APPENDIX A: QUANTUM THEORY OF ZEEMAN SPLITTING

The actual splitting of most atomic spectral lines in response to an applied magnetic field does not follow the classical, Lorentz-Zeeman theory. Observed splitting of the spectral lines of neon can be into from 2 to 9 lines each; only the two lines at 626.65nm and 585.25nm (wavelengths in air) behave as predicted. In this appendix we very briefly summarize the consequences of the modern, quantum-mechanical theory of atomic structure which can correctly describe the anomalous Zeeman splitting exhibited by the majority of neon’s spectral lines.

Angular momentum and magnetic moment of a single atomic electron

The Coulomb field of the nucleus forms, to an excellent approximation, a central potential well within which one or more electrons can be bound. As in the classical case, the total quantum-mechanical angular momentum of an isolated atom is a constant of the motion, and thus its angular momentum eigenstates may also be chosen to be eigenstates of the Hamiltonian (energy) operator \( H \) (i.e., stationary states). Consider first a single electron bound to the atom’s nucleus. The total angular momentum \( \vec{j} \) of the electron is the vector sum of two parts: its orbital angular momentum \( \vec{l} = \vec{r} \times \vec{p} \), which is determined by the electron’s spatial state (i.e. wave-function), and its intrinsic spin angular momentum \( \vec{s} \) (which is an inherent, quantum-mechanical property of the electron that has no classical analog). Thus, for any particular single-electron state \( \vec{j} = \vec{l} + \vec{s} \).

Because the three Cartesian components of any quantum-mechanical angular momentum operator \( \vec{J} \) do not commute, the complete, 3-dimensional angular momentum vector cannot be defined for any quantum state. States can be found, however, which are simultaneously eigenstates of the (squared) magnitude of the angular momentum operator, \( J^2 = \vec{J} \cdot \vec{J} \), and one Cartesian component (conventionally, the \( z \)-component), \( J_z \). In the case of a single electron, its orbital angular momentum eigenstates \( |\alpha;ll_z\rangle \) are characterized by two angular momentum quantum numbers \( l \) and \( l_z \) such that

\[
\begin{align*}
L^2 |\alpha;ll_z\rangle &= \hbar^2 l(l+1) |\alpha;ll_z\rangle; \quad l \in \{0, 1, 2, \ldots\} \\
L_z |\alpha;ll_z\rangle &= \hbar l_z |\alpha;ll_z\rangle; \quad l_z \in \{-l, -l+1, \ldots, l-1, l\}
\end{align*}
\]  

(27.A.1)

9 The discovery of electron spin involved many physicists during the 1920’s. Although demonstrated experimentally by the Germans Otto Stern and Walther Gerlach in 1922, their results were misinterpreted. The Dutch physicists Uhlenbeck and Goudsmit and the Austrian-Swiss Wolfgang Pauli are generally credited with the first successful theory of the effects of electron spin on atomic structure.

10 We use lower-case letters \( j, l, \) and \( s \) to represent the total, orbital, and spin angular momenta of a single atomic electron state. Upper-case letters \( J, L, \) and \( S \) are used for the net resulting angular momenta of an assemblage of atomic electrons. Bold, upper-case characters are used for the corresponding quantum-mechanical operators.
The extra \( \alpha \) in the state’s *ket vector* \( |\alpha; l_l z\rangle \) represents all the other quantum numbers required to uniquely define that state.\(^{11}\)

The electron’s intrinsic spin angular momentum is characterized by the permanently-fixed quantum number \( s = 1/2 \), making the electron a fermion subject to the Pauli Exclusion Principle: no two electrons may occupy identical quantum states. The \( z \)-component of the electron’s spin angular momentum has a quantum number which may take on only two values: \( s_z = \pm 1/2 \). Because the electron’s spin represents a non-independent degree of freedom, its eigenstates can be chosen to be simultaneously eigenstates of its orbital angular momentum, so a single-electron state vector, including spin, can be written as \( |\alpha; l_l z, s_z\rangle \). Any particular single-electron quantum state may be expanded as a linear combination (or *coherent superposition*) of the complete set of \( |\alpha; l_l z, s_z\rangle \) for all the various allowed values of the quantum numbers.

