Everything You Always Wanted to Know About the Hydrogen Atom (But Were Afraid to Ask)

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Abstract

A thorough review of the structure of the hydrogen atom will be presented with emphasis on the quantum-mechanical principles involved rather than calculational detail, which will be minimized. First, the relationship of the Heisenberg uncertainty principle to the hydrogen atom will be discussed briefly. This is followed by a discussion of the energy level structure of the hydrogen atom, including fine structure, in the context of the quantum-mechanical theories of Bohr, Schrödinger, and Dirac. Finally, smaller-order corrections to these theories will be discussed, including the Lamb shift, hyperfine structure, and the Zeeman effect.

1 The Uncertainty Principle

Before discussing specifics about the structure of the hydrogen atom, it is interesting to note what information about the hydrogen atom can be derived just from the Heisenberg uncertainty principle. A familiar form of the uncertainty principle looks like the following:

$$\Delta x \Delta p_x \sim \hbar, \tag{1}$$

where Δx and Δp_x are the uncertainty in the x-component of the position and momentum of a particle, respectively. Consider an electron in a classical circular orbit in the xy-plane. It is then reasonable to write $\Delta x \sim r$, where r is the radius of the orbit. Assuming a state of minimum uncertainty, Δp_x is then known from the uncertainty principle, and it should be roughly equal to the magnitude of the momentum for the circular orbit being considered. That is,

$$p \sim \Delta p_x \sim \frac{\hbar}{r}. \tag{2}$$

Classically, the energy is simply[1]

$$E = \frac{p^2}{2m} - \frac{e^2}{r} = \frac{\hbar^2}{2mr^2} - \frac{e^2}{r}, \tag{3}$$

where m is the electron mass and e the electron charge. The last step results from the substitution of p from equation 2. The value of r is unknown, but one would expect it to have a value that minimizes the energy, as Nature likes to do. Differentiating equation 3 with respect to r and setting equal to zero gives

$$\frac{dE}{dr} = -\frac{\hbar^2}{mr^3} + \frac{e^2}{r^2} = 0. \tag{4}$$

This yields

$$r = \frac{\hbar^2}{me^2} \equiv a_0 = 0.529 \text{ Å}, \tag{5}$$

where a_0 is the Bohr radius. Substituting into equation 3 gives

$$E = -13.6\text{eV}. \tag{6}$$

The Bohr radius is exactly the radius of the circular orbit in the ground state of the electron in Bohr theory, and it holds up as representative of the extent of the orbit in Schrödinger theory. The energy -13.6eV is the known ground state energy of the hydrogen atom. So, starting with only a very rough view of the structure of the atom and the uncertainty principle, one can make some reasonable assumptions and derive two extremely important fundamental results — the "size" if the hydrogen atom in its ground state and its ionization energy. Of course, to get precisely the right results one needs to make the right assumptions, and so this calculation is certainly not rigorously accurate. It merely illustrates the relation of the fundamental physical structure of the hydrogen atom to the uncertainty principle. The fact that these results were derived assuming minimum uncertainty leads to a rather important conclusion—the hydrogen atom in its ground state is essentially in a state of minimum uncertainty. This explains why the electron in its ground state cannot radiate, as one expects classically, and

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[1] To achieve consistency and avoid confusion, all equations are written in Gaussian units.

get drawn in towards the nucleus — to do so would violate the uncertainty principle. If the electron were confined closer to the nucleus, so that Δx were much smaller, then Δp_x would be much larger and so it would not be possible to consider the electron as necessarily bound to the nucleus.

2 The Bohr Model

With the use of spectroscopy in the late 19th century, it was found that the radiation from hydrogen, as well as other atoms, was emitted at specific quantized frequencies. It was the effort to explain this radiation that led to the first successful quantum theory of atomic structure, developed by Niels Bohr in 1913. He developed his theory of the hydrogenic (one-electron) atom from four postulates:

1. *An electron in an atom moves in a circular orbit about the nucleus under the influence of the Coulomb attraction between the electron and the nucleus, obeying the laws of classical mechanics.*
2. *Instead of the infinity of orbits which would be possible in classical mechanics, it is only possible for an electron to move in an orbit for which its orbital angular momentum L is and integral multiple of $\hbar$.*
3. *Despite the fact that it is constantly accelerating, an electron moving in such an allowed orbit does not radiate electromagnetic energy. Thus, its total energy E remains constant.*
4. *Electromagnetic radiation is emitted if an electron, initially moving in an orbit of total energy E_i, discontinuously changes its motion so that it moves in an orbit of total energy E_f. The frequency of the emitted radiation ν is equal to the quantity $(E_i - E_f)$ divided by h.* [2]

The third postulate can be written mathematically

$$\begin{aligned} L &= n\hbar \qquad (7) \\ n &= 1, 2, 3, \ldots \end{aligned}$$

For an electron moving in a stable circular orbit around a nucleus, Newton's second law reads

$$\frac{Ze^2}{r^2} = m\frac{v^2}{r}, \qquad (8)$$

where v is the electron speed, and r the radius of the orbit. Since the force is central, angular momentum should be conserved and is given by $L = |\mathbf{r} \times \mathbf{p}| = mvr$. Hence from the quantization condition of equation 7,

$$mvr = n\hbar. \tag{9}$$

Equations 8 and 9 therefore give two equations in the two unknowns r and v. These are easily solved to yield

$$\begin{aligned} r &= \frac{n^2\hbar^2}{mZe^2} = \frac{n^2}{Z}a_0 && (10) \\ v &= \frac{Ze^2}{n\hbar} = \frac{Z}{n}\alpha c, && (11) \end{aligned}$$

where

$$\alpha \equiv \frac{e^2}{\hbar c} \approx \frac{1}{137} \tag{12}$$

is a dimensionless number known as the *fine-structure constant* for reasons to be discussed later. Hence αc is the speed of the electron in the Bohr model for the hydrogen atom ($Z = 1$) in the ground state ($n = 1$). Since this is the maximum speed for the electron in the hydrogen atom, and hence $v \ll c$ for all n, the use of the classical kinetic energy seems appropriate. From equation 8, one can then write the kinetic energy,

$$K = \frac{1}{2}mv^2 = \frac{Ze^2}{2r}, \tag{13}$$

and hence the total energy,[2]

$$E = K + V = \frac{Ze^2}{2r} - \frac{Ze^2}{r} = -\frac{Ze^2}{2r}. \tag{14}$$

Having solved for r as equation 10, one can then write

$$E = -\frac{mZ^2e^4}{2\hbar^2}\frac{1}{n^2} = -\frac{mc^2}{2}(Z\alpha)^2\frac{1}{n^2}. \tag{15}$$

Numerically, the energy levels for a hydrogenic atom are

$$E = -13.6\text{eV}\frac{Z^2}{n^2}. \tag{16}$$

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[2] The reader may notice that $E = -K$, as a natural consequence of the virial theorem of classical mechanics.

One correction to this analysis is easy to implement, that of the finite mass of the nucleus. The implicit assumption previously was that the electron moved around the nucleus, which remained stationary due to being infinitely more massive than the electron. In reality, however, the nucleus has some finite mass M, and hence the electron and nucleus both move, orbiting about the center of mass of the system. It is a relatively simple exercise in classical mechanics to show one can transform into the rest frame of the nucleus, in which frame the physics remains the same except for the fact that the electron acts as though it has a mass

$$\mu = \frac{mM}{m+M}, \tag{17}$$

which is less than m and is therefore called the *reduced mass.* One can therefore use μ in all equations where m appears in this analysis and get more accurate results. With this correction to the hydrogen energy levels, along with the fourth Bohr postulate which gives the radiative frequencies in terms of the energy levels, the Bohr model correctly predicts the observed spectrum of hydrogen to within three parts in 10^5.

