

Ground and Excited States of the Hydrogen Atom in External Magnetic Field

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Abstract

Our main objective in this paper is to discuss and solve the necessary equations which explains the presence of a hydrogen atom in an external strong magnetic field. For this purpose we will discuss first the Maxwell's equations for point charge. After that, we will formulate the Schrödinger's equation which represents the interaction of electromagnetic field with a charged particle. As an example of this case we will discuss the solution of the Schrödinger's equation for a hydrogen atom which is presenting in an external strong magnetic field parallel to the z-axis. For this atom we will consider the cases of the ground and first two excited states. Variations of the calculated energy eigenvalues with respect to the intensity of the field are given.

1. Introduction

We can consider the point charge as the elementary part of electrodynamics. Now, what is a point charge? A point charge can be defined as a term that we use for a charge that exist at a single point in space and does not have neither area nor volume; it cannot be measured directly since it only exists in theory [1]. What makes it interesting is that, even though we may think that nothing major or drastic should happen to a point charge since it is just a single point in space, but, as a matter of fact, the point charge do have some interactions with its surrounding. Here, by surrounding, we mean the electromagnetic field as it concerns electrodynamics. We can specify some limiting aspects as we will solely focus on what happens with the point charge. In electrodynamics, basically, there ought to be an interaction of charges with an electromagnetic field. However, the physical concept of the field in electrodynamics differs essentially from the field concept in Newtonian mechanics [2]. Take gravitational field as an example, which is the space in which gravitational forces act. In Newtonian mechanics, the values of these forces at any point of the field is determined by the instantaneous positions of the gravitating bodies no matter how far they are from the given point [1]. Such a field representation is not satisfactory in electrodynamics: during the time that an electromagnetic disturbance takes to move from one charge to another, the latter can move at a very great distance. Often, elementary charges (electrons, protons) have velocities close to the velocity of propagation of electromagnetic disturbances [2].

In the electrodynamics of elementary charges, the finite velocity of propagation of electromagnetic disturbances is of fundamental significance. Considering point charges, the action of a field on the charge is always determined only by the field at the point where the charge is located, and only at the instant when the charge is at this point. As opposed to the action at Newtonian mechanics, such interactions are termed as short-range [2]. Simply put, the equations of electrodynamics must describe the propagation of electromagnetic disturbances in space and the interaction of charges with the field, directly. In order to do that, we shall establish the basic equations of electrodynamics, starting from certain elementary laws. These laws will be used in the absence of matter consisting of atoms or, as usually said in electrodynamics, in the absence of a "material medium". In other words, we can also say: in free space or vacuum. As is well-known, the four quantities that are used to describe electromagnetic field are the electric field,

the electric induction, the magnetic field and the magnetic induction [2]. The force acting on unit electric charge at a given point in space is called the electric field intensity, but, instead of the field intensity, we will simply state about the field at given point in space. Similarly, we just shorten magnetic field intensity to magnetic field.

The basic equations governing the motion of charges and currents in an electromagnetic field are the well-known Maxwell's equations [2]. In dealing with the interaction of an atom with external magnetic or electric field, it is necessary to derive a Hamiltonian describing the system with a suitably chosen vector and scalar potentials.

In the present paper we calculated the energy eigenvalues of the ground and first few excited states of the hydrogen atom in an external magnetic field, by solving the Schrödinger equation for these states

2. The Maxwell's System of Equations

The Maxwell's system of equations in Gaussian units in the vacuum are [2]:

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t} \quad (2.1)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (2.2)$$

$$\nabla \times \mathbf{B} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + \frac{4\pi}{c} \mathbf{j} \quad (2.3)$$

$$\nabla \cdot \mathbf{E} = 4\pi\rho \quad (2.4)$$

The conservation equation

$$\nabla \cdot \mathbf{J} + \frac{\partial \rho}{\partial t} = 0$$

is satisfied automatically.

