640-402 QUANTUM MECHANICS B – ASSIGNMENT

The Energy Levels and Spectrum of Hydrogenic Atoms

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1   Introduction

A hydrogenic atom is one with a nucleus of charge Z and a single electron. Therefore the physics of Hydrogen (H) with $Z = 1$, singly ionised Helium (He^+) with $Z = 2$, doubly ionised Lithium (Li^{++}) and so forth, is essentially the same. The quantum mechanics of the Hydrogen atom is applicable to other atoms which only have a single electron. A study of the spectrum of hydrogen was one of the earliests tests of quantum mechanics.

2   The Schrödinger Equation

2.1   Energy Levels

A hydrogenic atom can be thought of as an electron with charge $(-e)$ moving around the spherically symmetric Coulomb potential of the nucleus which has charge Z. The Hamiltonian for this atomic system can then be written down as

$$H = \frac{\mathbf{p}^2}{2\mu} - \frac{Ze^2}{4\pi\varepsilon_0 r}.$$

where the first term corresponds to the kinetic energy of the electron, and the second term corresponds to the Coulombic attraction between the electron and the nucleus. The momentum of the electron is $\mathbf{p}$, Z is the number of protons in the nucleus, r is the distance between the electron and the nucleus, e is the fundamental electric charge on an electron or proton and μ is the reduced mass of the system given by

$$\mu = \frac{Mm}{M+m}$$

The problem reduces to solving the time independent Schrödinger equation for the above Hamiltonian.

$$\left[\frac{\mathbf{p}^2}{2\mu} - \frac{Ze^2}{4\pi r} \right] \psi_{nlm} = E_n \psi_{nlm}$$

Solving for this equation gives the energy levels of hydrogenic atoms E_n, and and corresponding wavefunctions ψ_{nlm}. The energy levels only depend on the principle quantum number n, whereas the wavefunctions also depend on the orbital angular momentum quantum number l ($l = 0, 1, ... n-1$) and magnetic quantum number m ($m = -l, -l+1, ..., +l-1, +l$). The wavefunctions of hydrogenic atoms are given by

$$\psi_{nlm}(\mathbf{r}) = \psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

where $R_{nl}(r)$ are the radial wavefunctions and $Y_{lm}(\theta, \phi)$ are spherical harmonics. The corresponding energy levels of hydrogenic atoms are given by

$$E_n = -\frac{1}{2}\mu c^2 \frac{Z^2 \alpha^2}{n^2}$$

where α is the fine structure constant ($\alpha = e^2/(4\pi\varepsilon_0 \hbar c)$). Since the energy levels depend only on the principle quantum number n, we see that the energy levels are degenerate for different values of l and m at a given value of n. The diagram below shows the energy levels for the case when $Z = 1$ (Hydrogen). The degeneracy in l can be seen for the different values of n. The energy levels shown are known as the gross structure of atomic hydrogen.

2.2 Rydberg States

A highly excited hydrogenic atom, that is one with a large principal quantum number *n* is said to be known as a *Rydberg Atom*, or to be in a *Rydberg State*. The table below compares some properties of a hydrogen atom in a $n = 1$ state and one in a $n = 100$ state.

Quantity	n = 1	n = 100
Radius of Bohr Orbit (in m)	5.3×10^{-11}	5.3×10^{-7}
Binding Energy $|E_n|$ (in *eV*)	-13.6	1.36×10^{-3}

The Rydberg Atom with $n = 100$, is of an extremely large size – approximately the size of a simple bacteria. However, such an atom has a very small ionisation energy and hence the electron is very weakly bound.

2.3 Hydrogenic Spectrum

The diagram below shows the spectrum of atomic hydrogen as predicted by the Bohr model of the atom and by Schrödinger's equation. As can be seen there are a number of series of spectral lines – Lyman, Balmer, Paschen and Brackett.

The hydrogen series appear close together in the electromagnetic spectrum. For example, the Lyman Series is in the Ultra-Violet (UV) Region, the Balmer series is in the Visible-UV region and the Paschen, Brackett and Pfund series are in the Infra-Red (IR) Region.