Along with this excellent agreement with observation, the Bohr theory has an appealing aesthetic feature. One can write the angular momentum quantization condition as

$$L = pr = n\frac{h}{2\pi}, \tag{18}$$

where p is the linear momentum of the electron. Louis de Broglie's theory of matter waves predicts the relationship $p = h/\lambda$ between momentum and wavelength, so

$$2\pi r = n\lambda. \tag{19}$$

That is, the circumference of the circular Bohr orbit is an integral number of de Broglie wavelengths. This provided the Bohr theory with a solid physical connection to previously developed quantum mechanics.

Unfortunately, in the long run the Bohr theory, which is part of what is generally referred to as the *old quantum theory*, is unsatisfying. Looking at the postulates upon which the theory is based, the first postulate seems reasonable on its own, acknowledging the existence of the atomic nucleus, established by the scattering experiments of Ernest Rutherford in 1911, and assuming classical mechanics. However, the other three postulates introduce quantum-mechanical effects, making the theory an uncomfortable union of classical and quantum-mechanical ideas. The second and third postulates seem particularly ad hoc. The electron travels in a classical orbit, and yet its angular momentum is quantized, contrary to classical mechanics. The electron obeys Coulomb's law of classical electromagnetic theory, and yet it is assumed to not radiate, as it would classically. These postulates may result in good predictions for the hydrogen atom, but they lack a solid fundamental basis.

The Bohr theory is also fatally incomplete. For example, the Wilson-Sommerfeld quantization rule, of which the second Bohr postulate is a special case, can only be applied to periodic systems. The old theory has no way of approaching non-periodic quantum-mechanical phenomena, like scattering. Next, although the Bohr theory does a good job of predicting energy levels, it predicts nothing about *transition rates* between levels. Finally, the theory is really only successful for one-electron atoms, and fails even for helium. To correct these faults, one needs to apply a more completely quantum-mechanical treatment of atomic structure, and such an approach is used in Schrödinger theory.

3 Schrödinger Theory

The Schrödinger theory of quantum mechanics extends the de Broglie concept of matter waves by providing a formal method of treating the dynamics of physical particles in terms of associated waves. One expects the behavior of this wavefunction, generally called Ψ, to be governed by a wave equation, which can be written

$$\left(\frac{p^2}{2m} + V(\mathbf{x},t)\right)\Psi(\mathbf{x},t) = H\Psi(\mathbf{x},t), \tag{20}$$

where the first term of the left represents the particle's kinetic energy, the second the particle's potential energy, and H is called the Hamiltonian of the system. Making the assertion that p and H are associated with differential operators,

$$\begin{aligned} p &= -i\hbar\nabla & (21)\\ H &= i\hbar\frac{\partial}{\partial t}, & (22)\end{aligned}$$

this becomes

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x},t)\right)\Psi(\mathbf{x},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x},t), \tag{23}$$

which is known as the *time-dependent Schrödinger equation.* For the specific case of a hydrogenic atom, the electron moves in a simple Coulomb potential, and hence the Schrödinger equation is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\Psi(\mathbf{x},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{x},t). \tag{24}$$

The solution proceeds by the method of separation of variables. First one writes the wavefunction as a product of a space component and a time component, for which the solution for the time part is easy and yields

$$\Psi(\mathbf{x},t) = \psi(\mathbf{x})e^{-iEt/\hbar}. \tag{25}$$

Here E is the constant of the separation and is equal to the energy of the electron. The remaining equation for the spatial component is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{r}\right)\psi(\mathbf{x}) = E\psi(\mathbf{x}) \tag{26}$$

and is called the *time-independent Schrödinger equation.* Due to the spherical symmetry of the potential, this equation is best solved in spherical polar coordinates, and hence one separates the spatial wavefunction as

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi). \tag{27}$$

The equations are more difficult but possible to solve and yield

$$\begin{aligned} \Theta(\theta)\Phi(\phi) &= Y_l^{m_l}(\theta,\phi) && (28)\\ R(r) &= e^{-Zr/na_0}\left(\frac{Zr}{a_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2Zr}{na_0}\right), && (29) \end{aligned}$$

where L is an associated Laguerre polynomial, and for convenience the product of the angular solutions are written together in terms of a single function, the spherical harmonic Y. With foresight the separation constants $-m_l^2$ and and $l(l+1)$ were used. The meaning of the numbers n, l, and m_l will now be discussed.

The physics of the Schrödinger theory relies on the interpretation of the wave function in terms of probabilities. Specifically, the absolute square of the wavefunction, $|\Psi(\mathbf{x},t)|^2$, is interpreted as the probability density for finding the associated particle in the vicinity of $\mathbf{x}$ at time t. For this to make physical sense, the wavefunction needs to be a well-behaved function of $\mathbf{x}$ and t; that is, Ψ should be a finite, single-valued, and continuous function. In order to satisfy these conditions, the separation constants that appear while solving the Schrödinger equation can only take on certain discrete values. The upshot is, with the solution written as it is here, that the numbers n, l, and m_l, called *quantum numbers* of the electron, can only take on particular integer values, and each of these corresponds to the quantization of some physical quantity. The allowed values of the energy turn out to be exactly as predicted by the Bohr theory,

$$E = -\frac{mc^2}{2}(Z\alpha)^2\frac{1}{n^2}. \tag{30}$$

The quantum number n is therefore called the *principle quantum number.* To understand the significance of l and m_l, one needs to consider the orbital angular momentum of the electron. This is defined as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, or as an operator, $\mathbf{L} = -i\hbar\mathbf{r} \times \nabla$. With proper coordinate transformations, one can write the operators L^2 and the z-component of angular momentum L_z in spherical coordinates as

$$\begin{aligned} L^2 &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] && (31) \\ L_z &= -i\hbar\frac{\partial}{\partial\phi}. && (32) \end{aligned}$$

It can be shown that when these operators act on the solution Ψ, the result is

$$\begin{aligned} L^2\Psi &= l(l+1)\hbar^2\Psi && (33) \\ L_z\Psi &= m_l\hbar\Psi. && (34) \end{aligned}$$

It can also be shown that this means that an electron in a particular state has orbital angular momentum of constant magnitude $\sqrt{l(l+1)}\hbar$ and constant projection onto the z-axis of $m_l\hbar$. Since the electron obeys the time-independent Schrödinger equation $H\Psi = E\Psi$, and hence has constant energy, one says that the wavefunction Ψ is a *simultaneous eigenstate* of the operators H, L^2, and L_z. Table 1 summarizes this information and gives the allowed values for each quantum number. It is worth repeating that these numbers can have only these specific values because of the demand that Ψ be a well-behaved function.

It is common to identify a state by its principle quantum number n and a letter which corresponds to its orbital angular momentum quantum number l, as shown in table 2. This is called *spectroscopic notation.* The first four

Table 1: Some quantum numbers for the electron in the hydrogen atom.

Quantum number	Integer values	Quantized quantity
n	$n \geq 1$	Energy
l	$0 \leq l < n$	Magnitude of orbital angular momentum
m_l	$-l \leq m_l \leq l$	z-component of orbital angular momentum

Table 2: Spectroscopic notation.

Quantum number l	0	1	2	3	4	…
Letter	s	p	d	f	g	…

designated letters are of historical origin. They stand for sharp, primary, diffuse, and fundamental, and refer to the nature of the spectroscopic lines when these states were first studied.

Figure 1 shows radial probability distributions for some different states, labelled by spectroscopic notation. The radial probability density P_{nl} is defined such that

$$P_{nl}(r)dr = |R_{nl}(r)|^2 4\pi r^2 dr \tag{35}$$

is the probability of finding the electron with radial coordinate between r and $r + dr$. The functions are normalized so that the total probability of finding the electron at some location is unity. It is interesting to note that each state has $n - l - 1$ nodes, or points where the probability goes to zero. This is sometimes called the *radial node quantum number* and appears in other aspects of quantum theory. It is also interesting that for each n, the state with $l = n - 1$ has maximum probability of being found at $r = n^2 a_0$, the radius of the orbit predicted by Bohr theory. This indicates that the Bohr model, though known to be incorrect, is at least similar to physical reality in some respects, and it is often helpful to use the Bohr model when trying to visualize certain effects, for example the spin-orbit effect, to be discussed in the next section. The angular probability distributions will not be explored here[3], except to say that they have the property that if the solutions with all possible values of l and m_l for a particular n are summed together, the result is a distribution with spherical symmetry, a feature which helps to

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[3] See Eisberg and Resnick, chapter 7, for a more thorough discussion.

greatly simplify applications to multi-electron atoms.

