Perturbation treatment

We will treat $W(r)\hat{\vec{L}}\bullet\hat{\vec{S}}$ as a perturbation on the Schrodinger Hamiltonian and in first order we need its expectation value with respect to the zero order hydrogenic functions. Note that because $\boldsymbol{\Phi}_{jm\ell 1/2}$ is an eigenfuction of $\hat{\vec{L}}\bullet\hat{\vec{S}}$ we don't need to use degenerate perturbation theory. The required matrix element is

$$E^{(1)}_{j,\ell,m} = \left\langle R_{n\ell}(r)\Phi_{j,\ell,m,1/2}\right|\frac{1}{2}W(r)\left(\hat{J}^2-\hat{L}^2-\hat{S}^2\right)\left|R_{n\ell}(r)\Phi_{j,\ell,m,1/2}\right\rangle$$

which separates into the product of radial factor

$$\left\langle R_{n\ell}(r)\right|W(r)\left|R_{n\ell}(r)\right\rangle = \frac{Ze^2\hbar^2}{8\pi\varepsilon_0 c^2 m^2}\left\langle R_{n\ell}(r)\right|\frac{1}{r^3}\left|R_{n\ell}(r)\right\rangle = \frac{Ze^2\hbar^2}{8\pi\varepsilon_0 c^2 m^2}\left\langle\frac{1}{r^3}\right\rangle_{n\ell}$$

and an angular factor

$$\left\langle\Phi_{j,\ell,m,1/2}\right|\frac{1}{2}\left(\hat{J}^2-\hat{L}^2-\hat{S}^2\right)\left|\Phi_{j,\ell,m,1/2}\right\rangle = \frac{1}{2}\left(j(j+1)-\ell(\ell+1)-3/4\right)$$

using

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

we have

$$E^{(1)}_{j,\ell,m} = \frac{Z^4 e^2\hbar^2}{16\pi\varepsilon_0 c^2 m^2 a_0^3}\frac{\left(j(j+1)-\ell(\ell+1)-3/4\right)}{n^3\ell\left(\ell+1/2\right)\left(\ell+1\right)}$$

Using $R_\infty(energy)=\dfrac{e^2}{8\pi\varepsilon_0 a_0}$, $a_0=\dfrac{4\pi\varepsilon_0\hbar^2}{me^2}$ and the square of the fine structure constant $\alpha^2=\dfrac{2R_\infty}{mc^2}$ we have

$$\frac{Z^4 e^2\hbar^2}{16\pi\varepsilon_0 c^2 m^2 a_0^3}=\frac{\alpha^2 R_\infty Z^4}{2}$$

where R_∞ is expressed as an energy. Two convenient units are

$R_\infty(eV)=13.605693eV$ or $R_\infty(cm^{-1})=109{,}739.85cm^{-1}$

The first order spin-orbit shift to the $njm_j\ell$ level is

$$E^{(1)}_{n,j,\ell,m}=\frac{\alpha^2 R_\infty Z^4}{2}\frac{\left(j(j+1)-\ell(\ell+1)-3/4\right)}{n^3\ell\left(\ell+1/2\right)\left(\ell+1\right)}$$

where $\ell\neq 0$. Coupling the $l=1,s=1/2$ angular momenta results in the terms $j=3/2\,\&\,1/2$ with the energy shifts

$$E^{(1)}_{n,3/2,1,m}=\frac{\alpha^2 R_\infty Z^4}{2n^3}\times\frac{1}{3}\ \text{and}\ E^{(1)}_{n,1/2,1,m}=-\frac{\alpha^2 R_\infty Z^4}{2n^3}\times\frac{2}{3}$$

and the splitting

$$\Delta E_{SO}=E^{(1)}_{n,3/2,1,m}-E^{(1)}_{n,1/2,1,m}=\frac{\alpha^2 R_\infty Z^4}{2n^3}=2.92189\frac{Z^4}{n^3}cm^{-1}$$

Note that the splitting for p orbitals drops rapidly with increasing n and increases rapidly with increasing Z. The splitting for H is $0.3654cm^{-1}$ in excellent agreement with the experimental splitting $0.3652cm^{-1}$. The splitting of the n=2 level for the one electron atoms is predicted to be $\Delta E\left(Z\right)=0.3654Z^4 cm^{-1}$ and as the following table shows is remarkably accurate. The experimental values for ΔE are from Moore's Tables

Element	$\Delta E(cm^{-1})$	Z^4	$\Delta E / Z^4$
He^{+}	5.8434	16	0.3652
Li^{+2}	29.58	81	0.3652
Be^{+3}	93.5	256	0.3652
B^{+4}	228.3	625	0.3653
C^{+5}	473.3	1296	0.3652
N^{+6}	876.9	2401	0.3652
O^{+7}	1496	4096	0.3652