Spin in one-electron atoms

The electrostatic Hamiltonian for a one-electron atom is (in spherical coordinates)

$$H^{(0)} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{2\mu r^2}L^2 - \frac{Ze^2}{r},$$

where μ is the electron reduced mass, e its charge, Z the nuclear charge, and L^2 is the angular momentum operator, which includes terms in θ and φ but not in r. The eigenfunctions are $\psi^{(0)}_{nlm_l}$,

$$H^{(0)}\psi^{(0)}_{nlm_l} = E^{(0)}_n\psi^{(0)}_{nlm_l}.$$

$H^{(0)}$ describes an electron without internal degrees of freedom (spin). A full description must include the spin, with the wavefunctions χ_{sm_s} (2-dimensional vectors in the spin space), which satisfy

$$S^2\chi_{sm_s} = s(s+1)\hbar^2\chi_{sm_s}$$

$$S_z\chi_{sm_s} = m_s\hbar\chi_{sm_s}.$$

If we ignore the interaction between the spin and other degrees of freedom, we can express the wavefunction by

$$\psi^{(0)}_{nlm_lm_s} = \psi^{(0)}_{nlm_l}\chi_{sm_s}.$$

Obviously, if there were no such interaction, the spin could not be observed. The full Hamiltonian includes an interaction term H_{so},

$$H = H^{(0)}I + H_{so},$$

where I is a 2×2 unit matrix in the spin space. In general, the eigenfunctions of H will not be pure α or β functions; they will have the more general form

$$\psi = \begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = \psi_+ \begin{pmatrix} 1 \\ 0 \end{pmatrix} + \psi_- \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \psi_+\alpha + \psi_-\beta.$$

$|\psi_+(\vec{r})|^2 \, d\vec{r}$ is the probability of finding an electron with spin $+\frac{1}{2}\hbar$ in the volume element $d\vec{r}$ around $\vec{r}$.

Spin-orbit coupling

Because of the spin angular momentum, the electron has a magnetic moment $\vec{M}_s$, proportional to the spin $\vec{S}$. From the point of view of the electron, the nucleus with charge Ze moves around it, creating a magnetic field proportional to the angular momentum $\vec{L}$. The interaction is therefore proportional to the scalar product $\vec{S} \cdot \vec{L}$. The full expression is

$$H_{so} = \frac{Ze^2}{2\mu^2 c^2} \frac{1}{r^3} \vec{S} \cdot \vec{L}.$$

We can estimate the size of the interaction by taking $r \sim a_0$ and $\langle \vec{S} \cdot \vec{L} \rangle \sim \hbar^2$. We obtain (for $Z = 1$) $\langle H_{so} \rangle \sim 10^{-4}$eV, whereas atomic energies are of order of one eV. The interaction is relatively small, and we can use perturbation theory. We obtain in first order (ignoring degeneracy)

$$E_j \approx E_j^{(0)} + \langle \psi_j^{(0)} | H_{so} | \psi_j^{(0)} \rangle,$$

$$\psi_j \approx \psi_j^{(0)} + \sum_{k \neq j} \frac{\langle \psi_k^{(0)} | H_{so} | \psi_j^{(0)} \rangle}{E_j^{(0)} - E_k^{(0)}} \psi_k^{(0)}.$$

This is not an efficient approach. The $E_n^{(0)}$ energies have a $2n^2$ degeneracy, so that secular determinants of that order must be solved. In addition, while the perturbation splits some of the degenerate levels, the brute force diagonalization of the secular determinant does not give the physical reason for the nature of the splitting. Thus, the $n = 2$ level of the H atom, which is 8-fold degenerate, splits into three sublevels, with degeneracies 2, 2, 4. This result is obtained but not explained in the secular determinant treatment. We shall see that the splitting mode can be predicted from angular momentum considerations without any calculations.