3.1 The Spin-Orbit Effect

In order to further explain the structure of the hydrogen atom, one needs to consider that the electron not only has orbital angular momentum $\mathbf{L}$, but also intrinsic angular momentum $\mathbf{S}$, called *spin.* There is an associated spin operator $\mathbf{S}$, as well as operators S^2 and S_z, just as with $\mathbf{L}$. Usually written in matrix form, these operators yield results analogous to L^2 and L_z when acting on the wavefunction Ψ,

$$\begin{aligned} S^2\Psi &= s(s+1)\hbar^2\Psi && (36) \\ S_z\Psi &= m_s\hbar\Psi, && (37) \end{aligned}$$

where s and m_s are quantum numbers defining the magnitude of the spin angular momentum and its projection onto the z-axis, respectively. For an electron $s = 1/2$ always, and hence the electron can have $m_s = +1/2, -1/2$.

Associated with this angular momentum is an intrinsic magnetic dipole moment

$$\mu_{\mathrm{S}} = -g_s\mu_b\frac{\mathbf{S}}{\hbar}, \tag{38}$$

where

$$\mu_b \equiv \frac{e\hbar}{2mc} \tag{39}$$

is a fundamental unit of magnetic moment called the *Bohr magneton.* The number g_s is called the *spin gyromagnetic ratio* of the electron, expected from Dirac theory to be exactly 2 but known experimentally to be $g_s = 2.00232$. This is to be compared to the magnetic dipole moment associated with the orbit of the electron,

$$\mu_{\mathrm{l}} = -g_l\mu_b\frac{\mathbf{L}}{\hbar} \tag{40}$$

where $g_l = 1$ is the *orbital gyromagnetic ratio* of the electron. That is, the electron creates essentially twice as much dipole moment per unit spin angular momentum as it does per unit orbital angular momentum. One expects these magnetic dipoles to interact, and this interaction constitutes the spin-orbit effect.

The interaction is most easily analyzed in the rest frame of the electron, as shown in figure 2. The electron sees the nucleus moving around it with speed v in a circular orbit of radius r, producing a magnetic field

$$B = \frac{Zev}{cr^2}. \tag{41}$$

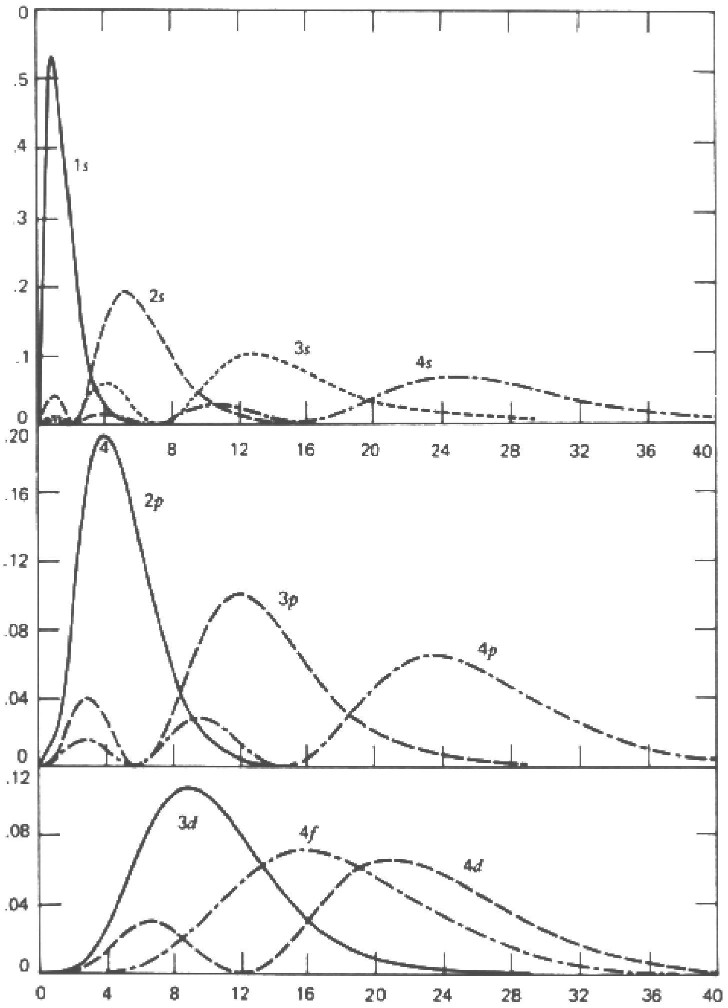

Figure 1: Radial probability distribution for an electron in some low-energy levels of hydrogen. The abscissa is the radius in units of a_0.

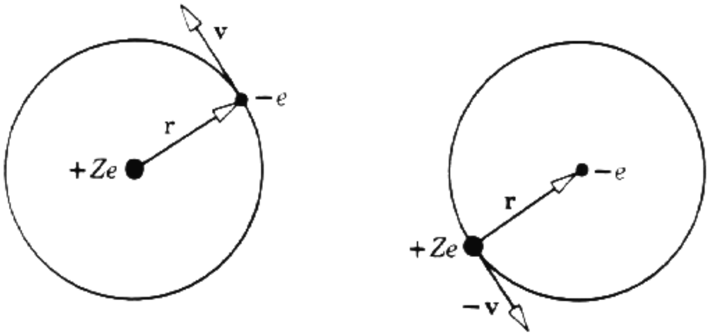

Figure 2: On the left, an electron moves around the nucleus in a Bohr orbit. On the right, as seen by the electron, the nucleus is in a circular orbit.

In terms of the electron orbital angular momentum $L = mrv$, the field may be written

$$\mathbf{B} = \frac{Ze}{mcr^3}\mathbf{L}. \tag{42}$$

The spin dipole of the electron has potential energy of orientation in this magnetic field given by

$$\Delta E_{so} = -\mu_{\mathrm{S}} \cdot \mathbf{B}. \tag{43}$$

However, the electron is not in an inertial frame of reference. In transforming back into an inertial frame, a relativistic effect known as *Thomas precession* is introduced, resulting in a factor of 1/2 in the interaction energy. With this, the Hamiltonian of the spin-orbit interaction is written

$$\Delta H_{so} = \frac{Ze^2}{2m^2c^2r^3}\mathbf{L} \cdot \mathbf{S}. \tag{44}$$

With this term added to the Hamiltonian, the operators L_z and S_z no longer commute with the Hamiltonian, and hence the projections of **L** and **S** onto the z-axis are not conserved quantities. However, one can define the total angular momentum operator

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{45}$$

It can be shown that the corresponding operators J^2 and J_z *do* commute with this new Hamiltonian. Physically what happens is that the dipoles associated with the angular momentum vectors **S** and **L** exert equal and opposite torques on each other, and hence they couple together and precess

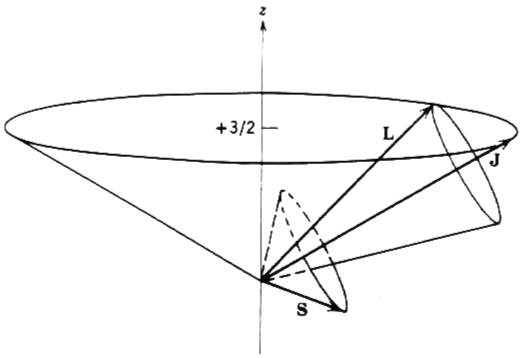

Figure 3: Spin-orbit coupling for a typical case of $s = 1/2$, $l = 2$, $j = 5/2$, $m_j = 3/2$, showing how **L** and **S** precess about **J**.

uniformly around their sum **J** in such a way that the projection of **J** on z-axis remains fixed. The operators J^2 and J_z acting on Ψ yield

$$\begin{aligned} J^2\Psi &= j(j+1)\hbar^2\Psi && (46) \\ J_z\Psi &= m_j\hbar\Psi, && (47) \end{aligned}$$

where j has possible values

$$j = |l-s|, |l-s|+1, \ldots, l+s-1, l+s. \tag{48}$$

For a hydrogenic atom $s = 1/2$, and hence the only allowed values are $j = l - 1/2, l + 1/2$, except for $l = 0$, where only $j = 1/2$ is possible. Figure 3 illustrates spin-orbit coupling for particular values of l, j, and m_j.