Because the electron carries electrical charge \( -e \), its orbital and spin angular momenta generate magnetic dipole moment vectors which add to produce an electron state’s total magnetic moment \( \vec{m} \). A magnetic dipole moment is associated with the orbital angular momentum of the single-electron state \( |\alpha; l_l z, s_z\rangle \) because the orbiting charge of the electron creates a tiny current loop, thus producing a magnetic dipole field. Therefore the magnetic moment quantum vector operator \( \vec{M} \) is proportional to the orbital angular momentum operator: \( \vec{M} = -\mu_b \vec{L} \). \( \mu_b \) is called the Bohr magneton and has a value of approximately \( 5.79 \times 10^{-5} \) eV/Tesla; its expression in terms of fundamental constants is shown in (27.A.2). The minus sign arises because the electron has a negative charge. Since \( \vec{M} \) and \( \vec{L} \) are parallel, the \( z \)-component magnetic moment operator \( M_z \) is proportional to \( L_z \), which has eigenvalue \( l_z \) for an electron in the state \( |\alpha; l_l z, s_z\rangle \). Therefore

\[
M_z |\alpha; l_l z, s_z\rangle = -\mu_b L_z |\alpha; l_l z, s_z\rangle = -\mu_b l_z |\alpha; l_l z, s_z\rangle; \quad \mu_b = \frac{e\hbar}{2m_e} \tag{27.A.2}
\]

Ignoring the effects of the electron’s spin for a moment, the presence of an externally applied magnetic field will shift the \( |\alpha; l_l z\rangle \) state’s energy by the potential energy of this dipole with respect to the field:\(^{12}\)

\[
\langle E_B \rangle = -\langle \alpha; l_l z | \vec{M} \cdot \vec{B} | \alpha; l_l z \rangle = \mu_b l_z B \tag{27.A.3}
\]

---

\(^{11}\) The concept of the state vector was integral to the matrix mechanics theory of quantum phenomena, first conceived by the German physicist Werner Heisenberg and later formulated by him and his colleagues Max Born and E. Pascual Jordan in a series of seminal papers in 1925; Heisenberg was awarded the 1932 Nobel Prize “for the creation of quantum mechanics.” The British physicist Paul Dirac introduced the modern *bra* and *ket* notations for quantum state vectors, as well as the *Dirac delta function* \( \delta(\vec{r}) \) and the notation \( \hbar \) for \( h/2\pi \). We shall have more to say about Dirac later.

\(^{12}\) This is strictly true only if \( E_s \ll \Delta E_0 \), where \( \Delta E_0 \) is the energy difference to the next closest state. The formula presented in (27.A.3) is a result of the application of *first order perturbation theory* to estimate effect of the operator \( (-\vec{M} \cdot \vec{B}) \) on the energy of a state.
The direction of the magnetic flux density $\vec{B}$ determines the “$z$-axis” for the single, specifiable component of the state’s orbital angular momentum ($l_z$). Thus the presence of the magnetic field can break the degeneracy of the $2l+1$ states $|\alpha; l l_z\rangle$ sharing the quantum number $l$ (for $l > 0$), generating energy shifts of $\mu_B B l_z$, one for each allowed value of $l_z$.

The electron’s spin also generates a magnetic dipole moment, but in a different, purely quantum-mechanical way: the electron’s intrinsic magnetic moment cannot be identified with a physical circulation of charge (a current loop). Again, the spin-induced dipole moment is proportional to the quantum-mechanical spin vector operator $\vec{S}$, but the constant of proportionality is different: $\vec{M} = \mu_B \vec{S}$ $\rightarrow$ $M_z |\alpha; l = 0, l_z = 0, s_z\rangle = -\mu_B |\alpha; 0, 0\rangle$, where $\mu_B$ is the gyromagnetic ratio of the electron. The most straightforward theory of the interaction of an s=1/2 electron with an external electromagnetic field requires that $\mu_B = 2$, and this value implies that the electron may have $M_z = \pm \mu_B$. An early calculation based on the current, more modern and comprehensive theory of the interaction between electrons and the electromagnetic field (quantum electrodynamics, or QED) predicted that $\mu_B = 1.0011614$, about a 0.1% correction. Since an electron’s orbital and spin angular momentum vectors need not be parallel, and magnetic moment due to spin is different from that due to orbital angular momentum, the total magnetic moment they generate and the resulting energy shift $\langle E_B \rangle = -\langle \vec{M} \cdot \vec{B} \rangle$ are not necessarily simple to calculate.

