Spin-Orbit Interactions

The perturbation Hamiltonian is: $H' = -\vec{\mu} \cdot \vec{B}$

The magnetic dipole moment of the electron is related to its spin angular momentum:

$$\vec{\mu} = -g_s \frac{\mu_B}{\hbar} \vec{S}$$

where μ_B is the Bohr magneton: $\mu_B = \frac{e\,\hbar}{2\,m_e}$

and the magnetic field at the site of the electron is:

$$\vec{B}_{internal} = \left(\frac{e}{4\,\pi\epsilon_o m_e c^2 r^3}\right) \vec{L}$$

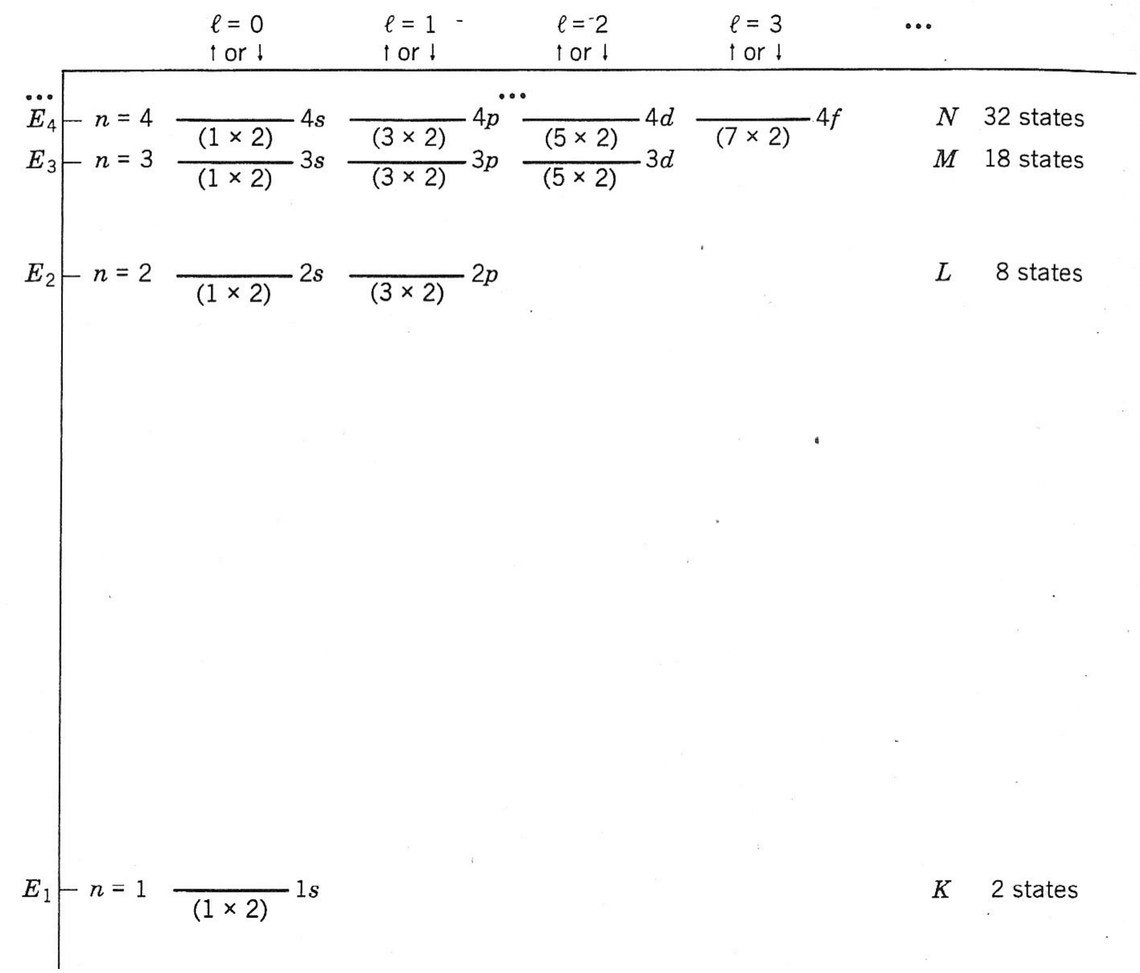
The perturbation Hamiltonian becomes: $H' = \frac{e^2}{4\,\pi\epsilon_o} \frac{\vec{S}\cdot\vec{L}}{2\,m_e^2\,c^2\,r^3}$

