118(4): Force Eigenvalues due to Spin Orbit Interaction in H

In this case the force equation is:

$$(\hat{H} - E)\,\underline{\nabla}\,\psi = \underline{F}\,\psi \quad -(1)$$

in spherical polar coordinates. The Hamiltonian is:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V + \hat{H}_{so} \quad -(2)$$

where:

$$H_{so} = \xi(r)\,\underline{s}\cdot\underline{L} \quad -(3)$$

The wavefunction for the state $|n\ell m_\ell\rangle$ is:

$$|n\ell m_\ell\rangle = R_{n\ell}(r)\,Y_{\ell m_\ell}(\theta,\phi) \quad -(4)$$

and the spin orbit interaction constant is:

$$\hbar c\,\zeta_{n\ell} = \hbar^2 \int_0^\infty \xi(r)\,R_{n\ell}^2(r)\,r^2\,dr \quad -(5)$$

This is the radial average of the Hamiltonian, and gives the interaction average energy of an electron in an orbital with its own spin. In a hydrogen-like atom with nucleus of atomic number Z, the Coulomb potential energy is:

$$V = -\frac{Ze^2}{4\pi\varepsilon_0 r} \quad -(6)$$

For H,

$$Z = 1. \quad -(7)$$

Therefore for H: $\xi(r) = \dfrac{e^2}{8\pi\varepsilon_0 m^2 c^2}\,\dfrac{1}{r^3} \quad -(8)$

Therefore:

2)

$$\left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \frac{1}{a_0^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)} \quad -(9)$$

where the Bohr radius is:

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m e^4} \quad -(10)$$

Therefore for an electron in H with quantum numbers n and ℓ:

$$\zeta_{n\ell} = \frac{\alpha^2 R_\infty}{n^3 \ell(\ell+\frac{1}{2})(\ell+1)} \quad -(11)$$

where the fine structure constant is:

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = 0.007297351 \quad -(12)$$

and

$$\left.\begin{aligned} hcR_\infty &= \frac{m e^4}{8\hbar^2 \epsilon_0^2} \\ &= 2.179908 \times 10^{-18}\ \text{J} \end{aligned}\right\} -(13)$$

In general:

$$\zeta_{n\ell} = \frac{\alpha^2 R_\infty Z^4}{n^3 \ell(\ell+\frac{1}{2})(\ell+1)} \quad -(14)$$

So spin orbit interaction is proportional to Z^4 and large atom is very important.

The first order correction of a state $|n\ell s; jm_j\rangle$ from perturbation theory is:

$$E_{so} = \langle n\ell s; jm_j | \hat{H}_{so} | n\ell s; jm_j \rangle \quad -(15)$$

5)

So:

$$\boxed{\left(\hat{H} - E + E_{so}\right) \underline{\nabla} \psi = \underline{F} \psi} \quad - (16)$$

We have:

$$\underline{\ell} \cdot \underline{s} \, |n\ell s; j m_j\rangle = \frac{1}{2}\left(j^2 - \ell^2 - s^2\right) |n\ell s; j m_j\rangle \quad - (17)$$

because:

$$j^2 = |(\underline{\ell} + \underline{s})|^2 = \ell^2 + s^2 + 2\,\underline{\ell} \cdot \underline{s} \quad - (18)$$

So:

$$E_{so} = \frac{1}{2} \hbar^2 \left(j(j+1) - \ell(\ell+1) - s(s+1)\right) \langle n\ell s; j m_j | \xi(r) | n\ell s; j m_j \rangle$$

$$= \frac{1}{2} hc \, \gamma_{n\ell} \left(j(j+1) - \ell(\ell+1) - s(s+1)\right).$$

$$\boxed{E_{so} = \alpha^2 hc R_\infty \left[\frac{j(j+1) - \ell(\ell+1) - s(s+1)}{2n^3 \ell\left(\ell + \frac{1}{2}\right)(\ell+1)}\right]} \quad - (17)$$

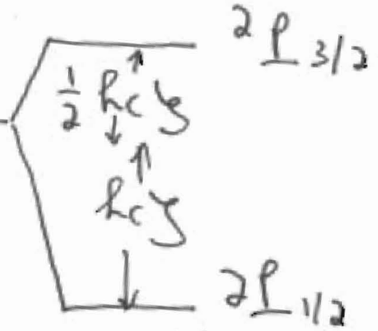
So the fine energy eigenvalues are evaluated from eqns. (16) and (17), with the H wavefunctions ψ in the first approximation. This is because spin-orbit splitting in H is very small. For example, for 2-p electron,

$$n = 2, \quad \ell = 1, \quad - (18)$$

energy level separation and transition wavenumber

4)
are of the order of $R_\infty \sim 10^5\ cm^{-1}$. The magnitude of the spin-orbit interaction constant is $\alpha^2 R_\infty / 24$, i.e. $R_\infty / (4.51 \times 10^5)$, fraction of a wavenumber. So using the H wavefunctions of is a very good approximation. The 2p level is split as follows:

Fig. (1)



The permitted states of total angular momentum from a system made up of two sources of angular momentum are given by the Clebsch Gordan series:

$$j = j_1 + j_2,\ j_1 + j_2 - 1,\ \ldots,\ |j_1 - j_2| \quad -(19)$$

$$m_j = m_{j1} + m_{j2}$$

so for a 2-p electron:

$$j = \frac{3}{2} \text{ and } \frac{1}{2} \quad -(20)$$

$$-(21)$$

So in eq. (17):

$$n = 2,\ \ell = 1,\ j = 3/2 \text{ or } 1/2,\ s = 1/2$$

and F can be worked out for eq. (16)