\frac{\hbar^2\ell(\ell+1)}{2mr^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right)}_{V_{eff}} R_{n\ell}(r) = E_{n\ell} R_{n\ell}(r)$$

Use $R_{n\ell}(r) = P_{n\ell}(r)/r \Rightarrow -\frac{\hbar^2}{2m}P''_{n\ell}(r) + V_{eff}(r)P_{n\ell}(r) = E_{n\ell}P_{n\ell}(r)$

Sketch $V_{eff}(r)$ and implications for different ℓ

See book for definition in Table 2.2 (beware $\rho = \frac{Zr}{na_0}$, different in each!)

Show plots

Useful expressions

$|\Psi(0)|^2 = \frac{1}{\pi}\left(Z/na_0\right)^3 \qquad \ell = 0$

$\ell > 0 \qquad \left\langle \frac{1}{r^3} \right\rangle = \frac{1}{\ell(\ell+1/2)(\ell+1)}\left(\frac{Z}{na_0}\right)^3$

$\left\langle \frac{1}{r} \right\rangle = \frac{1}{n^2}\frac{Z}{a_0}$

Estimate effect from finite nuclear radius

$V_{act}(r) - V_{pure}(r) \simeq \frac{e^2}{4\pi\varepsilon_0 r} \quad$ for $r < r_N \sim 10^{-15}\,m$

$$\langle \Delta V \rangle = \iiint \Delta V(r) \left|\Psi_{n\ell m}(\vec{r})\right|^2 d^3r \simeq \iiint_0^{r_N} \frac{e^2}{4\pi\varepsilon_0 r} |\Psi(\vec{r})|^2 r^2 dr \sin\theta\, d\theta\, d\phi$$

$$\simeq 4\pi |\Psi(0)|^2 \int_0^{r_N} \frac{e^2}{4\pi\varepsilon_0 r} r^2 dr = 2\pi |\Psi(0)|^2 \frac{r_N^2 e^2}{4\pi\varepsilon_0}$$

$$= 2\frac{Z^3}{n^3}\left(\frac{r_N}{a_0}\right)^2 \frac{e^2}{4\pi\varepsilon_0 a_0}$$

$$= 2\frac{Z^3}{n^3}\left(\frac{r_N}{a_0}\right)^2 27.21\,eV \sim \frac{Z^3}{n^3} 10^{-8}\,eV \sim \frac{Z^3}{n^3}\,MHz$$

In QM, you need to be able to find the "matrix elements" of operators

$$Q_{ab} = \langle \Psi_a | Q_{op} | \Psi_b \rangle$$

An important one in AMO is the effect from light

In length gauge, the operator part is

$$Q_{op} = \underbrace{\hat{\varepsilon}_{rad}}_{\text{polarization}} \cdot \vec{r} \qquad \hat{\varepsilon}_x = \hat{x} \cdot \hat{e}_{rad} \quad \text{etc}$$

Substitute the form for Ψ for H-atom

$$Q_{n_2 l_2 m_2, n_1 l_1 m_1} = D_{12} \, I_{ang}$$

$$D_{12} = \int_0^\infty R_{n_2 l_2}(r) \, r \, R_{n_1 l_1}(r) \, r^2 dr$$

$$I_{ang} = \iint_{\text{all ang}} Y^*_{l_2 m_2}(\theta,\phi) \left(\hat{\varepsilon}_x \sin\theta\cos\phi + \hat{\varepsilon}_y \sin\theta \sin\phi + \hat{\varepsilon}_z \cos\theta \right) Y_{l_1 m_1}(\theta,\phi) \, d\phi \, \sin\theta \, d\theta$$

Use $\cos\phi = \frac{1}{2}(e^{i\phi} + e^{-i\phi}) \qquad \sin\phi = \frac{-i}{2}(e^{i\phi} - e^{-i\phi})$

$$I_{ang} = \langle l_2 m_2 | \frac{\hat{\varepsilon}_x - i\hat{\varepsilon}_y}{\sqrt{2}} \frac{\sin\theta e^{i\phi}}{\sqrt{2}} + \frac{\hat{\varepsilon}_x + i\hat{\varepsilon}_y}{\sqrt{2}} \frac{\sin\theta e^{-i\phi}}{\sqrt{2}} + \hat{\varepsilon}_z \cos\theta | l_1 m_1 \rangle$$

Depending on polarization, different states can be connected.