The factor of “2” comes from the Thomas precession.

$$\boxed{H' = \alpha\,\frac{\hbar}{2\,m_e^2\,c}\,\frac{\vec{S}\cdot\vec{L}}{r^3}}$$

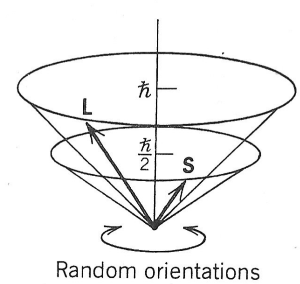
The spin-orbit interaction undermines the usefulness of the $|n\;l\;m_l\;m_s\rangle$ states. The $|n\;l\;m_l\;m_s\rangle$ states are shown on the next page.

Figure 8-13
Energy levels E_n and degenerate states $\Psi_{n\ell m_\ell m_s}$ for the one-electron atom. The dynamics of the atom is governed only by the Coulomb force, as in Figure 7-2. The spin of the electron may be either up (↑) or down (↓) for each assignment of the set of quantum numbers $(n\ell m_\ell)$.



We can use m_l and m_s as *"good quantum numbers"* to determine the stationary states as long as we are able to specify eigenvalues independently for the observables L_z and S_z. These two quantities are separately conserved whenever there exist states of definite energy in which L_z and S_z also have definite values.

Figure 8-26
Independently oriented **L** and **S** vectors representing a state with good quantum numbers m_ℓ and m_s. In this case **L** refers to the $\ell = 1$ state with $m_\ell = 1$.



Recall that our perturbation Hamiltonian is:

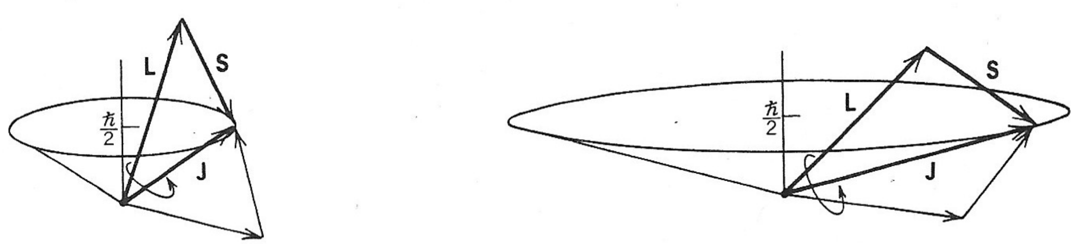
$$H' = \alpha \frac{\hbar}{2\, m_e^2\, c} \frac{\vec{S}\cdot\vec{L}}{r^3}$$

We need eigenstates described by quantum numbers that are eigenstates of the Hamiltonian *H′*. Why? Because we need to calculate the first-order correction to the stationary states in the H-atom due to the $-\vec{\mu}\cdot\vec{B}$ interaction (a.k.a. the $\vec{S}\cdot\vec{L}$ interaction).

$$E^1 = \langle\psi|H'|\psi\rangle \sim \left\langle\psi\left|\frac{\vec{S}\cdot\vec{L}}{r^3}\right|\psi\right\rangle$$

Since our *H′* implies a dependence of the energy on the *relative* orientation of $\vec{L}$ and $\vec{S}$, the two vectors must be coupled together as a result of this new dynamical variation of the energy. We can see the coupling in the figure if we fix the energy by fixing the angle between $\vec{L}$ and $\vec{S}$ while maintaining the *z* components of the two vectors.

