

SOME ELEMENTS OF ATOMIC STRUCTURE THEORY

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1 Review of facts and terminology

1.1 The nature of an atom

As everyone knows, an atom is the smallest unit of a chemical element, and atoms combine to form molecules and solids. Each element is uniquely specified by its **atomic number Z** . However a given element may occur in several different versions, called **isotopes**; these have the same Z but different **atomic mass number A** . A glance at the periodic table shows that for the naturally occurring elements Z and A vary from hydrogen ($Z = 1$, $A = 1$) to uranium ($Z = 92$, $A = 238$). The mass of an atom is given approximately by A , in terms of the **atomic mass unit**, or **amu**: $1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$. The sizes of atoms are conveniently measured in terms of a unit called the **Bohr radius**, a_0 , which has the value $1 a_0 = 5.3 \times 10^{-11} \text{ m} = 0.053 \text{ nm}$. Although atoms vary greatly in mass and other properties, their sizes are all comparable, being a few times a_0 . Since this size is small compared to the wavelength of light, atoms are not “visible” in the ordinary sense of the word – an optical microscope cannot form an image of a single atom. This is one of the reasons that the structure of an atom cannot be understood in the same familiar mechanical-geometrical terms that we use to describe the structure of a mountain, a tree, a crystal, or even a molecule. In many ways atomic physics is the prototype for the scientific study of objects which can be understood only by rather formal abstract ideas.

The classic experiments of Rutherford about 1911 established that the mass of the atom is concentrated almost entirely in a very small positively charged **nucleus**, the size of which is approximately 10^{-14} m . This nucleus contains Z protons, each having electrical charge $e = 1.60 \times 10^{-19} \text{ C}$, and $A - Z$ neutrons. Thus the masses of the **nucleons** (neutrons and protons) are approximately 1 *amu* each, and the neutral atom must contain Z **electrons**, each with a charge of $-e$. The electron mass, $m = 9.1 \times 10^{-31} \text{ kg}$, is only about 1/2000 of the nucleon mass. The study of atomic structure is primarily the study of how the electrons

are distributed in the space around the nucleus, which can usually be approximated by a point charge $+Ze$, fixed at the center of the atom.

Attempts to form a mental image of atomic structure can be misleading if taken too literally. There are two familiar kinds of pictures: in the first the electrons are particles moving in “Bohr orbits” forming a miniature “solar system”; in the second the electrons are “Schrödinger waves” forming diffuse clouds. In fact, these are both over-simplifications, but nevertheless useful. In his Complementarity Principle, Niels Bohr stressed the fact that we must accept the idea that an electron is neither a particle nor a wave, but has complementary properties of both. The crucial point is that particles and waves are mathematical abstractions, human inventions, useful concepts; the electron, however is a natural physical object. Given its extremely small size and mass compared to anything in our everyday experience, we shouldn’t be surprised that it doesn’t always move in trajectories like a baseball or waves like the surf.

Although a large amount of information has been accumulated about atoms by studying their chemical behavior and other properties, by far the most important means of studying atomic structure is by means of optical spectroscopy. In fact the two subjects almost coincide: the theory of atomic spectroscopy is by and large the same subject as atomic structure theory.

1.2 Energy quantization

The internal energy of an isolated atom can have only a discrete set of values - the “**allowed energy levels**”. This fact was a strong motivation for the invention and development of the quantum theory early in the twentieth century. Today we say that the energy is “quantized”, and we understand that in terms of the eigenvalues of the hamiltonian operator. For the purposes of this introduction, however, we will not discuss the theory, only the facts.

In discussing atomic energy levels, we mean only the energy of the electrons due to their motions within the atom. We do **not** include the atom’s interaction with other atoms, or its own motion through space: we assume the atom is at rest and isolated from all other objects. We also do **not** include the internal energy of the **nucleus**. We regard the nucleus as a very small, very heavy positively charged particle at the center of the atom.