Multiple-electron atoms; g-factor

An atom with $n$ electrons has a total angular momentum $\vec{J} = \vec{L} + \vec{S}$, where $\vec{L}$ and $\vec{S}$ are vector sums of the $n$ electrons’ respective individual orbital and spin momenta $\vec{l}$ and $\vec{s}$. Because the relative orientations of the individual electron’s vectors can assume a variety of

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13 “Spin” cannot be caused by something physically “going around,” because $\vec{l} \times \vec{s}$ angular momentum must have quantum numbers which are integers (any convenient quantum mechanics text should derive this result).

14 Paul Dirac developed the first comprehensive, relativistically-correct quantum theory of the electron and its interaction with the electromagnetic field in a historic, then-controversial paper of 1928. In the course of his investigations he postulated that not only should the spin-1/2 electron have $\mu_B = 2$, but that it must also be accompanied by what would later be interpreted as a companion antiparticle. Most relevant for our purposes, he used his theory to explain the anomalous Zeeman Effect in every detail. Dirac shared the 1933 Nobel Prize with Erwin Schrödinger. The positron (anti-electron) was identified by the Caltech physicist Carl Anderson in 1932, earning him the 1936 Nobel Prize.

15 This value calculated by the American physicist Julian Schwinger in 1948 is engraved on his tombstone; Schwinger shared the 1965 Nobel Prize with Feynman and the Japanese physicist Sin-Itiro Tomonaga for their development of modern QED. For many years, refinements in the predicted value of $\mu_B$ represented the most precise theoretical calculations of a fundamental physical constant, more precise than even the most accurate experimental measurements. This changed in 2006, with an experimental measurement by a team at Harvard (Odom, Hanneke, D’Urso, & Gabrielse, 2006) which included a Caltech alumnus (D’Urso) who, as an undergraduate, added the polarizer to our experiment’s apparatus. Current QED calculations and experimental measurements have precisions $\sim 10^{-12}$. 

arrangements, the magnitudes of $L$ and $S$ can generally take on many possible values, even for a fixed set of $n$ quantum numbers $l$ for the electrons (they each, of course, have $s = 1/2$). The total $L$ and $S$ are, of course, angular momenta, and eigenstates of the squared magnitude operators $L^2$ and $S^2$ may be found with eigenvalues $\hbar^2L(L+1)$ and $\hbar^2S(S+1)$, respectively, with quantum numbers $L$ and $S$. The quantum number $L$ for the total orbital angular momentum must be a nonnegative integer. The quantum number $S$ for the total spin angular momentum must be a nonnegative integer if the number of electrons $n$ is even; $S$ is half-integer for $n$ odd (e.g. $\frac{1}{2}$, $\frac{3}{2}$, etc.).

The total resultant angular momentum $J$ is similarly quantized, with $J^2$ and $J_z$ having eigenvalues $\hbar^2J(J+1)$ and $\hbar J_z$ associated with quantum numbers $J$ and $J_z$. In terms of $L$ and $S$, the range of possible values for the quantum numbers $J$ and $J_z$ are

$$J \in \{ |L - S|, |L - S| + 1, \ldots, L + S - 1, L + S \}$$
$$J_z \in \{ -J, -J + 1, \ldots, J - 1, J \}$$

(27.A.4)

(Note that if $S$ is half-integer, then so will be $J$ and $J_z$.) These relations are generally satisfied for the addition of any two angular momenta, not just $L$ and $S$. For example, two electrons, both in states with $l = 1$, may have a total, combined orbital angular momentum quantum number of $L = 1 - 1 = 0$, or $L = 1$, or $L = 1 + 1 = 2$. Their total spin angular momentum quantum number may be either $S = \frac{1}{2} + \frac{1}{2} = 1$ or $S = \frac{3}{2} - \frac{1}{2} = 0$. Using (27.A.4), the possible values for the total angular momentum quantum number $J$ are then:

<table>
<thead>
<tr>
<th></th>
<th>$L = 0$</th>
<th>$L = 1$</th>
<th>$L = 2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S = 0$</td>
<td>$J = 0$</td>
<td>$J = 1$</td>
<td>$J = 2$</td>
</tr>
<tr>
<td>$S = 1$</td>
<td>$J = 1$</td>
<td>$J = 0$ or $J = 1$ or $J = 2$</td>
<td>$J = 1$ or $J = 2$ or $J = 3$</td>
</tr>
</tbody>
</table>

