Exact solution of the Zeeman effect in single-electron systems

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Abstract

Contrary to popular belief, the Zeeman effect can be treated exactly in single-electron systems, for arbitrary magnetic field strengths, as long as the term quadratic in the magnetic field can be ignored. These formulas were actually derived already around 1927 by Darwin, using the classical picture of angular momentum, and presented in their proper quantum-mechanical form in 1933 by Bethe, although without any proof. The expressions have since been more or less lost from the literature; instead, the conventional treatment nowadays is to present only the approximations for weak and strong fields, respectively. However, in fusion research and other plasma physics applications, the magnetic fields applied to control the shape and position of the plasma span the entire region from weak to strong fields, and there is a need for a unified treatment. In this paper we present the detailed quantum-mechanical derivation of the exact eigenenergies and eigenstates of hydrogen-like atoms and ions in a static magnetic field. Notably, these formulas are not much more complicated than the better-known approximations. Moreover, the derivation allows the value of the electron spin gyromagnetic ratio $g_s$ to be different from 2. For completeness, we then review the details of dipole transitions between two hydrogenic levels, and calculate the corresponding Zeeman spectrum. The various approximations made in the derivation are also discussed in details.

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1 Introduction

At the end of the 19th century, when Maxwell’s theory of electromagnetism had been established, it was known that electromagnetic radiation is produced by oscillating electric charges. The charges that produce light were however still a mystery. At the same time, it was generally believed that an electric current was made up of charged particles. Lorentz suggested that atoms might also consist of charged particles, and that the oscillations of these particles inside the atoms might be the source of light. If this were true, then a magnetic field ought to have an effect on the oscillations and therefore on the wavelength of the light thus produced. In 1896 Zeeman, a pupil of Lorentz, demonstrated this phenomenon, known as the Zeeman effect, and in 1902 they were awarded the Nobel Prize.

Lorentz was thus one of the first to predict the existence of the electron, which, within a year later, was discovered by Thomson, at least as a free particle. This, in combination with the results obtained by Planck and Einstein regarding the nature of black-body radiation and the photo-electric effect, led to the subsequent emergence of Bohr’s atomic theory.

A full understanding of the Zeeman effect can only be obtained from quantum mechanics, but Lorentz was nevertheless soon after the initial discovery by Zeeman able to produce a simple classical theory which predicted certain aspects of the polarization of the different spectral components. These were later verified experimentally by Zeeman. Soon after the discovery of the so-called anomalous Zeeman effect (the weak-field limit), around 1905, came the development of the Landé vector model of the atom. Using this model, with its semi-empirical rules, basically all aspects of the observed Zeeman spectra could be explained and predicted. This was however most fortuitous, since the classical Landé $g$-factor happens to be identical to its quantum-mechanical counterpart.

Based on the Landé vector model of angular momentum, in combination with the wave-mechanics of Schrödinger, Darwin was in 1927 able to solve "the problem of a spinning electrified body moving in a central orbit in a magnetic field [...] by the method of the wave mechanics in spherical harmonics". The formalism presented there bears very little resemblance to how the problem is formulated nowadays, but the treatment is actually equivalent to an exact solution of the Schrödinger equation for the Zeeman effect.

It is certainly amusing to read Darwin’s statement that "The proper attack on this problem would undoubtedly be by way of the recent work of Heisenberg [...] but this theory is still in the making, so it has not been practicable to apply it here"; the article goes on to say that the work of Heisenberg "could give all the results of this paper; but it would have been harder to follow because the matrix methods are not so easy for most readers as are spherical harmonics."

Today the situation is rather the opposite, and we shall therefore in this paper present the exact eigenvalues and eigenvectors for the Zeeman effect in single-electron ions (i.e. hydrogenic systems), using the matrix formulation of quantum mechanics. These expressions are not new; they appeared as early as 1933, due to Bethe, and they have also been published in the well-known book by Bethe and Salpeter, where several aspects of the fundamental properties of the Zeeman effect, as well as certain approximations made in the treatment, are discussed in depth.

However, in neither of the above quoted works is given any indication – or reference – of how to derive these exact formulas. Due to this, perhaps, the presentation of the Zeeman effect found in modern text-books on atomic physics (see e.g. Ref. Section 5.2), is limited to the discussion of the weak and strong field limits, known respectively as the anomalous and normal Zeeman effect, and perhaps some particular intermediate cases, where the Zeeman effect is also known as the Paschen–Back effect. (By strong and weak fields, we mean that the energy contribution from the magnetic field is large or small compared to the spin–orbit interaction.)

For many-electron atoms, this is naturally the proper attack on the problem, since an exact solution is unattainable. However, for the particular case of hydrogenic atoms and ions, the exact treatment is not much more complicated; in fact, the resulting expressions for the eigenvalues and eigenvectors are quite simple. The spectral properties of single-electron ions have recently received rekindled interest due to a variety of applications within plasma spectroscopy (for a review, see Ref. and references therein). In e.g. fusion research, strong magnetic fields are used to control the shape and position of the plasma. A detailed understanding of the influence of these fields on the spectral lines is crucial for a correct interpretation of the observed line-widths, which are employed for temperature measurements, among other things. Moreover, the magnetic field strengths employed often span the entire scale from weak to strong fields, and there is therefore a clear need for a unified treatment of the Zeeman effect, valid for all fields.

The structure of this paper is as follows: in Section we will show how to solve the Schrödinger equation exactly for a hydrogenic system in a magnetic field, under the assumption that the quadratic term in the
magnetic field strength can be ignored. We then show in Section 3 how expansions of the exact expressions reproduce the traditional results of weak and strong fields. As a bonus, a quantitative expression is found for determining the validity of these approximations. States with zero angular momentum must be considered separately, and actually correspond to an extreme case of the strong-field approximation, as discussed in Section 4. Section 5 contains a review of the dipole transition matrix elements and selection rules, and finally we discuss in Section 6 the approximations made during the derivations.

2 Exact solution of the Schrödinger equation

As pointed out above, the traditional treatment of the Zeeman effect in most text-books is limited to the cases where the influence of the magnetic field can be separated from the effects of the spin–orbit interaction. In the weak-field limit, the magnetic interaction is introduced as a perturbation to the spin–orbit eigenstates, and vice-versa in the strong-field case. In this picture, all perturbations are already diagonal and the formalism is trivial.

In the general case, to be presented here, these two effects must however be treated simultaneously. Our method will be to diagonalize the combined perturbation in a basis set consisting of the solutions of the field-free, non-relativistic Schrödinger equation for a single-electron ion. Depending on the orbital quantum number \( \ell \) of the states considered, the matrices will be of various dimensions. A significant simplification will however emerge from the algebra, and the final energy matrix will separate into a number of 2 \( \times \) 2 sub-matrices which are easily diagonalized. The case \( \ell = 1 \) is treated in some detail in Ref. 10, from where the idea for the method has been adopted and further developed.