When we speak of the **structure** of an atom, in practice this usually means not so much the arrangement of the electrons in *space*, but rather the set of allowed energy levels. This set of numbers, often displayed in an “energy level diagram,” is unique to the particular kind of atom being studied, and in principle gives us most of the information we need about the atom. Each atom has a *lowest* energy level, called the “ground state” energy. It also has an *upper limit* to its energy levels, called the **ionization energy** E_I . If a ground-state atom is suddenly given an amount of energy greater than E_I it may lose one or more of its electrons and become “ionized.” In general, the lower energy levels are separated by relatively large energy differences (lie far apart on the energy level diagram) while the higher energy levels crowd together more and more closely as the ionization energy is approached. In principle there are an infinite number of energy levels, all lying below the ionization energy, which is often called the ionization limit for this reason.

1.3 Spectroscopy

Our detailed knowledge of atomic energy levels comes almost entirely from optical spectroscopy. When an atom is excited into a state with more energy than the ground state, it will stay in that excited state for only a short time, after which it will make a “*quantum jump*” to a lower level. Since energy must always be conserved, the atom must somehow lose its excess energy during this process. It often does so by emitting light (electromagnetic radiation). The wavelength of the emitted light is determined by the energy difference of the initial and final levels. This wavelength can be measured in the laboratory very precisely with a *spectrometer*. By recording all the different wavelengths emitted by a hot gas of a given element, we acquire a list of the energy level *differences* characteristic of that atom. From these differences, the energy levels themselves can be deduced, although this is not necessarily a simple process.

In most cases, the atom emits a single *photon*, or “quantum” of light when it jumps from one energy level to another. The wave nature of light and the quantum nature of light are related by the simple equations

$$E = h\nu \quad \text{and} \quad c = \nu\lambda \quad (1)$$

where ν is the frequency of the light, λ is its wavelength, and E is the energy of a single photon. The velocity of light $c = 3.0 \times 10^8 m/s$ and Planck’s constant $h = 6.63 \times 10^{-34} Js$ are universal constants.

We label the atom we are discussing by means of two numbers: the atomic number Z , and the electron number N . We often specify Z indirectly by giving the standard symbol for the element. For example He means $Z = 2$ and Fe means $Z = 26$. The electron number N is simply the number of electrons in the atom; for a neutral atom of course $N = Z$. We are often interested in the spectra of positive ions, for which $N < Z$. For example, in a hot gas such as the upper atmosphere of the sun, many atoms are ionized because of the violent collisions between atoms. The higher the temperature, the higher will be the degree of ionization of the atoms, i.e. the difference $Z - N$. We often give N indirectly also, by giving the *spectrum number* in roman numerals. Thus C I means the first spectrum of carbon, namely neutral carbon, so $Z = N = 6$; but C III means the third spectrum of carbon, namely *twice-ionized* carbon, so that $Z = 6, N = 4$. All the ions of equal N are said to form an *isoelectronic sequence*. Sequences are typically named for the neutral member; for example C III belongs to the Be sequence, and all ions with 4 electrons are called “beryllium-like”.

1.4 Quantum numbers

In addition to establishing the energies of the atom’s quantum states, it is the job of the spectroscopist to assign each state a set of *quantum numbers*. These numbers serve as identifying labels for the energy levels, and also provide some information about the physical nature of the states.

