HW 6: Solutions. Albers

The first order Stark effect shift for these levels is

$$\Delta^{(1)} = 3eaE = \frac{3e^2}{\beta^2 a} = \frac{3\alpha^2 m}{\beta^2} \qquad \text{(S7.86)}$$

Write the second-order shift from parts (a) and (b) as

$$\Delta^{(2)} = -\gamma \frac{1}{\alpha^3 m^3} E^2 = -\gamma \frac{\alpha^2 m}{\beta^4} \qquad \text{(S7.87)}$$

Evidently for the ground state, γ is about 2. The ratio of the second order ground state splitting to the first order $n = 2$ splitting is about

$$\left| \frac{\Delta^{(2)}}{\Delta^{(1)}} \right| = \frac{\gamma}{3\beta^2} \qquad \text{(S7.88)}$$

When $\beta = 10$, this ratio is about

$$\left| \frac{\Delta^{(2)}}{\Delta^{(1)}} \right| \approx 0.007 \qquad \text{(S7.89)}$$

Part d) When $\beta = 2$

$$\left| \frac{\Delta^{(2)}}{\Delta^{(1)}} \right| \approx 0.16 \qquad \text{(S7.90)}$$

The two effects become comparable when $\beta \approx \sqrt{\gamma/3}$.

Problem 7.10 Some Magnetic Field Effects

Part a) The fine-structure splitting between the $n = 2$ levels is

$$\Delta_{FS} = \frac{\alpha^4 m}{32} \qquad \text{(S7.91)}$$

which is about 4.523×10^{-5}eV.

The shift due to an external magnetic field B is of the order $\mu_o B$, where $\mu_o = e/2m$ which is about 5.79×10^{-9} electron volts per gauss.[2] When B = .5 gauss, this is much smaller than the fine structure splitting. But when $B = 10^5$ gauss, the magnetic energy is larger than the fine-structure splitting, comparable to the spacing between the gross-structure energy levels.

Part b) The $\mathbf{A}^2$ term is of the order $(e^2/m)B^2a^2$, since r is of the order of the Bohr radius a. Therefore it is comparable to the term linear in B when $\mu_o B = B^2 a^2 e^2/m$, or

$$B = \frac{m\mu_o}{e^2 a^2} = \frac{m^2\alpha^2}{e} \qquad \text{(S7.92)}$$

or

$$B^2 = m^4 \alpha^3 \qquad \text{(S7.93)}$$

A gauss is a cgs unit equivalent to energy^2 in natural units. But this isn't enough to tell you the cgs units. There are some conventions, and you have to know something else. Remember that in cgs units, **B** and **E** have the *same* units. You can figure it out from the Lorentz force law, equation (1.20), or from any number of books that tell you that $\mu_o = e\hbar/2mc$. Remember that in cgs, e^2 has the same dimensions as $\hbar c$. The upshot is that gauss^2 is a cgs unit equivalent to erg/cm^3. Thus

$$\begin{aligned} B^2 &= \alpha^3 \times (511{,}000\text{eV})^4 \times 1.602189 \times 10^{-12} \frac{\text{erg}}{\text{eV}} \times \left(\frac{1}{1.97 \times 10^{-5}\text{evcm}} \right)^3 \\ &= 5.552 \times 10^{18} \text{gauss}^2 \end{aligned} \qquad \text{(S7.94)}$$

and the desired magnetic field is of the order 2.3×10^9gauss. For some other atoms and molecules, the size of B for which the $\mathbf{A}^2$ term becomes important turns out to be rather lower.

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[2] See Equation (6.39).

Part c) In the strong field limit, label the states by $|n, l, m_l, m_s\rangle$. The energies in the field along the z-axis are (ignoring the fine structure effects)

$$E^o_{n,l,m_l,m_s} = -\frac{\alpha^2 m}{2n^2} - \mu_o B(m_l + 2m_s) \tag{S7.95}$$

so the difference between the energies of the highest and lowest states is $4\mu_o B$. This is comparable to the fine-structure splitting when

$$4\mu_o B = \Delta_{FS} = \frac{\alpha^4 m}{32} \tag{S7.96}$$

or

$$B = \frac{\Delta_{FS}}{4\mu_o} = \frac{4.523 \times 10^{-5}\text{eV}}{4 \times 5.79 \times 10^{-9}\text{eV/gauss}} = 1953 \text{ gauss} \tag{S7.97}$$

Part d) We want to compute the first order perturbed energy.

$$\Delta_{FS} = \left\langle \Psi^{nl}_{m_l m_s} \right| H_{LS} + H_{kin} \left| \Psi^{nl}_{m_l m_s} \right\rangle \tag{S7.98}$$