π - Polarization

$$\langle l_2 m_2 | \cos\theta | l_1 m_1 \rangle = \delta_{m_2 m_1} \left[\delta_{l_2, l_1+1} \sqrt{\frac{l_2^2 - m_1^2}{(2l_2-1)(2l_2+1)}} + \delta_{l_2+1, l_1} \sqrt{\frac{l_1^2 - m_1^2}{(2l_1-1)(2l_1+1)}} \right]$$

$$= \delta_{m_2 m_1} \left[\delta_{l_2, l_1+1} + \delta_{l_2+1, l_1} \right] \sqrt{\frac{l_>^2 - m_1^2}{4l_>^2 - 1}} \qquad l_> = \max(l_1, l_2)$$

σ - Polarization

$$\langle l_2 m_2 | \sin\theta \, e^{\pm i\phi} | l_1 m_1 \rangle = \delta_{m_2, m_1 \pm 1} \left[\mp \delta_{l_2, l_1+1} \sqrt{\frac{(l_2 \pm m_1)(l_2 + 1 \pm m_1)}{(2l_2+1)(2l_2-1)}} \pm \delta_{l_2+1, l_1} \sqrt{\frac{(l_1 \mp m_1)(l_1 - 1 \mp m_1)}{(2l_1+1)(2l_1-1)}} \right]$$

Note the selection rules!

The spin orbit interaction comes from a relativistic correction to the Hamiltonian. One way to think about: In the frame of the electron, the proton going around makes a B-field that interacts with the electron spin.

$$H_{so} \simeq \frac{1}{2m_e^2 c^2} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r^3} \vec{L}\cdot\vec{S}$$

(book eq. 2.51 uses $\vec{l} = \frac{\vec{L}}{\hbar}$, $\vec{s} = \frac{\vec{S}}{\hbar}$)

Instead of using states $|l, m_l\rangle |s, m_s\rangle$ combine them into total angular momentum states. This uses Clebsch-Gordan coefficients

$$\vec{J} = \vec{L} + \vec{S} \quad \rightarrow \quad \vec{L}\cdot\vec{S} = \frac{1}{2}\left[\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right]$$

Look at the general case $\vec{J} = \vec{J}_1 + \vec{J}_2$ with eigenstates $|j_1 j_2 j m_j\rangle$ and eigenvalues

$$\vec{J}^2 |j_1 j_2 j m_j\rangle = \hbar^2 j(j+1) |j_1 j_2 j m_j\rangle \qquad J_z |j_1 j_2 j m_j\rangle = \hbar m_j |j_1 j_2 j m_j\rangle$$

The allowed values are $j = j_1 + j_2, j_1 + j_2 - 1, \ldots, |j_1 - j_2|$; $-j \le m_j \le j$

Often need the connection between $|j_1 j_2 j m_j\rangle$ and the $|j_1 j_2 m_1 m_2\rangle = |j_1 m_1\rangle |j_2 m_2\rangle$. These are the Clebsch-Gordan coefficients

$$|j_1 j_2 j m_j\rangle = \sum_{m_1 m_2} |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | j_1 j_2 j m_j\rangle$$

Example $l=1$, $s=\frac{1}{2}$

$$|1, \tfrac{1}{2}, \tfrac{3}{2}, \tfrac{3}{2}\rangle = |1,1\rangle |\tfrac{1}{2}, \tfrac{1}{2}\rangle$$

$$|1, \tfrac{1}{2}, \tfrac{3}{2}, \tfrac{1}{2}\rangle = \frac{1}{\sqrt{3}} |1,1\rangle |\tfrac{1}{2}, -\tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}\, |1,0\rangle |\tfrac{1}{2}, \tfrac{1}{2}\rangle$$

$$|1, \tfrac{1}{2}, \tfrac{3}{2}, -\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\, |1,0\rangle |\tfrac{1}{2}, -\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}\, |1,-1\rangle |\tfrac{1}{2}, \tfrac{1}{2}\rangle$$

$$|1, \tfrac{1}{2}, \tfrac{3}{2}, -\tfrac{3}{2}\rangle = |1,-1\rangle |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

$$|1, \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}}\, |1,1\rangle |\tfrac{1}{2}, -\tfrac{1}{2}\rangle - \frac{1}{\sqrt{3}} |1,0\rangle |\tfrac{1}{2}, \tfrac{1}{2}\rangle$$

$$|1, \tfrac{1}{2}, \tfrac{1}{2}, -\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}}\, |1,0\rangle |\tfrac{1}{2}, -\tfrac{1}{2}\rangle - \sqrt{\tfrac{2}{3}}\, |1,-1\rangle |\tfrac{1}{2}, \tfrac{1}{2}\rangle$$

The main effect is to split the energy levels. The total energies are

$$E_{n\ell j} = E_{n\ell} + \frac{1}{2}\beta_{n\ell}\left[j(j+1) - \ell(\ell+1) - s(s+1)\right]$$

$$\beta_{n\ell} = \frac{\hbar^2}{2m_e c^2}\,\frac{e^2}{4\pi\varepsilon_0}\,\frac{Z^3}{n^3 a_0^3}\,\frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)} = \underbrace{\frac{\hbar^2}{2m_e a_0^2}}_{hcR_\infty}\alpha^2\,\frac{Z^3}{n^3}\,\frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)}$$

Get the form for some states

$E_{n0\frac{1}{2}} = E_{n0}$

$E_{n1\frac{3}{2}} = E_{n1} + \frac{1}{2}\beta_{n1}$ $\qquad$ $E_{n1\frac{1}{2}} = E_{n1} - \beta_{n1}$