For the neutral hydrogen atom, the situation is simple: each quantum state is labeled by four quantum numbers, namely n, l, m_l, m_s . If relativistic effects are ignored to begin

with, these numbers have direct physical interpretations as follows. The first three are integers which describe the motion of the electron in space. The **principal quantum number** is a positive integer $n = 1, 2, 3, \dots$ which determines the energy of the state and the semi-major axis of the elliptical Bohr orbit. The energy is $E_n = -E_I/n^2$ where E_I is the ionization energy of hydrogen, also called the Rydberg energy unit, approximately equal to 13.6 eV. The **orbital quantum number** l is a nonnegative integer less than n , namely $l = 0, 1, 2, \dots, n-1$. This determines the magnitude of the **angular momentum** of the electron's motion, and the eccentricity of the Bohr orbit. The orbital angular momentum magnitude is $|\vec{L}| = \sqrt{l(l+1)} \hbar$ where $\hbar = h/2\pi$. The **magnetic quantum number** is an integer m_l in the range $-l \leq m_l \leq +l$, which determines the component of the orbital angular momentum in a particular direction. In a given coordinate system, the z component of the orbital angular momentum is $L_z = m_l \hbar$.

In addition to its orbital motion around the nucleus, the electron has an intrinsic angular momentum called **spin**. The magnitude of the spin angular momentum is $|\vec{S}| = \sqrt{s(s+1)} \hbar$, exactly analogous to the orbital angular momentum, except that the spin quantum number is not an integer, but rather $s = 1/2$. In a given coordinate system, the z component of the spin angular momentum is $S_z = m_s \hbar$. Here m_s is analogous to m_l except that it has only two possible values: $m_s = \pm 1/2$. We say that the spin must be either “up” or “down”.

For reasons of convenience in speaking and writing, a historical system of letters instead of l values, known as **spectroscopic notation**, continues to be used. In this system $s=0$, $p=1$, $d=2$, $f=3$, $g=4$, $h=5$, etc. Thus for example a state with $n = 3, l = 2$ is called **3d** for convenience. This **3d orbital** is taken to include states with all possible values of m_l, m_s for the given values $n = 3, l = 2$. The possible hydrogen orbitals are thus $1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, \dots$.

1.5 The Pauli Exclusion Principle

For atoms other than hydrogen we may consider labeling the states by giving the set of quantum numbers n, l, m_l, m_s for each electron. In fact, the physical N -electron state may not be well represented in this way, but it is a reasonable starting point for a labeling system. The Pauli Principle states that no two electrons can have the same set of these 4 quantum numbers. Thus there is a maximum number $(2(2l+1))$ of electrons which can occupy each orbital. These numbers are familiar from chemistry: $s : 2, p : 6, d : 10, \dots$. An electronic **configuration** is specified by giving the orbital for each electron, or in other words by giving the **occupation number** of each orbital. Thus the ground state of the carbon atom has the configuration $(1s^2 2s^2 2p^2)$; sometimes filled orbitals (those containing the maximum allowed number of electrons) are omitted and this is written simply $(2p^2)$.

Since the principal quantum numbers determine the energy to a first approximation, all states with the same n value are said to belong to a given **shell**, and as we consider increasing values of N , the shells are filled “from the bottom up”, in order of increasing energy, and increasing distance from the nucleus. However this approximation soon breaks down — for example the ground configuration of potassium ($Z = 19$) is $(3s^2 3p^6 4s)$ rather than $(3s^2 3p^6 3d)$. This effect which causes orbitals of low l to have lower energies is called

penetration, since electrons in these orbitals can penetrate closer to the nucleus. The shells can be designated by upper case letters; this notation is less common in optical spectroscopy than in chemistry or X-ray spectroscopy. The letter K denotes the $n = 1$ shell; L, $n = 2$; M, $n = 3$, etc.

In summary, the atomic shell structure can be represented as follows:

<i>SHELL</i>	<i>ORBITALS</i>	<i>STATES</i>
<i>K</i>	$1s^2$	2
<i>L</i>	$2s^2 2p^6$	8
<i>M</i>	$3s^2 3p^6 3d^{10}$	18
<i>N</i>	$4s^2 4p^6 4d^{10} 4f^{14}$	32

(2)

and so forth.

