11/30/05

Case II. $H_z \gg H_{SO}$, but not so much that H_{SO} can be dropped.

We ignore H_D and H_{RKE} for simplicity, not because it's realistic.

Write $\quad H_{SO} = f(r)\, \vec{L}\cdot\vec{S}$, where $f(r) = \frac{\alpha^2}{2}\frac{1}{r}\frac{dV}{dr}$.

Thus for perturbation theory, take:

$$H_0 = \frac{p^2}{2} + V(r) + H_z$$
$$H_1 = H_{SO} = f(r)\, \vec{L}\cdot\vec{S}$$

Eigenstates of H_0 are (some of them) degenerate, as shown under Case I. Can only use the uncoupled basis, since the coupled basis is not an eigenbasis of H_0. So we look at matrix elements (think of $n=2$ levels in H)

$$\langle n\, \ell\, m_\ell\, m_s \,|\, H_{SO} \,|\, n\, \ell'\, m_\ell'\, m_s' \rangle$$

where we put primes to cover all degenerate eigenspaces of H_0, as they appeared in Case I (there were 3 2-fold degenerate levels). However, we see right away that $[H_{SO}, L^2] = 0$, so the prime on ℓ is not necessary, and in fact we can do perturbation theory in the 2s and 2p sets of states separately. This means there is only one 2-fold degeneracy, that between states $|2\,1, -1, \tfrac{1}{2}\rangle$ and $|2\,1, 1, -\tfrac{1}{2}\rangle$ (these are $|n\,\ell\, m_\ell\, m_s\rangle$). This makes one 2x2 matrix. Look at the off-diagonal element,

$$\langle 2\,1\,{-1}\,\tfrac{1}{2} \,|\, f(r)\, \vec{L}\cdot\vec{S} \,|\, 2\,1\,1, -\tfrac{1}{2}\rangle .$$

Use the identity, $\quad \vec{L}\cdot\vec{S} = \frac{1}{2}\left(L_+ S_- + L_- S_+\right) + L_z S_z$.

The term L_+S_- vanishes, because you can't raise m_ℓ or lower m_s in $|21\,1,-1/2\rangle$. The term L_-S_+ gives a ket proportional to $|210\,1/2\rangle$, but this is orthog. to the bra in the M.E. and it vanishes too. The term L_zS_z vanishes for the same reason. Thus, the off-diagonal element vanishes, and once again there are no matrices to diagonalize. (at least for $n=2$.)

So to get the energy shifts we need only look at diagonal matrix elements,

$$\Delta E = \langle n\ell m_\ell m_s | f(r)\, \underbrace{\vec{L}\cdot\vec{S}}_{\frac{1}{2}(L_+S_- + L_-S_+) + L_zS_z} | n\ell m_\ell m_s\rangle$$

Terms L_+S_-, L_-S_+ give 0 as above w. the off-diag. ME, while L_zS_z brings out $m_\ell m_s$. Thus,

$$\Delta E = m_\ell m_s \;\langle n\ell m_\ell m_s | \frac{\alpha^2}{2}\frac{1}{r}\frac{dV}{dr} | n\ell m_\ell m_s\rangle$$

$$= m_\ell m_s \frac{\alpha^2}{2} \underbrace{\langle n\ell 0 | \frac{1}{r^3} | n\ell 0\rangle}_{\frac{1}{2}\frac{\alpha^2}{n^3}\frac{1}{\ell(\ell+1/2)(\ell+1)}} \qquad \text{(in H)} \qquad (\ell\neq 0).$$

This is for $\ell\neq 0$ (the 2p state). For the 2s state, $\vec{L}=0$ (the zero operator) and $\Delta E = 0$.

