IV. Atoms in B fields

a) The Zeeman Effect

We already have determined the Hamiltonian for an H atom in an external B field. For multi-electron atoms nothing changes greatly, so we will take here the example of H_2.

Then, with a static B field, picking the z axis along the field direction,

$$H_z = \frac{\mu_0}{h} B (L_z + 2 S_z)$$

(28)

Weak B fields:

When $E_{Zeeman} < E_{fs}$, we can just take the diagonal perturbations within a given term, such as $2 \frac{\mu}{h} B \frac{1}{2}$. So the only off-diagonal matrix elements we might need are in $m$, and we evaluate

$$\langle L, S, J, m | L_z + 2 S_z | L, S, J, m' \rangle$$

Since $L_z$ and $S_z$ are both g-total components of 1st rank tensors, we have $\Delta m = 0$ and only $m' = m$ contributes. Thus the first-order energies are

$$E_z = \frac{\mu_0}{h} B \langle L, S, J, m | L_z + 2 S_z | L, S, J, m \rangle$$

The matrix elements can be found using the W-E theorem and the theorems on Pauli as you did in the problem sets. Even easier, we can get the diagonal matrix elements using the Landé formula (following Weissbluth):

$$\langle L, S, J, m | L_z + 2 S_z | L, S, J, m \rangle = \frac{\langle L, S, J, m | \left( L_z + 2 S_z \right) \cdot \epsilon | L, S, J, m \rangle}{J(J+1)}$$

$$= m \hbar \delta_{m, m_0} = m \hbar$$
Now, \((L+2S)\cdot J = \frac{3}{2} J^2 + \frac{1}{2} (S^2 - L^2)\), so

\[
\frac{\langle L S J m' | (L+2S) \cdot \vec{B} | L S J m \rangle}{J(J+1)} = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2 J(J+1)}
\]

\[\equiv g_J, \text{ the Landé g factor}\]

Thus, \(E_Z = \mu_B g_J m \cdot B\)

This works for complex atomic systems in LS coupling as well. For example, in the \((3d)^7 4s\) configuration of Fe, we have:

- \(5F_5\) \(1.40021\)
- \(5F_4\) \(1.39004\)
- \(5F_3\) \(1.24938\)
- \(5F_2\) \(\approx 1.00044\)

These \(g\) factors are much used to study relativistic corrections, configuration mixing effects, and as a means of identifying molecular transitions by comparing experimental \(g\) factors with those predicted for the various states that might be involved in a transition.

Notes regarding \(Hfs\) -

We implicitly assumed \(E_Z \gg E_{hf}\) and ignored the smaller splittings. For very weak fields we must instead directly diagonalize the Hamiltonian,

\[
H_{\text{Hfs}} + \text{Zeeman} = -2 \alpha \vec{I} \cdot \vec{J} + \frac{\mu_B}{\hbar} (L + 2S) \cdot \vec{B} + \frac{\mu_B}{\hbar} (\vec{I} \cdot \vec{B})
\]
Only \((L+2 S) \cdot B\) has a large effect in 1st order, and we get

\[
E_z^{(1st \, order)} = M_B \cdot g_F \cdot m_F \cdot B
\]

where \(g_F = g_J \left( \frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} \right)\) \(\text{(32)}\)

At slightly larger fields we must diagonalize the hamiltonian explicitly, inserting the appropriate values for the 6-j symbols that arise in the off-diagonal matrix elements of \(\text{(31)}\). For the ground state of \(\text{H}\), \(I = J = \frac{1}{2}\) and we get something like this:

![Diagram showing energy levels for \(I, J\) coupling with \(B\)]

**Very Low Fields:**

- For \(F = 1\):
  - \(m_I = \frac{1}{2}, m_J = \frac{1}{2}\)
  - \(m_I = -\frac{1}{2}, m_J = -\frac{1}{2}\)
  - \(m_I = 0, m_J = 0\)

**Higher Fields:**

- \(I, J\) couple to form \(F\), classically.
  - \(F\) then precesses about \(B\).

**Strong \(B\) fields**

When \(E_z > E_{fs}\), the coupling between \(\hat{L}\) and \(\hat{S}\) is disrupted just as is the coupling of \(\hat{I}\) and \(\hat{J}\) above.

- \(DI\) can be ignored as long as the small hyperfine separations are below the scale of interest.
- Otherwise, use \(m_I, m_J\) separately.
So we need to diagonalize,

\[ H_{\text{L+Zeeman}} = \hat{S} \cdot \hat{L} + \frac{\mu_B B}{h} (L_z + 2S_z) \]

This is the same Hamiltonian as Eq. (28), but with the addition of the \( \hat{L} \cdot \hat{S} \) term. For the \( 2p \) state of \( H \), we have,

\[
\begin{array}{c|c|c|c|c}
\hline
m_L & m_S & \frac{1}{2} \beta & \frac{1}{2} \beta & \frac{1}{2} \beta \\
\hline
1 & \frac{1}{2} & 1 & \frac{1}{2} & \frac{1}{2} \\
0 & \frac{1}{2} & 0 & \frac{1}{2} & \frac{1}{2} \\
-1 & \frac{1}{2} & -1 & \frac{1}{2} & \frac{1}{2} \\
\hline
\end{array}
\]

In the high field or Paschen-Back regime, the \( \hat{L} \cdot \hat{S} \) term is negligible compared with the magnetic interaction, so the energies are just

\[ E_2 = \mu_B m_L B + \frac{3}{2} \mu_B m_S B \]

as shown above.