1.6 States of complex atoms

For atoms with two or more electrons, there are many possible quantum states, and we need a systematic way of naming them. The standard spectroscopic notation is based on the *vector model* of angular momentum addition. The quantum theory of angular momentum is a large and very well-developed subject, but many of its results can be summarized as follows. A good reference to begin the study of the structure of complex atoms is the small book by Woodgate [1].

An angular momentum vector \mathbf{J} is specified by two quantum numbers J, M so that its magnitude is $|\mathbf{J}| = \sqrt{J(J+1)} \hbar$ and its z -component is $\mathbf{J}_z = M \hbar$. As with the orbital and magnetic quantum numbers given above for a single electron, for a given J the M quantum number can have $2J+1$ values, namely $M = -J, -J+1, \dots, J-1, J$. In the vector model we imagine that the various ways in which the vector \mathbf{J} is allowed to point are restricted so that its z component is always one or the other of these $2J+1$ values. The angular momentum quantum number J may be either an integer or a half-integer, so that the range $-J \leq M \leq J$ always involves an integer number of steps: $2J+1$ is always an integer.

Now if we add two angular momentum vectors \mathbf{J}_1 and \mathbf{J}_2 , using the above restrictions on the z components, we see that there are a total of $(2J_1+1)(2J_2+1)$ states. We can specify these states by the values of M_1 and M_2 . But we can also group the states according to *total* angular momentum quantum numbers J and M , using the ordinary vector sum $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$, but with the above conditions on the values of J, M . If we work this out carefully we see that the possible values of J range from a minimum of $J_{min} = |J_1 - J_2|$ to a maximum of $J_{max} = J_1 + J_2$ including all values in integral steps in between. Then for each J we have the usual values of M . This turns out to give the same number of states:

$$\sum_{J=|J_1-J_2|}^{J_1+J_2} (2J+1) = (2J_1+1)(2J_2+1) \quad (3)$$

It turns out, as we will see later in discussing the quantum theory of atomic structure, that the most generally useful scheme for labeling atomic states consists of combining all the

orbital angular momenta of the individual electrons into a **total orbital angular momentum** $\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 + \dots$, and also combining all the spin angular momenta of the individual electrons into a **total spin angular momentum** $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \dots$. Only after that are these two added together to get the **total angular momentum** $\mathbf{J} = \mathbf{L} + \mathbf{S}$. This is called **L-S coupling** or **Russell-Saunders coupling**. Since the energy of an isolated atom cannot depend on the direction of the total angular momentum, the three quantum numbers L, S, J are sufficient to determine the energy in all but the most complicated configurations, and are thus a very convenient label for atomic energy levels.

For example, in an excited state of helium, we may have the configuration $1s2p$, so that there are four angular momenta to combine: $l_1 = 0, l_2 = 1, s_1 = s_2 = 1/2$. We know there will be 12 possible states, since there are three possible values of m_l for the p electron, and for each of these we can have 4 possible combinations of m_{s1} and m_{s2} , namely *up-up*, *up-down*, *down-up*, and *down-down*. We describe these 12 states in L-S coupling as follows: Adding 0 and 1 gives only one possible value of L , namely $L = 1$. But there are two possible values of S , since we can have either $|s_1 - s_2| = 0$ or $s_1 + s_2 = 1$, but nothing in between. Thus we have states with $(L = 1, S = 0)$ and states with $(L = 1, S = 1)$. Finally we form the J values. For $S = 0$ we must have $J = L = 1$; but for $S = 1$ we can have J running from $|L - S|$ to $L + S$ in integer steps, namely $J = 0, 1, 2$. Putting all this together we see that we expect 4 energy levels within the $1s2p$ excited configuration of helium. We label them $\{L=1, S=0, J=1\}$, $\{L=1, S=1, J=0\}$, $\{L=1, S=1, J=1\}$, and $\{L=1, S=1, J=2\}$.