Since the coupling is weak and hence the interaction energy is small relative to the principle energy splittings, it is sufficient to calculate the energy correction by first-order perturbation theory using the previously found wavefunctions. The energy correction is then

$$\Delta E_{so} = \langle \Delta H_{so} \rangle = \int \Psi^* \Delta H_{so} \Psi d^3x. \tag{49}$$

The value of $\mathbf{L}\cdot\mathbf{S}$ is easily found by calculating

$$J^2 = \mathbf{J}\cdot\mathbf{J} = L^2 + S^2 + 2\mathbf{L}\cdot\mathbf{S}, \tag{50}$$

and hence when acting on Ψ,

$$\mathbf{L}\cdot\mathbf{S}\Psi = \frac{1}{2}\hbar^2[j(j+1) - l(l+1) - s(s+1)]\Psi. \tag{51}$$

One then needs to calulate the expectation of r^{-3}, which is more complicated. The answer is

$$\Delta E_{so} = (Z\alpha^4)mc^2 \frac{[j(j+1) - l(l+1) - \frac{3}{4}]}{4n^3 l(l+\frac{1}{2})(l+1)}, \tag{52}$$

where the value $s = 1/2$ has been included.

3.2 Kinetic Energy Correction

Before claiming that this formula explains the fine structure of the hydrogen atom, however, one needs to be careful. The correction is of the order α^4, which means it of the order v^4, where v is the electron speed. The kinetic energy used in the Hamiltonian when solving the Schrödinger equation was just $p^2/2m$, which contributed to order α^2. However, the next term in the expansion of the true relativistic kinetic energy is of order p^4 and hence will contribute to order α^4. So if one wishes to quote the energy splittings of the hydrogen atom accurate to order α^4, one had better include the contribution from this further correction.

The relativistic kinetic energy of the electron can be expanded in terms of momentum as

$$T = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \dots \tag{53}$$

Therefore, the correction to the Hamiltonian is

$$\Delta H_{rel} = -\frac{1}{8m^3c^2} p^4. \tag{54}$$

At first sight, this looks quite complicated, since it involves the operator $p^4 = \hbar^4 \nabla^4$. However, one can make use of the fact that

$$\frac{p^2}{2m} = E_n - V \tag{55}$$

to get

$$\Delta H_{rel} = -\frac{1}{2mc^2}(E_n^2 - 2E_nV + V^2). \tag{56}$$

With $V = -Ze^2/r$, applying first-order perturbation theory to this Hamiltonian reduces to the problem of finding the expectation values of r^{-1} and r^{-2}. This can be done with some effort, and the result is

$$\Delta E_{rel} = -(Z\alpha)^4 mc^2 \frac{1}{2n}\left[\frac{1}{(l+\frac{1}{2})} - \frac{3}{4n}\right]. \tag{57}$$

Combining equations 57 and 52 and using the fact that $j = l - 1/2, l + 1/2$, the complete energy correction to order $(Z\alpha)^4$ may be written

$$\Delta E_{fs} = \Delta E_{rel} + \Delta E_{so} = -(Z\alpha)^4 mc^2 \frac{1}{2n}\left[\frac{1}{(j+\frac{1}{2})} - \frac{3}{4n}\right]. \tag{58}$$

This energy correction depends only on j and is called the *fine structure* of the hydrogen atom, since it is of order $\alpha^2 \sim 10^{-4}$ times smaller than the principle energy splittings. This is why α is known as the fine-structure constant. The fine structure of the hydrogen atom is illustrated in figure 4. Note that all levels are shifted down from the Bohr energies, and that for every n and l there are two states corresponding to $j = l - 1/2$ and $j = l + 1/2$, except for s states. Also note that states with the same n and j but different l have the same energies, though this will be shown later not to be true due an effect know as the Lamb shift. As an aside, these fine structure splittings were derived by Sommerfeld by modifying the Bohr theory to allow elliptical orbits and then calculating the energy differences between the different states due to differences in the average velocity of the electron. By using the wrong method he got exactly the right answer, a coincidence which caused much confusion at the time.

Strictly speaking, equation 58 has only been shown to be correct for $l \neq 0$ states, although it turns out to be correct for all l. To do the calculation correctly for $l = 0$, one needs to include the effect of an additional term in the Hamiltonian known as the Darwin term, which is purely an effect of relativistic quantum mechanics and can only be understood in the context of the Dirac theory. It is therefore appropriate to discuss the Dirac theory to achieve a more complete understanding of the fine structure of the hydrogen atom.

4 Dirac Theory

The theory of Paul Dirac represents an attempt to unify the theories of quantum mechanics and special relativity. That is, one seeks a formulation of quantum mechanics which is Lorentz invariant, and hence consistent with special relativity. For a free particle, relativity states that the energy is given by $E^2 = p^2c^2 + m^2c^4$. Associating E with a Hamiltonian in quantum mechanics, one has

$$H^2 = p^2c^2 + m^2c^4. \tag{59}$$

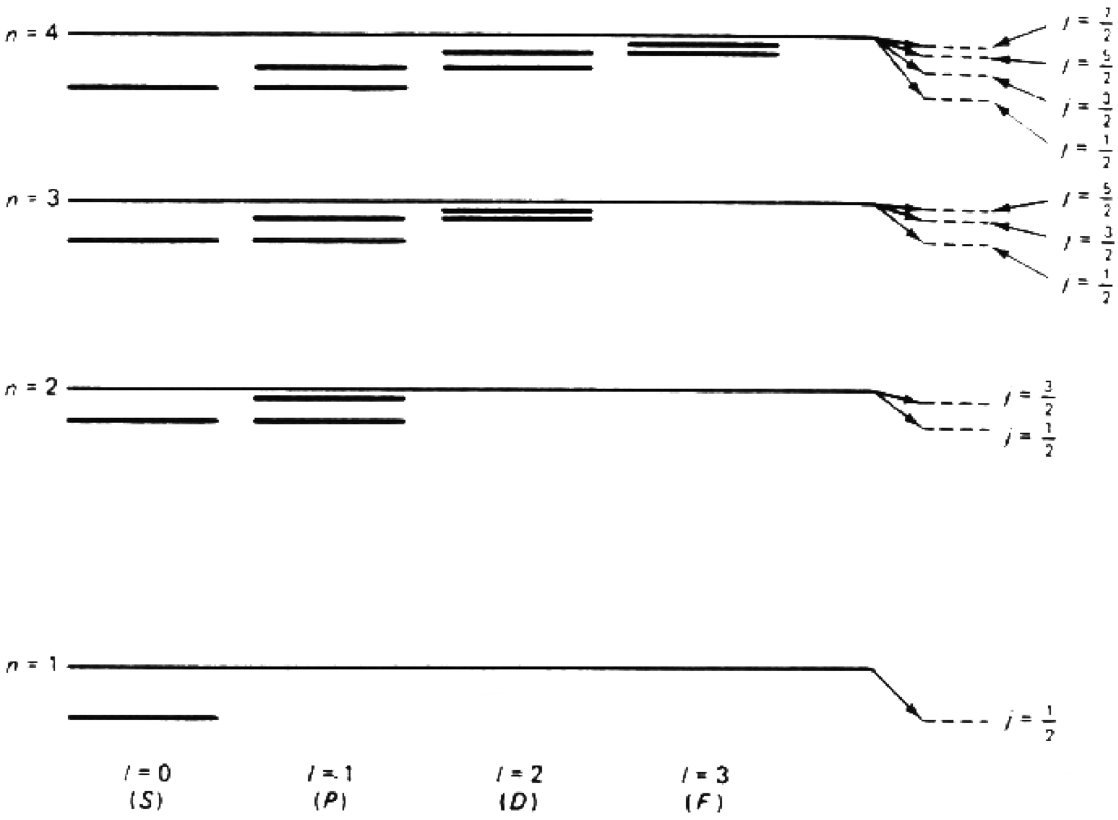

Figure 4: The fine structure of the hydrogen atom. The diagram is not to scale.