Clearly in many cases a given amount of total angular momentum $J$ might be obtained by combining different amounts of total orbital and spin angular momenta $L$ and $S$, even from a set of atomic electrons with fixed values for their individual orbital angular momentum quantum numbers $l$. Upon examination of the above table, two electrons, each with $l = 1$, could have $J = 1$ in the multi-electron eigenstates $|JLS\rangle = |101\rangle$ or $|110\rangle$ or $|111\rangle$ or $|121\rangle$. In general, we should expect that such a two-electron atomic state with $J = 1$ would arise from some coherent superposition (mixture) of these four $|1LS\rangle$ orthogonal eigenstates.

It may turn out, though, that a given $J$ arises in a particular multi-electron atomic state from a single, pure $|JLS\rangle$ state. Thus the multi-electron state is an eigenstate of both $L^2$ and $S^2$ as well as $J^2$ (rather than a coherent superposition of several such states as mentioned in the last paragraph). Such a state is said to be $LS$ or Russell-Saunders coupled. These $|JLS\rangle$ states are

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16 Herbert. N. Russell was a very influential American astronomer of the early 20th century. Frederick A. Saunders was an accomplished American physicist who made important contributions to atomic spectroscopy. They described their angular momentum coupling scheme in a paper published in 1925.
particularly well suited for the calculation of energy shifts due to an externally-applied magnetic field, as we now show.

In general, for small values of the magnitude of an externally applied magnetic field \( B \) oriented along the z-axis, eigenstates of \( J^2 \) and \( J_z \) will experience proportional energy shifts of

\[
\langle E_n \rangle = -\langle \mathbf{M} \cdot \mathbf{B} \rangle = g \mu_n J_z B \tag{27.A.5}
\]

For atomic states with a given quantum number \( J \), the coefficient \( g \) is independent of \( J_z \) and is called the atomic state’s \( g \)-factor. Thus the energy shift of the state is proportional to \( J_z \). Since the orientation of the z-axis is arbitrary, then as far as eigenstates of \( J^2 \) and \( J_z \) are concerned, the atom’s total magnetic moment vector \( \mathbf{M} \) must be parallel to and proportional to its total angular momentum vector \( \mathbf{J} \). However, \( \mathbf{J} = \mathbf{L} + \mathbf{S} \), whereas we would expect that the magnetic moment vector \( \mathbf{M} \propto \mathbf{L} + g_e \mathbf{S} = \mathbf{J} + (g_e - 1) \mathbf{S} \). This vector \( \mathbf{M} \) would generally not be parallel to \( \mathbf{J} \). The quantum-mechanical resolution to this conundrum is to require that the quantum operator \( \mathbf{M} \) be proportional to the projection of this latter vector onto the direction of \( \mathbf{J} \): \(^{17}\)

\[
\mathbf{M} \propto \mathbf{J} \left[ 1 + (g_e - 1) \frac{\mathbf{J} \cdot \mathbf{S}}{J^2} \right] \tag{27.A.6}
\]

We can find the value of \( \mathbf{J} \cdot \mathbf{S} \) as follows: since \( \mathbf{J} = \mathbf{L} + \mathbf{S} \), then \( \mathbf{L} = \mathbf{J} - \mathbf{S} \) and

\[
\mathbf{L}^2 = (\mathbf{J} - \mathbf{S}) \cdot (\mathbf{J} - \mathbf{S}) = \mathbf{J}^2 + \mathbf{S}^2 - 2 \mathbf{J} \cdot \mathbf{S}
\]

\[
\therefore \ 2 \mathbf{J} \cdot \mathbf{S} = \mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2
\]

The \( LS \) coupled, \( |JLS\rangle \) states are eigenstates of the RHS of the above expression, so for these states (27.A.6) becomes

\[
\mathbf{M} \propto \mathbf{J} \left[ 1 + (g_e - 1) \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \right]
\]

Comparing this result to (27.A.5), we find that an \( LS \) coupled, \( |JLS\rangle \) state’s \( g \)-factor is given by

\[
g = 1 + (g_e - 1) \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \tag{27.A.7}
\]

Setting \( g_e \equiv 2 \) in (27.A.7) results in what is called the \textit{Landé g-factor} for the \( LS \) coupled state.\(^{18}\)

Applying this result to the example we presented earlier (the \( J = 1 \) states of a two-electron system, each with orbital quantum number \( l = 1 \)), possible values for the Landé \( g \)-factor are:

\[
|JLS\rangle = |101\rangle: g = 2; \ |110\rangle: g = 1; \ |111\rangle: g = 3/2; \ |121\rangle: g = 1/2.
\]

\(^{17}\) Rigorously, the results presented here follow from the \textit{Wigner-Eckart theorem}, part of the representation theory of Lie groups (physicists Eugene Wigner and Carl Eckart).