For convenience, so that we do not have to write out all these quantum numbers, we extend our spectroscopic notation as follows. We use an upper case letter to represent L according to the previous scheme S, P, D, F, \dots ; then we use the integer $2S+1$ as a super-prefix, and J as a sub-suffix. Without J , using only L, S , this is called a **term**; including J gives a **level**. Within the level are $2J+1$ **states**, which have the same energy since they differ only in M , that is only in the direction of \mathbf{J} . The energy is often determined mainly by L, S ; the weak dependence on J is called the **fine structure**. Finally we pronounce the spin state as “singlet” for $2S+1 = 1$, “doublet” for $2S+1 = 2$, “triplet” for $2S+1 = 3$, and so forth. If the fine structure is small, this terminology tells us to expect a grouping of $1, 2, 3, \dots$ closely-spaced energy levels.

So for our helium example we have 2 terms, “singlet P” 1P , and “triplet P” 3P , with the 4 levels $^1P_1, ^3P_0, ^3P_1, ^3P_2$. Finally, note that there really are 12 states in these 4 levels: if we count the possible values of $M = -J, \dots, +J$, we see that 1P_1 has 3 states, 3P_0 has 1, 3P_1 has 3, and 3P_2 has 5. (Also see the carbon example below.)

In more complex cases, it is important to make use of the simplicity afforded by a **closed shell**. If we have the maximum allowed number of electrons in a shell, they always couple together to give a system with $L = 0$ and $S = 0$. Thus for example, the beryllium ($Z = 4$) atom has a set of excited states $1s^22s2p\ ^1P, 1s^22s2p\ ^3P$, which are exactly analogous to the helium $1s2p$ states described above.

Finally there is a complication for configurations containing **equivalent electrons**, that is two or more electrons in the same orbital (same values of n, l). For example, in the $2p3p$ configuration, the terms are $^1S, ^3S, ^1P, ^3P, ^1D, ^3D$. These are determined by considering all possible values of L, S when we add one electron with $l_1 = 1, s_1 = 1/2$ to another

electron with $l_2 = 1, s_2 = 1/2$. However for the $2p^2$ configuration, some of these terms are forbidden. The reason is that electrons are **fermions**, that is they satisfy Fermi-Dirac statistics, which means that any state of 2 or more electrons must be antisymmetric — it must change sign if we interchange the quantum numbers of any pair of electrons. (This is really not understandable until you learn about the quantum theory of multi-particle states.) The Pauli Exclusion Principle is just one consequence of the fact that electrons are fermions. Another consequence is that certain of the terms that occur for $2p3p$ do not occur for $2p^2$. In fact, the configuration $2p^2$ has just 3 terms, namely 1S , 3P , and 1D .

In summary, the states of an atom are traditionally named in four steps, which we illustrate with the ground configuration of carbon.

First we specify the **configuration**: $1s^22s^22p^2$ (15 states)

then the **terms**: 1S (1 state), 3P (9 states), 1D (5 states)

then the **levels** and **states**:

1S_0 (1 state):	$M = 0$
3P_0 (1 state):	$M = 0$
3P_1 (3 states):	$M = -1, 0, +1$
3P_2 (5 states):	$M = -2, -1, 0, +1, +2$
1D_2 (5 states):	$M = -2, -1, 0, +1, +2$

2 Electron wavefunctions

2.1 Hydrogen: Nonrelativistic

The probability of finding the electron at a particular place within the atom is given by the square of the wavefunction $\psi(\vec{r})$ [2]. That is, the **position probability density** (probability per unit volume) for finding the electron at a displacement \vec{r} relative to the nucleus is $|\psi(\vec{r})|^2$. If we integrate over some volume V , we get the probability of finding the electron within that volume:

$$P(V) = \int_V |\psi(\vec{r})|^2 d^3r. \quad (4)$$

Note this is a three-dimensional integral; if we use rectangular coordinates, $d^3r = dx dy dz$; in spherical polar coordinates, $d^3r = r^2 \sin \theta dr d\theta d\phi$. We often combine the angular parts of this by writing $d\Omega = \sin \theta d\theta d\phi$; then the full 3-dimensional volume element is $d^3r = r^2 dr d\Omega$. (Here Ω stands for a solid angle and is measured in steradians, with the total solid angle surrounding a point being 4π steradians.) Since the probability of finding the electron somewhere must be 1 (100%), it must be a fact that

$$\int |\psi(\vec{r})|^2 d^3r = 1 \quad (5)$$

if the integral is taken over all space.