In these equations, we consider ρ and \mathbf{j} to be known. The unknowns, to be determined, are the fields \mathbf{E} and \mathbf{B} . In order to satisfy equations (2.1) and (2.2), it is enough to put

$$\mathbf{H} = \nabla \times \mathbf{A} \quad (2.5)$$

and

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} - \nabla \phi \quad (2.6)$$

From equation (2.5) if we add the gradient of an arbitrary function to the vector potential, the magnetic field will not change, so that

$$\mathbf{A} = \mathbf{A}' + \nabla f(x, y, z, t) \quad (2.7)$$

In order that the addition of ∇f should not affect the electric field, we must also change the scalar potential:

$$\phi = \phi' - \frac{1}{c} \frac{\partial f}{\partial t} \quad (2.8)$$

Then, for the electric field, we obtain

$$\mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{A}'}{\partial t} - \nabla \phi = -\frac{1}{c} \frac{\partial \mathbf{A}'}{\partial t} - \nabla \phi' \quad (2.9)$$

The transformation equations (2.7), (2.8) are called the Gauge transformations [2]. Substituting (2.5) and (2.6) in (2.3) gives

$$\nabla \times \nabla \times \mathbf{A} = -\frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} - \frac{1}{c} \frac{\partial}{\partial t} \nabla \phi + \frac{4\pi}{c} \mathbf{j} \quad (2.10)$$

Since $\nabla \times \nabla \times \mathbf{A} = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$, then, (2.9) is reduced to the following form:

$$-\nabla^2 \mathbf{A} + \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} + \nabla \left(\nabla \cdot \mathbf{A} + \frac{1}{c} \frac{\partial \phi}{\partial t} \right) = \frac{4\pi}{c} \mathbf{j} \quad (2.11)$$

Putting $a = \nabla \cdot \mathbf{A} + \frac{1}{c} \frac{\partial \phi}{\partial t}$ and applying the transformations (2.7) and (2.8) on the potentials, we have

$$a = \nabla \cdot \mathbf{A} + \frac{1}{c} \frac{\partial \phi}{\partial t} = \nabla \cdot \mathbf{A}' + \frac{1}{c} \frac{\partial \phi'}{\partial t} + \nabla^2 f - \frac{1}{c^2} \frac{\partial^2 f}{\partial t^2} \quad (2.12)$$

If the arbitrary function f has been chosen to satisfy the equation

$$\nabla^2 f - \frac{1}{c^2} \frac{\partial^2 f}{\partial t^2} = a \quad (2.13)$$

Then, from (2.12), it is obvious that the potentials will be subject to the condition

$$\nabla \cdot \mathbf{A}' + \frac{1}{c} \frac{\partial \phi'}{\partial t} = 0 \quad (2.14)$$

This is called the Lorentz condition [2]. If we consider that the transformation (2.7) and (2.8) are performed so that the Lorentz condition is satisfied; the primes in the potentials can then be omitted, by setting a equals to zero.

From the Lorentz condition and (2.11), we obtain the equation for a vector potential:

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = -\frac{4\pi}{c} \mathbf{j} \quad (2.15)$$

From (2.4) and (2.6), we have

$$\nabla \cdot \mathbf{E} = -\frac{1}{c} \frac{\partial}{\partial t} \nabla \cdot \mathbf{A} - \nabla^2 \phi = 4\pi\rho$$

Substituting $\nabla \cdot \mathbf{A}$ from the Lorentz condition (2.14), we obtain

$$\nabla^2 \phi - \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = -4\pi\rho \quad (2.16)$$

Equations (2.15) and (2.16) each contains only one unknown. Therefore, each equation for potential does not depend on the rest and can be solved separately. The equations for potentials are second order with respect to coordinate and time derivatives. For a solution, it is necessary to give not only the initial values of the potentials, but also the initial values of their time derivatives.

3. The Schrödinger Equation for an Electron in an Electromagnetic Field

In the absence of interaction with the electromagnetic field, it is easily seen that the Hamilton equations [3]

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial x_i} \quad (3.1)$$

with

$$H = \frac{\mathbf{P}^2}{2\mu} + V(\mathbf{r}) \quad (3.2)$$

yield

$$\mu \frac{\partial^2 x_i}{\partial t^2} = -\frac{\partial V}{\partial x_i} = F_i \quad (3.3)$$

The Hamiltonian for the interaction of an electron with an external electromagnetic field, represented by the potentials $\mathbf{A}(\mathbf{r}, t)$, $\phi(\mathbf{r}, t)$ is given by [3]

$$H = \frac{(\mathbf{P} + \frac{e}{c}\mathbf{A}(\mathbf{r}, t))^2}{2\mu} - e\phi(\mathbf{r}, t) \quad (3.4)$$

The Hamilton equations of motion are

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial p_i} = \frac{p_i + \frac{e}{c}A_i}{\mu} \quad (3.5)$$

and

$$\frac{dp_i}{dt} = -\frac{\partial H}{\partial x_i} = -\frac{e}{\mu c} \left(p_k + \frac{e}{c} A_k \right) \frac{\partial A_k}{\partial x_i} + e \frac{\partial \phi}{\partial x_i} \quad (3.6)$$