\(^{18}\) The German physicist Alfred Landé published this result in 1921.
superposition of these states, the resultant g-factor to be used in equation (27.A.5) would be a weighted average of these four values.

**Spectroscopic term notation**

The individual electrons in an atom occupy stationary states with various values for each electron’s angular momentum quantum numbers \( l, l_z, \) and \( s_z \). In addition, the principal quantum number \( n \) determines how deeply into the nuclear Coulomb potential well an electron state resides and determines the electron state’s binding energy (except for usually relatively small corrections due to spin-orbit coupling, mutual electrostatic repulsion among the electrons, and several other effects). The principal quantum number \( n \) can assume only positive integer values, with \( n = 1 \) representing the most strongly bound states (binding energy decreases with increasing \( n \) approximately as \( n^2 \)).

For any particular \( n \), the orbital angular momentum quantum number \( l \) is restricted to an integer value in the set \( l \in \{0, 1, \ldots, n-1\} \). Thus, for example, \( l \) must equal 0 in the \( n = 1 \) states, but \( l \) can equal 0 or 1 in the \( n = 2 \) states, etc. For any particular value of \( l \), single electron states exist with \( l_z \in \{-l, -l+1, \ldots, l-1, l\} \) and with \( s_z = \pm 1/2 \). Thus for a particular choice of \( n \) and \( l \), there are a total of \( 2(2l+1) \) single-electron states, and counting all allowable choices for \( l, l_z, \) and \( s_z \), there are a total of \( 2n^2 \) single-electron states with principal quantum number \( n \). Because electrons are fermions, there can exist at most one electron occupying each of these states. The \( 2n^2 \) single-electron states with principal quantum number \( n \) collectively make up an atomic shell. The \( 2n^2 \) single-electron states with a specified \( n \) and \( l \) make up a subshell. It can be shown that a completely filled atomic subshell holding \( 2n^2 \) electrons will form a multi-electron state which is completely spherically-symmetric and therefore have total \( J = L = S = 0 \). This is then also true for any completely filled shell as well.

**Spectroscopic notation** denotes the orbital angular momentum quantum numbers of the various occupied atomic subshells using letter symbols from the following table:

<table>
<thead>
<tr>
<th>( l ) value</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>…</th>
</tr>
</thead>
<tbody>
<tr>
<td>symbol</td>
<td>( s )</td>
<td>( p )</td>
<td>( d )</td>
<td>( f )</td>
<td>( g )</td>
<td>( h )</td>
<td>…</td>
</tr>
</tbody>
</table>

A specific subshell is prefixed with its \( n \) value, as in: \( 1s, 2s, 2p, 3s, 3p, 3d, \) etc. If more than one electron occupies a subshell, then the number of electrons is denoted by a superscript, e.g. \( 2p^5 \).

For example, the electron configuration of the ground state of neon is written as \( 1s^22s^22p^6 \), the ground state of sodium is \( 1s^22s^22p^63s^1 \).

A **spectroscopic term** expression describes a multi-electron, \( LS \) coupled \( |JLS\rangle \) state using the following format: \( ^2S_{1/2}L_J \), where the spin multiplicity prefix is an integer (the number of possible values for \( S_z \in \{-S, -S+1, \ldots, S-1, S\} \)), the value for \( L \) is denoted by an upper-case version of the appropriate letter found in the previous table, and a number suffix (integer or half-integer) is used for the total angular momentum quantum number \( J \). Thus \( ^1S_0 \) represents \( |000\rangle \), the term
for any completely filled or empty subshell; $^2P_{1/2}$ for $|\frac{1}{2}\frac{1}{2}\rangle$; etc. If the multi-electron state has odd spatial parity, i.e. $\langle -\vec{r} | J LS \rangle = - \langle \vec{r} | J LS \rangle$, then the term includes a trailing "°" as in $^2P°_{1/2}$. For example, one particular singly-ionized, LS coupled state of neon could be described as: $1s^22s^22p^5(^2P°_{3/2})$, which, according to equation (27.A.7), would be expected to have a Landé g-factor of $4/3$ ($J = \frac{1}{2}$, $L = 1$, $S = \frac{1}{2}$).