altogether, for 2p levels

$$\Delta E = \frac{\alpha^2}{n^3} \frac{m_\ell m_s}{\ell(\ell+1/2)(\ell+1)}$$

$$= \frac{\alpha^2}{48} m_\ell m_s \quad \text{in A.U.}$$

Case III. $H_{FS} \gg H_Z$ (weak B fields). Take

$$H_0 = \frac{p^2}{2} + V(r) + H_{FS}$$

$$H_1 = H_Z$$

Now unpert. energies are E_{nj} (H) or $E_{n\ell j}$ (alkalis). Must use degen. pert. theory. Must use coupled basis $|n\ell j m_j\rangle$ since uncoupled basis is not eigenbasis of H_0. Naively might expect

$$\langle n\ell j m_j | H_Z | n\ell' j\, m_j' \rangle \quad \text{(H)}$$

$$\text{or} \quad \langle n\ell j m_j | H_Z | n\ell j\, m_j' \rangle \quad \text{(Alk)},$$

for ME's in degen. pert. th., but since $[L^2, H_Z] = [J_z, H_Z] = 0$, in fact primes can be dropped and we need compute only diagonal matrix elements. So we need

$$\Delta E = \langle n\ell j m_j | H_Z | n\ell j m_j \rangle$$

$$H_Z \to (\mu_B B)\underbrace{(L_z + 2S_z)}_{\to J_z + S_z}$$

$$= (\mu_B B)\left[m_j + \langle n\ell j m_j | S_z | n\ell j m_j \rangle \right].$$

To evaluate remaining ME, we make a digression to cover the <u>projection theorem</u>. This follows from ~~and~~ an identity due to Dirac:

$$[J^2,[J^2,\vec V]] = 2(J^2\vec V + \vec V J^2) - 4(\vec V\cdot\vec J)\vec J.$$

Accepting this identity, we sandwich both side by $\langle \alpha' j m'|$ and $|\alpha j m\rangle$, bra and ket from a std. angular momentum basis, with j values equal on both sides (the α and m values are allowed to be different).

To analyze the LHS, let

$$\vec X = [J^2, \vec V],$$

so $\langle \alpha' j m' | \text{LHS} | \alpha j m\rangle = \langle \alpha' j m' | J^2 \vec X - \vec X J^2 | \alpha j m\rangle = 0$

since each $\vec X$ brings out $j(j+1)$ (we set $\hbar = 1$). So,

$\langle \alpha' j m' | \text{RHS} | \alpha j m\rangle = 0$

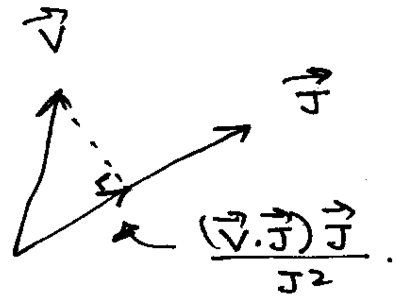
$$= 2\underbrace{\langle \alpha' j m' | J^2\vec V + \vec V J^2 | \alpha j m\rangle}_{} - 4\langle \alpha' j m' | (\vec V\cdot\vec J)\vec J | \alpha j m\rangle$$

$\to 2j(j+1)\langle \alpha' j m' | \vec V | \alpha j m\rangle.$ Thus we find

$$\boxed{\langle \alpha' j m' | \vec V | \alpha j m\rangle = \frac{1}{j(j+1)}\langle \alpha' j m' | (\vec V\cdot\vec J)\vec J | \alpha j m\rangle}$$

This is the <u>projection theorem</u>. It is called this because if $\vec V$ and

$\vec{J}$ were classical vectors, then $\dfrac{(\vec{V}\cdot\vec{J})\vec{J}}{J^2}$ would be the projection of $\vec{V}$ onto $\vec{J}$,



So to go back to our matrix element,

$$\langle n\,l\,j\,m_j |\; S_z \;| n\,l\,j\,m_j\rangle$$

$$= \frac{1}{j(j+1)}\,\langle n\,l\,j\,m_j |\, \underbrace{(\vec{S}\cdot\vec{J})}_{\frac{1}{2}\left[J^2+S^2-L^2\right]}\, \overbrace{J_z}^{m_j} \,| n\,l\,j\,m_j\rangle$$

using $L^2 = (\vec{J}-\vec{S})^2$

$$= \frac{m_j}{2j(j+1)}\left[\,j(j+1)+s(s+1)-l(l+1)\right].$$

altogether,

$$\boxed{\Delta E = (\mu_B B)\, m_j \left[1 + \frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}\right]}$$

weak field limit, [ ] = Landé g-factor.

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