The generalized angular momentum $\vec{J}$

The Hamiltonian of a 1-e atom, including spin-orbit interaction, was given above as $H = H^{(0)}I + H_{so}$. Without H_{so}, the functions $\psi^{(0)}_{nlm_lm_s}$ are eigenfunctions of the five operators $H^{(0)}, L^2, L_z, S^2, S_z$. This is possible since all the operators commute. The question is now: what happens if $H^{(0)}$ is replaced by H?

Since $H^{(0)}$ commutes with all the other operators, the only problem may come from H_{so}. This operator includes physical constants, the term $1/r^3$, and $\vec{S}\cdot\vec{L}$. $1/r^3$ commutes with the other operators, since they only involve angular and spin coordinates, so we need to check $\vec{S}\cdot\vec{L}$.

$$[\vec{S}\cdot\vec{L}, L_z] = [L_xS_x, L_z] + [L_yS_y, L_z] + [L_zS_z, L_z] =$$

$$= [L_x, L_z]S_x + [L_y, L_z]S_y + [L_z, L_z]S_z = -i\hbar L_yS_x + i\hbar L_xS_y.$$

Note that any $[S_i, L_j] = 0$. The result is that $\vec{S}\cdot\vec{L}$ does not commute with L_z; therefore, $[H, L_z] \neq 0$, and m_l is not a good quantum number. Similarly, we can get

$$[\vec{S}\cdot\vec{L}, S_z] = -i\hbar L_x S_y + i\hbar L_y S_x,$$

so that S_z also does not commute with H. If we define
$\vec{J} \equiv \vec{L} + \vec{S}$,
J_z commutes with H. It is easily shown that $\vec{J}$ is a generalized angular momentum, since

$$[J_x, J_y] = [L_x + S_x, L_y + S_y] = [L_x, L_y] + [S_x, S_y] =$$
$$= i\hbar(L_z + S_z) = i\hbar J_z.$$

We can now define $J^2 \equiv J_x^2 + J_y^2 + J_z^2$ in the usual way, and the 5 operators H, L^2, S^2, J^2, J_z commute. The exact wave functions will be defined by the quantum numbers $n, l, s(= 1/2), j, m_j$:
$H\psi_{nljm_j} = E_{nlj}\psi_{nljm_j}$
$L^2\psi_{nljm_j} = l(l+1)\hbar^2\psi_{nljm_j}$
$S^2\psi_{nljm_j} = (3/4)\hbar^2\psi_{nljm_j}$
$J^2\psi_{nljm_j} = j(j+1)\hbar^2\psi_{nljm_j}$
$J_z\psi_{nljm_j} = m_j\hbar\psi_{nljm_j}$.
Note that s is always $\frac{1}{2}$ and is therefore omitted.

We start with the functions $\psi^{(0)}_{nlm_lm_s}$, which are eigenfunctions of $H^{(0)}, L^2, L_z, S^2, S_z$. We want the exact functions ψ_{nljm_j}, eigenfunctions of H, L^2, S^2, J^2, J_z. The best way is to go via $\psi^{(0)}_{nljm_j}$, eigenfunctions of $H^{(0)}, L^2, S^2, J^2, J_z$. This step is relatively easy, and it gives important information about the final states. The energies depend on nlj, so that the splitting may be obtained by looking at the values these quantum numbers can have for a given case. In addition, the integrals of H_{so} vanish between functions which do not have the same $lsjm_j$, so that nondegenerate perturbations may be used.

Proof that integrals of H_{so} vanish between degenerate zero-order functions $\psi^{(0)}_{nljm_j}$ with the same n:
$J^2 = (\vec{S} + \vec{L})^2 = S^2 + L^2 + 2(\vec{S} \cdot \vec{L}) \quad (\vec{S} \cdot \vec{L} = \vec{L} \cdot \vec{S})$

$$H_{so} = K \frac{1}{r^3} \vec{S} \cdot \vec{L} = \frac{1}{2} K \frac{1}{r^3} (J^2 - L^2 - S^2).$$

