Eigenfunctions of the Spin-Orbit Hamiltonian

We know that $\hat{H}^0$ commutes with the orbital angular momentum operators $\hat{\vec{L}}^2$ & $\hat{L}_\alpha$ where $\alpha = x, y, \text{ or } z$, What about the spin-orbit term? Since $W(r)$ is a radial function it will commute with these operators and we need only consider the effect of $\hat{\vec{L}} \bullet \hat{\vec{S}}$. We know that the atom is isolated so the total angular momentum due to the electrons spin and orbital motion must be a constant of the motion. We write this vector operator as

$\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$ and, by general principles we anticipate that the wavefunction for $\hat{H}$ will be an eigenfunction of $\hat{J}^2$ & $\hat{J}_z$ with eigenvalues $j(j+1)$ & m_j (in multiples of $\hbar^2$ & $\hbar$) with j being $0,\ 1/2\ ,1\ \ /3/2,\ \cdots$ and $-j \le m_j \le j$ in multiples of 1. Note further that since

so

$$\hat{\vec{L}} \bullet \hat{\vec{S}} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)$$

the eigenvalue problem of interest is

$$\left(\hat{H}^0 + \frac{W(r)}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right)\right)\Psi = E\Psi$$

Because both the coulomb potential and $W(r)$ are radially symmetric we must have $\Psi = R(r)\Phi(\theta,\phi)$ and we can choose $\Phi(\theta,\phi)$ to be an eigenfunction of $\hat{J}^2,\ \hat{J}_z,\ \hat{L}^2$ & $\hat{S}^2$. The radial function is then determined by

$$\left(-\frac{\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \frac{l(l+1)\hbar^2}{2mr^2} - \frac{e^2 Z}{4\pi\varepsilon_0 r} + \frac{W(r)}{2}\left(j(j+1) - l(l+1) - \frac{1}{2}\left(\frac{1}{2}+1\right)\right)\right)R(r) = ER(r)$$

and clearly the energy will depend on $j\,\&\,l$ but not m_j so the various states will be $2j+1$ degenerate. There are several ways to determine the explicit form of the angular function Φ, the most general using angular momentum coupling rules and the Clebsch-Gordon or Wigner coefficients. We derive the explicit form in appendix 2 of these notes and simply state the result for $j = l \pm 1/2$

$$\Phi_{jml1/2} = \pm\sqrt{\frac{l \pm m + 1/2}{2l+1}}\alpha Y_l^{m-1/2} + \sqrt{\frac{l \mp m + 1/2}{2l+1}}\beta Y_l^{m+1/2}$$

Note that j must be positive so when $l = 0$ we have $j = 1/2$ and the coefficient of $W(r)$ vanishes and there is no spin-orbit effect for *s* states. Additionally we take the upper sign when $j = l + 1/2$ and the lower sign when $j = l - 1/2$. The splitting of energy levels due to the spin-orbit interaction is known as fine structure splitting.

Lets write out a few of these angular terms explicitly. For $\ell = 0$ we have

$$\left| j = 1/2, m_j, \ell = 0 \right\rangle = \left(\sqrt{+m_j + 1/2}\ \alpha Y_0^{m_j - 1/2} + \sqrt{-m_j + 1/2}\ \beta Y_0^{m_j + 1/2} \right)$$

and for the two possible values of $m_j = \pm 1/2$ we have

$$\left| j = 1/2, m_j = +1/2, \ell = 0 \right\rangle = \alpha Y_0^0 \text{ and } \left| j = 1/2, m_j = -1/2, \ell = 0 \right\rangle = \beta Y_0^0$$

from which we see that for $\ell = 0$ the total angular momentum is that due to the electrons spin. For $\ell = 1$ we can have $j = 1/2\,\&\,3/2$ so

$$\left| j = 1/2, m_j, \ell = 1 \right\rangle = \frac{1}{\sqrt{3}}\left(-\sqrt{-m_j + 3/2}\ \alpha Y_1^{m_j - 1/2} + \sqrt{m_j + 3/2}\ \beta Y_1^{m_j + 1/2} \right)$$

and since $m_j = \pm 1/2$ we have

$$\left| j = 1/2, 1/2, \ell = 1 \right\rangle = \frac{1}{\sqrt{3}}\left(-\ \alpha Y_1^0 + \frac{2}{\sqrt{2}}\ \beta Y_1^1 \right)$$

and

$$\left| j = 1/2, -1/2, \ell = 1 \right\rangle = \frac{1}{\sqrt{3}}\left(-\frac{2}{\sqrt{2}}\ \alpha Y_1^{-1} + \beta Y_1^0 \right)$$

The $j = 3/2$ functions are

$$\left| j = 3/2, m_j, \ell = 1 \right\rangle = \frac{1}{\sqrt{3}}\left(+\sqrt{m_j + 3/2}\ \alpha Y_1^{m_j - 1/2} + \sqrt{-m_j + 3/2}\ \beta Y_1^{m_j + 1/2} \right)$$

and since $m_j = \pm 1/2 \,\&\, \pm 3/2$ we have

$$\left| j = 3/2, -3/2, l = 1 \right\rangle = \beta Y_1^{-1}$$

$$\left| j = 3/2, -1/2, l = 1 \right\rangle = \frac{1}{\sqrt{3}}\left(\alpha Y_1^{-1} + \sqrt{2}\ \beta Y_1^0 \right)$$

$$\left| j = 3/2, 1/2, l = 1 \right\rangle = \frac{1}{\sqrt{3}}\left(+\sqrt{2}\ \alpha Y_1^0 +\ \beta Y_1^1 \right)$$

$$\left| j = 3/2, 3/2, l = 1 \right\rangle = \alpha Y_1^1$$

Note that because

$$\mathbf{\Phi}_{jml1/2} = \pm\sqrt{\frac{l \pm m + 1/2}{2l+1}}\alpha Y_l^{m-1/2} + \sqrt{\frac{l \mp m + 1/2}{2l+1}}\beta Y_l^{m+1/2}$$

is an eigenfunction of $\hat{\hat{L}}^2 \,\&\, \hat{L}_z$ the eigenfunctions of the spin free Schrodinger equation are $R_{n\ell}(r)\boldsymbol{\Phi}_{jm\ell 1/2}$ so that

$$\hat{H}^0 R_{n\ell}(r)\boldsymbol{\Phi}_{jm\ell 1/2} = E_n R_{n\ell}(r)\boldsymbol{\Phi}_{jm\ell 1/2}\,.$$