2.1 The unperturbed system

The non-relativistic Schrödinger equation for a hydrogenic system in vacuum, ignoring for now the spin–orbit interaction, is

\[
\left[ -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi \epsilon_0 r} \right] \psi(r) = H_0 \psi(r) = E_0 \psi(r),
\]

where \( \mu = m_e M / (m_e + M) \) is the reduced electron mass (\( m_e \) and \( M \) are the electron and nuclear masses, respectively) and \( Z \) the nuclear charge. Because of the spherical symmetry, the wavefunction \( \psi \) can be written as a product

\[
|n\ell m_\ell\rangle = \psi_{n\ell m_\ell}(r, \theta, \phi) = R_{n\ell}(r) Y_{\ell m_\ell}(\theta, \phi)
\]

of an angular part, given by the spherical harmonics \( Y_{\ell m_\ell}(\theta, \phi) \), and a radial part \( R_{n\ell}(r) \).

The energy of each eigenstate \( |n\ell m_\ell\rangle \) will depend only on the principal quantum number \( n \) as

\[
E_0 = -\frac{\mu c^2 (Z\alpha)^2}{2} \frac{n^2}{\ell^2},
\]

where \( \alpha = e^2 / 4\pi \epsilon_0 \hbar c \approx 1/137.036 \) is the fine-structure constant. Introducing relativistic corrections for the momentum operator adds another term

\[
\Delta E_{rel} = \frac{1}{2} m_e c^2 (Z\alpha)^2 \frac{3}{4} \left[ \frac{3}{4} - \frac{n}{\ell + 1/2} \right]
\]

to the energy, breaking the degeneracy in the \( \ell \) quantum number. The degeneracy in the \( m_\ell \) quantum number is only broken through an external field such as the magnetic field about to be studied.

It is not entirely obvious which value of the electron mass to use in Eq. 4, but since the perturbation in itself is a small correction, it will make an insignificant difference whether we use the electron mass \( m_e \) or the reduced mass \( \mu \) [footnote on p. 196]. Therefore, we shall in what follows always use the standard electron mass in perturbation theory.

2.2 Interaction with an external field

The interaction between an atom and an external electromagnetic field is introduced through the vector potential \( \mathbf{A} \). From Maxwell’s equation \( \nabla \cdot \mathbf{B} = 0 \) (there are, probably, no magnetic monopoles), it is clear that one can choose to represent any magnetic field \( \mathbf{B} \) as \( \mathbf{B} = \nabla \times \mathbf{A} \). The choice of \( \mathbf{A} \) is not unique, but one
can generally write $A = (\mathbf{B} \times \mathbf{r})/2 + \nabla \Psi$, where $\Psi$ is an arbitrary scalar potential. Note that over atomic distances, the macroscopic magnetic field can be assumed to be constant in magnitude and direction.

The non-relativistic Schrödinger equation (relativistic corrections and other approximations are discussed in Section 6) for a spin-less electron in an external magnetic field can be derived from the Klein–Gordon equation \[3\], and is

$$\left[ -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} - \frac{i\hbar \mathbf{A} \cdot \nabla}{m_e} + \frac{e^2}{2m_e} \mathbf{A}^2 \right] \psi(r) = E\psi(r), \tag{5}$$

where we also have used the freedom of gauge invariance to set $\nabla \cdot \mathbf{A} = 0$ (the Coulomb gauge), which means that the scalar field $\Psi$ must be a constant, which we arbitrarily may choose as zero.

The term linear in $\mathbf{A}$ can be written

$$-\frac{i\hbar \mathbf{A} \cdot \nabla}{m_e} = \frac{e}{2m_e} \mathbf{B} \cdot \mathbf{L},$$

where $\mathbf{L} = -i\hbar (\mathbf{r} \times \nabla)$ is the angular momentum operator. Similarly, the quadratic term becomes

$$\frac{e^2}{2m_e} \mathbf{A}^2 = \frac{e^2}{2m_e} (\mathbf{B} \times \mathbf{r})^2.$$

Comparing the magnitudes of the linear and quadratic terms, one finds \[6\] that their ratio is of the order $B \cdot 10^{-6}/\text{Tesla}$ for atomic systems. Except for extreme cases, such as neutron stars, the quadratic term is hence completely negligible, which simplifies the mathematics a great deal. (When included, the quadratic term will lead to diamagnetism \[5\].) For very strong magnetic fields, when the spin–orbit interaction can be neglected altogether but the quadratic term not, the energy levels can be found by different methods \[11\].

So far we have used a semi-classical picture of the electron by ignoring the spin, which however contributes an additional, intrinsic, angular momentum. To the magnetic moment of the electron from the classical angular momentum

$$\mathbf{M}_L = -\frac{e}{2m_e} \mathbf{L} = -\mu_B \mathbf{L}/\hbar, \tag{6}$$

where $\mu_B$ is the Bohr magneton, we should therefore add a contribution from the spin

$$\mathbf{M}_S = -g_s \frac{e}{2m_e} \mathbf{S} = -g_s \mu_B \mathbf{S}/\hbar. \tag{7}$$

According to the original Dirac theory, the magnetic moment of the electron due to its intrinsic spin is determined by $g_s \equiv 2$. However, using quantum electrodynamics (QED), one finds that the value of the spin gyromagnetic ratio $g_s$ is not exactly integer, but

$$\frac{g_s}{2} = 1 + \frac{\alpha}{2\pi} + \frac{0.328\alpha^2}{\pi^2} + \ldots \approx 1.0011595. \tag{8}$$

This correction is called the anomalous magnetic moment of the electron. Since it poses no problems to retain a general value of $g_s$ in our calculations, we will do so. Moreover, this allows the formalism to be extended (with proper modifications, accounting for the relative dielectric constant and the electron effective mass) to e.g. solids, where the values of the gyromagnetic ratio may differ significantly from 2, and even be negative \[12\].

