Phys 506 lecture 17: Degenerate Perturbation Theory II: Atomic Fine Structure

1 Nonrelativistic hydrogen

Note, we will use the Gottfried normalization for $\hat{L}$, where $\hbar$ is factored out: $\hat{L}_{\text{Gottfried}} = \frac{\hat{L}}{\hbar}$.

The Hamiltonian for the hydrogen atom is

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

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

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

we also write

$$E_n^0 = -\frac{e^2}{2a_0 n^2}, \quad \text{where} \quad a_0 = \frac{\hbar^2}{\mu e^2} = \text{ Bohr radius } = 0.529\text{Å}$$

$$E_1^0 = -13.6 eV$$

2 Relativistic corrections to $\hat{H}_0$

1.) Relativistic effects in the kinetic energy

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

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

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

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

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 election interacts with. We describe it as follows. The electron magnetic moment gives an energy

$\boldsymbol{\mu} \cdot \mathbf{H}$, with $\boldsymbol{\mu} =$ magnetic moment not reduced mass and $\mathbf{H} =$ magnetic field not Hamiltonian

$$\boldsymbol{\mu} = \frac{e\hbar}{2m_e c} \boldsymbol{\sigma}, \qquad \text{with} \quad \boldsymbol{\sigma} = \text{ Pauli spin matrix}$$

$$\mathbf{H} = -\frac{1}{c}\mathbf{v}\times\mathbf{E} = \frac{1}{ec}\mathbf{v}\times\mathbf{e}_r \underbrace{\frac{dV}{dr}}_{\text{Coulomb potential energy}}$$

$$= -\underbrace{\frac{\hbar}{em_e c}}_{\text{from Gottfried normalization}}\mathbf{L}\frac{1}{r}\frac{dV}{dr}, \qquad \text{with } V(r) = -\frac{e^2}{r}.$$

We add the term

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

which has an extra factor of $\frac{1}{2}$ multiplying it (called the Thomas precession factor which is very hard to derive and arises from the fact that the circular motion is accelerating). This is called spin-orbit coupling.

Note that there is another term called the Darwin term as well. We will not cover this term in detail. It is zero except in s-wave states, and it gives the result of the spin-orbit coupling term in the limit as $s \to 0$, which we will just implement by hand.

3 Perturbation theory for relativistic effects

So,

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

with

$$\hat{H}_0 = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{\hat{r}}$$

and

$$\hat{V} = -\frac{1}{8}\frac{\hat{p}^4}{\mu^3c^2} + \frac{1}{2}\left(\frac{\hbar}{mc}\right)^2\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}\frac{1}{\hat{r}},$$

where $\hat{\mathbf{S}} = \boldsymbol{\sigma}/2$ because of the Gottfried normalization.

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

Note that

$$\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} = \frac{\hat{L_+}\hat{S}_- + \hat{L}_-\hat{S}_+}{2} + \hat{L}_z\hat{S}_z.$$

So,

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

But, we also have that

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

Then,

$$[\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}, \hat{L}_z + \hat{S}_z] = 0.$$

So, a set of mutually commuting variables is $\hat{J}^2, \hat{J}_z, \hat{L}^2, \hat{S}^2$, (Note that $\hat{J}^2 = \hat{\mathbf{L}}^2 + 2\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} + \hat{\mathbf{S}}^2$ commutes with $\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}$ too). So, we label the states by $|j, m; l, s = \frac{1}{2}\rangle$.

We use spectroscopic notation to label the states:

$$\begin{array}{rl} nl_j & n = \text{ principal quantum number} \\ & l = S \to (l=0),\ P \to (l=1),\ D \to (l=2),\ F \to (l=3) \\ & j = \text{ half odd integer} \\ \text{Like} & 1S_{1/2} \quad 2S_{1/2} \quad 2P_{3/2} \quad 2P_{1/2} \text{ etc.} \\ \text{Since} & \hat{\mathbf{J}}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}})^2 = \hat{\mathbf{L}}^2 + 2\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} + \hat{\mathbf{S}}^2 \\ \text{We have} & \hat{\mathbf{L}}\cdot\hat{\mathbf{S}} = \dfrac{\hat{J}^2 - \hat{L}^2 - \hat{S}^2}{2} \quad \text{(a useful identity).} \end{array}$$

Hence

$$\langle jm; ls = \tfrac{1}{2}|\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}|jm; ls = \tfrac{1}{2}\rangle = \frac{j(j+1) - l(l+1) - \frac{3}{4}}{2}$$

So

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

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

$$\begin{aligned} \hat{V}_{SO} &= \frac{1}{4}\frac{\hbar^2 e^2}{m^2c^2}\frac{1}{\hat{r}^3}\left[(l \pm \frac{1}{2})(l + |^{3/2}_{1/2}) - l(l+1) - \frac{3}{4}\right] \\ &= \frac{1}{4}\frac{\hbar^2 e^2}{m^2c^2}\frac{1}{\hat{r}^3}\begin{cases} +l & j = l + \frac{1}{2} \\ -l-1 & j = l - \frac{1}{2} \end{cases} \\ \langle nljm|\hat{V}_{S0}|nljm\rangle &= \frac{1}{4}\left(\frac{\hbar}{ma}\right)^2 e^2\langle nl|\tfrac{1}{\hat{r}^3}|nl\rangle \times \begin{cases} l & j = l + \frac{1}{2} \\ -l-1 & j = l - \frac{1}{2} \end{cases} \end{aligned}$$