If H and p are associated with the same operators as in Schrödinger theory, then one expects the wave equation

$$-\hbar^2 \frac{\partial^2}{\partial t^2}\Psi = (-\hbar^2\nabla^2 c^2 + m^2c^4)\Psi. \tag{60}$$

This is known as the *Klein-Gordan Equation.* Unfortunately, attempts to utilize this equation are not successful, since that which one would wish to interpret as a probability distribution turns out to be not positive definite. To alleviate this problem, the square root may be taken to get

$$H = (p^2c^2 + m^2c^4)^{1/2}. \tag{61}$$

However, this creates a new problem. What is meant by the square root of an operator? The approach is to guess the form of the answer, and the correct guess turns out to be

$$H = c\alpha \cdot \mathbf{p} + \beta mc^2. \tag{62}$$

With this form of the Hamiltonian, the wave equation can be written

$$i\hbar\frac{\partial \chi}{\partial t} = (c\alpha \cdot \mathbf{p} + \beta mc^2)\chi. \tag{63}$$

In order for this to be valid, one hopes that when it is squared the Klein-Gordan equation is recovered. For this to be true, equation 63 must be interpreted as a matrix equation, where α and β are at least 4×4 matrices and the wavefunction χ is a four-component column matrix.

It turns out that equation 63 describes only a particle with spin 1/2. This is fine for application to the hydrogen atom, since the electron has spin 1/2, but why should it be so? The answer is that the linearization of the Klein-Gordan equation is not unique. The particular linearization used here is the simplest one, and happens to describe a particle of spin 1/2, but other more complicated Hamiltonians may be constructed to describe particles of spin $0, 1, 5/2$ and so on. The fact that the relativistic Dirac theory automatically includes the effects of spin leads to an interesting conclusion—spin is a relativistic effect. It can be added by hand to the non-relativistic Schödinger theory with satisfactory results, but spin is a natural consequence of treating quantum mechanics in a completely relativistic fashion.

Including the potential now in the Hamiltonian, equation 63 becomes

$$i\hbar\frac{\partial \chi}{\partial t} = (c\alpha \cdot \mathbf{p} + \beta mc^2 - \frac{Ze^2}{r})\chi. \tag{64}$$

When the square root was taken to linearize the Klein-Gordan equation, both a positive and a negative energy solution was introduced. One can write the wavefunction

$$\chi = \begin{pmatrix} \Psi_+ \\ \Psi_- \end{pmatrix}, \tag{65}$$

where Ψ_+ represents the two components of χ associated with the positive energy solution and Ψ_- represents the components associated with the negative energy solution. The physical interpretation is that Ψ_+ is the particle solution, and Ψ_- represents an anti-particle. Anti-particles are thus predicted by Dirac threory, and the discovery of anti-particles obviously represents a huge triumph for the theory. In hydrogen, however, the contribution of Ψ_- is small compared to Ψ_+. With enough effort, the equations for Ψ_+ and Ψ_- can be decoupled to whatever order is desired. When this is done[4], the Hamiltonian to order v^2/c^2 can be written

$$H = H_s + \Delta H_{rel} + \Delta H_{so} + \Delta H_d, \tag{66}$$

where H_s is the original Schrödinger Hamiltonian, ΔH_{rel} is the relativistic correction to the kinetic energy, ΔH_{so} is the spin-orbit term, and ΔH_d is the previously mentioned Darwin term. The physical origin of the Darwin term is a phenomenon in Dirac theory called *zitterbewegung*, whereby the electron does not move smoothly but instead undergoes extremely rapid small-scale fluctuations, causing the electron to see a smeared-out Coulomb potential of the nucleus.

The Darwin term may be written

$$\Delta H_d = -\frac{e\hbar^2}{8m^2c^2}\nabla^2\Phi. \tag{67}$$

For the hydrogenic-atom potential $\Phi = Ze/r$, this is

$$H_d = -\frac{Ze^2\pi\hbar^2}{2m^2c^2}\delta^3(\mathbf{r}). \tag{68}$$

When first-order perturbation theory is applied, the energy correction depends on $|\Psi(0)|^2$. This term will only contribute for s states ($l = 0$), since only these wavefunctions have non-zero probability for finding the electron at the origin. The energy correction for $l = 0$ can be calculated to be

$$\Delta E_d = (Z\alpha)^4 mc^2 \frac{1}{2n^3}. \tag{69}$$

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[4] See Bjorken and Drell chapter 4 for a thorough discussion of the transformation.

Including this term, the fine-structure splitting given by equation 58 can be reproduced for all l. All the effects that go into fine structure are thus a natural concequence of the Dirac theory.

The hydrogen atom can be solved exactly in Dirac theory, where the states found are simultaneous eigenstates of H, J^2, and J_z, since these operators can be shown to mutually commute. The exact energy levels in Dirac theory are

$$E_{nj} = mc^2 \left[1 + \left(\frac{Z\alpha}{n - (j + \frac{1}{2}) + \sqrt{(j + \frac{1}{2})^2 - (Z\alpha)^2}} \right)^2 \right]^{-1/2} . \tag{70}$$

This can be expanded in powers of $Z\alpha$, yielding

$$E_{nj} = mc^2 \left\{ 1 - \frac{1}{2} \frac{(Z\alpha)^2}{n^2} \left[1 + \frac{(Z\alpha)^2}{n} \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right) \right] + \ldots \right\} . \tag{71}$$

This includes an amount mc^2 due to the relativistic energy associated with the rest mass of the electron, along with the principle energy levels and fine structure, in exact agreement to order $(Z\alpha)^4$ with what was previously calculated. However, even this exact solution in Dirac theory is not a complete description of the hydrogen atom, and so the the next section describes further effects not yet discussed.

5 Smaller Effects[5]

One correction to the Dirac theory involves the use of the reduced electron mass, which was previously discussed. Another involves considering that the proton has some finite size and is not exactly a point charge. Instead of having a $V = -Ze^2/r$ potential energy, one might imagine something like

$$V = \begin{cases} -\frac{Ze^2}{r} & r > r_0 \\ -V_0 & r \le r_0, \end{cases} \tag{72}$$

where r_0 is some representative size of the proton $\sim 10^{-13}$ cm. Like the Darwin term, this will only affect s states, since only in these states can the electron be found at the origin. However, even for s states this correction turns out to be of the order $\Delta E \sim 10^{-10}$eV, and hence it is not very important. Other effects will now be discussed which are more important, not

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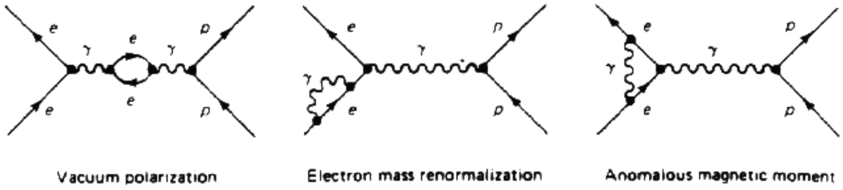
[5] From this point on, effects will only be discussed only in terms of the hydrogen atom, although they can be extended to other one-electron atoms.