Optical pumping

Since \( B \) fields split the \( m \) degeneracy completely, one can play a lot of clever games with atoms in a small magnetic field. One nice scheme is the following:

Use circularly polarized light to excite an atom, so \( \Delta m = \pm 1 \). Now use a broadband source that can excite any of the transitions between the \( m \) components of states \( |1\rangle \) and \( |2\rangle \):
Solid lines show allowed $\Delta m = +1$ transitions; wavy lines show allowed routes for spontaneous decay. If we leave the light on long enough, all of the atoms will be trapped on the right hand side, since there is no way out of it (as you noticed in problem set 7). This is referred to as an optical pumping cycle, and gives a completely oriented population in the polarized state $|1\rangle$, $m=1$ when the field is turned off.

Incidentally, all of these Zeeman effects can be measured carefully by exciting radio frequency magnetic dipole transitions.

In the hyperfine case, $\Delta m_J = 0$, $\Delta m_z = \pm 1$ transitions are called nuclear magnetic resonance; they measure $g_J$. "Magnetic resonance imaging" exploits this.

In the fine structure case, $\Delta J = 0$, $\Delta m_J = \pm 1$ transitions are called electron paramagnetic resonance; they measure $g_J$. A related case is called electron spin resonance. Biologists and chemists use these methods extensively since the $g$ factors are sensitive to the environment of the atom in a solid or large molecule.
b) \( H \) in very strong B fields

Classically the Hamiltonian, 
\[
H = \frac{p^2}{2m} - \frac{1}{r} + \frac{1}{8} R^2 \frac{1}{r^5}
\]
becomes chaotic for high fields.

(Original theory -- Wentzen & Friedrich. Not surprisingly, Friedrich's text has an excellent discussion.)

The q.m. problem is not separable and has no dynamical symmetry, so it is surprisingly intractable -- no good simple analytical solutions. Delos & others have obtained very accurate solutions, though, by direct numerical solution of the Schrödinger equation.

Several experimentalists (notably D. Kleppner and K. Welge's group) have studied Rydberg states in large static B fields, where laboratory fields can cause perturbation that equal or exceed the binding energies.

The plots on p. SF-39 show numerical solutions for "moderate" strong fields, where \( n \) is still a good quantum number.

At stronger fields, the quantum mechanical level structure is profoundly altered. For example, at 6 T, the spectrum near the TP looks like this:

\[ \begin{array}{c}
\text{Energy (cm}^{-1}\text{)} \\
-20 \quad -10 \quad 0 \quad 10 \quad 20
\end{array} \]
HYDROGEN IN A MAGNETIC FIELD can assume a third set of shapes for the family of $n = 8, m = 0$ states, where the angular momentum has a mixture of values from $l = 0$ to $l = 7$. (Other shapes for the same family of states are shown to the same scale in the illustrations on pages 132 and 140.) Little is known about the properties of atoms in a strong magnetic field. In the hydrogen atom the system is quite simple and the equations describing the system are easily stated, but no general methods for solving the equations are known. The difficulty in developing a general theory of magnetic atoms is in part that the nodal lines cannot be described by any known coordinate system. Near the proton the nodal surfaces are spherical because the Coulomb force dominates, but far from the proton the nodal surfaces are cylindrical because the magnetic force is more important. (The magnetic force is directed not toward the proton but to the axis of the field.)
These oscillations are "quasi-landau" resonances. They are transverse semiclassical orbital structure for a nearly free electron. The spacing is

$$\gamma \approx \frac{eB}{mc},$$

$$\gamma \approx 1.5,$$ well below $5\gamma$.

A WKB solution (Edmonds, Størmer) clearly shows the factor of $\frac{3}{2}$, smoothly changing to $\gamma=1$ well above the $5\gamma$.

Higher-resolution spectra are even stranger (see p. SF-41.) The structure corresponds to stable classical orbits. To see clearly,

1) Take experimental data with constant "scaled energy"

$$E = E_B^{-3/4}.$$  

The classical egri's of motion are then held the same within a similarity transformation.

2) Plot as a function of scaled field $B^{1/4}$. The Fourier transform shows the classical action spectrum directly. (Friedrich's way of saying this is that scaling the quantization conditions $\gamma = n$ we vary the effective value of $\gamma$; when it matches the action of a classical orbit, we see structure.

In any case, the illustrated spectra (for $E = -a_2$) show periodicities corresponding to the classical closed orbits, either along $\hat{x}$ (vibrators), $\hat{y}$ to $\hat{z}$ (rotators), or in 3 dimensions ("exotics.") At higher scaled energies, $E = -0.1$, nearly all classical orbits are chaotic.

The q.m. reflection can be seen by looking at the statistics of nearest-neighbor spacings

$$\frac{1}{\gamma} \frac{n+1}{n-1}.$$
FIG. 1. (a) Scaled-energy spectrum at $\bar{E} = -0.45$ as a function of $\gamma^{-1/3}$. Range of excitation energy $-77.7 \text{ cm}^{-1} \leq E \leq -54.3 \text{ cm}^{-1}$ and field strength $5.19 \leq B \leq 3.03 \text{ T}$. (b) Fourier-transformed action spectrum of (a); closed orbits correlated to respective resonances in $(\rho, z)$ projection; $z$ coordinate vertically.
\[ P(x) \quad \text{(Poisson distribution)} \]
\[ x = -0.4 \]

\[ P(x) \quad x = -0.25 \]

\[ P(x) \quad x = -0.1 \]

- Higher distribution, characteristic of chaotic systems. (Spectrum of random matrices or Gaussian orthogonal ensemble)

- No good quantum #'s \( \Rightarrow \) all levels repel, so close spacings unlikely.

Can also see period doubling as a function of \( x \), other signs of classical chaos — see Friedrick.

Nevertheless, the Schrödinger equation is always integrable. The exact meaning of "quantum chaos" is still a very lively subject of discussion. (see R. Blumen's work, for example.)