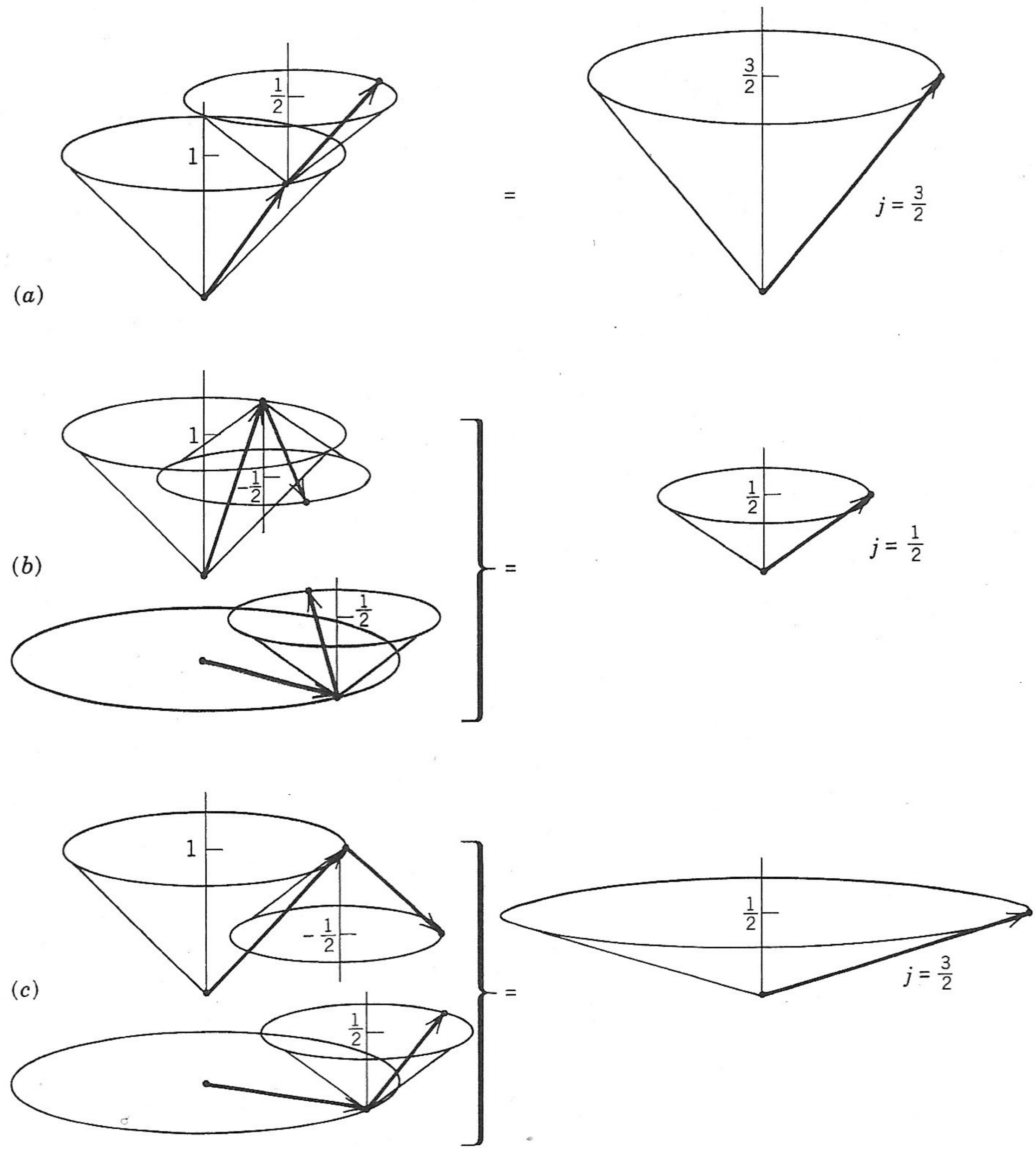
Figure 8-27
Coupling of spin and orbital angular momenta owing to the spin–orbit interaction. The effect is represented as a precession of **L** and **S** about **J**. The indicated vector additions correspond to the configurations displayed in parts (*b*) and (*c*) of Figure 8-22.



L_z and S_z cannot be assigned definite values; however a state of definite energy can still have a definite value of J_z. The total angular momentum is conserved as long as the atom is isolated.