Vacuum polarization Electron mass renormalization Anomalous magnetic moment

Figure 5: Feynman loop diagrams showing some effects that contribute to the Lamb shift.

Table 3: Contribution of different effects to the energy splitting of $2s_{1/2}$ and $2p_{1/2}$ in hydrogen. Numbers are given in units of frequency $\nu = E/h$.

Effect	Energy contribution
Vacuum polarization	-27 MHz
Electron mass renormalization	+1017 MHz
Anomalous magnetic moment	+68 MHz
Total	+1058 MHz

only because the energy shifts are larger, but because they split the energy levels of states that would otherwise be degenerate.

5.1 The Lamb Shift

According to Dirac and Schrödinger theory, states with the same n and j quantum numbers but different l quantum numbers ought to be degenerate. However, a famous experiment by Lamb and Retherford in 1947 showed that the $2s_{1/2}(n = 2, l = 0, j = 1/2)$ and $2p_{1/2}(n = 2, l = 1, j = 1/2)$ states of the hydrogen atom were not degenerate, but that the s state had slightly higher energy by an amount now known to be $E/h = 1057.864\text{MHz}$. The effect is explained by the theory of quantum electrodynamics, in which the electromagnetic interaction itself is quantized. Some of the effects of this theory which cause the Lamb shift are shown in the Feynman diagrams of figure 5. Table 3 shows how much each of these contribute to the splitting of $2s_{1/2}$ and $2p_{1/2}$. The most important effect is illustrated by the center diagram, which is a result of the fact that the ground state of the electromagnetic field is not zero, but rather the field undergoes "vacuum fluctuations" that interact with the electron. Any discussion of the calculation is beyond the scope of this paper, so the answers will merely be given. For $l = 0$,

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3}\{k(n,0)\}, \tag{73}$$

where $k(n,0)$ is a numerical factor which varies slightly with n from 12.7 to 13.2. For $l \neq 0$,

$$\Delta E_{Lamb} = \alpha^5 mc^2 \frac{1}{4n^3}\left\{k(n,l) \pm \frac{1}{\pi(j+\frac{1}{2})(l+\frac{1}{2})}\right\} \tag{74}$$

for $j = l \pm 1/2$, where $k(n,l)$ is a small numerical factor < 0.05 which varies slightly with n and l. Notice that the Lamb shift is very small except for $l = 0$.

5.2 Hyperfine Structure

To this point, the nucleus has been assumed to interact with the electron only through its electric field. However, like the electron, the proton has spin angular momentum with $s = 1/2$, and associated with this angular momentum is an intrinsic dipole moment

$$\mu_{\mathrm{p}} = \gamma_p \frac{e}{Mc}\mathbf{S}_{\mathrm{p}}, \tag{75}$$

where M is the proton mass and γ_p is a numerical factor known experimentally to be $\gamma_p = 2.7928$. Note that the proton dipole moment is weaker than the electron dipole moment by roughly a factor of $M/m \sim 2000$, and hence one expects the associated effects to be small, even in comparison to fine structure, so again treating the corrections as a perturbation is justified. The proton dipole moment will interact with both the spin dipole moment of the electron and the orbital dipole moment of the electron, and so there are two new contributions to the Hamiltonian, the nuclear spin-orbit interaction and the spin-spin interaction. The derivation for the nuclear spin-orbit Hamiltonian is the same as for the electron spin-orbit Hamiltonian, except that the calculation is done in the frame of the proton and hence there is no factor of 1/2 from the Thomas precession. The nuclear spin-orbit Hamiltonian is

$$\Delta H_{pso} = \frac{\gamma_p e^2}{mMc^2 r^3}\mathbf{L}\cdot\mathbf{S}_{\mathrm{p}}. \tag{76}$$

The spin-spin Hamiltonian can be derived by considering the field produced by the proton spin dipole, which can be written

$$\mathbf{B}(\mathbf{r}) = \frac{1}{r^3}\left[3\frac{(\mu_{\mathrm{p}}\cdot\mathbf{r})\mathbf{r}}{r^2} - \mu_{\mathrm{p}}\right] + \frac{8\pi}{3}\mu_{\mathrm{p}}\delta^3(\mathbf{r}). \tag{77}$$

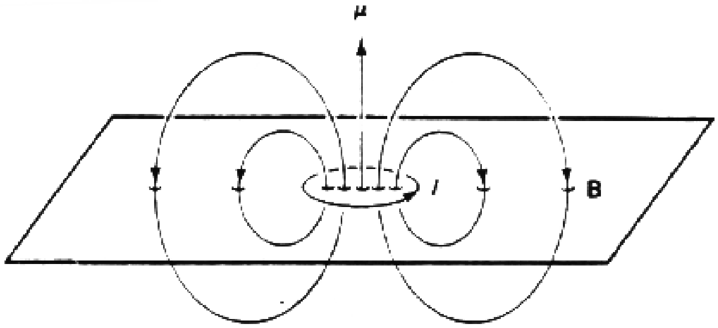


Figure 6: The field of a magnetic dipole. All **B** field lines cross the plane of the dipole going up inside the loop and down outside the loop.

The first term is just the usual field associated with a magnetic dipole, but the second term requires special explanation. Normally, when one considers a dipole field, it is implicit that one is interested in the field far from the dipole—that is, at distances far from the source compared to the size of the current loop producing the dipole. However, every field line outside the loop must return inside the loop, as shown in figure 6. If the size of the current loop goes to zero, then the field will be infinite at the origin, and this contribution is what is reflected by the second term in equation 77. The electron has additional energy

$$\Delta E_{ss} = -\mu_{\mathrm{e}} \cdot \mathbf{B} \tag{78}$$

due to the interaction of its spin dipole with this field, and hence the spin-spin Hamiltonian is

$$\Delta H_{ss} = \frac{\gamma_p e^2}{mMc^2}\left\{\frac{1}{r^3}[3(\mathbf{S}_{\mathrm{p}}\cdot\hat{r})(\mathbf{S}_{\mathrm{e}}\cdot\hat{r}) - (\mathbf{S}_{\mathrm{p}}\cdot\mathbf{S}_{\mathrm{e}})] + \frac{8\pi}{3}(\mathbf{S}_{\mathrm{p}}\cdot\mathbf{S}_{\mathrm{e}})\delta^3(\mathbf{r})\right\}. \tag{79}$$

The operator J_z does not commute with this Hamiltonian. However, one can define the total angular momentum

$$\mathbf{F} = \mathbf{L} + \mathbf{S}_{\mathrm{e}} + \mathbf{S}_{\mathrm{p}} = \mathbf{J} + \mathbf{S}_{\mathrm{p}}. \tag{80}$$

The corresponding operators F^2 and F_z commute with the Hamiltonian, and they introduce new quantum numbers f and m_f through the relations

$$F^2\Psi = f(f+1)\hbar^2\Psi \tag{81}$$

$$F_z\Psi = m_f\hbar\Psi. \tag{82}$$

The quantum number f has possible values $f = j + 1/2, j - 1/2$ since the proton is spin 1/2, and hence every energy level associated with a particular set of quantum numbers n, l, and j will be split into two levels of slightly different energy, depending on the relative orientation of the proton magnetic dipole with the electron state.