The energy of a magnetic dipole – which the electron effectively becomes due to its magnetic moment – in a magnetic field is

$$H'_{\text{magn}} = -(\mathbf{M}_L + \mathbf{M}_S) \cdot \mathbf{B} = \frac{\mu_B}{\hbar} (\mathbf{L} + g_s \mathbf{S}) \cdot \mathbf{B}, \tag{9}$$

and we now also introduce the energy from the spin–orbit interaction

$$H'_{\text{so}} = \xi(r) (\mathbf{L} \cdot \mathbf{S}), \tag{10}$$

where for the one-electron central-field case

$$\xi(r) = \frac{1}{2m_e^2 c^2} \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r^3}. \tag{11}$$

In the field-free Schrödinger equation, Eq. \[1\], the geometry is spherically symmetric, whereas the magnetic field defines a particular direction of symmetry. We make this direction the $z$-axis of our system, which reduces the scalar product in Eq. \(9\) to $\mathbf{B} \cdot (\mathbf{L} + g_s \mathbf{S}) = B (L_z + g_s S_z)$, where $B = |\mathbf{B}|$. \[4\]
The total non-relativistic Hamiltonian for the electron in a hydrogen-like atom in an external magnetic field thus becomes

\[ H = H_0 + H'_{\text{so}} + H'_{\text{magn}} \]

\[ = \frac{\hbar^2}{2\mu} \sum_{n} - Z e^2 + \frac{1}{2m^2c^2} \frac{Z e^2}{4\pi\epsilon_0} \frac{1}{r^3} (L \cdot S) + \frac{\mu_B B}{\hbar} (L_z + g_s S_z). \] (12)

We assume that the relativistic correction \( \Delta E_{\text{rel}} \) is still given by Eq. (4) in the presence of the external field.

### 2.3 Perturbed energies and eigenstates

To diagonalize the perturbation

\[ H' = H'_{\text{so}} + H'_{\text{magn}} \] (13)

we first need to introduce a proper set of basis states. This is actually not trivial [5, Section 45\( \beta \)], but to simplify matters we shall use the Pauli approximation, in which each state is a two-component spinor and the spin operators are described by the Pauli spin matrices.

We can therefore use as basis the eigenstates of the unperturbed Hamiltonian \( H_0 \), arranged in a proper spinor notation. In the unperturbed system, the good quantum numbers are, in addition to \( n \) and \( \ell \), also \( m_\ell \) and \( m_s \), although the eigenstates are degenerate in the \( m_s \). In the presence of the external field, the individual \( m_s \) are no longer good quantum numbers, but only their sum \( m = m_\ell + m_s \).

We can therefore anticipate that each new eigenstates will be a linear combination of exactly two unperturbed eigenstates, corresponding to \( m_s = \pm \frac{1}{2} \) and \( m_\ell \) chosen accordingly. But since the spin–orbit interaction is not diagonal in the unperturbed eigenstates, we need to carry out the derivation using the full expansion in the unperturbed eigenstates

\[ |n\ell m⟩ = \sum_{m_\ell} \sum_{m_s} |n\ell m_\ell m_s⟩ \langle n\ell m_\ell m_s|n\ell m⟩, \] (14)

where \( m_s \) and \( m_\ell \) take on all allowed values. To avoid unnecessary notation, the indices \( n \) and \( \ell \) will be suppressed most of the time, as all calculations are performed for fixed values of these quantum numbers. In all matrices below, the basis states are assumed to be arranged in the following order:

\( (m_\ell, m_s) = (\ell, \uparrow), (\ell, \downarrow), (\ell - 1, \uparrow), (\ell - 1, \downarrow), \ldots, (-\ell, \uparrow), (-\ell, \downarrow) \)

where up and down arrows mean \( m_s = \pm \frac{1}{2} \) respectively.

The contribution to the energy due to \( H' \) is

\[ \Delta E_{n\ell m}(B) = \langle n\ell m| H' |n\ell m⟩ \]

\[ = W \sum_{m_\ell, m_s} \langle n\ell m|m_\ell m_s⟩ \left\langle m_\ell m_s \left\{ \frac{2L \cdot S}{\hbar^2} + \frac{L_z + g_s S_z}{\hbar} \beta \right\} m'_\ell m'_s \right\rangle \langle m'_\ell m'_s|n\ell m⟩, \] (15)

where we have defined

\[ \beta = B/B_0, \] (16)

with \( B_0 = W/\mu_B \)

\[ W = \frac{\hbar^2}{2} \langle \xi(r) \rangle = \frac{\mu_B^2}{4\pi\epsilon_0 c^2} \left\langle \frac{1}{r^3} \right\rangle_{n\ell}, \] (17)

The expectation value \( W \) is not defined for \( \ell = 0 \), since then there is no spin–orbit interaction, but instead an energy contribution named the Darwin term. We will consider that case separately in Section [6] and may assume \( \ell \neq 0 \) in what follows. One can then show [6] that for the hydrogenic eigenfunctions,

\[ \left\langle \frac{1}{r^3} \right\rangle_{n\ell} = \frac{Z^3}{a_0^3 n^3 \ell (\ell + 1/2)(\ell + 1)}, \] (18)

and thus

\[ W = \frac{m_ec^2}{4} \frac{(Z\alpha)^4}{n^3 \ell (\ell + 1/2)(\ell + 1)}. \] (19)
The magnetic field term,
\[ \langle m_ℓm_s | \mathbf{L}^z + g_s S^z | m'_ℓm'_s \rangle = \frac{\hbar}{\hbar} m_\ell m_s \delta_{m_\ell m'_\ell} \delta_{m_s m'_s}, \]  
(20)
is already diagonal in the present basis, but the spin–orbit interaction \( \mathbf{L} \cdot \mathbf{S} = L_x S_x + L_y S_y + L_z S_z \) is not. Since the orbital angular momentum operator \( \mathbf{L} \) and the spin angular moment operator \( \mathbf{S} \) act on separate vector spaces, spin and position space respectively, they trivially commute. Therefore, we can separate space and spin, so that
\[ \langle m_ℓm_s | L_i S_i | m'_ℓm'_s \rangle = \langle m_ℓ | L_i | m'_ℓ \rangle \langle m_s | S_i | m'_s \rangle \quad (i = x, y, z). \]  
(21)
This expression corresponds to an outer or Kronecker product between the space and spin matrices. This is defined as
\[ \mathbf{A} \otimes \mathbf{B} = \left( \begin{array}{ccc} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{array} \right) \otimes \left( \begin{array}{cc} b_{11} & b_{12} \\ b_{21} & b_{22} \end{array} \right) = \left( \begin{array}{cccc} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{array} \right), \]  
from which generalizations to larger matrices should be obvious. Each element in the product matrix is a product of one element in the first row and one in the second matrix, spanning all possible combinations. Within each marked sub-matrix, one finds the matrix \( \mathbf{B} \) multiplied with the subsequent elements in \( \mathbf{A} \).