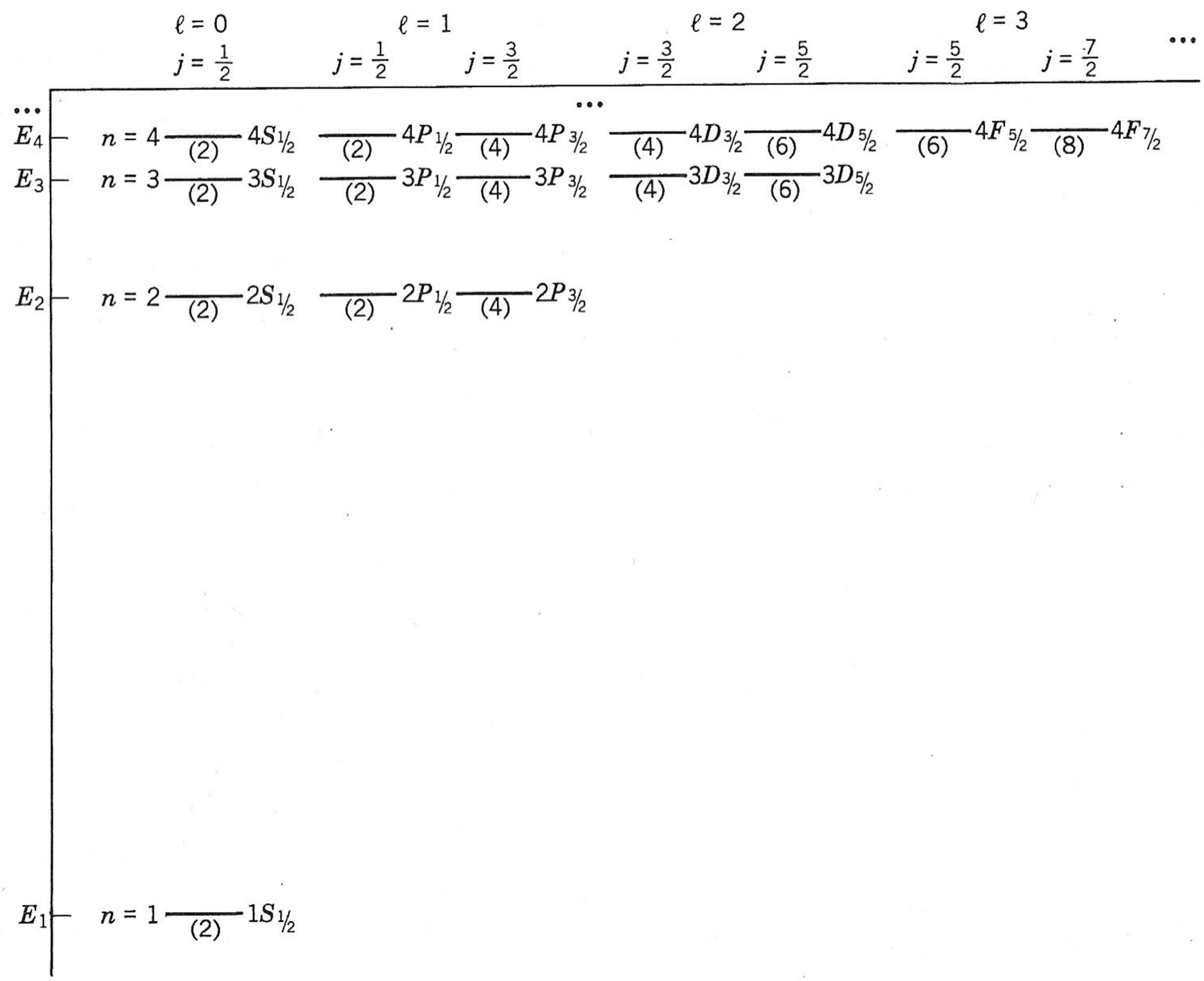
Let's look at the following figure to see how we can construct states of $j = \ell + \frac{1}{2}$ and $j = \ell - \frac{1}{2}$.

Figure 8-22
Vector addition of orbital and spin angular momenta. The factors of $\hbar$ are suppressed, and the $\ell = 1$ case is chosen for $\mathbf{L}$. The sum $1 + \frac{1}{2}$ produces the results $\frac{3}{2}$ and $\frac{1}{2}$ for the vector $\mathbf{J}$.



