Lecture 4: Fine-structure of hydrogen-like ions

1. Non-relativistic limit of Dirac equation (reminder)

At the previous lecture we have derived the non-relativistic limit (up to the order $\frac{\alpha^2}{\alpha^3}$) of the Dirac equation:

$$\left[ \frac{\hat{P}^2}{2m} + V(r) - \frac{P^4}{8m^3} + \frac{1}{2m^2} \int \frac{dV}{dr} \left( -\frac{1}{2m^2} (2e^2) \delta(r) \right) \right] \psi(r) = E \psi(r) \quad (1)$$

which is the equation for the large component of the Dirac wave function. Today we want to use this equation to see how the spectrum of hydrogen-like ions will be affected by three relativistic corrections. First, let us remind that for the pure Schrödinger case:

$$\left[ \frac{\hat{P}^2}{2m} + V(r) \right] \psi_0(r) = E \psi_0(r) \quad (2)$$

the $\psi_0(r) = \psi_{n\ell m\mu}(r)$ is the "usual" non-relativistic wave function, and:

$$E = E_n = -\frac{(2\alpha)^2}{2m} \mu \quad (3)$$

Again, we remind here that we are working in relativistic units where $\hbar = c = 1$.

We can estimate corrections to this energy by using perturbation approach. Let us consider three corrections term by term.

2. Relativistic correction toionic energy

We start with the correction $H_1 = -\frac{P^4}{8m^3}$. First we need to find unperturbed basis.
Such a basis is clearly formed by solutions $\Psi_{\text{new}} (\mathbf{r})$ of unperturbed Schrödinger Hamiltonian. Of course, we need to "add" spin in our analysis (actually not for $H_0$ term, which is spin-independent, but for $V$ term):

$$\Psi_{\text{new}} (\mathbf{r}) = \Psi_{\text{new}} (\mathbf{r}) \cdot \chi_{m_s}$$ (4)

where $\chi_{m_s=1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ and $\chi_{m_s=-1/2} = \begin{pmatrix} 0 \\ i \end{pmatrix}$ (5)

We are ready now to calculate the energy correction:

$$\Delta E_1 = \left< \Psi_{\text{new}} \right| - \frac{P^4}{8m^2} \left| \Psi_{\text{new}} \right> \quad (6)$$

We note that this matrix element is diagonal in $m_s, m_e$, and $l$. (And we will see, it is diagonal in $n$).

Let us consider:

$$\frac{P^4}{8m^2} = \frac{1}{2m} \left( \frac{P^2}{2m} \right)^2 = \frac{1}{2m} \left( \hat{H}_0 - V(\mathbf{r}) \right)^2 \quad (7)$$

By inserting Eq (7) into (6) we obtain:

$$\Delta E_1 = -\frac{1}{2m} \left( \left< \Psi_{\text{new}} \right| \hat{H}_0 \hat{H}_0 + 2 \hat{H}_0 V(\mathbf{r}) + V(\mathbf{r}) V(\mathbf{r}) \left| \Psi_{\text{new}} \right> \right) =$$

$$= -\frac{1}{2m} \left( E_n^2 + 2E_n \left< \Psi_{\text{new}} | V(\mathbf{r}) | \Psi_{\text{new}} \right> + \left< \Psi_{\text{new}} | V^2(\mathbf{r}) | \Psi_{\text{new}} \right> \right) \quad (8)$$

To proceed further we need to remind that:

$$\left< \Psi_{\text{new}} \left| \frac{1}{r^2} \right| \Psi_{\text{new}} \right> = \frac{2}{a_0 m^2}, \quad \left< \Psi_{\text{new}} \left| \frac{1}{r^3} \right| \Psi_{\text{new}} \right> = \frac{2^2}{a_0^2 n^3} \quad (9)$$
where $a_0$ is the Bohr radius. (Please, prove Eqs (5) in your homework).

By using the fact that $U(r) = -\frac{2\epsilon e^2}{r}$

we obtain:

$$\Delta E_1 = -\frac{1}{2\hbar} \left[ \frac{2(\hbar \gamma)^4}{4\hbar^4} - \frac{2(\hbar \gamma)^2}{2\hbar^2} \left( \frac{2e^2}{a_0\hbar} \right)^2 + \right]$$

$$+ \frac{2^2 (\hbar \gamma)^2}{a_0^2 \hbar^3 (\epsilon + 112)} = -\frac{1}{2\hbar} \left[ \frac{2(\hbar \gamma)^4}{4\hbar^4} - \frac{(\hbar \gamma)^4}{\hbar^4} \frac{2e^2}{a_0\hbar} + (\hbar \gamma)^2 \right]$$

$$\times \frac{2 \frac{2e^2}{a_0\hbar}}{\hbar^3 (\epsilon + 112)} = \frac{1}{2\hbar} \left[ \frac{2e^2}{a_0\hbar} \left( \frac{3}{4} - \frac{\hbar}{\epsilon + 112} \right) = \right]$$

$$= -E_n \left( \frac{2e^2}{a_0\hbar} \right) \left( \frac{3}{4} - \frac{\hbar}{\epsilon + 112} \right) \quad (10)$$

3. Spin-orbit term

Now let us consider the second term:

$$\hat{H}_2 = \zeta(r) \overline{L} \overline{S} \quad (11)$$

where $\zeta(r) = \frac{1}{2\hbar^2} \frac{1}{r} \frac{dV}{dr} \quad (12)$

As we discussed already that the problem with this term that it does not commute with operators $L$ and $S$. In this sense, the use of the basis states (4) is not convenient for the perturbation calculations. One would need to couple $\overline{L}$ and $\overline{S}$ into total angular momentum $\overline{J} = \overline{L} + \overline{S}$. In principle, we know how to do it: to use Clebsch-Gordan coefficients.