2.3.1 The Lyman Series – Ultra Violet Region

Spectral Line	Wavelength (Angstroms)
Ly_α	1216
Ly_β	1026
Ly_γ	972.5
Ly_δ	949.7

2.3.2 The Balmer Series – Visible-Ultra Violet Region

Spectral Line	Wavelength (Angstroms)
H_α	6563
H_β	4861
H_γ	4340

The schematic spectral diagram below shows the Balmer series of atomic hydrogen. It shows the positions of the spectral lines in the electromagnetic spectrum.

2.3.3 The Paschen Series – Infra Red Region

Spectral Line	Wavelength (Angstroms)
P_α	18751
P_β	12818

3 Fine Structure

Although the energy levels for hydrogenic atoms shown above agree qualitatively with experiment, very precise measurements of the hydrogen spectrum reveal the existence a finer structure which can not be explained with the Hamiltonian used above. Experiments reveals that some of the energy levels are split into many smaller levels and therefore many of the degeneracies are lifted.

The fine structure of the energy levels of hydrogenic atoms are due to relativistic effects and the spin of the electron which were not taken into account in the previous section. We can obtain an estimate on how much the energy levels are shifted, by using perturbation theory if we assume the the relativistic and spin effects are small. We can treat the Hamiltonian, energy eigenfunctions and energy levels as the unperturbed case and use first order perturbation theory for the perturbing components of the Hamiltonian. The Schrödinger equation is then of the following form

$$\left[H_0 + H_1' + H_2' + H_3' \right] \psi_{nlm} = E\psi_{nlm}$$

where H_0 corresponds to the unperturbed Hamiltonian used in the previous section, and H_1', H_2' and H_3' correspond to small perturbations involving relativistic corrections to the kinetic energy, the effect of spin-orbit coupling and the Darwin interaction. These three perturbations are described individually below. The process then involves determining the shift in energy to first order for each of the perturbing terms in the Hamiltonian. The unperturbed Schrödinger equation needs to be slightly modified in order to treat perturbing Hamiltonians which take the spin of the electron into account. The modified 'unperturbed' equation is given by

$$H_0 \psi_{nlm_l m_s}^{(0)} = E_n^{(0)} = \psi_{nlm_l m_s}^{(0)}$$

, where $E_n^{(0)}$ are the Schrödinger energy eigenvalues (with $\mu = m$) and the zero order wave functions $\psi_{nlm_l m_s}^{(0)}$ are modified two component wave functions (also known as Pauli wave functions or spin-orbitals) given by

$$\psi_{nlm_l m_s}^{(0)}(q) = \psi_{nlm_l}^{(0)}(\mathbf{r}) \chi_{\frac{1}{2}, m_l}$$

. The parameter q represents the combined spin and space coordinate, and $\chi_{\frac{1}{2}, m_l}$ are two component spinors (spin eigenfunctions for particle of spin one half). For spin-up ($m_s = +1/2$) and spin-down ($m_s = -1/2$), the normalised spinors are denoted by

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

Since the unperturbed Hamiltonian does not depend on the spin variable, the Pauli wavefunctions are separable in the spin and coordinate variables. To describe the state of an electron in a hydrogenic atom, we now have the four quantum number n, l, m_l and m_s. As a result of this, each of the unperturbed energy levels are E_n are $2n^2$ degenerate.

Finally the new perturbed energy levels to first order are given by

$$E = E_n^{(0)} + \Delta E_1' + \Delta E_2' + \Delta E_3'$$

where $\Delta E_{(k)}'$ is the energy shift resulting from the k'th perturbation.

3.1 Relativistic Correction to the Kinetic Energy

$$H_1' = -\frac{p^4}{8m^3 c^2}$$

Since relativistic effects were not taken into account previously, the perturbing Hamiltonian H_1' represents the relativistic correction to the kinetic energy of the electron. Using first order perturbation theory the energy shift is given by

$$\Delta E_1' = \left\langle nlm_l m_s \left| \frac{-p^4}{8m^3 c^2} \right| nlm_l m_s \right\rangle$$

$$\Delta E_1' = -E_n \frac{Z^2\alpha^2}{n^2}\left[\frac{3}{4} - \frac{n}{l+\frac{1}{2}}\right]$$

3.2 Spin Orbit Interaction

$$H_2' = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{L}\cdot\mathbf{S}$$

