Atomic Fine Structure

Note, we will use the Gottfried normalization for $\hat{L}$

~~$\hat{L}$~~ where $\hbar$ is factored out $\hat{L}_{Gottfried} = \frac{\hat{L}}{\hbar}$

The Hamiltonian for the Hydrogen atom is

$$\hat{H}_0 = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{r} \qquad \mu = \frac{m_e m_p}{m_e + m_p} = 0.9995\, m_e = \text{reduced mass}$$

$$E_n^0 = -\frac{\alpha^2 \mu c^2}{2n^2} \qquad n = 1, 2, 3, \ldots$$

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137.04} = \text{fine structure constant}$$

also write

$$E_n^0 = -\frac{e^2}{2a_0 n^2} \qquad a_0 = \frac{\hbar^2}{\mu e^2} = \text{Bohr radius} = 0.529\,\mathring{A}$$

$$E_1^0 = -13.6\text{ eV}$$

Corrections to $\hat{H}_0$.

1.) Relativistic effects

In reality the kinetic energy is $\sqrt{\mu^2 c^4 + p^2 c^2} - \mu c^2$

$$= \mu c^2 \left[1 + \frac{1}{2}\frac{p^2}{\mu^2 c^2} - \frac{1}{8}\frac{p^4}{\mu^4 c^4} + \cdots \right] - \mu c^2$$

$$= \frac{p^2}{2\mu} - \frac{1}{8}\frac{p^4}{\mu^3 c^2}$$

so $$\boxed{\hat{V}_{rel} = -\frac{1}{8}\frac{\hat{p}^4}{\mu^3 c^2}}$$

2.) Spin-orbit coupling

Since the proton and electron both rotate about their center of mass, the electron sees a moving proton in its rest frame. This moving charge creates a magnetic field that the electron interacts with

The electron magnetic moment gives an energy

$$-\vec{\mu}\cdot\vec{H} \qquad \vec{\mu} = \text{magnetic moment not reduced mass}$$

$$\vec{H} = \text{magnetic field not Hamiltonian}$$

$$\vec{\mu} = \frac{e\hbar}{2m_e c}\vec{\sigma} \qquad \vec{\sigma} = \text{Pauli spin matrix}$$

Coulomb potential energy

$$\vec{H} = -\frac{1}{c}\vec{v}\times\vec{E} = \frac{1}{ec}\vec{v}\times\hat{r}\,\frac{dV}{dr}$$

$$= -\frac{\hbar}{e m_e c}\vec{L}\,\frac{1}{r}\frac{dV}{dr} \qquad \text{with } V(r) = -\frac{e^2}{r}$$

from Gottfried normalization

we add the term

$$\frac{1}{4}\left(\frac{\hbar}{mc}\right)^2 \vec{L}\cdot\vec{\sigma}\,\frac{1}{r}\frac{dV}{dr}$$

which has an extra factor of $\frac{1}{2}$ multiplying it (called Thomas precession factor and very hard to derive)
This is called spin-orbit coupling

so $\hat{H} = \hat{H}_0 + \hat{V}$

$$\hat{H}_0 = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{r} \qquad \hat{V} = -\frac{1}{8}\frac{\hat{p}^4}{\mu^3 c^2} + \frac{1}{2}\left(\frac{\hbar}{mc}\right)^2 \hat{\vec{L}}\cdot\hat{\vec{S}}\,\frac{1}{r}\frac{dV}{dr}$$

$$\vec{S} = \vec{\sigma}/2$$

The relativistic perturbation $\hat{p}^4$ is a scalar and commutes with all angular momenta and spin

Note $\hat{\vec{L}}\cdot\hat{\vec{S}} = \frac{\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+}{2} + \hat{L}_z\hat{S}_z$

so $[\hat{\vec{L}}\cdot\hat{\vec{S}}, \hat{L}_z] = -\frac{\hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+}{2} \neq 0$