Racah’s $Jl$ coupling scheme for excited atomic states

One other common angular momentum coupling scheme should be mentioned, because it is particularly relevant to the theoretical analyses of the observed Zeeman splitting of the transitions in neon between the excited state configurations ($1s^22s^22p^5$ $3p\rightarrow 3s$ and $4d \rightarrow 3p$), transitions which produce most of the bright spectral lines shown in Figure 1. This scheme, known as $Jl$ coupling, combines the orbital angular momentum $l$ of a lone excited electron with the total angular momentum $J_{\text{core}}$ of the remaining LS coupled core electrons ($1s^22s^22p^5$ for the neon lines we’re considering). The resulting combined angular momentum $K$ would be chosen from the set of possibilities $K \in \{ |J_{\text{core}} - l|, |J_{\text{core}} + l|-1, J_{\text{core}} + l \}$. The excited electron’s spin $s$ is then combined with $K$ to give a final total $J$ of $|K \pm \frac{1}{2}|$, as first described in (Racah, 1942).

The accepted spectroscopic term notation used for a state defined by $Jl$ coupling is, for example, $1s^22s^22p^5(^2P°_{3/2})3p^2[5/2]_2$, with $2^{2s+1}[K]_L$ as the term descriptor of the final, $Jl$ coupled term, and the term describing the core electron’s LS coupled state is listed in parenthesis. This is the notation used to describe neon’s atomic configurations on the NIST website (Martin & Wiese, 2007). The g-factor for $Jl$ coupled states is given in (Racah, 1942) as $(J_{\text{core}}$ and $g_{\text{core}}$ are the total angular momentum and g-factor of the LS coupled state of the core electrons, and we use the simple approximation $g_e = 2$):

$$g_{Jl} = \frac{2J + 1}{2K + 1} + 2(g_{\text{core}} - 1) \frac{K(K+1) + J_{\text{core}}(J_{\text{core}} + 1) - l(l+1)}{(2K+1)(2J+1)}$$

For the neon example given above, $1s^22s^22p^5(^2P°_{3/2})3p^2[5/2]_2$, then $J_{\text{core}} = 3/2$, $g_{\text{core}} = 4/3$ (using equation (27.A.7)), $l = 1$, $K = 5/2$, and $J = 2$. The resulting $g = 16/15 \approx 1.067$. The two other $Jl$ coupled combinations which also result in $J = 2$ are: $1s^22s^22p^5(^2P°_{3/2})3p^2[3/2]_2$ ($g = 43/30 \approx 1.433$) or $1s^22s^22p^5(^2P°_{1/2})3p^2[3/2]_2$ ($g = 7/6$). In contrast, if we were to simply LS couple the complete $1s^22s^22p^53p$ electron configuration (keeping in mind the limitations on the possible core electron states demanded by Pauli exclusion), the possible states with total $J = 2$ then have terms of $^3P_2$ ($g = 3/2$), $^3D_2$ ($g = 7/6$), or $^1D_2$ ($g = 1$). The consequences of these various possibilities on the expected Zeeman splitting of the neon spectral lines are analyzed in a

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19 Giulio Racah was a mid-twentieth-century Italian-Israeli physicist who made several important contributions to the modern quantum theory of multi-electron atomic states and atomic spectroscopy.
later section. Of course, any $Jl$ coupled state may be expressed as a coherent superposition of $LS$ coupled states.