Since $\psi^{(0)}_{nljm_j}$ are eigenfunctions of L^2, S^2, J^2 and J_z, integrals of H_{so} between two functions which differ in one of the eigenvalues $ljsm_j$ will vanish. Since the degenerate functions have the same n, they must differ in one (at least) of the other numbers, which proves the statement. The function correct to first order will therefore be

$$\psi_{nljm_j} \approx \psi^{(0)}_{nljm_j} + \sum_{n' \neq n} \frac{\langle \psi^{(0)}_{n'ljm_j} | H_{so} | \psi^{(0)}_{nljm_j} \rangle}{E^{(0)}_n - E^{(0)}_{n'}}.$$

The energy is given to first order by

$$E_{nlj} = E^{(0)}_n + \langle \psi^{(0)}_{nljm_j} | H_{so} | \psi^{(0)}_{nljm_j} \rangle =$$

$$= E^{(0)}_n + \frac{Z^2 |E^{(0)}_n| \, \alpha^2}{2n} \, \frac{[j(j+1) - l(l+1) - \frac{3}{4}]}{l(l+\frac{1}{2})(l+1)},$$

where the dimensionless fine structure constant is $\alpha \equiv \frac{e^2}{\hbar c} \approx \frac{1}{137}$. The correction vanishes for $l = 0$. The fine structure splittings are of order 10^{-4} eV in light atoms. There are other relativistic effects of the same order. In addition, there are hyperfine structure terms of order 10^{-7} eV, resulting from the electron interaction with the nuclear spin.

The first order energy correction depends on $Z^2\alpha^2$. It is small for light elements, but increases with Z^2, and for heavy elements it becomes large, as do other relativistic effects. They cannot be treated as perturbation, and the starting point must be relativistic quantum mechanical formulation (Dirac equation). This is true not only for the one-electron atoms discussed here. Looking at Au ($Z = 79$), the lowest ionization potential is higher than non-relativistic predictions by more than 3 eV, while relativistic calculations agree with experiment. Trends in the periodic table change in the 6th and 7th row.

The energy cannot depend on the value of m-type quantum numbers as long as spherical symmetry is retained. These values are changed by $L^{\pm}$-type operators, which commute with H. Therefore,

$$H\psi_{nlm} = E\psi_{nlm} \Rightarrow HL^{\pm}\psi_{nlm} = L^{\pm}H\psi_{nlm} = EL^{\pm}\psi_{nlm},$$

and $L^{\pm}\psi_{nlm}$ has the same energy as ψ_{nlm}.

The functions $\psi^{(0)}_{nljm_j}$ are linear combinations of the $\psi^{(0)}_{nlm_lm_s}$, with the same nl:

$$\psi^{(0)}_{nljm_j} = \sum_{m_lm_s} a_{m_lm_s}\psi^{(0)}_{nlm_lm_s}.$$

The combination coefficients are a special case of the Clebsch-Gordan parameters, which appear whenever two angular momenta are coupled to form a new angular momentum. There are well known (but complicated) expressions for these coefficients, but in most cases they can be found by simple arguments (example follows).

The main advantage of coupling $\vec{L}$ and $\vec{S}$ is that we know immediately how the levels will split under the spin-orbit coupling. The allowed j values go from $|l - s|$ to $l + s$ in steps of one. Consequently, j can be $l - \frac{1}{2}$ or $l + \frac{1}{2}$ for $l \geq 1$; for $l = 0$ j can only be $+\frac{1}{2}$. This means that all levels of a one-electron atom, except s, will split into two sublevels with $j = l \pm \frac{1}{2}$, which will show up as doublets in the spectrum. The degeneracy will be $2j+1$. An s level does not split.

Looking at $2n^2$ functions with the main quantum number n, the energy will now depend on nlj. Counting the functions, we find for each l two levels, with degeneracies $2(l+\frac{1}{2})+1$ and $2(l-\frac{1}{2})+1$. The total number of the functions is

$$\sum_{l=0}^{n-1}[2(l+\frac{1}{2})+1+2(l-\frac{1}{2})+1] = \sum_{l=0}^{n-1}(4l+2) = \frac{2+4n-2}{2}\cdot n = 2n^2,$$

so all functions are accounted for.