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

For the kinetic energy term, we have

$$\begin{aligned} \hat{V}_{\text{rel}} = -\frac{1}{8}\frac{\hat{p}^4}{\mu^3c^2} &= -\left[\hat{H}_0 + \frac{e^2}{\hat{r}}\right]^2 \cdot \frac{1}{2\mu c^2} \quad \text{another useful trick} \\ \langle nljm|\hat{V}_{\text{rel}}|nljm\rangle &= -\langle nljm|\left[\hat{H}_0 + \frac{e^2}{\hat{r}}\right]^2|nljm\rangle\frac{1}{2\mu c^2} \\ &= -\left[{E_n^0}^2 + 2E_n^0 e^2\langle nl|\frac{1}{\hat{r}}|nl\rangle + e^4\langle nl|\frac{1}{\hat{r}^2}|nl\rangle\right]\frac{1}{2\mu c^2}. \end{aligned}$$

These radial integrals are also known

$$\langle nl|\tfrac{1}{\hat{r}}|nl\rangle = \frac{1}{a_0 n^2}$$

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

and

$$E_n^0 = -\frac{e^2}{2a_0 n^2}.$$

4 Final results

So we get

$$\begin{aligned}\langle nljm|\hat{V}_{\text{rel}}|nljm\rangle &= -\frac{e^4}{4a_0^2}\left[\frac{1}{n^4}-\frac{4}{n^4}+\frac{4}{n^3(l+\frac{1}{2})}\right]\frac{1}{2\mu c^2} \\ &= E_n^0\frac{e^2}{a_0}\frac{1}{n^2}\left[\frac{n}{l+\frac{1}{2}}-\frac{3}{4}\right]\frac{1}{\mu c^2} \\ &= E_n^0\alpha^2\frac{1}{n^2}\left[\frac{n}{l+\frac{1}{2}}-\frac{3}{4}\right] \quad \text{and } \alpha=\frac{e^2}{\hbar c}.\end{aligned}$$

Similarly, we find

$$\begin{aligned}\langle nljm|\hat{V}_{SO}|nljm\rangle &= \frac{1}{4}\frac{\hbar^2}{m^2c^2}\frac{\mu^2e^4}{\hbar^4}\frac{1}{n^3}\frac{1}{(l+1)(l+\frac{1}{2})l}\times\begin{cases} l & j=l+\frac{1}{2} \\ -l-1 & j=l-\frac{1}{2}\end{cases} \\ &= -E_n^0\alpha^2\frac{1}{n}\frac{1}{2(l+1)(l+\frac{1}{2})l}\times\begin{cases} l & j=l+\frac{1}{2} \\ -l-1 & j=l-\frac{1}{2}\end{cases}\end{aligned}$$

Now, we examine the $j=l+\frac{1}{2}$ case:

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

while the $j=l-\frac{1}{2}$ case is given by:

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

Recall $E_n^0<0$ so the shift is negative (Gottfried's 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 (we need to evaluate the Darwin term to prove it);

2.) The lowest excited states are $2P_{1/2}$ and $2S_{1/2}$ which are not split from each other since the 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 $jmls$ basis we did not need to actually use degenerate perturbation theory because we found the $\|$ subspace.

In the next lecture, we will need the degenerate formalism when we examine the Zeeman effect.

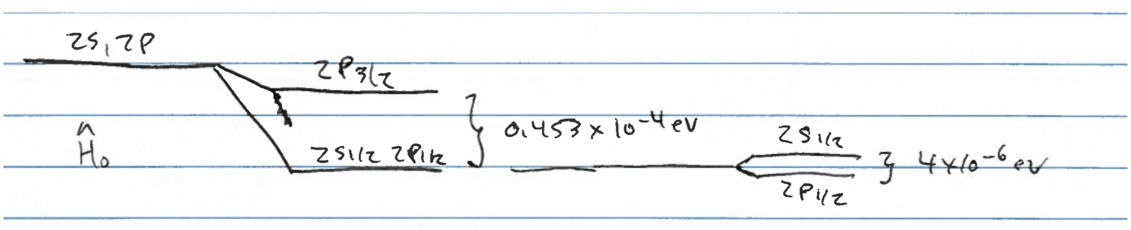

Figure 1: Hierarchy of the splittings of the $n = 2$ shell of hydrogen. For $\hat{H}_0$, the $2s$ and $2p$ levels are degenerate. The fine structure splits the $2P_{3/2}$ lies above the still degenerate $2S_{1/2}$ and $2P_{1/2}$ states by 0.453×10^{-4} eV. Adding in the Lamb shift, splits the $2S_{1/2}$ (above) and $2P_{1/2}$ (below) with a splitting of 4×10^{-6} eV.