The required matrix elements for the spin part are immediately given by the Pauli spin matrices
\[ \sigma_x = \langle m_s | S_x | m'_s \rangle = \frac{\hbar}{2} \left( \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \right), \]
\[ \sigma_y = \langle m_s | S_y | m'_s \rangle = \frac{\hbar}{2} \left( \begin{array}{cc} 0 & -i \\ i & 0 \end{array} \right), \]
\[ \sigma_z = \langle m_s | S_z | m'_s \rangle = \frac{\hbar}{2} \left( \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right), \]
(23)
whereas for the space part we make use of the ladder operators
\[ L_\pm = L_x \pm i L_y \ \Leftrightarrow \ \left\{ \begin{array}{l} L_x = (L_+ + L_-)/2, \\ L_y = (L_+ - L_-)/2i. \end{array} \right. \]  
(24)
whose action on the unperturbed eigenstates is defined through the relations (with conventional phase choices)
\[ L_\pm | \ell, m_\ell \rangle = \hbar \sqrt{\ell(\ell + 1) - m_\ell(m_\ell + 1)} | \ell, m_\ell \pm 1 \rangle. \]  
(25)
To write down the matrices corresponding to the operators \( L_x \) and \( L_y \) is somewhat tricky, since the sizes of the matrices depend on the value of \( \ell \); the dimensions will be \( 2\ell + 1 \), i.e. the number of possible \( m \)-values. The \( z \)-component is however diagonal, since the operators \( L_z \) and \( S_z \) correspond to the good quantum numbers \( m_\ell \) and \( m_s \) of the basis eigenstates, so we can write it generally as
\[ \langle m_\ell | L_z | m'_\ell \rangle \langle m_s | S_z | m'_s \rangle = m_\ell m_s \hbar^2 \delta_{m_\ell m'_\ell} \delta_{m_s m'_s}. \]  
(26)
This will be the only contribution to the diagonal of the spin–orbit term, since the ladder operators \( L_\pm \) (and hence \( L_x \) and \( L_y \)) do not couple states with the same \( m_\ell \) or \( m_s \).

Moreover, although each of the matrices \( \langle m_\ell | L_z | m'_\ell \rangle \) and \( \langle m_\ell | L_y | m'_\ell \rangle \) contain several off-diagonal elements, an important simplification takes place when they are added together to form \( \langle m_\ell m_s | \mathbf{L} \cdot \mathbf{S} | m'_\ell m'_s \rangle \), and the matrix separates into a sequence of \( 2 \times 2 \) sub-matrices, plus the corner elements which are uncoupled. Clearly, this represents what was predicted earlier: only states of equal \( m = m_\ell + m_s \) are coupled.
Using these two observations, it becomes possible to present the structure of the spin–orbit matrix as

\[
\langle m_\ell m_s | \frac{2L \cdot S}{\hbar^2} | m'_\ell m'_s \rangle = \begin{pmatrix}
\ell & 0 & 0 & 0 & 0 \\
0 & -\ell & ? & 0 & 0 \\
0 & ? & -\ell & 0 & 0 \\
0 & 0 & 0 & -(\ell - 1) & ? \\
0 & 0 & 0 & ? & \ell - 2
\end{pmatrix},
\]

(27)

where the so-far undetermined elements are denoted "?". The structure is emphasized by the dotted lines, which enclose 2 × 2 areas in which all matrix elements correspond to given quantum numbers m and m'. It should be apparent that the non-zero matrix elements will be confined to the block-diagonal, and that in each such block the relation \( m = m' \) will hold.

The corner elements of the matrix are trivial, so we focus on the interior of the matrix. To find the unknown matrix elements, we may use the same matrix but with a different division into sub-blocks:

\[
\langle m_\ell m_s | \frac{2L \cdot S}{\hbar^2} | m'_\ell m'_s \rangle = \begin{pmatrix}
\ell & 0 & ? & 0 & 0 \\
0 & -\ell & 0 & 0 & 0 \\
0 & ? & -\ell & 0 & 0 \\
0 & 0 & 0 & -(\ell - 1) & ? \\
0 & 0 & 0 & ? & \ell - 2
\end{pmatrix}.
\]

(27')

This division corresponds exactly to the direct matrix product (22), and we can therefore easily trace the contributions to the unknown elements.

First consider the top right question mark (boxed) in Eq. (27'). In this area of the matrix, \( m_\ell' = \ell - 1 \) and \( m_\ell = \ell \). These states are coupled by \( L_+ \) and we get for the sub-matrix

\[
\frac{\hbar^2}{2} \begin{pmatrix}
0 & 0 \\
0 & 0
\end{pmatrix} = L_x \sigma_x + L_y \sigma_y \\
= \langle m_\ell = \ell | L_+ | m_\ell' = \ell - 1 \rangle \left( \frac{1}{2} \sigma_x + \frac{1}{2} \sigma_y \right)
\]

\[
= \frac{\hbar^2}{2} \sqrt{\ell (\ell + 1)} - m_\ell^2 (m_\ell' + 1) \begin{pmatrix}
0 & 0 \\
0 & 0
\end{pmatrix}.
\]

For the unknown element in the third row, second column, the only difference is that the involved states are coupled by \( L_- \) instead. The prime is only a book-keeping label; \( m_\ell \) and \( m'_\ell \) are interchangeable as long as \( L_+ \) is replaced by \( L_- \) and vice versa, and hence this second unknown element is exactly the same as the first one, with the only change of removing the primes.

In the positions of the matrix where the question marks appear, we always have \( m_s = 1/2 \) or \( m'_s = 1/2 \). Therefore, on these positions, \( m_\ell = m - 1/2 \) (with or without primes). These observations are however not particular for this sub-block of the matrix, but apply generally, and thus all non-zero off-diagonal elements can be written on the same identical form \( \sqrt{\ell (\ell + 1)} - (m - 1/2)(m + 1/2) \), since furthermore \( m = m' \) within each sub-block on the diagonal, as noted above.

Finally we rewrite the diagonal elements, which have contributions from both the \( L_z S_z \) matrix elements, Eq. (26), and the magnetic interaction, Eq. (20):

\[
\mathcal{D}(m_\ell, m_s) = \langle m_\ell m_s | \frac{2L \cdot S}{\hbar^2} + \beta \frac{L_z + g_s S_z}{\hbar} | m_\ell m_s \rangle
\]

\[
= 2m_\ell m_s + \beta (m_\ell + g_s m_s)
\]

When \( m_s = \pm 1/2 \) we must have \( m_\ell = m \mp 1/2 \) and thus

\[
\mathcal{D}(m_\ell = m \mp 1/2, m_s = \pm 1/2) = \pm \left( m \mp \frac{1}{2} \right) + \beta \left[ m \pm \frac{g_s}{2} \right] = \pm \left( m \mp \frac{1}{2} \right) + \beta \left[ m \pm \frac{g_s - 1}{2} \right].
\]

(28)
Again, these expressions will be valid anywhere on the diagonal, and we have thus proven that all the $2 \times 2$ blocks along the block diagonal can be written on a common form,

\[
\begin{pmatrix}
-(m + 1/2) + \beta [m - (g_s - 1)/2] & \sqrt{\ell(\ell + 1) - (m + 1/2)(m + 1/2)} \\
\sqrt{\ell(\ell + 1) - (m + 1/2)(m + 1/2)} & m - 1/2 + \beta [m + (g_s - 1)/2]
\end{pmatrix},
\]

valid for all allowed values of $m$, except of course the corner elements $|m| = \ell + 1/2$. These are however trivial, and give the eigenvalues (cf. Eq. (15))

\[
\Delta E_{\pm(\ell+1/2)} = W \left[ \ell \pm \beta (\ell + g_s/2) \right].
\]