$[\hat{\vec{L}}\cdot\hat{\vec{S}}, \hat{S}_z] = \frac{\hat{L}_+\hat{S}_- - \hat{L}_-\hat{S}_+}{2} \neq 0$

but $[\hat{\vec{L}}\cdot\hat{\vec{S}}, \hat{L}_z + \hat{S}_z] = 0$

so, a set of mutually commuting variables is

$\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$

($\hat{J}^2 = \hat{L}^2 + 2\hat{\vec{L}}\cdot\hat{\vec{S}} + \hat{S}^2$ commutes with $\hat{\vec{L}}\cdot\hat{\vec{S}}$ too)

so label states by $|j, m; l, s=\tfrac{1}{2}\rangle$

We use spectroscopic notation to label the states

$n l_j$ $\quad$ $n =$ principal quantum number

$l = s, p, d, f$ $\quad$ ($l=0$, $l=1$, $l=2$, $l=3$)

$j =$ half odd integer

like $1S_{1/2}$ $\quad 2S_{1/2}$ $\quad 2P_{3/2}$ $\quad 2P_{1/2}$ etc.

since $\hat{J}^2 = (\hat{\vec{L}} + \hat{\vec{S}})^2 = \hat{L}^2 + 2\hat{\vec{L}}\cdot\hat{\vec{S}} + \hat{S}^2$

so $\hat{\vec{L}}\cdot\hat{\vec{S}} = \frac{\hat{J}^2 - \hat{L}^2 - \hat{S}^2}{2}$ (a useful identity)

hence $\langle j\, m; l\; s=\tfrac{1}{2} | \hat{\vec{L}}\cdot\hat{\vec{S}} | j\, m; l\; s=\tfrac{1}{2}\rangle = \frac{j(j+1) - l(l+1) - \frac{3}{4}}{2}$

so $\boxed{\hat{V}_{SO} = \frac{1}{4}\frac{\hbar^2}{m^2c^2}\left[j(j+1) - l(l+1) - \tfrac{3}{4}\right]\frac{e^2}{r^3}}$ when acting on these states

Now, since $j = l \pm \frac{1}{2}$ we have

$$\hat{V}_{so} = \frac{1}{4}\frac{\hbar^2 e^2}{m^2c^2}\frac{1}{r^3}\left[\left(l\pm\tfrac{1}{2}\right)\left(l+1\,{}^{3/2}_{1/2}\right) - l(l+1) - \tfrac{3}{4}\right]$$

$$= \frac{1}{4}\frac{\hbar^2 e^2}{m^2c^2}\frac{1}{r^3}\left[\begin{array}{ll} +l & j=l+\frac{1}{2} \\ -l-1 & j=l-\frac{1}{2}\end{array}\right.$$

$$\langle n l j m | \hat{V}_{so} | n l j m\rangle = \frac{1}{4}\left(\frac{\hbar}{mc}\right)^2 e^2 \langle n l | \tfrac{1}{r^3} | n l\rangle * \left\{\begin{array}{ll} l & j=l+\frac{1}{2} \\ -l-1 & j=l-\frac{1}{2}\end{array}\right.$$

The radial integral is known $\langle n l | \frac{1}{r^3} | n l\rangle = \frac{1}{a_0^3}\frac{1}{n^3 (l+1)(l+\frac{1}{2}) l}$ for $l \neq 0$

$$\hat{V}_{kin} = -\frac{1}{8}\frac{\hat{p}^4}{\mu^3 c^2} = -\left[\hat{H}_0 + \frac{e^2}{r}\right]^2 \cdot \frac{1}{2\mu c^2}$$ another useful trick

$$\langle n l j m | \hat{V}_{kin} | n l j m\rangle = -\langle n l j m | \left[\hat{H}_0 + \frac{e^2}{r}\right]^2 | n l j m\rangle \frac{1}{2\mu c^2}$$

$$= -\left[{E_n^0}^2 + 2E_n^0 e^2 \langle n l | \tfrac{1}{r} | n l\rangle + e^4 \langle n l | \tfrac{1}{r^2} | n l\rangle\right]\frac{1}{2\mu c^2}$$