How do we go from the $|n\ \ell\ m_\ell\ m_s\rangle$ states to the $|n\ \ell\ j\ m_j\rangle$ states?

Figure 8-24
Energy levels E_n and degenerate states $\Psi_{n\ell jm_j}$ for the one-electron atom. Each assignment of quantum numbers $(n\ell j)$ implies $2j+1$ possible values of m_j, as indicated in parentheses at each level. The spectroscopic notation nL_j is used to designate the states. This scheme is an alternative to the one described in Figure 8-13. The Coulomb force provides the only interaction in each of the two figures.



All "fine and good," but how are these states eigenstates of the $\vec{S}\cdot\vec{L}$ operator in our perturbation Hamiltonian, *H'* ?

First of all, the total angular momentum of the atom is $\vec{J}=\vec{L}+\vec{S}$, and

$$\vec{J}\cdot\vec{J}=\left(\vec{L}+\vec{S}\right)\cdot\left(\vec{L}+\vec{S}\right)$$

Solving this for $\vec{S}\cdot\vec{L}$ we find:

$$\vec{S}\cdot\vec{L} = \frac{J^2 - L^2 - S^2}{2}$$

We can now find the expectation value for $\vec{S}\cdot\vec{L}$ by using our new eigenstates $\left|n\,\ell\,j\,m_j\right\rangle$:

For example:

$$\langle J^2\rangle = \left\langle n\,\ell\,j\,m_j\middle|J^2\middle|n\,\ell\,j\,m_j\right\rangle = j(j+1)\hbar^2$$

Continuing on with the other expectation values we find the following:

$$\langle \vec{S}\cdot\vec{L}\ \rangle = \frac{\langle J^2\rangle - \langle L^2\rangle - \langle S^2\rangle}{2}$$
$$= \frac{j(j+1)\hbar^2 - \ell(\ell+1)\hbar^2 - s(s+1)\hbar^2}{2}$$

We still have to calculate the expectation value of $\frac{1}{r^3}$.

$$\langle\tfrac{1}{r^3}\rangle = \left(\frac{\alpha m_e c}{n\,\hbar}\right)^3 \frac{2}{\ell(\ell+1)(2\ell+1)}$$

Collecting our calculations, we find the following:

$$\langle H'\rangle = \frac{\alpha\hbar}{2\,m_e^2\,c}\ \langle n\,\ell\,j\,m_j\left|\frac{\vec{S}\cdot\vec{L}}{r^3}\right| n\,\ell\,j\,m_j\rangle$$

$$\langle H'\rangle_{\vec{S}\cdot\vec{L}} = \frac{\alpha^2}{n}\ E_n^0\ \frac{j(j+1) - \ell(\ell+1) - \frac{3}{4}}{\ell(\ell+1)(2\ell+1)}$$

where $\quad E_n^0 = \frac{1}{2}m_e c^2\,\frac{\alpha^2}{n^2}$.

Let's combine our two contributions to the fine structure splitting:
1) The relativistic kinetic energy, and
2) The spin-orbit coupling

$$\langle H' \rangle_{fs} = \langle H' \rangle_{rel} + \langle H' \rangle_{\vec{S}\cdot\vec{L}}$$

$$\langle H' \rangle_{fs} = -\frac{E_n^0\,\alpha^2}{4n^2}\left[\frac{4n}{\ell+\frac{1}{2}} - 3\right] + \frac{\alpha^2}{n}\,E_n^0\,\frac{j(j+1)-\ell(\ell+1)-\frac{3}{4}}{\ell(\ell+1)(2\ell+1)}$$

$$\langle H' \rangle_{fs} = \frac{\alpha^2}{n}\,E_n^0\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)$$