$E_{n2\frac{5}{2}} = E_{n2} + \beta_{n2}$ $\qquad$ $E_{n2\frac{3}{2}} = E_{n2} - \frac{3}{2}\beta_{n2}$

Note that the weighted average doesn't change. (The trace of $\vec{L}\cdot\vec{S}$ is zero.)

$$\left(6E_{n2\frac{5}{2}} + 4E_{n2\frac{3}{2}}\right)/10 = E_{n2} + \frac{6}{10}\beta_{n2} - \frac{6}{10}\beta_{n2} \overset{\checkmark}{=} E_{n2}$$

Compare to e iment

$$\left(E_{21\frac{3}{2}} - E_{21\frac{1}{2}}\right)/hc = R_\infty\,\alpha^2\,\frac{1}{8}\,\frac{3/2}{1\,\frac{3}{2}\,2} = \overset{\text{CODATA}}{109\,737.31568160\ \text{cm}^{-1}}\,\left(\overset{\text{CODATA}}{7.2973525693\times10^{-3}}\right)^2/16$$

$$= 0.365229\ \text{cm}^{-1}$$

From NIST $= 82259.2850014\ \text{cm}^{-1} - 82\,258.9191133\ \text{cm}^{-1} = 0.3658881\ \text{cm}^{-1}$

Why the difference?

What is the frequency? $f = 0.366\ \text{cm}^{-1}\ 3\times10^{10}\ \frac{\text{cm}}{\text{s}} = 11\ \text{GHz}$

Note the spin orbit splitting is proportional to $\frac{Z^3}{n^3}\,\frac{1}{\ell(\ell+1)}$

Other relativistic effects? Mass (that is relativistic KE), magnetic dipole of proton (hyperfine), QED (Lamb shift)

The spin-orbit effect changes the selection rules for transitions

$$\langle n_1 l_1 j_1 m_1 | z | n_2 l_2 j_2 m_2 \rangle = D_{12} \langle l_1 s j_1 m_1 | \cos\theta | l_2 s j_2 m_2 \rangle$$

Still must have $|l_1 - l_2| = 1$ and $m_1 = m_2$. Can have $|j_1 - j_2| = 1$ or 0

Example $n_1 S\ m_1 = \frac{1}{2} \to n_2 P\ j\ m_2$

$$|l_1 s j_1 m_1\rangle = |0\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle = |0,0\rangle |\tfrac{1}{2},\tfrac{1}{2}\rangle$$

$$\langle 0\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2} | \cos\theta | 1\ \tfrac{1}{2}\ \tfrac{3}{2}\ \tfrac{3}{2}\rangle = \underbrace{\cancel{\langle \tfrac{1}{2},\tfrac{1}{2} | \tfrac{1}{2},\tfrac{1}{2}\rangle}}_{\to 1} \underbrace{\cancel{\langle 0,0 | \cos\theta | 1,1\rangle}}_{\to 0}$$

$$|1\ \tfrac{1}{2}\ \tfrac{3}{2}\ \tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}} \langle \tfrac{1}{2},\tfrac{1}{2} | \tfrac{1}{2},\tfrac{1}{2}\rangle \langle 0,0 | \cos\theta | 1,0\rangle \neq$$

$$|1\ \tfrac{1}{2}\ \tfrac{3}{2}\ -\tfrac{1}{2}\rangle = \sqrt{\tfrac{2}{3}} \underbrace{\cancel{\langle \tfrac{1}{2},\tfrac{1}{2} | \tfrac{1}{2},-\tfrac{1}{2}\rangle}}_{\to 0} \langle 0,0 | \cos\theta | 1,0\rangle = 0$$

$$|1\ \tfrac{1}{2}\ \tfrac{3}{2}\ -\tfrac{3}{2}\rangle = \langle \tfrac{1}{2},\tfrac{1}{2} | \tfrac{1}{2},-\tfrac{1}{2}\rangle \langle 0,0 | \cos\theta | 1,-1\rangle = 0$$

$$|1\ \tfrac{1}{2}\ \tfrac{1}{2}\ \tfrac{1}{2}\rangle = -\tfrac{1}{\sqrt{3}} \langle \tfrac{1}{2},\tfrac{1}{2} | \tfrac{1}{2},\tfrac{1}{2}\rangle \langle 0,0 | \cos\theta | 1,0\rangle \neq 0$$

$$|1\ \tfrac{1}{2}\ \tfrac{1}{2}\ -\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{3}} \langle \tfrac{1}{2},\tfrac{1}{2} | \tfrac{1}{2},-\tfrac{1}{2}\rangle \langle 0,0 | \cos\theta | 1,0\rangle = 0$$

Note the matrix element is 2x bigger to $j = \frac{3}{2}$ than to $\frac{1}{2}$. Also note sum of squares is same as without spin orbit.