These radial integrals are also known $\langle n l | \frac{1}{r} | n l\rangle = \frac{1}{a_0 n^2}$

$$\langle n l | \tfrac{1}{r^2} | n l\rangle = \frac{1}{a_0^2 n^3 (l+\frac{1}{2})}$$

and $E_n^0 = -\frac{e^2}{2a_0 n^2}$ so we get

$$\langle n l j m | \hat{V}_{kin} | n l j m\rangle = -\frac{e^4}{4a_0^2}\left[\frac{1}{n^4} - \frac{4}{n^4} + \frac{4}{n^3(l+\frac{1}{2})}\right]\frac{1}{2\mu c^2}$$

$$= E_n^0 \frac{e^2}{a_0}\frac{1}{n^2}\left[\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right]\frac{1}{\mu c^2}$$

$$= E_n^0 \alpha^2 \frac{1}{n^2}\left[\frac{n}{l+\frac{1}{2}} - \frac{3}{4}\right] \qquad \alpha = \frac{e^2}{\hbar c}$$

similarly, we find

$$\langle n\,l\,j\,m|\,\hat{V}_{so}\,|n\,l\,j\,m\rangle = \frac{1}{4}\frac{\hbar^2}{m^2c^2}\frac{e^2}{a_0}\frac{\omega^2 e^4}{\hbar^4}\frac{1}{n^3}\frac{1}{(l+1)(l+\frac{1}{2})l} * \begin{cases} l & j=l+\frac{1}{2} \\ -l-1 & j=l-\frac{1}{2}\end{cases}$$

$$= -E_n^0\,\alpha^2\frac{1}{n}\frac{1}{2(l+1)(l+\frac{1}{2})l}\begin{cases} l & j=l+\frac{1}{2} \\ -l-1 & j=l-\frac{1}{2}\end{cases}$$

$j=l+\frac{1}{2}$ case

$$E_n = E_n^0\left[1+\frac{\alpha^2}{n^2}\left[\frac{n}{j}-\frac{3}{4}-\frac{n}{(j+\frac{1}{2})2j}\right]\right]$$

$$= E_n^0\left[1+\frac{\alpha^2}{n^2}\left[\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right]\right]$$

$j=l-\frac{1}{2}$ case

$$E_n = E_n^0\left[1+\frac{\alpha^2}{n^2}\left[\frac{n}{j+1}-\frac{3}{4}+\frac{n\,(j+\frac{3}{2})}{2(j+\frac{3}{2})(j+1)(j+\frac{1}{2})}\right]\right]$$

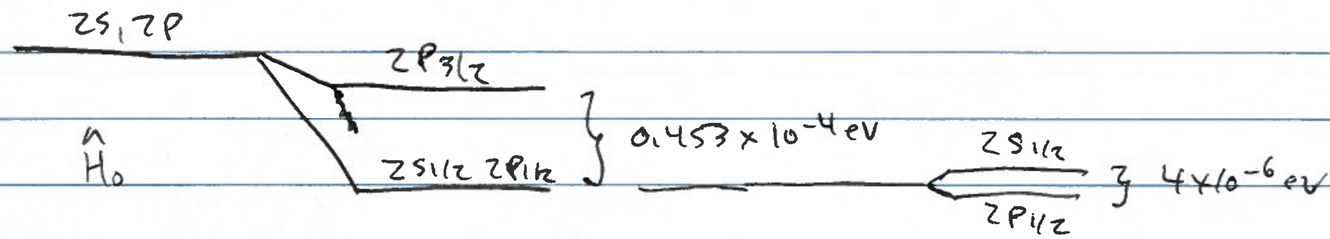
$$= E_n^0\left[1+\frac{\alpha^2}{n^2}\left[\frac{n}{j+\frac{1}{2}}-\frac{3}{4}\right]\right]$$

recall $E_n^0 < 0 \Rightarrow$ shift is negative (book has a typo)

Comments

1.) even though this shift wasn't calculated for $j=\frac{1}{2}$, $l=0$, it holds for that case as well (need dirac equation to prove it)

2.) The lowest excited states are $2P_{1/2}$ $2S_{1/2}$
which are not split from each other since shift depends only on j
experimentally they are split (called the Lamb shift)
which can be understood only with quantum electrodynamics (field theory)



3.) By choosing the jm ls basis, we did not need to actually use degenerate perturbation theory because we found the ll subspace.

In next lecture, we will need the degenerate formalism.