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Quantum Mechanics

Lecture 11

Quiz 2;
Spin-orbit coupling;
Fine structure of Hydrogen.

A quick recap

Suppose a complicated Hamiltonian splits into two pieces,

$$H = H_0 + \lambda H_1$$

and that an eigenspace of H_0 with energy E is **degenerate** with N states.

$$|\chi_j\rangle := |\phi_E^{(0)}, j\rangle \qquad j = 1, \ldots, N \qquad H_0 |\chi_j\rangle = E |\chi_j\rangle \qquad E = E^{(0)}$$

Then the first order corrections to the eigenstates and eigenvalues are found by diagonalizing the perturbing Hamiltonian:

$$\sum_{j=1}^{N} |\chi_j\rangle\langle\chi_j| = 1_E \qquad 1_E H_1 1_E |\psi_E\rangle = E^{(1)} |\psi_E\rangle$$

Perturbations will in general break the degeneracy.

Spin-orbit coupling

Moving charges generate currents, and hence magnetic fields:

Biot-Savart Law

In the electron's rest frame: $$\mathbf{B} = \frac{-Ze\mathbf{v}\times\mathbf{r}}{cr^3}$$ $\mathbf{v} = \mathbf{p}/m_e$ = electron velocity in proton rest frame

This B-field will couple to the electron spin:

$$H = -\boldsymbol{\mu}\cdot\mathbf{B} = -\left(\frac{-ge}{2m_e c}\mathbf{S}\right)\cdot\left(\frac{-Ze\mathbf{v}\times\mathbf{r}}{cr^3}\right) = \frac{Ze^2}{m_e^2c^2r^3}\mathbf{S}\cdot\mathbf{L}$$

g = 2 is the **Landé g factor**, relating the spin and magnetic moment of an electron.

This argument ignores relativistic effects. A complete treatment includes an effect called Thomas precession and gives the spin-orbit Hamiltonian:

$$H_{SO} = \frac{Ze^2}{2m_e^2c^2|\hat{\mathbf{r}}^3|}\mathbf{S}\cdot\mathbf{L}$$

It's a natural dipole coupling term.

Spin-orbit coupling

We will consider the spin-orbit interaction as a perturbation that will split the degenerate states of a hydrogen atom. To that end, define:

$$|l, m_l, s, m_s\rangle = |l, m_l\rangle \otimes |s, m_s\rangle \qquad [\mathbf{L}, \mathbf{S}] = 0 \qquad s = \frac{1}{2} \text{ for an electron}$$

$$S^2|s, m_s\rangle = s(s+1)\hbar^2|s, m_s\rangle \qquad S_z|s, m_s\rangle = m_s\hbar|s, m_s\rangle$$

$$L^2|l, m_l\rangle = l(l+1)\hbar^2|l, m_l\rangle \qquad L_z|l, m_l\rangle = m_l\hbar|l, m_l\rangle$$

$$\mathbf{J} = \mathbf{L} + \mathbf{S}$$

orbital + spin = total angular momentum

To do degenerate perturbation theory, we must diagonalize:

$$H_{SO} \propto \mathbf{S} \cdot \mathbf{L}$$

Total angular momentum is conserved

Total J and J_z also give good quantum numbers for H_{SO}:

$$\mathbf{J} = \mathbf{S} + \mathbf{L} \qquad J^2 = L^2 + S^2 + 2\,\mathbf{S}\cdot\mathbf{L}$$

$$J_z = L_z + S_z \qquad 2\,\mathbf{S}\cdot\mathbf{L} = J^2 - L^2 - S^2$$

$$[\mathbf{J}, \mathbf{S}\cdot\mathbf{L}] = [J_z, \mathbf{S}\cdot\mathbf{L}] = 0$$

Explicitly:
$$\begin{aligned}[J_z, \mathbf{S}\cdot\mathbf{L}] &= [L_z + S_z, L_xS_x + L_yS_y + L_zS_z] \\ &= [L_z, L_x]S_x + [L_z, L_y]S_y + L_x[S_z, S_x] + L_y[S_z, S_y] \\ &= i\hbar L_yS_x - i\hbar L_xS_y + i\hbar L_xS_y - i\hbar L_yS_x = 0\end{aligned}$$

Note: $[L_z, H_{SO}] \neq 0\,, \quad [S_z, H_{SO}] \neq 0$ So m and z are not **separately** good quantum numbers anymore!

We conclude that s, l, j and $m_j = m_l + m_s$ are **all** good quantum numbers for H_{SO}.

Degenerate perturbation theory for H_{SO}

There are now $2n^2$ degenerate states for each n (due to electron spin). We can again use symmetry to our advantage to diagonalize in each subspace.

Since l is still a good quantum number, we can solve for each value of l separately.

$$|\, l, m_l, s, m_s\rangle \longrightarrow |\, j, m_j\rangle$$

Suppress l and s in this notation.

Original unperturbed eigenbasis

Symmetry-adapted eigenbasis

$$s = \frac{1}{2}, \; m_s = \pm\frac{1}{2}$$

Electrons have spin 1/2

Of the original eigenstates, which can possibly contribute as a linear combination of the new eigenstates? At most two states are consistent:

$$|\, j, m_l + \tfrac{1}{2}\rangle = a\,|\, l, m_l, \tfrac{1}{2}, \tfrac{1}{2}\rangle + b\,|\, l, m_l + 1, \tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

Set $b = 0$ if $m_l = l$.

$$m_j = (m_l) + \left(\tfrac{1}{2}\right) = (m_l + 1) + \left(-\tfrac{1}{2}\right)$$

Adding other states would violate conservation of J_z.