To find the other solutions, we need only diagonalize the matrix (29), which has eigenvalues

\[
\Delta E_m^\pm = \frac{W}{2} \left[ 2m\beta - 1 \pm \sqrt{\beta^2(g_s - 1)^2 + 4m\beta(g_s - 1) + (2\ell + 1)^2} \right],
\]

which thus is the total energy shift due to the spin–orbit interaction and the magnetic field. The corresponding eigenstates can be expressed in terms of the original $|m_\ell, m_s\rangle$ states as

\[
|m\rangle_+ = \sin \varphi |m + 1/2, \downarrow\rangle + \cos \varphi |m - 1/2, \uparrow\rangle,
\]

\[
|m\rangle_- = \cos \varphi |m + 1/2, \downarrow\rangle - \sin \varphi |m - 1/2, \uparrow\rangle,
\]

where the angle $\varphi$ is given by

\[
\varphi = \frac{1}{2} \arctan \left( \sqrt{\frac{4\ell(\ell + 1) - 4m^2 + 1}{2m + \beta(g_s - 1)}} \right).
\]

The absolute signs appear here since an explicit sign convention has been introduced in Eq. (32a).

Examples of the calculated Zeeman levels based on these results are shown in Figs. 1 and 2.

3 Strong and weak field expansions

The formalism as presented above makes no assumptions of the relative strength between the spin–orbit interaction and the magnetic field. In the traditional derivation, however, the one of the two which is stronger is first treated as a perturbation to the central-field Hamiltonian, which gives a set of new eigenfunctions. Subsequently, the other effect is treated as a perturbation to this new system, using its eigenfunctions as a basis set.

In many practical cases the magnetic fields in question are either "weak" – laboratory field strengths are typically of the order 10–100 mT – or "strong" (superconducting electromagnets or astrophysical objects), making the traditional approach seemingly more appealing, since the algebra and the resulting expressions are somewhat simpler (but only very little!).

It is therefore desirable to attempt to derive these limits from the general case, and also to obtain a quantitative criterion for when these approximations are valid, which is generally brushed over in the traditional texts, where "strong" or "weak" fields are merely assumed. For the weak-field case, it is necessary to assume $g_s = 2$, and therefore we will also assume this for strong fields, in order to facilitate the comparison with expressions in the literature.

As our starting point we will use the expression for $\Delta E_m^\pm$, Eq. (31). The parameter determining the relative strength of the magnetic interaction to the spin–orbit interaction is $\beta$. Assuming that this quantity is large, i.e. $\beta \gg (2\ell + 1)$, we can neglect both $(2\ell + 1)^2$ and the term linear in $\beta$ in the square-root, and also the term $(-1)$ outside, giving

\[
\Delta E_m^\pm = B\mu_B (m \pm 1/2).
\]

The solutions to the corner elements given by Eq. (30) also reduce to this expression if we ignore $\ell$ compared to $(\ell + 1)\beta$. This result is trivially obtained from Eq. (14) if the spin–orbit term $\mathbf{L} \cdot \mathbf{S}$ is ignored, and thus corresponds to the well-known expression for the normal Zeeman effect.

In this strong-field limit, the states are split in $m$ but degenerate in $\ell$ (except of course for the dependence on $\ell$ in the relativistic correction, Eq. (11)), as seen in Fig. 2. The eigenstates are particularly simple, since the
denominator in Eq. (33) becomes very large, and so \( \varphi \approx \pi/4 \). Since the levels tend to group, and because of the selection rule \( \Delta m = 0, \pm 1 \) to be discussed shortly, the spectrum for normal Zeeman effect of a transition \( n \rightarrow n' \) will consist of three equidistant lines – a Lorentz triplet \( [6, \text{p. 211}] \).

In the opposite limit, where \( \beta \ll (2\ell + 1) \), we get

\[
\Delta E_{m}^{\pm} \approx \frac{W}{2} \left\{ 2m\beta - 1 \mp (2\ell + 1) \left( 1 + \frac{1}{2} \frac{4m\beta}{(2\ell + 1)^2} \right) \right\}
\]

\[
= \begin{cases} 
W\ell + B\mu_{B}m & \frac{2\ell + 2}{2\ell + 1}, \\
-W(\ell + 1) + B\mu_{B}m & \frac{2\ell}{2\ell + 1},
\end{cases}
\]

if we neglect the term quadratic in \( B \). The solutions to the corner elements are also incorporated in this formula (the top expression), which is easily shown – without approximations – from Eq. (30), if we realize that \( m/(\ell + 1/2) = \pm 1 \).

We can identify the first term in Eq. (35) as the contribution from the spin–orbit interaction if the magnetic field is ignored. The two cases correspond to \( j = \ell \pm 1/2 \), where \( j \) is the quantum number associated with the total angular momentum \( J = L + S \) which is conserved in the absence of a magnetic field. The energy contribution from the magnetic field can now be evaluated, within this approximation, through the expression \( [6] \)

\[
\Delta E_{\text{magn}}(m_{j}) = \frac{\mu_{B}}{\hbar}B\left\langle L_{z} + 2S_{z} \right\rangle = \frac{\mu_{B}}{\hbar}B\left\langle J_{z} + S_{z} \right\rangle
\]

(this is where we need \( g_{s} = 2 \)). The expectation value of \( J_{z} \) is \( \hbar m_{j} \) by definition, and one may show that

\[
\langle nlsjm_{j} | S_{z} | nlsjm_{j} \rangle = (g - 1)m_{j}\hbar
\]

where \( s \) is the spin (i.e. 1/2 for an electron) and

\[
g = 1 + \frac{j(j + 1) + s(s + 1) - \ell(\ell + 1)}{2j(j + 1)}
\]

is the Landé factor. Thus \( \Delta E_{\text{magn}} = g\mu_{B}Bm_{j} \), which can be shown to give exactly the remaining part of Eq. (35). We now also realize why the corner solutions ended up in the top expression of Eq. (35), since \( |m| = \ell + 1/2 \) only is allowed for the triplet state \( j = \ell + 1/2 \).

In the weak-field case the distance between two levels corresponding to subsequent values of \( m \) within the same multiplet will be the same for all levels (cf. Fig. 1). This case is, for historical reasons, called anomalous Zeeman effect, but is actually the more commonly encountered one. Since the splitting of the levels for different multiplets is different (i.e. dependent on \( j \)), there will be more lines in the spectrum than for the normal Zeeman effect.