We start from the definition of the total
\[ J = \bar{L} + \bar{S} \quad (13) \]

Which operators commute with \( \bar{L} \bar{S} \) term?

Obviously: \( \bar{L}^2, \bar{S}^2, \bar{J}^2 \) and \( \bar{J}_z \). The coupled \( |\bar{L}\bar{S}\bar{J}\bar{m}\rangle \) basis is, therefore, the best for the perturbation calculations. We know how to construct such a basis:

\[ Y_{\bar{L}\bar{S}\bar{J}\bar{m}} \equiv \langle \bar{F} | \bar{L}\bar{S}\bar{J}\bar{m} \rangle = \sum_{\bar{m}_w} (\bar{c} \bar{w} \bar{m}_w | \bar{J}\bar{m}_j \rangle \cdot Y_{\bar{m}_w} (\bar{r}) \cdot Y_{\bar{m}_w} (\bar{t}) ) \]

\[ Y_{\bar{m}_w} (\bar{r}) \]

We know that this function is eigenfunction of operators \( \bar{L}^2, \bar{S}^2 \) and \( \bar{J}^2 \). Therefore, we can obtain in this basis:

\[ \Delta E_2 = \langle \bar{J}\bar{m}_w | \bar{J} (\bar{r}) \bar{L}\bar{S} | \bar{J}\bar{m}_w \rangle = \]

\[ = \langle \bar{J}\bar{m}_w | \bar{J} (\bar{r}) \left( \frac{1}{2} \left( \bar{L}^2 - \bar{S}^2 \right) \right) | \bar{J}\bar{m}_w \rangle = \]

\[ = \frac{1}{2} \left( j (j+1) - L (L+1) - S (S+1) \right) \langle \bar{J}\bar{m}_w | \bar{J} (\bar{r}) | \bar{J}\bar{m}_w \rangle \]

\[ \quad (15) \]

We can calculate the mean value of \( \bar{J} (\bar{r}) \) (this will be your homework) to obtain:

\[ \langle \bar{J}\bar{m}_w | \bar{J} (\bar{r}) | \bar{J}\bar{m}_w \rangle = \frac{1}{2m^2} (2m^2) \langle \bar{J}\bar{m}_w | \frac{1}{\bar{r}^3} | \bar{J}\bar{m}_w \rangle = \]

\[ = \frac{1}{2m^2} (2m^2) \frac{2^3 (2m)^3}{\hbar^3 (2+12) (2+1)} \quad (16) \]

We note that the \( \Delta E_2 \) is non-vanishing only for \( L \neq 0 \). It is clear already from the fact that operator itself is \( \bar{L} \bar{S} \bar{L} \bar{S} \).

By combining (15) and (16) we obtain:
\[ \Delta E_2 = -E_n \cdot \frac{(d\varphi)^2}{2\hbar (e^{+\frac{\ell}{2}})(e^{+\frac{\ell+1}{2}})} \begin{cases} \ell & \text{for } j = e^{+\frac{\ell+1}{2}} \\ -\ell - 1 & \text{for } j = e^{-\frac{\ell}{2}} \end{cases} \] (13)

4. Darwin term

By using expression for the Darwin correction to the Hamiltonian, we obtain:

\[ \Delta E_3 = \frac{-11}{2m^2} (2e^2) \langle \Psi_{\text{He}} \mid \delta(\vec{r}) \mid \Psi_{\text{He}} \rangle = \]

\[ = \frac{-11}{2m^2} (2e^2) \left| \Psi_{\text{He}}(0) \right|^2 \] (18)

We see that Darwin correction is defined by the value at the wavefunction at the origin. Only s-wave functions \( l=0 \) are non-zero at \( r=0 \). By using the property of s-wave functions at \( r=0 \) (that will be your homework) we find:

\[ \Delta E_3 = \frac{1}{2} m (\frac{d\varphi}{d\theta})^2 \cdot \frac{(d\varphi)^2}{n} = -E_n \cdot \frac{(d\varphi)^2}{n}, \; l=0 \] (19)

5. Fine structure of hydrogen-like systems

By combining now Eqs (10), (17) and (18) we obtain the overall relativistic correction at the order of \( \beta^2 c^2 \):

\[ \Delta E = \Delta E_1 + \Delta E_2 + \Delta E_3 = E_n \left( \frac{(d\varphi)^2}{n^2} \left( \frac{n}{j^{+\frac{1}{2}}} - \frac{3}{4} \right) \right) \] (20)

Adding this to the non-relativistic Schrödinger energy we obtain:

\[ E_{nj} = E_n \left[ 1 + \frac{(d\varphi)^2}{n^2} \left( \frac{n}{j^{+\frac{1}{2}}} - \frac{3}{4} \right) \right] \] (21)

We see that in contrast to the non-relativistic energy, we have now energy that depends both on principal quantum number \( n \), and total momentum \( j \).