Matrix elements for H_{SO}

What are the matrix elements $\langle \chi_j | H_{SO} | \chi_k \rangle$ of H_{SO} in this basis?

Order the original basis as follows: $|\chi_1\rangle = |\, l, m_l, \frac{1}{2}, \frac{1}{2} \rangle, \quad |\chi_2\rangle = |\, l, m_l + 1, \frac{1}{2}, -\frac{1}{2} \rangle$

Rewrite in terms of raising and lowering operators:

$$2\,\mathbf{S} \cdot \mathbf{L} = L_+ S_- + L_- S_+ + 2 L_z S_z$$

Easily verified from definitions.

Matrix elements are now straightforward to calculate. Example:

$$\begin{aligned}
\langle \chi_1 | 2\,\mathbf{S} \cdot \mathbf{L} | \chi_1 \rangle &= \langle l, m_l, \tfrac{1}{2}, \tfrac{1}{2} | 2\,\mathbf{S} \cdot \mathbf{L} | l, m_l, \tfrac{1}{2}, \tfrac{1}{2} \rangle \\
&= \langle l, m_l, \tfrac{1}{2}, \tfrac{1}{2} | L_+ S_- + L_- S_+ + 2 L_z S_z | l, m_l, \tfrac{1}{2}, \tfrac{1}{2} \rangle \\
&= \langle l, m_l, \tfrac{1}{2}, \tfrac{1}{2} | 2 L_z S_z | l, m_l, \tfrac{1}{2}, \tfrac{1}{2} \rangle \\
&= m_l \hbar^2
\end{aligned}$$

Eigenvalues

The matrix in this basis (for fixed l, n) is:

$$2\,\mathbf{S}\cdot\mathbf{L} \longrightarrow \hbar^2 \begin{pmatrix} m_l & \sqrt{l(l+1) - m_l(m_l+1)} \\ \sqrt{l(l+1) - m_l(m_l+1)} & -(m_l+1) \end{pmatrix}$$

Diagonalizing this gives us the new eigenstates and eigenvalues.

Eigenvalues:

$$\{l, -(l+1)\}$$

For consistency, use:

$$J^2 = L^2 + S^2 + 2\,\mathbf{S}\cdot\mathbf{L}$$

Two choices:

$$j(j+1) = l(l+1) + \tfrac{1}{2}\left(\tfrac{1}{2}+1\right) + \begin{cases} l \\ -(l+1) \end{cases} \quad \Rightarrow \quad j = \begin{cases} l + \frac{1}{2} \\ l - \frac{1}{2} \end{cases}$$

Total angular momentum adds nicely!

Eigenvectors

The eigenvectors are as follows:

Recall: $m_j = m_l + \frac{1}{2}\,,\ j = l \pm \frac{1}{2}\,,\quad |\chi_1\rangle = |\,l, m_l, \frac{1}{2}, \frac{1}{2}\rangle\,,\quad |\chi_2\rangle = |\,l, m_l + 1, \frac{1}{2}, -\frac{1}{2}\rangle$

Eigenstates are:

$$|\,l \pm \frac{1}{2}, m_j\rangle = \sqrt{\frac{l \pm m_j + \frac{1}{2}}{2l+1}}\,|\chi_1\rangle \pm \sqrt{\frac{l \mp m_j + \frac{1}{2}}{2l+1}}\,|\chi_2\rangle$$

Expressed in terms of m_j, we find:

$$|\chi_1\rangle = |\,l, m_j - \frac{1}{2}, \frac{1}{2}, \frac{1}{2}\rangle\,,\quad |\chi_2\rangle = |\,l, m_j + \frac{1}{2}, \frac{1}{2}, -\frac{1}{2}\rangle$$

As in the Stark effect, the new energy eigenstates will now have distinct energies.

Energy corrections

The final step is to compute the corrections to the energy at 1st order:

$$
\begin{aligned}
E_{SO}^{(1)} &= \langle n, j, m_j | H_{SO} | n, j, m_j \rangle \\
&= \frac{Ze^2}{4m_e^2c^2} \langle n, j, m_j | \frac{1}{|\hat{\mathbf{r}}|^3} 2\,\mathbf{S}\cdot\mathbf{L} | n, j, m_j \rangle \\
&= \frac{Ze^2\hbar^2}{4m_e^2c^2} \langle n, j, m_j | |\hat{\mathbf{r}}|^{-3} | n, j, m_j \rangle \cdot \begin{cases} l & \text{if } \; j = l + \frac{1}{2} \\ -(l+1) & \text{if } \; j = l - \frac{1}{2} \end{cases} \\
&= \frac{m_e c^2 Z^4 \alpha^4}{4n^3 l\left(l + \frac{1}{2}\right)\left(l+1\right)} \cdot \begin{cases} l & \text{if } \; j = l + \frac{1}{2} \\ -(l+1) & \text{if } \; j = l - \frac{1}{2} \end{cases}
\end{aligned}
$$