The approximate expressions for strong and weak fields can thus be derived as expansions of the exact result, Eq. (35). We may now also specify quantitatively under what conditions these approximations hold, since this is determined by whether \( B/B_{0} = B\mu_{B}/W \) is much greater or much smaller than \( 2\ell + 1 \). Inserting the constants into Eq. (35) gives

\[
W = \frac{Z^{4}}{\gamma} \cdot 3.62261 \cdot 10^{-4} \text{ eV} = \frac{Z^{4}}{\gamma} \cdot 2.92183 \text{ cm}^{-1},
\]

\[
B_{0} = \frac{Z^{4}}{\gamma} \cdot 6.2584 \text{ Tesla}
\]

where \( \gamma = n^{3}(\ell + 1/2)(\ell + 1) \). Thus the approximations are valid if \( B \) is much larger or smaller than

\[
\frac{(Z\alpha)^{4} m_{e}c^{2}}{n^{3}(\ell + 1) 2\mu_{B}} = \frac{Z^{4}}{n^{3}(\ell + 1)} \cdot 12.5 \text{ Tesla}.
\]

For light atoms and states with \( n \) and \( \ell \) less than 4, this expression takes values between 0.1 and 10 Tesla; for heavier atoms the fourth power of \( Z \) will dominate and, except for high shells and strong fields, the weak-field approximation will almost always be valid.
As an example, let us consider the states \( n = 3 \) and 4 in HeII \((Z = 2)\). Inserting \( \ell = 1 \) and 2 for \( n = 3 \) (for \( \ell = 0 \) the strong-field approximation is exact; see the following section) the threshold field strengths come out as 3.70 and 1.23 Tesla respectively. For \( n = 4 \) the corresponding values for \( \ell = 1, 2 \) and 3 become 1.56, 0.52 and 0.26 Tesla. As briefly mentioned in the Introduction, a modern application of Zeeman effect is to use fusion plasma spectroscopy in order to determine the plasma temperature, by e.g. studying the transition between precisely these states in HeII [13]. Typical magnetic fields in a tokamak the size of JET’s lie in the range 1–3 Tesla, and we thus clearly see that such an investigation cannot be carried out using either of the traditional approximations.

4 Treatment of s-states

As mentioned above, the expectation value \( W \) is only defined for \( \ell \neq 0 \) (cf. Eq. (19)). But, in light of the previous section, we now realize that \( \ell = 0 \) corresponds to an extreme case of Eq. (34), where the magnetic field is infinitely much stronger than the spin–orbit interaction. Hence, without approximation, the energy eigenvalues are (here we may keep a general value of \( g_s \))

\[
\Delta E^\pm_m = B\mu_B \left( m \pm \frac{g_s - 1}{2} \right) = \pm B\mu_B g_s/2, \quad (\ell = 0),
\]

since for \( \ell = 0 \) we have \( m = m_s = \pm 1/2 \). To this we should also add the Darwin term \[6\]

\[
\Delta E_D = \frac{\pi \hbar^2}{2m_e^2c^2} \frac{Z^2}{4\pi\varepsilon_0} \langle n00|\delta(r)|n00 \rangle = \frac{m_e c^2 (Z\alpha)^4}{2 n^3},
\]

(40)

5 Transitions and matrix elements

To calculate the Zeeman pattern of the spectral line from a transition between two different \( n\ell \) states, we need to consider the selection rules and the transition matrix elements. Since the eigenstates \((32ab)\) of the total Hamiltonian, Eq. (12), are simply linear combinations of hydrogenic states \(|n\ell m \rangle \), it is however enough to employ the well-known results for transitions between two hydrogenic states (derived in the absence of any magnetic field).

The derivation of the matrix elements for spontaneous emission is a procedure found in any textbook on the theory of atomic spectra (see e.g. Ref. 6, Chapter 4). We therefore merely state the results in order that this paper can be used as a self-contained reference on how to calculate the Zeeman spectrum. We will then give an illustrative example of the resulting spectrum when these expressions are applied to the Zeeman problem at hand.

5.1 Spontaneous emission matrix elements

In the dipole approximation, the transition probability for spontaneous emission from a state \( b \) to a lower state \( a \) is found from Fermi’s Golden Rule to be

\[
W^s_{ab}(\Omega) \, d\Omega = C(\omega_{ba}) |\hat{\epsilon} \cdot \mathbf{r}_{ba}|^2 \, d\Omega,
\]

(41)

where \( d\Omega \) is the solid angle element in which the radiation is observed, and \( \hat{\epsilon} \) is a unit vector in the polarization direction of the radiation. The overlap matrix element

\[
\mathbf{r}_{ba} = \langle n'\ell' m' | \mathbf{r} | n\ell m \rangle = \langle n'\ell' m' | \mathbf{r} | n\ell m \rangle \delta_{m', m},
\]

(42)

where we introduced the prime notation for the higher state \( b \) for a cleaner notation, and used the fact that the operator \( \mathbf{r} \) does not act on the spin space. Hence we obtain the first selection rule, \( \Delta m_s = 0 \).

The pre-factor in Eq. (41) is

\[
C(\omega_{ba}) = \left( \frac{2Z}{a_\mu} \right)^2 \frac{(\Delta E)^3}{\hbar(\mu c^2)^2} \frac{1}{8\pi Z^2\alpha^3},
\]

(43)

where \( \Delta E = h\omega_{ba} = E_b - E_a \). It is generally only meaningful to compare the relative intensities of Zeeman components for the same chemical element (same \( Z \) and \( \mu \)), and hence the only factor we really need to
retain in $\mathcal{C}$ is the energy difference $\Delta E$. When calculating the spectral line intensity from the transition probability, an extra factor $\Delta E$ enters, making the observed intensity proportional to $(\Delta E)^4$.

Introducing the spherical tensor components of $\hat{\epsilon}$

$$
\epsilon_0 = \epsilon_z \quad \epsilon_{\pm 1} = \mp \frac{1}{\sqrt{2}} (\epsilon_x \pm i \epsilon_y),
$$

(44)

and correspondingly for $r_{ba}$, we can write

$$
\hat{\epsilon} \cdot r_{ba} = \sum_{q=-1}^{1} \epsilon_q^a r_{qba}^q = \sum_{q=-1}^{1} \epsilon_q^a T_{n'\ell' m' \ell m \ell}^q
$$

(45)

where

$$
T_{n'\ell' m' \ell m \ell}^q = \sqrt{\frac{4\pi}{3}} R_{n'\ell'}(r) \int_{\Omega} Y_{\ell m \ell}^* Y_{\ell' m' q} Y_{-\ell' m' q} d\Omega.
$$

(46)

with the radial overlap integral

$$
R_{n'\ell'} = \int_0^{\infty} R_{n'\ell'}(r) R_{n\ell}(r) r^3 dr.
$$

(47)

Here $R_{n\ell}(r)$ is the radial part of the hydrogenic wavefunction, to which we will shortly return.