**Electric dipole radiation selection rules and Zeeman splitting**

Visible light has wavelengths of $\sim 400–800$ nm, thousands of times greater than a atomic diameter ($\sim 1–3\text{Å}$). Consequently, an electromagnetic wave in this wavelength range primarily affects an atom’s electrons through oscillations of its electric field in the atom’s vicinity. This oscillating field can exchange energy (in the form of photons) with the atom and cause transitions between atomic states whose energy difference $\Delta E = h\omega$, where $\omega$ is the angular frequency of the electric field oscillation. Such transitions correspond to the classical, electric dipole radiation discussed in the main text (pages 27-ff.), and are therefore known as *electric dipole* transitions. In fact, the analogy is more than just a casual resemblance to the classical situation. As you will learn in your quantum mechanics course, one can represent a perturbing force by an operator $G$ applied to the quantum state $|\psi\rangle$ to generate the new state $|\psi'\rangle = G|\psi\rangle$. The probability that this new state is observed to correspond to some specified state $|\phi\rangle$ is given by the squared magnitude of the matrix element of $G$ connecting $|\psi\rangle$ and $|\phi\rangle$:

$$|\langle\phi|\psi'\rangle|^2 = |\langle\phi|G|\psi\rangle|^2$$

In the case of an oscillating electric field experienced by a single electron (such as the transverse electric field produced by a passing electromagnetic wave), the relevant operator is proportional to the dot product of the field’s polarization vector $\vec{E}$ and the electron’s electric dipole moment vector $-e\vec{R}$ ($\vec{R}$ is the electron’s position operator): $\vec{E} \cdot -e\vec{R} = e(E_x\hat{x} + E_y\hat{y} + E_z\hat{z})$. Thus to determine the probability of such a field leading to an observed transition between two single-electron spatial states $|nll_z\rangle$ and $|n'l'l'_z\rangle$, we must evaluate the *matrix elements* of the three Cartesian position operators:

$$\langle n'l'l'_z | X | nll_z \rangle, \quad \langle n'l'l'_z | Y | nll_z \rangle, \quad \langle n'l'l'_z | Z | nll_z \rangle$$

As shown in *Leighton* as well as in many elementary quantum mechanics texts, these matrix elements will all generally vanish unless the following electric dipole transition *selection rules* obtain ($\Delta n = n' - n$ can be anything, including 0, as long as $n > l$ and $n' > l'$):

$$\begin{align*}
X, Y, Z : \quad & \Delta l = l' - l = \pm 1 \quad \text{and} \quad \Delta s_z = 0 \\
X, Y : \quad & \Delta l_z = l'_z - l_z = \pm 1 \\
Z : \quad & \Delta l_z = 0
\end{align*} \quad (27.A.9)$$

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20 We ignore the electron’s spin quantum number $s_z$ because the oscillating electric field of the passing visible-light photon has little effect on a magnetic dipole moment, and the photon’s oscillating magnetic field is relatively insignificant because of the photon’s long wavelength (low frequency). *Magnetic dipole* transitions can occur, however, but at a very low rate (and are thus known as a class of *forbidden transitions*).
These electric dipole transition selection rules may be extended in a straightforward manner to $LS$ coupled multi-electron states $|JLS\rangle$. The most basic requirements for an electric dipole transition is that only one electron changes its state, and this electron must have its $\Delta l = \pm 1$ (for the case of $JL$ coupling, the lone excited electron transitions). Additionally, the electrons’ combined spatial wave function must change parity. As for the atom as a whole,\[ \Delta J = 0, \pm 1 \quad (J = 0 \rightarrow J = 0 \text{ forbidden})
\]
\[ \Delta J_z = 0, \pm 1 \quad (J_z = 0 \rightarrow J_z = 0 \text{ forbidden if } \Delta J = 0) \]
\[ \Delta L = 0, \pm 1 \quad (L = 0 \rightarrow L = 0 \text{ forbidden}) \]
\[ \Delta S = 0 \]

(27.A.10)

Justification for the rules may be found in Leighton. The relationship between the polarization of the emitted radiation and $\Delta J_z$ is the same as that for $\Delta l_z$ in (27.A.9): for linear polarization purely in a plane containing the $z$-axis, $\langle J' L' S J_z | Z | J L S J_z \rangle$ is non-vanishing, and $\Delta J_z = 0$; if $\Delta J_z \neq 0$, then the polarization is generally elliptical with a non-vanishing component perpendicular to the $z$-axis.