This perturbation corresponds to the shift in the energy as a result of the interaction between the internal spin of the electron and it's orbital angular momentum as it orbits the nucleus. Since the potential $V(r) = -Ze^2/(4\pi\varepsilon_0 r)$ for a hydrogenic atom, the perturbing Hamiltonian becomes

$$H_2' = \frac{1}{2m^2c^2}\frac{Ze^2}{4\pi\varepsilon_0 r^3}\mathbf{L}\cdot\mathbf{S}$$

The energy shift for this perturbing Hamiltonian using first order perturbation theory is

$$\Delta E_2' = -E_n \frac{Z^2\alpha^2}{2nl(l+\frac{1}{2})(l+1)}\begin{cases} l, & j = l+\frac{1}{2} \\ -l-1, & j = l-\frac{1}{2}\end{cases}$$

3.3 Darwin Interaction

$$H_3' = \frac{\pi\hbar^2}{2m^2c^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\delta(\mathbf{r})$$

The Darwin term does not act on the spin variable and only applies when the orbital angular moment is zero ($l = 0$). The shift energy from the Darwin term is given by

$$\Delta E_3' = -E_n\frac{Z^2\alpha^2}{n}, \quad l = 0$$

3.4 Fine Structure Energy Levels to First Order

Based on the energy levels obtained for hydrogenic atoms from the Schrödinger equation, and the energy shifts obtained from the three perturbation when relativistic and spin effects are taken into account we get

$$E_{nj} = E_n + \Delta E_1' + \Delta E_2' + \Delta E_3'.$$

Now subtracting from the binding energy $E = mc^2 - E_{nj}$

$$E = mc^2\left[1 - \frac{(Z\alpha)^2}{2n^2} - \frac{(Z\alpha)^4}{2n^3}\left(\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right)\right].$$

This result is valid if the perturbation is small, and therefore it begins to break down for hydrogenic atoms with large atomic numbers Z.

3.5 The Dirac Equation

The equation which provides the correct energy eigenvalues and eigenstates for the fine structure of hydrogenic atoms is the Dirac equation, shown below for a Hydrogenic atom,

$$\left[c\alpha\cdot\mathbf{p} + \beta mc^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right]\psi = E\psi$$

where ψ is a 4-component spinor. The Dirac equation takes special relativistic effects and the spin of the electron (or any spin-$\frac{1}{2}$ particle) into account, and gives the following solutions for the energy eigenvalues for hydrogenic atoms.

$$E_{nj}^{Dirac} = \frac{mc^2}{\sqrt{1 + \frac{(Z\alpha)^2}{n-j-\frac{1}{2}+\sqrt{\left(j+\frac{1}{2}\right)^2-(Z\alpha)^2}}}}$$

Expanding the above equation in a series we obtain

$$E = mc^2 \left[1 - \frac{(Z\alpha)^2}{2n^2} - \frac{(Z\alpha)^4}{2n^2}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right) - ...\right].$$

This can be seen to agree with the result obtained previously using the perturbation theory for the first few terms.

4 Hyperfine Structure

Until now, the nucleus of hydrogenic atoms has been treated as a point charge. effectively of infinite mass. However, precise spectroscopic measurements of hydrogenic atoms reveal some very small effects on the energy levels which cannot be explained if the nucleus is treated in this way. These effects are known as *hyperfine effects* because they are much smaller then the fine structure effects predicted by the Dirac equation. The hyperfine effects can be grouped into two types.

Hyperfine Structure effects give rise to splittings in energy levels

Isotope Shifts slightly shift the energy levels and can usually be detected by observing the differences between two or more different isotopes.

Hyperfine structure effects arise from the electric multipole moments of the nucleus which can interact with the electromagnetic field produced at the nucleus by the electrons. The two main multipole moments are the magnetic dipole moment associated with the spin of the nucleus and the electric quadrupole moment due to the departure of the spherical charge distribution in the nucleus. Perturbation theory can be used to determine the shift in the energy these two multipole effects will have.