Consider first the case $l = 0$, since the hyperfine splitting of the hydrogen atom ground state is of the most interest. Since the electron has no orbital angular momentum, there is no nuclear spin-orbit effect. It can be shown that because the wavefunction has spherical symmetry, only the delta function term contributes from the spin-spin Hamiltonian. First order perturbation theory yields

$$\Delta E_{hf} = \frac{8\pi\gamma_p e^2}{3mMc^2}(\mathbf{S}_{\mathrm{p}} \cdot \mathbf{S}_{\mathrm{e}})|\Psi(0)|^2. \tag{83}$$

Like the Darwin term, this depends on the probability of finding the electron at the origin. The value of $\mathbf{S}_{\mathrm{p}} \cdot \mathbf{S}_{\mathrm{e}}$ can be found by squaring $\mathbf{F}$, which with $l = 0$ gives

$$F^2 = S_e^2 + S_p^2 + 2\mathbf{S}_{\mathrm{e}} \cdot \mathbf{S}_{\mathrm{p}}. \tag{84}$$

Hence

$$\mathbf{S}_{\mathrm{p}} \cdot \mathbf{S}_{\mathrm{e}} = \frac{\hbar^2}{2}[f(f+1) - s_p(s_p+1) - s_e(s_e+1)] = \frac{\hbar^2}{2}\left[f(f+1) - \frac{3}{2}\right], \tag{85}$$

where the last step includes the values $s_e = s_p = 1/2$. The hyperfine energy shift for $l = 0$ is then

$$\Delta E_{hf} = \left(\frac{m}{M}\right)\alpha^4 mc^2 \frac{4\gamma_p}{3n^3}\left[f(f+1) - \frac{3}{2}\right]. \tag{86}$$

It is easy to see from this expression that the hyperfine splittings are smaller than fine structure by a factor of M/m. For the specific case of the ground state of the hydrogen atom ($n = 1$), the energy separation between the states of $f = 1$ and $f = 0$ is

$$\Delta E_{hf}(f = 1) - \Delta E_{hf}(f = 0) = 5.9 \times 10^{-6}\mathrm{eV}. \tag{87}$$

The photon corresponding to the transition between these two states has frequency and wavelength

$$\begin{aligned} \nu &= 1420.4057517667(10)\mathrm{MHz} && (88)\\ \lambda &= 21.1\mathrm{cm}. && (89) \end{aligned}$$

This is the source of the famous "21 cm line," which is extremely useful to radio astronomers for tracking hydrogen in the interstellar medium of galaxies. The transition is exceedingly slow, but the huge amounts of interstellar hydrogen make it readily observable. It is too slow to be seen in a terrestrial laboratory by spontaneous emission, but the frequency can be measured to very high accuracy by using stimulated emission, and this frequency is in fact one of the best-known numbers in all of physics.

For $l \neq 0$, the δ term does not contribute but the other terms in the spin-spin Hamiltonian as well as the nuclear spin-orbit Hamiltonian do contribute. The calculation is much harder but yields

$$\Delta E_{hf} = \left(\frac{m}{M}\right) \alpha^4 mc^2 \frac{\gamma_p}{2n^3} \frac{\pm 1}{(f+\frac{1}{2})(l+\frac{1}{2})} \tag{90}$$

for $f = j \pm 1/2$.

Figure 7 shows a revised version of the structure of the hydrogen atom, including the Lamb shift and hyperfine structure. Note that each hyperfine state still has a $2f+1$ degeneracy associated with the different possible values of m_f which correspond to different orientations of the total angular momentum with respect to the z-axis. For example, in the ground state, the higher-energy state $f = 1$ is actually a triplet, consisting of three degenerate states, and the $f = 0$ state is a singlet. This degeneracy can be broken by the presence of an external magnetic field.

5.3 The Zeeman Effect

When considering the Zeeman effect, it is easiest first to consider the hydrogen atom without hyperfine structure. Then m_j is a good quantum number, and the atom has a $2j+1$ degeneracy associated with the different possible values of m_j. In the presence of an external magnetic field, these different states will have different energies due to having different orientations of the magnetic dipoles in the external field. The splitting of these energy levels is called the Zeeman effect.

Figure 8 illustrates the geometry of the Zeeman effect. The total magnetic dipole moment of the electron is

$$\mu = \mu_{\mathrm{l}} + \mu_{\mathrm{s}} = -\frac{\mu_b}{\hbar}(\mathbf{L} + 2\mathbf{S}), \tag{91}$$

where $g_l = 1$ and $g_s = 2$ have been used. Because of the difference in the orbital and spin gyromagnetic ratios of the electron, this is not in general parallel to

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \tag{92}$$

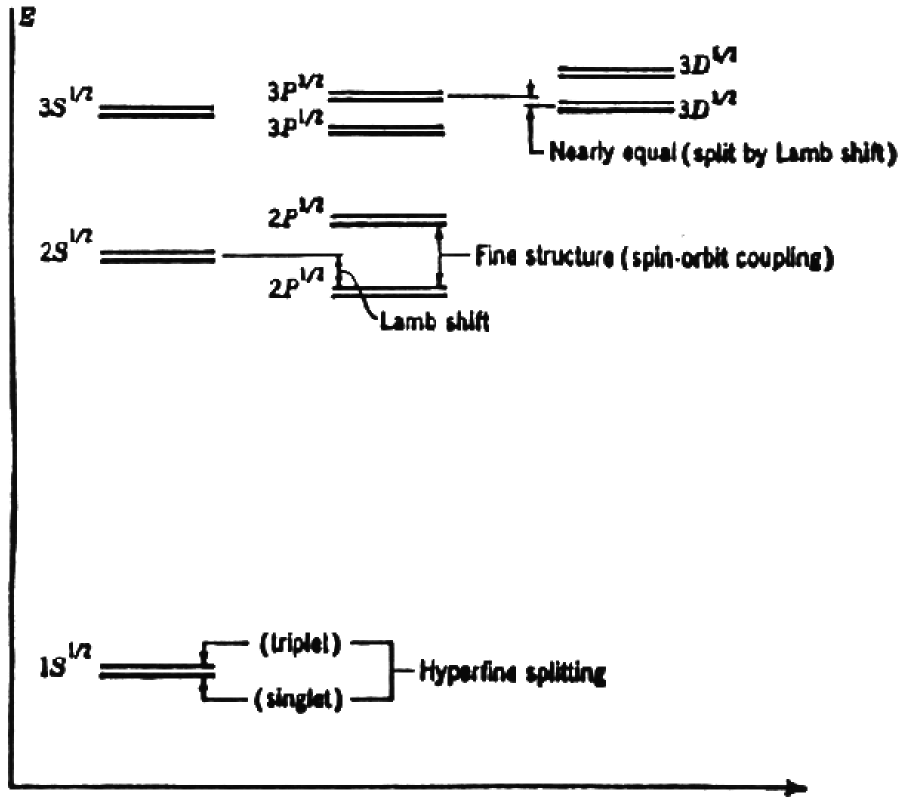


Figure 7: Some low-energy states of the hydrogen atom, including fine structure, hyperfine structure, and the Lamb shift.

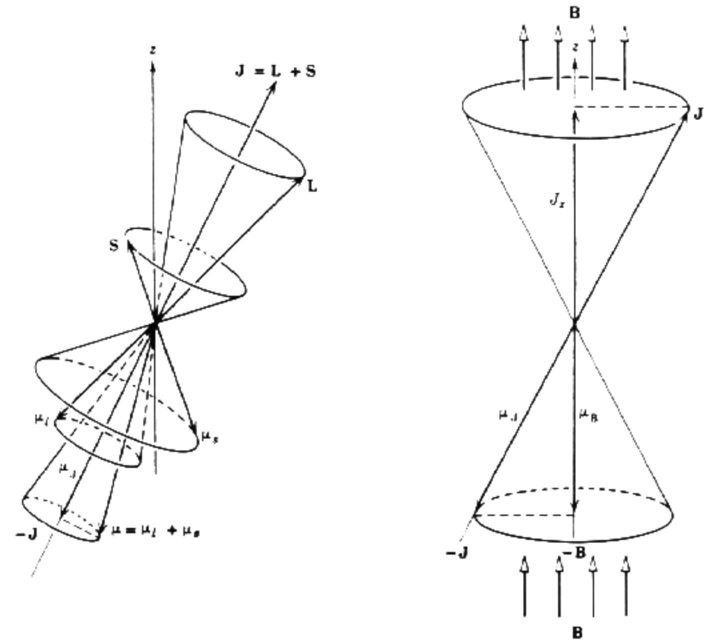


Figure 8: Geometry of the Zeeman effect. On the left, the total dipole moment μ precesses around the total angular momentum **J**. On the right, **J** precesses much more slowly about the magnetic field.

