

PHYS852 Quantum Mechanics II, Spring 2010  
 HOMEWORK ASSIGNMENT 8

Topics covered: hydrogen fine structure

1. [10 pts] Let the hamiltonian  $H$  depend on the parameter  $\lambda$ , so that  $H = H(\lambda)$ . The eigenstates and eigenvalues of  $H$  are then also functions of  $\lambda$ , i.e.  $E_n = E_n(\lambda)$  and  $|n\rangle = |n(\lambda)\rangle$ . Use the property  $H|n\rangle = E_n|n\rangle$  to prove the Feynman-Hellmann theorem:

$$\frac{\partial E_n(\lambda)}{\partial \lambda} = \langle n(\lambda) | \frac{\partial H(\lambda)}{\partial \lambda} | n(\lambda) \rangle$$

2. [15 pts] The effective hamiltonian which governs the radial wave equation is

$$H = -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial r^2} + \frac{\hbar^2 \ell(\ell+1)}{2Mr^2} - \frac{e^2}{4\pi\epsilon_0 r}.$$

The exact eigenvalues in terms of  $e$  and  $\ell$  are

$$E_n = -\frac{Me^4}{32\pi^2\epsilon_0^2\hbar^2 n(\ell)^2},$$

where  $n(\ell) = n_r + \ell + 1$ , with  $n_r$  being the highest power in the series expansion or  $R_{n\ell}(r)$ .

Apply the Feynman-Hellman theorem with  $\lambda = e$  to derive:

$$\langle n\ell^{(0)} | R^{-1} | n\ell^{(0)} \rangle = \frac{1}{n^2 a_0}.$$

Then use  $\lambda = \ell$ , with  $\ell$  treated as a continuous parameter, to derive:

$$\langle n\ell^{(0)} | R^{-2} | n\ell^{(0)} \rangle = \frac{1}{(\ell + 1/2)n^3 a_0^2}.$$

3. [20 pts] Deriving Kramer's relation:

- a.) First, show via integration by parts that  $\int dr ur^s u' = -\frac{s}{2} \int dr ur^{s-1} u$ . Then use this result to show that  $\int dr u' r^s u' = -\frac{2}{s+1} \int dr u' r^{s+1} u''$ .
- b.) With  $R_{n\ell}(r) = u(r)/r$ , the radial eigenvalue equation of the hydrogen atom becomes

$$u'' = \left[ \frac{\ell(\ell+1)}{r^2} - \frac{2}{a_0 r} + \frac{1}{n^2 a_0^2} \right] u.$$

Use this to express  $\int dr ur^s u''$  in terms of  $\langle n\ell^{(0)} | R^s | n\ell^{(0)} \rangle$ ,  $\langle n\ell^{(0)} | R^{s-1} | n\ell^{(0)} \rangle$ , and  $\langle n\ell^{(0)} | R^{s-2} | n\ell^{(0)} \rangle$ .

- c.) Set aside your result from part b.), and now integrate  $\int dr ur^s u''$  by parts, assuming the boundary terms vanish. Apply the identities derived in part a.) to each of the resulting terms in the obvious manner, and then again use the eigenvalue equation to eliminate  $u''$ .
- d.) You now have two distinct expressions for  $\int dr ur^s u''$ . Equate the them and collect like terms to derive a relation between  $\langle n\ell^{(0)} | R^s | n\ell^{(0)} \rangle$ ,  $\langle n\ell^{(0)} | R^{s-1} | n\ell^{(0)} \rangle$ , and  $\langle n\ell^{(0)} | R^{s-2} | n\ell^{(0)} \rangle$ . This is called Kramer's relation.

4. [15 pts] Spin-orbit interaction:

- a.) Use Kramer's relation with  $s = -1$ , together with your results from problem 2, to evaluate  $\langle n\ell^{(0)} | R^{-3} | n\ell^{(0)} \rangle$ .
- b.) Use this expression to show that the first-order spin-orbit interaction shift, given by the Dirac equation as

$$E_{n\ell j}^{(1)} = \frac{e^2}{8\pi\epsilon_0 M^2 c^2} \langle n\ell j^{(0)} | \frac{\vec{L} \cdot \vec{S}}{R^3} | n\ell j^{(0)} \rangle,$$

can be expressed as

$$E_{n\ell j}^{(1)} = \frac{[E_n^{(0)}]^2}{M c^2} \frac{n [j(j+1) - \ell(\ell+1) - 3/4]}{\ell(\ell+1/2)(\ell+1)}.$$

5. [15 pts] From the Dirac equation, it is found that the fine-structure of hydrogen is given by three terms: the relativistic mass correction, the spin-orbit interaction, and the Darwin term. In the atomic physics lecture notes, the Feynman-Hellman theorem is used to show that the first-order relativistic mass-correction is

$$E_{n\ell}^{(1)} = -\frac{[E_n^{(0)}]^2}{2m_e c^2} \left( \frac{4n}{\ell+1/2} - 3 \right).$$

Due to symmetry, the spin-orbit interaction term is exactly zero for  $\ell = 0$ , while the combined mass-correction and Darwin terms give a net shift of

$$E_{n0\frac{1}{2}}^{(1)} = -\frac{m_e c^2 \alpha^4}{4n^4} \left( 2n - \frac{3}{2} \right).$$

For  $\ell \neq 0$ , on the other hand, the Darwin term vanishes, while the spin-orbit shift is non-zero.

Consider separately the two possible cases  $j = \ell + 1/2$  and  $j = \ell - 1/2$ , and show that for  $\ell \neq 0$ , the full fine-structure shift is given by

$$E_{nj}^{(1)} = -\frac{m_e c^2 \alpha^4}{4n^4} \left( \frac{2n}{j+1/2} - \frac{3}{2} \right).$$

Using the above expression for  $E_{n0\frac{1}{2}}^{(1)}$ , show that this formula also works for the  $\ell = 0$  case.

Based on this formula, make a sketch of the hydrogen energy levels for  $n = 1, 2, 3$ , showing the fine structure splittings. For each  $n$ , give the degeneracy of each  $j$  sub-level, and compute the level separations in eV.

**Practice problem:**

This problem will not be graded and no points will be awarded. The solution will be included with the solutions to the required problems.

**DC Stark Effect to first-order for the  $n = 3$  level of the hydrogen atoms:** The stark shift is governed by the potential:

$$V_E = -eE_0Z.$$

- a.) List all of the degenerate  $|n\ell m_\ell^{(0)}\rangle$  states in the  $n = 3$  subspace. Then use the selection rules to group the levels into closed sets of coupled states.
- b.) Write the matrix element  $\langle 3\ell m_\ell^{(0)} | Z | 3\ell' m_\ell'^{(0)} \rangle$  out as an integral over  $r, \theta, \phi$ . Evaluate the integral for all transitions which obey the selection rules.
- c.) For each group in part a.) having more than one element, find the ‘good’ eigenstates, by diagonalizing  $V_E$  in the subspace of the states in the group.
- d.) Give the number of distinct sublevels that the  $n = 3$  level splits into. State the degeneracy of each sub-level, and list the ‘good’ basis states which belong to each sub-level. Include a sketch of the energy levels versus  $E_0$ .