Thus, from (3.1)

$$\begin{aligned} \mu \frac{d^2 x_i}{dt^2} &= \frac{d}{dt} \left(p_i + \frac{e}{c} A_i \right) \\ &= \frac{dp_i}{dt} + \frac{e}{c} \left(\frac{\partial A_i}{\partial t} + \frac{\partial A_i}{\partial x_k} \frac{dx_k}{dt} \right) = e \frac{\partial \phi}{\partial x_i} + \frac{e}{c} \frac{\partial A_i}{\partial t} - \frac{e}{c} \frac{\partial A_k}{\partial x_k} \frac{dx_k}{dt} + \frac{e}{c} \frac{\partial A_i}{\partial x_k} \frac{dx_k}{dt} \end{aligned} \quad (3.7)$$

The first two terms are seen to be equal to $-eE_i$ and the second two terms can be checked to equal $-\frac{e}{c} \mathbf{v} \wedge \mathbf{B}$. Thus H given by (3.4) is the correct choice of Hamiltonian.

The Schrödinger equation for an electron in an electromagnetic field takes the form [3]

$$\left[\frac{(\frac{\hbar}{i}\nabla + \frac{e}{c}\mathbf{A}(\mathbf{r}, t))^2}{2\mu} - e\phi(\mathbf{r}, t) \right] \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad (3.8)$$

where we have replaced the operator \mathbf{P} by $\frac{\hbar}{i}\nabla$. Before proceeding with the solution of the energy eigenvalue equation, we need to ask what happens to gauge invariance. If we write the equation in terms of \mathbf{A}' and ϕ' , defined in (2.7) and (2.8), the preceding equation takes the form

$$\left[\frac{(\frac{\hbar}{i}\nabla + \frac{e}{c}\mathbf{A}(\mathbf{r}, t) + \frac{e}{c}\nabla f(\mathbf{r}, t))^2}{2\mu} - e\phi'(\mathbf{r}, t) + \frac{e}{c} \frac{\partial f(\mathbf{r}, t)}{\partial t} \right] \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad (3.9)$$

which looks like a different equation. It is easy to see that if the transformations (2.7) and (2.8) are accompanied by a phase change with a wave function $\psi(\mathbf{r}, t)$ to $\psi'(\mathbf{r}, t)$ where [3]

$$\psi'(\mathbf{r}, t) = e^{i\Lambda(\mathbf{r}, t)}\psi(\mathbf{r}, t) \quad (3.10)$$

then, since

$$\frac{\partial \psi}{\partial t} = -i \frac{\partial \Lambda}{\partial t} \psi + e^{-i\Lambda} \frac{\partial \psi'}{\partial t} \quad (3.11)$$

and

$$\frac{\hbar}{i} \nabla \psi = -\hbar (\nabla \Lambda) \psi - e^{-i\Lambda} \frac{\hbar}{i} \nabla \psi' \quad (3.12)$$

we get the original equation in terms of \mathbf{A}' , ϕ' and ψ' provided

$$\Lambda(\mathbf{r}, t) = \frac{e}{\hbar c} f(\mathbf{r}, t) \quad (3.13)$$

Let us return to Schrödinger equation, we shall specialize to time-independent field so that $\mathbf{A} = \mathbf{A}(\mathbf{r})$ and $\phi = \phi(\mathbf{r})$. In that case we can write

$$\psi(\mathbf{r}, t) = e^{-i\frac{Et}{\hbar}} \psi(\mathbf{r}) \quad (3.14)$$

and

$$\left[\frac{1}{2\mu} \left(\frac{\hbar}{i} \nabla + \frac{e}{c} \mathbf{A} \right) \cdot \left(\frac{\hbar}{i} \nabla + \frac{e}{c} \mathbf{A} \right) - e\phi(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (3.15)$$

Equation (3.15) can be written in the form

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi - \frac{ie\hbar}{\mu c} \mathbf{A} \cdot \nabla \psi - \frac{ie\hbar}{2\mu c} (\nabla \cdot \mathbf{A}) \psi + \frac{e^2}{2\mu c^2} A^2 \psi - e\phi(\mathbf{r}) \psi = E\psi \quad (3.16)$$

We now make use of the freedom to choose a gauge function $f(\mathbf{r})$ such that $\nabla \cdot \mathbf{A}(\mathbf{r}) = 0$ to get