So, as **L** and **S** precess about **J**, the total dipole moment μ also precesses about **J**. Assuming the external field to be in the z direction, this field causes **J** to precess about the z-axis. Typical internal magnetic fields in the hydrogen atom can be shown to be of the order 1 Tesla. If the external field is much weaker than 1 Tesla, which it is for almost all practical purposes, then the precession of **J** around the z-axis will take place much more slowly than the precession of μ around **J**. The Hamiltonian of the Zeeman effect is

$$\Delta H_z = -\mu \cdot \mathbf{B} = -\mu_B B, \tag{93}$$

where μ_B is the projection of the dipole moment onto the direction of the field, the z-axis. Because of the difference in the precession rates, it is reasonable to evaluate μ_b by first evaluating the projection of μ onto **J**, called μ_J, and then evaluating the projection of this onto **B**, thus giving some average projection of μ onto **B**. First, the projection of μ onto **J** is

$$\mu_J = \frac{\mu \cdot \mathbf{J}}{J} = -\frac{\mu_b}{\hbar} \frac{(\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S})}{J}. \tag{94}$$

Then

$$\mu_B = \mu_J \frac{\mathbf{J} \cdot \mathbf{B}}{JB} = \mu_J \frac{J_z}{J} = -\frac{\mu_b}{\hbar} \frac{(\mathbf{L} + 2\mathbf{S}) \cdot (\mathbf{L} + \mathbf{S}) J_z}{J^2}. \tag{95}$$

Evaluating the dot product using again that $J^2 = L^2 + S^2 + 2\mathbf{L} \cdot \mathbf{S}$, this becomes

$$\mu_B = -\frac{\mu_b}{\hbar} \frac{(3J^2 + S^2 - L^2)}{2J^2} J_z. \tag{96}$$

So when first order perturbation theory is applied, the energy shift is

$$\Delta E_z = \mu_b B g m_j, \tag{97}$$

where

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \tag{98}$$

is called the Landé g factor for the particular state being considered. Note that if $s = 0$, then $j = l$ so $g = 1$, and if $l = 0$, $j = s$ so $g = 2$. The Landé g factor thus gives some effective gyromagnetic ratio for the electron when the total dipole moment is partially from orbital angular momentum and partially from spin. From equation 97, it can be seen that the energy shift caused by the Zeeman effect is linear in B and m_j, so for a set of states with particular values of n, l, and j, the individual states with different m_j will be equally spaced in energy, separated by $\mu_b B g$. However, the spacing will

Table 4: Differences in energy of some particular pairs of states in the hydrogen atom. The state of lower energy is listed first.

Effect	States	Energy difference(eV)
Principle splitting	$1s_{1/2}$,$2s_{1/2}$	10.2
Fine structure	$2p_{1/2}$,$2p_{3/2}$	4.5×10^{-5}
Lamb shift	$2p_{1/2}$,$2s_{1/2}$	4.4×10^{-6}
	$3d_{3/2}$,$3p_{3/2}$	1.7×10^{-8}
Hyperfine structure	$1s_{1/2}(f = 0)$,$1s_{1/2}(f = 1)$	5.9×10^{-6}
Zeeman effect ($B = 10$gauss)	$2s_{1/2}(m_j = -1/2)$,$2s_{1/2}(m_j = +1/2)$	1.2×10^{-7}

in general be different for a set of states with different n, l, and j due to the difference in the Landé g factor.

Including hyperfine structure with the Zeeman effect is more difficult, since the field associated with the proton magnetic dipole moment is weak, and hence it does not take a particularly strong external field to make the Zeeman effect comparable in magnitude to the strength of the hyperfine interactions. The approximation of small external field is thus not practical when discussing the Zeeman splitting of hyperfine structure. However, it can be treated, and the result for the most important case of the Zeeman splitting of the hyperfine levels in the ground state of hydrogen[6] is shown in figure 9. The degeneracy of the triplet state is lifted, the three states of $m_f = -1, 0, +1$ having different energies in the external field. Notice how the splitting is linear for small external field, but then deviates as the field gets larger. The "21 cm" transitions shown on the right will have slightly different energies, and measuring the amount of this splitting is a good tool for radio astronomers to measure magnetic fields in the interstellar medium.

6 Conclusions

To summarize the relative strengths of the effects discussed in this paper, table 4 gives some numbers for comparison of some energy splittings in the hydrogen atom. Note how much larger the principle energy splittings are than any of the other effects.

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[6] See Feynman, volume III, chapter 12 for a discussion of the calculation of the splittings.

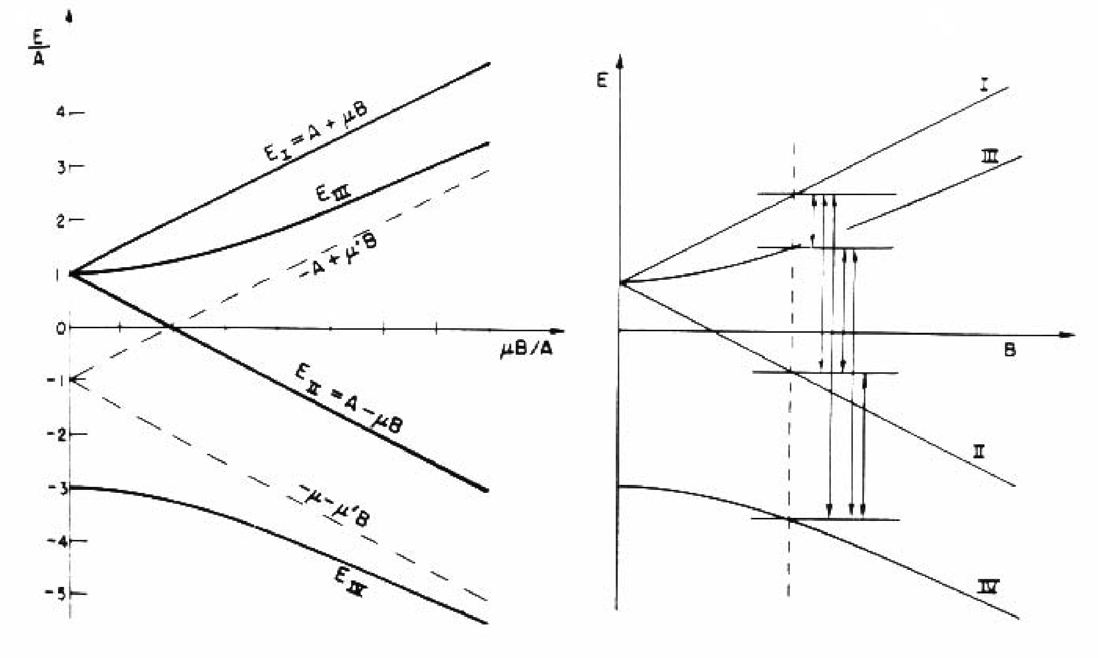

Figure 9: On left, Zeeman splitting of the hyperfine levels in the ground state ($1s_{1/2}$) of hydrogen. On right, some possible transitions between these states.

The hydrogen atom is one of the most important dynamical systems in all of physics, for several reasons:

1. Hydrogen is the most abundant stuff in the known universe. About 92% by number of the nuclei in the universe are hydrogen, 75% by mass.
2. Even though it is a relatively simple system, the physics of the hydrogen atom contains many important quantum mechanical concepts that extend to more complex atoms and other systems.
3. Because of its relative simplicity, the hydrogen atom can be solved theoretically to very high precision. Experimental measurements involving hydrogen thus offer very sensitive tests of modern physical theories, like quantum electrodynamics.

Every physicist should therefore have a solid understanding of the physics of the hydrogen atom.

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