Using either the Wigner–Eckart theorem or the properties of the spherical harmonics, one can show that [14, Section 11-4 and Chapter 14]

$$
T_{n'\ell' m' \ell m \ell}^q = (-1)^{\ell_s - m_s'} \sqrt{\ell_s \ell_{\ell}} R_{n'\ell'} \left( \begin{array}{ccc} \ell & 1 & \ell' \\ m_q & -m_{\ell}' \end{array} \right),
$$

(48)

where $\ell_s = \max(\ell', \ell)$. The properties of the Wigner 3j-symbol now enable us to identify further selection rules, since the 3j-symbol vanishes unless $\ell' = \ell + 1$ and $m_q + m_{\ell}'$. Thus we obtain the $\ell$ selection rule which requires change of parity; dipole transitions only connect states of opposite parity, and the parity of a hydrogenic state is $(-1)^\ell$. Moreover, since $q = 0, \pm 1$ we may write the other selection rule as $\Delta m_\ell = 0, \pm 1$.

In summary, the dipole selection rules for hydrogenic states are

$$
\Delta m_s = 0, \quad \Delta \ell = 1, \quad \Delta m_\ell = 0, \pm 1.
$$

(49)

### 5.2 The radial integral

Including proper normalization, the radial part of the hydrogenic wavefunction becomes

$$
R_{n\ell}(r) = \sqrt{\frac{(2Z)^3}{a_\mu}} \left( \frac{n - \ell - 1}{2n^4(n + \ell)} \right) e^{\rho/2n} \left( \frac{\rho}{n} \right)^\ell L_{n-\ell-1}^{2\ell+1}(\rho/n),
$$

(50)

where $L_n^{2\ell+1}(x)$ are the associated Laguerre polynomials, $a_\mu = 4\pi \epsilon_0 h^2 / mc^2$ is the Bohr radius (adjusted for finite nuclear mass), and we have also introduced $\rho = 2Zr/a_\mu$ as the dimensionless length scale.

Inserting this into the integral [14], one arrives at

$$
R_{n'\ell'} = \frac{a_\mu}{2Z} F_{n'\ell'}
$$

(51)

with the dimensionless form factor

$$
F_{n'\ell'} = \frac{1}{2} \sqrt{\frac{(n - \ell - 1)! (n' - \ell' - 1)!}{(n + \ell)! (n' + \ell')!}} \frac{1}{n^{\ell + 2}} \frac{1}{n'^{\ell' + 2}}
$$

$$
\times \int_0^{\infty} e^{-\frac{1}{2}(\frac{\rho}{n} + \frac{\rho'}{n'})} \rho^{\ell + \ell' + 3} L_{n-\ell-1}^{2\ell+1}(\rho/n) L_{n'-\ell'-1}^{2\ell'+1}(\rho/n') d\rho.
$$

(52)
5.3 Polarization

We now return to Eqs. (41) and (45) to study the polarization of the emitted radiation. Any arbitrary polarization can be expressed as a linear combination of two independent directions $\hat{e}_1$ and $\hat{e}_2$, such as left and right circularly polarized, or two perpendicular linear polarizations. For this discussion we choose the latter. We also introduce a wavevector $\mathbf{k}$ of unit length (as are the $e$-vectors) pointing in the direction of propagation of the emitted light, so that the three vectors $\hat{e}_1$, $\hat{e}_2$ and $\mathbf{k}$ form a right-handed system (see Fig. 3). As before we let the $z$-axis be the direction of the magnetic field. Taking, arbitrarily, $\hat{e}_2$ to lie in the $xy$-plane and $\hat{e}_1$ pointing downwards, we have

$$\hat{k} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta),$$

(53a)

$$\hat{e}_1 = (\cos \theta \cos \phi, \cos \theta \sin \phi, -\sin \theta),$$

(53b)

$$\hat{e}_2 = (-\sin \phi, \cos \phi, 0).$$

(53c)

Next we use the properties of the 3j-symbol in Eq. (48), which is non-zero if and only if $m_{\ell}' = m_{\ell} + q$, as already stated. Since each of the three values of $q = 0$ or $\pm 1$ only may be satisfied one at a time, we have three separate cases to study. These are for historical reasons referred to as $\pi$ and $\sigma^\pm$ (from the German words for parallel and perpendicular, "senkrecht").

$\pi$ In this case $\Delta m_{\ell} = 0$, and consequently we only need to consider $\mathcal{I}^0$ (we suppress the quantum numbers in this part). This gives the transition rate

$$W^\pi_{ab}(\pi) = C(\omega_{ba}) \sin^2 \theta |\mathcal{I}^0|^2$$

(54)

for a photon with polarization $\hat{e}_1$, whereas the rate is zero for polarization $\hat{e}_2$. Since the $\hat{k}$-vector is defined as the direction in which the radiation is observed, we find that if the emission is viewed longitudinally ($\mathbf{k}$ parallel to the magnetic field), $\theta = 0$ and so the $\pi$ component is absent. In the transverse direction ($\theta = \pi/2$), i.e. in a direction perpendicular to the magnetic field, we have $\hat{e}_1 = (0, 0, -1)$ and thus the $\pi$ component will be plane polarized with $\hat{e} = \hat{e}_1$ in the direction of the negative $z$-axis.

$\sigma^+$ This case corresponds to $\Delta m_{\ell} = m_{\ell}' - m_{\ell} = -1$. Now the only contribution will be from $\mathcal{I}^{-1}$, and since the two polarization directions are orthogonal and independent, we may sum the probabilities instead of the amplitudes. In result, we obtain

$$W^{\sigma^+}_{ab}(\sigma^+) = C(\omega_{ba}) \frac{1 + \cos^2 \theta}{2} |\mathcal{I}^{-1}|^2 .$$

(55)

The $\sigma^+$ component is plane polarized with $\hat{e} = \hat{e}_2$ in transverse observation, whereas in longitudinal observation it is circularly (left-hand) polarized. The intensity of each $\sigma$ component is always half of the $\pi$ component in transverse observation.

$\sigma^-$ For the case $\Delta m_{\ell} = 1$ we get the analogous expression

$$W^{\sigma^-}_{ab}(\sigma^-) = C(\omega_{ba}) \frac{1 + \cos^2 \theta}{2} |\mathcal{I}^{+1}|^2 .$$

(56)

The $\sigma^-$ component is also plane polarized in transverse observation, and (right-hand) circularly polarized in longitudinal.

From here on it is a simple matter to calculate the intensities of all transitions in the Zeeman pattern; see Fig. 4 for an example. The number of components increases rapidly with the quantum numbers; for a $7 - 8$ transition the total number is 512, although many will be very weak.