Example: The $n=2$ levels of the H atom.
There are 8 functions in the (nlm_lm_s) representation:

$$\begin{array}{cccc l}
2 & 0 & 0 & \pm\frac{1}{2} & (2s\alpha, 2s\beta) \\
2 & 1 & 0 & \pm\frac{1}{2} & (2p_0\alpha, 2p_0\beta) \\
2 & 1 & 1 & \pm\frac{1}{2} & (2p_1\alpha, 2p_1\beta) \\
2 & 1 & -1 & \pm\frac{1}{2} & (2p_{-1}\alpha, 2p_{-1}\beta)
\end{array}$$

There must also be 8 functions in the $(nljm_j)$ representation:

$$\begin{array}{cccc c cccc c cccc}
2 & 0 & \frac{1}{2} & \frac{1}{2} & & 2 & 1 & \frac{3}{2} & \frac{3}{2} & & 2 & 1 & \frac{1}{2} & \frac{1}{2} \\
2 & 0 & \frac{1}{2} & -\frac{1}{2} & & 2 & 1 & \frac{3}{2} & \frac{1}{2} & & 2 & 1 & \frac{1}{2} & -\frac{1}{2} \\
 & & & & & 2 & 1 & \frac{3}{2} & -\frac{1}{2} & & & & & \\
 & & & & & 2 & 1 & \frac{3}{2} & -\frac{3}{2} & & & & &
\end{array}$$

How are the functions in the second set expressed in terms of the first? There are two conditions: l must be the same, and $m_j = m_l + m_s$. This gives immediately the following expressions: $(20\frac{1}{2}\frac{1}{2}) = 2s\alpha$, $(20\frac{1}{2}-\frac{1}{2}) = 2s\beta$, $(21\frac{3}{2}\frac{3}{2}) = 2p_1\alpha$, $(21\frac{3}{2}-\frac{3}{2}) = 2p_{-1}\beta$.

What about the others? For example, $(21\frac{3}{2}\frac{1}{2})$ must be a linear combination of $2p_1\beta$ and $2p_{-1}\alpha$. To find the combination, we start from $(20\frac{3}{2}\frac{3}{2}) = 2p_1\alpha$ and apply the operator J^-.

$$J^-(21\frac{3}{2}\frac{3}{2}) = N^-(21\frac{3}{2}\frac{1}{2}).$$

It has been shown (in an exercise) that N^- for applying L^- to the general Y_{lm} is $\hbar\sqrt{(l+m)(l-m+1)}$. In this case, l is $j = \frac{3}{2}$ and m is $m_j = \frac{3}{2}$, so that $N^- = \hbar\sqrt{3}$. In order to apply J^- to $2p_1\alpha$ we must use $J^- = L^- + S^-$. The l, m in N^- are l, m_l for L^- and s, m_s for S^-. The result of operating $L^- + S^-$ on the rhs is

$$\hbar\sqrt{2}p_0\alpha + \hbar\sqrt{1}p_1\beta,$$

which must be equal to $\hbar\sqrt{3}(21\frac{3}{2}\frac{1}{2})$ obtained above. (p is used here rather than $2p$ to avoid confusion.) We thus find

$$(21\frac{3}{2}\frac{1}{2}) = \frac{1}{\sqrt{3}}(p_1\beta + \sqrt{2}p_0\alpha).$$

We can now find $(21\frac{1}{2}\frac{1}{2})$ by noting it must be orthogonal to $(21\frac{3}{2}\frac{1}{2})$. The orthogonal combination is $\sqrt{2}p_1\beta - p_0\alpha$, and upon normalization we get

$$(21\frac{1}{2}\frac{1}{2}) = \frac{1}{\sqrt{3}}(\sqrt{2}p_1\beta - p_0\alpha).$$

Since the energy depends on nlj and not on m_j, we normally need only one function for each nlj level.

Conclusion: Using only angular momentum arguments, we found the fine structure of one-electron atoms including SO coupling. The new $\psi^{(0)}_{nljm_j}$ form the basis for a simple, non-degenerate perturbation theory treatment.