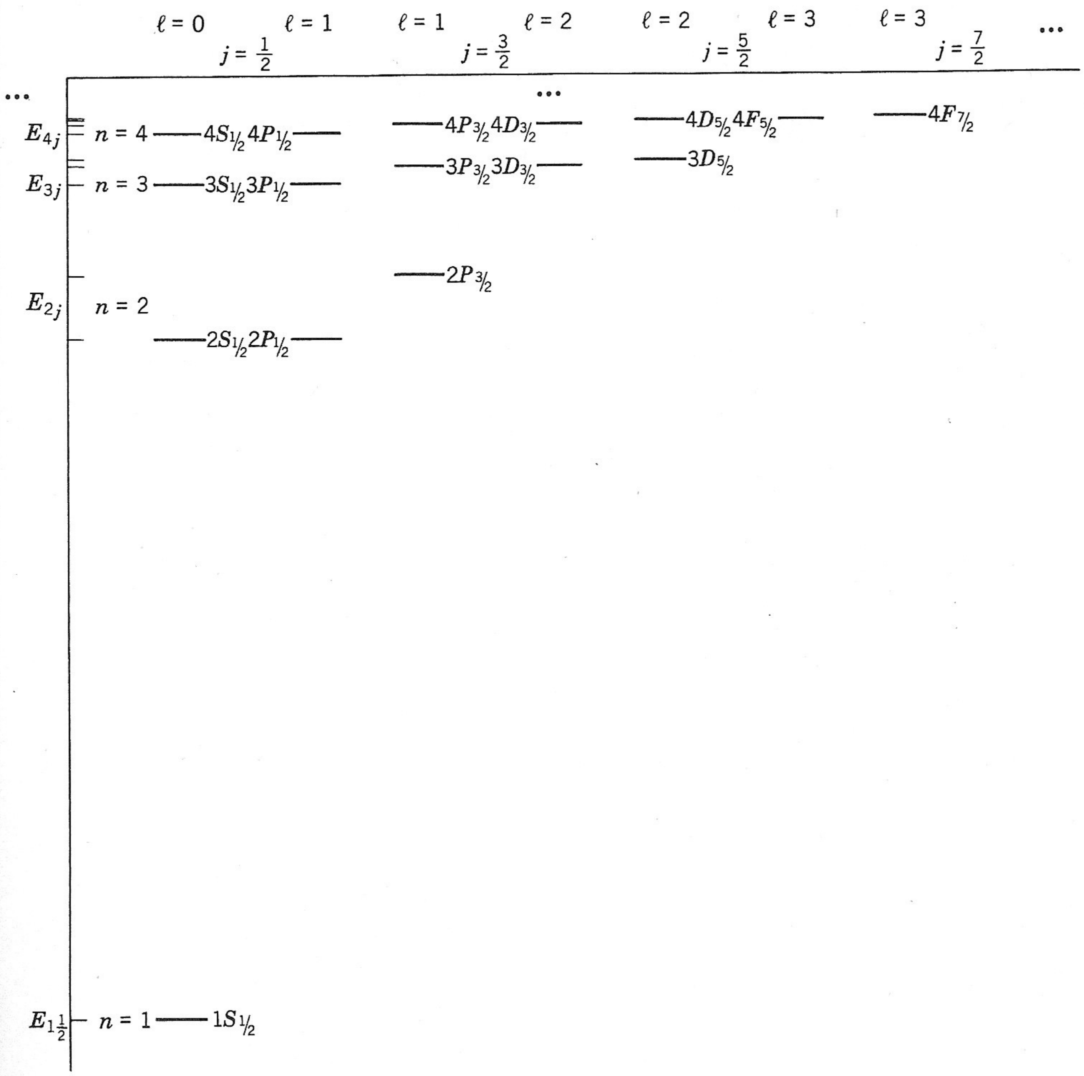
Now we can calculate the total energy of each $n\,j$ state.

$$E_{nj} = E_n^0 + \langle H' \rangle_{fs}$$

$$E_{nj} = -E_n^0\left[1 + \frac{\alpha^2}{n^2}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right]$$

The corresponding energy level diagram is shown in the following figure:

Figure 8-29
Energy levels E_{nj} for the one-electron atom. Each choice of n and j gives a pair of degenerate states nL_j with two different values of ℓ. The fine structure effects shift the levels away from their positions in Figure 8-24. The greatly exaggerated splittings indicate how the shifts diminish with increasing values of the quantum numbers.



These are the energy levels for the $|n\ \ell\ j\ m_j\rangle$ eigenstates for a one-electron atom.