4.1 Magnetic Dipole Interaction

The perturbation which describes the interaction of the nuclear magnetic dipole moment consists of two expressions depending on the orbital angular momentum l. For the case of $l \neq 0$ we have

$$H'_{MD} = \frac{2\mu_0}{4\pi\hbar} g_I \mu_B \mu_N \frac{1}{r^3} \mathbf{G} \cdot \mathbf{I}$$

where

$$\mathbf{G} = \mathbf{L} - \mathbf{S} + 3\frac{(\mathbf{S} \cdot \mathbf{r})\mathbf{r}}{r^2}$$

and the total spin of the atom (nucleus and electron) is given by

$$\mathbf{F} = \mathbf{I} + \mathbf{J}.$$

For the case when $l = 0$, the perturbation is given by

$$H'_{MD} = \frac{\mu_0}{4\pi} 2g_I \mu_B \mu_N \frac{8\pi}{3} \delta(\mathbf{r}) \mathbf{S} \cdot \mathbf{I}.$$

4.2   Electric Quadrupole Interaction

The interaction Hamiltonian between the electric quadrupole moment of the nucleus and the electrostatic potential create by an electron at the nucleus is given (in atomic units) by

$$H'_{EQ} = B \frac{\frac{3}{2}\mathbf{I} \cdot \mathbf{J}(2\mathbf{I} \cdot \mathbf{J} + 1) - \mathbf{I}^2 \mathbf{J}^2}{2I(2I-1)j(2j-1)}$$

4.3   Hyperfine Spectrum

The magnetic dipole and electric quadrupole interactions above correspond to a total hyperfine energy shift of

$$\Delta E = \frac{C}{2}K + \frac{B}{4} \frac{\frac{3}{2}K(K+1) - 2I(I+1)j(j+1)}{I(2I-1)j(2j-1)}$$

where B is the quadrupole coupling constant given by

$$B = Q \left\langle \frac{\partial^2 V}{\partial z^2} \right\rangle$$

and

$$K = F(F+1) - I(I+1) - j(j+1)$$

$$C = \frac{\mu_0}{4\pi} 2g_I \mu_B \mu_N \frac{l(l+1)}{j(j+1)} \frac{Z^3}{a_\mu^3 n^3 l(l+l/2)(l+1)}$$

The energy level diagram above shows the splittings of the different energy in a Hydrogen atom for n = 1 and n = 2. The diagram is not to scale and are magnified form the left to the right. The diagram qualitatively shows the effect on the Bohr/Schrödinger energy from the various corrections such as the Dirac fine structure, the Lamb Shift (described in the next section) and the hyperfine structure.

4.4   The 21 cm Line of Atomic Hydrogen

The energy level splitting diagram above shows that the ground state of the hydrogen atom splits into two hyperfine levels with the total angular momentum of the atom being $F = 0$ and $F = 1$. The difference in energy between these two levels is 1420 MHz which corresponds to a wavelength of $\lambda \approx 21$ cm. The probability of a transition occurring between these two levels is very low and occurs on average only once every few million years. However, there is a large amount of hydrogen gas in the galaxy allowing radio telescopes easily detect this 21 cm transition and therefore allow the mapping of hydrogen in the galaxy.

5 The Lamb Shift

Investigation of the fine structure of hydrogenic atoms using spectroscopic techniques in the 1930's showed that there were small differences between the observed spectra and the theoretical predictions made by the Dirac equation. For example, according to the Dirac equation the $2s_{1/2}$ and the $2p_{1/2}$ states coincide at the same energy level. Observations showed that the $2s_{1/2}$ was shifted slightly upwards by about 0.03 cm^{-1}. A very accurate measurement of the shift was made in 1947 by Lamb and Retherford using microwave techniques to stimulate a direct radio-frequency transition between the $2s_{1/2}$ and the $2p_{1/2}$ levels. This small shift of energy levels became known as the Lamb shift.

The physics of the Lamb shift are described in the theory of quantum electrodynamics, in which radiative corrections to the Dirac equation are obtained by taking into account the interaction of a quantised electromagnetic field with an electron. The Lamb shift arises because of the zero point energy of a quantised electromagnetic field is non zero, similar to the zero point energy of a quantum harmonic oscillator. In a vacuum, fluctuations of the zero point energy of the quantised radiation field act on the electron. The effect of the electron is to cause it to oscillate rapidly about some equilibrium position. As a result of this oscillatory motion, the electron does not appear to be point charge – instead the electron charge is slightly smeared at in a sphere of some small radius. When the electron is bound by an electric field as it is in an atom, the potential it experiences is slightly different to that experienced by the electron in it's mean position. Therefore electrons which are most sensitive to short distance modifications such as those in the ground state are raised in energy with respect to other states to which the shift is much smaller.

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