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi - \frac{ie\hbar}{\mu c} \mathbf{A} \cdot \nabla \psi + \frac{e^2}{2\mu c^2} A^2 \psi - e\phi(\mathbf{r}) \psi = E\psi. \quad (3.17)$$

4. The Small B-field and the Normal Zeeman Effect

For a constant uniform magnetic field, \mathbf{B} , we may take [3]

$$\mathbf{A} = \frac{-1}{2} \mathbf{r} \wedge \mathbf{B} \quad (4.1)$$

This means that the three components of \mathbf{A} are

$$\mathbf{A} = \frac{-1}{2} (y B_z - z B_y, z B_x - x B_z, x B_y - y B_x). \quad (4.2)$$

and consequently $\nabla \wedge \mathbf{A} = \mathbf{B}$. Hence the second term in (3.17) becomes

$$-\frac{ie\hbar}{2\mu c} (\mathbf{B} \wedge \mathbf{r}) \cdot \nabla \psi = \frac{e}{2\mu c} \mathbf{B} \cdot \mathbf{r} \wedge \frac{\hbar}{i} \nabla \psi = \frac{e}{2\mu c} \mathbf{B} \cdot \mathbf{L} \psi \quad (4.3)$$

If the \mathbf{B} -field is small and parallel to the z -axis, equation (3.17) after neglecting the term $\frac{e^2}{2\mu c^2} A^2 \psi$ and setting $\phi(\mathbf{r}) = 0$, is solved by the perturbation theory with

$$H' = \frac{e}{2\mu c} \mathbf{B} \cdot \mathbf{L} = \frac{e}{2\mu c} B L_z = \omega_L L_z \quad (4.4)$$

where ω_L is known as the Larmor frequency [3].

If the unperturbed Hamiltonian has spherical symmetry, the eigenstates are given by $u_{n\ell m}$ such that the perturbation energy for such a state is given by

$$E' = \hbar \omega_L m \quad (4.5)$$

where m is the z -component of the angular momentum eigenvalue, with

$$m = -\ell, -\ell + 1, -\ell + 2, \dots, \ell.$$

This result is called the normal Zeeman effect [3], the splitting of the energy levels into components (as m varies) due to the application of the constant weak magnetic field on the atom. Note that in the current model, we have not included the spin of the electron.

5. Large Magnetic Field

If we take into account the quadratic term in \mathbf{B} , the Schrödinger equation (3.17), with $\phi = 0$, takes the form

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi + \frac{eB}{2\mu c} L_z \psi + \frac{e^2 B^2}{8\mu c^2} (x^2 + y^2) \psi = E \psi \quad (5.1)$$

The presence of the potential $(x^2 + y^2)$ suggests the use of cylindrical coordinates for the separation of the variables. Writing

$$x = \rho \cos \varphi, y = \rho \sin \varphi \quad (5.2)$$

the Laplacian operator is then given by

$$\nabla^2 = \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \varphi^2}.$$

We now write [3]

$$\psi(\mathbf{r}) = u_m(\rho) e^{im\varphi} e^{ikz} \quad (5.3)$$

The differential equation satisfied by $u_m(\rho)$ is then given by

$$\frac{d^2 u}{d\rho^2} + \frac{1}{\rho} \frac{du}{d\rho} - \frac{m^2}{\rho^2} u - \frac{e^2 B^2}{4\hbar^2 c^2} \rho^2 u + \left(\frac{2\mu E}{\hbar^2} - \frac{eB\hbar m}{\hbar^2 c} - k^2 \right) u = 0 \quad (5.4)$$

If we introduce the dimensionless variable

$$x = \sqrt{\frac{eB}{2\hbar c}} \rho \quad (5.5)$$

we can rewrite (5.4) in the form

$$\frac{d^2u}{dx^2} + \frac{1}{x} \frac{du}{dx} - \frac{m^2}{x^2} u - x^2 u + \lambda u = 0 \quad (5.6)$$

where

$$\lambda = \frac{4\mu c}{eB\hbar} \left(E - \frac{\hbar^2 k^2}{2\mu} \right) - 2m \quad (5.7)$$

The asymptotic behaviours of (5.6) require that we assume that the solution of (5.6) can be given by

$$u(x) = x^{|m|} e^{-\frac{x^2}{2}} G(x) \quad (5.8)$$

where $G(x)$ satisfies the following differential equation

$$\frac{d^2G}{dx^2} + \left(\frac{2|m|+1}{x} - 2x \right) \frac{dG}{dx} + (\lambda - 2 - 2|m|)G = 0 \quad (5.9)$$