We know the matrix elements in the $\left|\Phi^{nl}_{jm}\right\rangle$ basis, where $H_{LS} + H_{kin}$ is diagonal. So in the m_l, m_s basis

$$\begin{aligned}
&\sum_j \left\langle \Psi^{nl}_{m_l m_s} \middle| \Phi^{nl}_{jm} \right\rangle \left\langle \Phi^{nl}_{jm} \right| H_{FS} \left| \Phi^{nl}_{jm} \right\rangle \left\langle \Phi^{nl}_{jm} \middle| \Psi^{nl}_{m_l m_s} \right\rangle \\
&= \frac{l \pm m + 1/2}{2l+1} \left\langle \Phi^{nl}_{l+\frac{1}{2}, m_l \pm \frac{1}{2}} \right| H_{FS} \left| \Phi^{nl}_{l+\frac{1}{2}, m_l \pm \frac{1}{2}} \right\rangle \\
&+ \frac{l \mp m + 1/2}{2l+1} \left\langle \Phi^{nl}_{l-\frac{1}{2}, m_l \pm \frac{1}{2}} \right| H_{FS} \left| \Phi^{nl}_{l-\frac{1}{2}, m_l \pm \frac{1}{2}} \right\rangle \\
&= \frac{\alpha^4 m}{2n^4} \left[\frac{l \pm m + 1/2}{2l+1} \left(\frac{3}{4} - \frac{2n}{2l+2} \right) + \frac{l \mp m + 1/2}{2l+1} \left(\frac{3}{4} - \frac{2n}{2l} \right) \right]
\end{aligned} \tag{S7.99}$$

When $l = 0$, there is no $j = l - 1/2$ state, and the second term is absent.

In the $n = 2$ level, the energies of the three states with $m = \frac{1}{2}$ in this limit are:

$$\begin{aligned}
E(2S) &= -\frac{\alpha^2 m}{8} - \frac{5}{4}\Delta - \mu_o B \\
E(2P)_{m_s = +\frac{1}{2}} &= -\frac{\alpha^2 m}{8} - \frac{7}{12}\Delta - \mu_o B \\
E(2P)_{m_s = -\frac{1}{2}} &= -\frac{\alpha^2 m}{8} - \frac{11}{12}\Delta
\end{aligned} \tag{S7.100}$$

Problem 7.11 The van der Waals Effect

The problem is simplified if you exploit the remaining axial symmetry. Write

$$\mathbf{r}_1 \cdot \mathbf{r}_2 - 3z_1 z_2 = x_1 x_2 + y_1 y_2 - 2z_1 z_2 \tag{S7.101}$$

In spherical-tensor notation.

$$r^{\pm} = \mp \frac{x \pm iy}{\sqrt{2}} \qquad r^o = z \tag{S7.102}$$

so that

$$H' = -\frac{e^2}{R^3}\left(r_1^+ r_2^- + r_1^- r_2^+ + 2r_1^o r_2^o \right) \tag{S7.103}$$

Now let us look at the $m = 2$, 1, and 0 separately:

Since the variational estimate of the ground state energy is always an upper bound.,

$$\Delta < -2E^2a^3 \tag{S7.203}$$

In problem 7.9, with three terms in the perturbation series we found

$$\Delta < -1.746a^3E^2 \tag{S7.204}$$

So the variational method does better than that. It is still above the lower bound from equation (7.47):

$$\Delta > ge - \frac{8}{3}a^3E^2 = -2.6666\ldots a^3E^2 \tag{S7.205}$$

Our estimate of course does not contradict the exact second order answer (7.59):

$$\Delta = -\frac{9}{4}a^3E^2 = -2.25a^3E^2 \tag{S7.206}$$

Problem 7.17 Born-Oppenheimer Approximation—A Simple Model

Part a)

$$V = \frac{\beta}{2}\left[(x_2 - x_3 - a)^2 + (x_2 - x_1 + a)^2\right] = \beta(x_2 - R)^2 + \beta\left(\frac{r}{2} - a\right)^2 \tag{S7.207}$$

where

$$R = \frac{x_1 + x_3}{2} \quad \text{and} \quad r = x_1 - x_3 \tag{S7.208}$$

are the nuclear cm and relative coordinates. If we fix R and r, this is just a harmonic oscillator with the zero of the energy shifted: The electron energies are

$$E_n(r) = \omega'\left(n + \frac{1}{2}\right) + \beta\left(\frac{r}{2} - a\right)^2 \tag{S7.209}$$

with $\omega'^2 = 2\beta/m$.

Part b) Now use $E_n(r)$ as the effective potential for the nuclear motion. The Hamiltonian is

$$H = \frac{P^2}{2M_{\text{tot}}} + \frac{p^2}{2\mu} + E_n(r) \tag{S7.210}$$

where P and p are the total and center of mass frame momentum, M_{tot} is the total mass $2M$, and μ is the reduced mass $M/2$. The energy has a constant term $\omega'\left(n + \frac{1}{2}\right)$, plus

$$\beta\left(\frac{r}{2} - a\right)^2 = \frac{\mu\omega''^2}{2}(r - 4a)^2 \tag{S7.211}$$

In the center of mass frame, $P = 0$, and the energy is the constant term plus the allowed energies of a harmonic oscillator with frequency ω'':

$$E_{nm} = \omega'\left(n + \frac{1}{2}\right) + \omega''\left(m + \frac{1}{2}\right) \tag{S7.212}$$

where

$$\omega''^2 = \frac{\beta}{2\mu} = \frac{\beta}{M} \tag{S7.213}$$

Part c) Now compare with the exact solution from problem 3.7. That is

$$\omega''^2 = \frac{\beta}{2\mu} = \frac{\beta}{M} \qquad \omega'^2 = 2\frac{\beta}{m}\left(1 + \frac{m}{2M}\right) \tag{S7.214}$$

The error is of order m/M, as expected.