6 Discussion of approximations

In this section we summarize the approximations made in the treatment. They are not many, as we have strived to keep things as general and exact as possible. For an even more detailed discussion, see Ref. 5, Sections 47α–ε.
- **The quadratic term**
  In Section 2.2 we ignored the term in the Hamiltonian quadratic in $A$, and we also showed that for fields of normal strengths (less than 1000 Tesla or so), this approximation is certainly valid, and simplifies the algebra considerably.

  A particular effect which enters if the quadratic term is retained is the possibility of mixing states with different $\ell$ quantum numbers. The linear term in $A$ commutes with $L^2$, making $\ell$ a good quantum number, but the quadratic term does not. Specifically, it introduces mixing between states with $\ell$-values differing by $\pm 2$. Again, this will only be of importance for very strong magnetic fields and can often safely be ignored.

- **Relativistic corrections**
  Using the Pauli approximation instead of the Dirac theory means we are only calculating the Zeeman effect to lowest order in $\alpha^2$. Assuming that all perturbations (magnetic field and spin–orbit interaction) are small, we remedy this by using the same correction Eq. \((4)\) as for the field-free case to correct for the non-relativistic momentum operator. Effects beyond this should be negligible.

- **The anomalous magnetic moment**
  In the approximate treatment of the anomalous Zeeman effect (weak fields) it is necessary to use the value $g_s = 2$. As it turned out, we were not restricted by this approximation in our exact derivations (note the factors $g_s - 1$ and $g_s/2$ appearing in the final expressions, Eqs. \((30)\) and \((31)\)), although the influence is very small – unless of course $g_s$ differs significantly from 2.

- **Nuclear motion and hyperfine structure**
  We have already taken into account the nuclear motion by using the reduced mass $\mu$ of the electron for the central-field Hamiltonian. In the perturbations, we have kept the electron mass since the perturbations themselves are small, so any corrections to them are even smaller \([6]\).

  Hyperfine structure due to the nuclear magnetic moment is in general orders of magnitude smaller than the fine-structure splitting (spin–orbit interaction). Therefore, we expect that hyperfine structure will not perturb the Zeeman spectrum except for extremely weak magnetic fields, where the Zeeman pattern can be heavily influenced.

7  **Summary**

  In conclusion, this paper has demonstrated how the problem of a single-electron atom or ion in a static magnetic field can be solved exactly, under the only simplifying approximation that the term which is quadratic in the field strength can be neglected in the Hamiltonian. No assumption was made regarding the value of the electron spin gyromagnetic ratio, which allows the obtained results to be readily generalized to applications in e.g. solids.

  By using the results presented here, a unified treatment of the Zeeman effect becomes possible over the entire range of fields presently employed in e.g. fusion plasma, where the influence of the Zeeman effect on the plasma temperature measurements has been demonstrated to be significant in many cases. The well-known formulas for the weak and strong field limits are easily obtained as expansions of the general results, and in addition it was possible to obtain a quantitative expression for the fields at which these approximations are valid.

  The obtained general expressions for the eigenstates and their corresponding energies are not very complicated. As a final remark, one may therefore point out that the derivation, as presented here, has certain pedagogical merits and provides a good example of how to apply the power of matrix algebra to quantum-mechanical problems.

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References

[1] Zeeman, P., Philosophical Magazine 43, 226 (1897).
[2] White, H. E., "Introduction to Atomic Spectra," (McGraw-Hill Book Co., New York, 1934), Chapter X.
[3] Darwin, C. G., Proc. Royal Soc. London 115, 1 (1927).
[4] Bethe, H., in "Handbuch der Physik," (edited by Smekal, A.) (Springer Verlag, Berlin, 2nd edition, 1933), vol. XXIV, part 1, pp. 396–399.
[5] Bethe, H. A. and Salpeter, E. E., "Quantum Mechanics of One- and Two-Electron Systems" (Springer Verlag, Berlin, 1957).
[6] Bransden, B. H. and Joachain, C. J., "Physics of Atoms and Molecules" (Longman Scientific & Technical, Harlow, 1983).
[7] Isler, R. C., Plasma Phys. Control. Fusion 36, 171 (1994).
[8] Blom, A. and Jupén, C., Plasma Phys. Control. Fusion 44, 1229 (2002).
[9] Hey, J. D., Lie, Y. T., Rusbüldt, D. and Hintz, E., Contrib. Plasma Phys. 34, 725 (1994).
[10] Fano, U. and Fano, L., "Physics of Atoms and Molecules. An Introduction to the Structure of Matter" (University of Chicago Press, Chicago, 1972).
[11] Simola, J. and Virtamo, J., J. Phys. B: Atom. Molec. Phys. 11, 3309 (1978).
[12] Callaway, J., "Quantum Theory of the Solid State," (Academic Press, San Diego, 2nd edition, 1991), pp. 526–529.
[13] von Hellermann, M. et al., Plasma Phys. Control. Fusion 37, 71 (1995).
[14] Cowan, R. D., "The Theory of Atomic Structure and Spectra" (University of California Press, Berkeley, 1981).
Figure 1: The total energy shift due to both spin–orbit interaction and an applied magnetic field for the $n = 2$ shell in HeII. The energy zero-point is chosen at $2s \, ^2S_{1/2}$ at $B = 0$. The states are marked by their quantum number $m$ with a following $\pm$ corresponding to the notation in Eqs. 31 and 32, except for the states with $|m| = \ell + 1/2$ for which there only are two unique solutions, Eq. 30. For small magnetic fields, the states are split linearly according to Eq. 35. Note that without any magnetic field, the two levels $2s \, ^2S_{1/2}$ and $2p \, ^2P_{1/2}$ are degenerate (the small difference due to the Lamb shift is ignored). Also see Fig. 2 where the field scale is extended.
Figure 2: In this figure, the same system as in Fig. 1 is shown, but for stronger fields. As the magnetic field approaches high values, the pattern converges into five states, according to Eq. (34). Since \( m \) takes on the values \( \pm \frac{1}{2}, \pm \frac{3}{2} \), there are only five possible values of \( m \pm \frac{1}{2} \), namely \( 0, \pm 1, \pm 2 \), and the degeneracy will obviously be one for the \( \pm 2 \) cases (only reached from \( m = \pm \frac{3}{2} \)), and two for the other, as is also seen in the figure. Noteworthy is also the anti-crossing rule: even if some lines cross as \( B \) increases, no lines with the same \( m \)-values ever cross. This is an effect of level repulsion between states of equal quantum mechanical symmetry (cf. Ref. 14, pp. 292–295 and Fig. 10-2 therein.)
Figure 3: Definition of the polarization vectors.
Figure 4: The complete Zeeman pattern for the HeII line at 4687 Å (vacuum) consists of 146 components. It is here calculated for $B = 2$ Tesla at a viewing angle $\theta = 40^\circ$ relative to the magnetic field axis (cf. Fig. 3). Only components with intensity greater than one (in the plot units) are included; the $\pi$ components are conventionally drawn with negative intensity.