If we change the variable to $y = x^2$, we get

$$\frac{d^2G}{dy^2} + \left(\frac{|m|+1}{y} - 1 \right) \frac{dG}{dy} + \frac{(\lambda - 2 - 2|m|)}{4y} G = 0 \quad (5.10)$$

Solving this equation in series

$$G(y) = \sum_0^\infty a_n y^n \quad (5.11)$$

we get the following recurrence relation for the coefficients a_n

$$a_{n+1} = \frac{n + \frac{|m|}{2} + \frac{1}{2} - \frac{\lambda}{4}}{\{(n+1)(n+|m|+1)\}} a_n \quad (5.12)$$

In order that the eigenfunction $\psi(\mathbf{r})$, and so is $G(y)$, is a well-behaved function, it must be finite as its variables tend to $\pm\infty$ and accordingly it must terminate. Let the last term in (5.11) is a_{n_r} then

$$n_r = \frac{\lambda}{4} - \frac{|m|+1}{2}, \quad n_r = 0, 1, 2, \dots$$

and we finally obtain

$$\lambda = \frac{4\mu c}{eB\hbar} \left(E - \frac{\hbar^2 k^2}{2\mu} \right) - 2m = 4 n_r + 2(|m| + 1) \quad (5.13)$$

where $\frac{\hbar^2 k^2}{2\mu}$ is the energy with the kinetic energy of the free motion in the z -direction. Accordingly, the perturbed energy due to the presence of the magnetic field is then given by

$$E = \frac{\hbar^2 k^2}{2\mu} + \frac{eB\hbar}{2\mu c} (2 n_r + (|m| + 1) + m) \quad (5.14)$$

The function $G(y)$ defined as given by (5.11) and (5.12) is the associated Laguerre polynomial [4]

$$G(y) = L_{n_r}^{|m|}(y) \quad (5.15)$$

If we compare the magnitudes of the quadratic term in B to that of the linear one in equation (5.1) we see that the ratio is of the order of [3]

$$\left[\frac{\text{quadratic term}}{\text{linear term}} \right] \approx \frac{B}{9 \times 10^9} \text{ gauss}$$

Thus, in atomic systems, with the kind of fields available in the Laboratory, that is $B \leq 10^5$ gauss, the quadratic term is certainly negligible.

6. The Hydrogen Atom in the Presence of Magnetic Field

6.1 The Ground State (1s)

Since the principal quantum number $n = n_r + \ell + 1$, where n_r is the radial quantum number, ℓ is the orbital angular momentum quantum number and m is the z -component of ℓ , the ground state of the hydrogen atom [5]: (1s) has, $n_r = m = 0$ and $n = 1$, $k = 0$. Taking into account the potential energy due to the interaction between the nucleus and the electron of mass m_e and charge $-e$, the total energy in the presence of the field is then obtained.

In Table-1 we present the values of the ground state energy of the hydrogen atom in the presence of the magnetic field as function of the field intensity B .

Table-1 Variation of the ground state energy (E) of the hydrogen atom in the presence of the magnetic field as function of the field intensity (B).

B in gauss	E in atomic units
0.0	-0.4997300
10	-0.4632100
20	-0.4267000
30	-0.3901800
40	-0.3536600
50	-0.3171500
60	-0.2806300
70	-0.2441200
80	-0.2076000
90	-0.1710800
100	-0.1345700
102.64	-0.1249325
136.85	0.0000039

In Table-1, the value of B which equals 102.64 corresponds to the first excited state energy of the hydrogen atom in free space, while the value 136.85 corresponds to the ionization energy.

6.2 Excited States of Hydrogen

The first excited state of hydrogen [5] has $n = 2$, so that $n_r + \ell = 1$. Hence, $n_r = 0$ and $\ell = 1, m = 1, 0, -1$. This state is known as the 2p-state. Also, $n_r = 1, \ell = 0, m = 0$. This state is known as the 2s-state. So that, we have the states: 2p, $m = 0$, 2p, $m = 1$, 2p, $m = -1$, 2s, $m = 0$. The next excited states have $n = 3$. Hence, we have the states: 3d, $m = 2, 1, 0, -1, -2$. Also, the states: 3p, $m = 1, 0, -1$, and the state: 3s, $m = 0$. And so on for the other excited states.

In Table-2 we present the energy eigenvalues of the first excited state 2p, $m = 0$ of the hydrogen atom in the presence of the magnetic field as function of the field intensity B .