Now consider an electric dipole transition in the presence of an applied magnetic field aligned with the $z$-axis. The field will shift the energies of states having different $J_z$ in accordance with equation (27.A.5): $\langle E_B \rangle = -\langle \mathbf{M} \cdot \mathbf{B} \rangle = g \mu_p J_z B$. Assume that a single electron transitions from $4d$ to $3p$, with initial and final $LS$ coupled states $|JLS\rangle_i = |2 2 1\rangle$ (or $^3D_2$) and $|JLS\rangle_f = |1 1 1\rangle$ (or $^3P_1$). The electric dipole selection rules listed above are satisfied, and equation (27.A.7) gives $g$-factors of $g_i = 7/6$ and $g_f = 3/2$. The resulting allowable state transitions are shown in Figure 12.

![Figure 12: An example of Zeeman splitting of a hypothetical electric dipole transition of a single electron (4d→3p). The term symbols of the initial and final LS coupled states are also shown. Applying a magnetic field splits the energy degeneracy of the various initial and final $J_z$ states (the splitting is greatly exaggerated). The selection rules in (27.A.10) allow 9 different transitions; each has a different energy $\Delta E$ because the initial and final states’ $g$-factors differ (see text). A diagram showing the relative locations of the 9 resulting spectral lines is also shown, along with each line’s initial and final $J_z$.](image-url)
If the two states’ $g$-factors were the same, then the application of a magnetic field would split the spectral line into only three distinct wavelengths, rather than the nine shown in Figure 12. Only if both $g$-factors $= 1$, would the splitting match the normal Zeeman Effect predicted by Lorentz (or one of the states has $J = 0$ and the other has $J = 1$ and $g = 1$).

### Normal Zeeman lines of neon

Now consider the two prominent normal Zeeman lines in the neon spectrum at wavelengths of 585.2 nm and 626.6 nm. Each line is generated by a transition between the configurations $1s^22s^22p^53p \rightarrow 1s^22s^22p^53s$. For each of these lines, both the initial and final states have 9 core electrons ($1s^22s^22p^5$) combined via LS-coupling to give the odd-parity term $^2P_{1/2} (J = 1/2, L = 1, S = 1/2)$. The excited electron’s orbital and spin angular momenta may assume different orientations relative to the $\vec{J}$, $\vec{L}$, and $\vec{S}$ of the core, resulting in the energy difference between the transitions generating the two spectral lines.

In the case of the 585.2 nm spectral line, the excited, $n = 3$ electron combines with the core electrons to form a nearly pure LS coupled term $1s^22s^22p^5(^2P_{1/2})3p \rightarrow 1s^22s^22p^5(^2P_{1/2})3s \; ^1P_0$ (i.e., $|000\rangle \rightarrow |110\rangle$). In both states the excited electron’s orbital angular momentum cancels that of the core, giving a total net $J = L = S = 0$: the overall angular momentum of the atom’s six $p$ electrons ($2p^53p$) is the same as that of its filled, ground state configuration ($2p^6$). Since the excited electron’s spin does not change orientation during its electric dipole transition to $3s$, the total spin $S$ of the atom’s electrons remains 0, while the loss of the excited electron’s orbital angular momentum ($\Delta l = -1$) leaves a net $L = 1$ for the atom’s total orbital angular momentum. Thus $J = 0$ in the initial state, and $J = 1$ and $g = 1$ in the final state, making this transition a good example of the quantum analog to Lorentz’s theory. The experimentally determined $g$-factor of the 585.2 nm final state is $1.037 \pm 0.002$, only 4% away from the pure LS coupled $^1P_0$ state Landé value.\(^{21}\)

In the 626.6 nm normal Zeeman transition, on the other hand, it is the initial state which has net angular momentum. As in the previous case, the $3p$ electron’s spin cancels that of the core electrons to give an overall net $S = 0$. The $L = 1$ orbital angular momentum of the core’s $^2P_{1/2}$ term combines with the $3p$ electron’s $l = 1$ to yield $J = L = 1$ for the atom’s total orbital angular momentum. Thus the initial state term is the very nearly pure, $LS$ coupled $1s^22s^22p^5(^2P_{1/2})3p \; ^1P_1$ ($|110\rangle$). Following the excited electron’s transition to $3s$, however, it assumes the $Jl$ coupled state $1s^22s^22p^5(^2P_{1/2})3s \; ^2[\frac{1}{2}]_0$, in which its spin combines with that of the core’s total angular momentum of $1/2$ to yield $J = 0$. The measured $g$-factor of the 626.6 nm initial state is $0.994 \pm 0.004$.

\(^{21}\) Measured $g$-factors are from (Pinnington, 1967).