Table-2 Variation of the energy of the first excited state 2p, $m = 0$ of the hydrogen atom in the presence of the magnetic field as function of the field intensity B .

B in gauss	E in atomic units
0	-0.1249325
2	-0.1176300
4	-0.1103300
6	-0.1030200
8	-0.0957190
10	-0.0884160
12	-0.0811130
14	-0.0738100
16	-0.0665060
18	-0.0592030
19.007	-0.055526

The last value in Table-2 corresponds to the excited state 3s of hydrogen in free space.

6.3 The Second Excited State (2s, $m = 0$): (Same as (2p, $m = 1$)).

For this state we have $n = 2, n_r = 1, \ell = 0, m = 0$

In Table-3 we present the energy eigenvalues of the excited state 2s, $m = 0$ of the hydrogen atom in the presence of the magnetic field as functions of the field intensity B . These values are the same for the excited state (2p, $m = 1$).

Table-3 Variations of the energies of the excited state ($2p, m = 1$) of the hydrogen atom in the presence of the magnetic field as functions of the field intensity B .

B in gauss	E in atomic units
0	-0.1249325
1	-0.1139800
2	-0.1030200
3	-0.0920680
4	-0.0811130
5	-0.0701580
6	-0.0592030
6.3357	-0.0555260

The last value in Table-3 corresponds to the excited state $3s$ of hydrogen in free space.

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Appendix I

1) Hydrogen atom reduced mass is $\mu = \frac{m_e M}{m_e + M} = \frac{1}{1 + \frac{m_e}{M}} = \frac{1}{1 + \frac{0.00054858}{1.007276}} = 0.99946$.

2) Atomic units
($\hbar = e = m_e = a_0 = 1, c = 137.036$).

3) Ground state energy eigenvalue of hydrogen in free space ($n = 1$)

$$-\frac{\mu e^4}{2\hbar^2 n^2} = -\frac{\mu}{2} = -\frac{0.99946}{2} = -0.49973 \text{ (a.u.)}$$

4) Energy of the hydrogen atom in external magnetic field:

$$E = -\frac{\mu e^4}{2\hbar^2 n^2} + \frac{eB\hbar}{2\mu c} (2n_r + (|m| + 1) + m) = -\frac{\mu}{2n^2} + \frac{B}{2\mu \times 137} (2n_r + (|m| + 1) + m) = -\frac{0.99946}{2n^2} + \frac{B}{2 \times 0.99946 \times 137} (2n_r + (|m| + 1) + m) = -\frac{0.49973}{n^2} + \frac{B}{273.85} (2n_r + |m| + m + 1).$$

5) Ground state energy of the hydrogen atom in external magnetic field:

$$E = -\frac{0.49973}{n^2} + \frac{B}{273.85} = -0.49973 + \frac{B}{273.85}.$$

6) First excited state energy of the hydrogen atom ($2p, m = 0$) in external magnetic field:

$$E = -\frac{0.49973}{4} + \frac{B}{273.85} = -0.1249325 + \frac{B}{273.85}$$

7) Excited state energy of the hydrogen atom ($2p, m = 1$) in external magnetic field

$$E = -\frac{0.49973}{4} + \frac{3B}{273.85} = -0.1249325 + \frac{3B}{273.85}.$$

8) Excited State energy of the hydrogen atom ($2p, m = -1$) in external magnetic field

$$E = -\frac{0.49973}{4} + \frac{B}{273.85} = -0.1249325 + \frac{B}{273.85}. \text{ The same as } (2p, m = 0). \text{ This is because we did not used the effect of the electron spin.}$$

9) Second excited state of the hydrogen atom ($2s$): $n = 2, n_r = 1, \ell = 0, m = 0$

$$E = -\frac{0.49973}{4} + \frac{3B}{273.85} = -0.1249325 + \frac{3B}{273.85}. \text{ The same as } (2p, m = 1). \text{ This is because we did not used the effect of the electron spin.}$$

10) If the spin of the electron is taken into account, then equation (5.1) is replaced by [6]

$$-\frac{\hbar^2}{2\mu} \nabla^2 \psi + \frac{eB}{2\mu c} (L_z + 2S_z) \psi + \frac{e^2 B^2}{8\mu c^2} (x^2 + y^2) \psi = E\psi \quad (\text{A.1})$$

where s_z is the z-component of the electron spin. $s = \frac{1}{2}, s_z = \pm \frac{1}{2}$.