For hydrogen we know the wavefunction quite well. It is simplest to use spherical polar coordinates, because it turns out that the angular dependence of $\psi(\vec{r})$ is determined by

the electron's orbital angular momentum, which we know is both conserved and quantized. Thus the functional form of the electron wavefunction is closely connected to the quantum numbers used to classify the states and energy levels. For given values of the three quantum numbers (n, l, m) the wavefunction is written

$$\psi_{nlm}(\vec{r}) = R_{nl}(r)Y_{lm}(\theta, \phi). \quad (6)$$

(Here m stands for the quantum number m_l ; we are just using m for simplicity.) The functions Y_{lm} are known as **spherical harmonics**. They are not specific to the hydrogen atom, but occur in many problems in mathematics in which spherical coordinates are used. For the first few values of l, m they are easy to write down:

$$Y_{0,0} = \sqrt{\frac{1}{4\pi}} \quad (7)$$

$$Y_{1,0} = \sqrt{\frac{3}{4\pi}} \cos(\theta) \quad (8)$$

$$Y_{1,1} = -\sqrt{\frac{3}{8\pi}} \sin(\theta)e^{i\phi} \quad (9)$$

$$Y_{1,-1} = \sqrt{\frac{3}{8\pi}} \sin(\theta)e^{-i\phi} \quad (10)$$

Of course $e^{i\phi} = \cos \phi + i \sin \phi$ and $i = \sqrt{-1}$. The spherical harmonics are so well known that we normally do not write them out in formulas like these, but simply use $Y_{lm}(\theta, \phi)$ in our equations just as we use any familiar function such as $\sin \theta$ for example. One simple feature of the Y_{lm} is their normalization:

$$\int |Y_{lm}(\theta, \phi)|^2 d\Omega = \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta |Y_{lm}(\theta, \phi)|^2 = 1. \quad (11)$$

The functions $R_{nl}(r)$ are called the **radial wavefunctions** for hydrogen, and are also well known. In complex atoms, we often assume that each electron has a wavefunction of form $\psi_{nlm}(\vec{r})$, with the same spherical harmonics Y_{lm} , but then the radial functions must be found in some approximate way, and will not be as simple as for hydrogen. Also we often define a different radial function $P_{nl}(r)$ by writing $P_{nl}(r) = rR_{nl}(r)$. Then the full wavefunction is

$$\psi_{nlm}(\vec{r}) = \frac{1}{r} P_{nl}(r) Y_{lm}(\theta, \phi). \quad (12)$$

One advantage of $P_{nl}(r)$ is that its normalization is simple. If we combine the two normalizing equations from above, we get

$$\int |\psi|^2 d^3r = \int_0^\infty r^2 R_{nl}(r)^2 dr = \int_0^\infty P_{nl}(r)^2 dr = 1. \quad (13)$$

Thus $P_{nl}(r)^2$ has the meaning of probability per unit length: in other words $P_{nl}(r)^2 dr$ is the probability for the electron to be at a distance between r and $r + dr$ from the nucleus.

For the first few states of hydrogen, we have the following radial functions, sometimes called *orbitals*. In these equations we are using the atomic unit of length a_0 , the first Bohr radius. So r is measured in units of a_0 and R in units of $a_0^{-3/2}$ so that R^2 is probability density per unit volume.

$$1s : R_{10}(r) = 2e^{-r} \quad (14)$$

$$2s : R_{20}(r) = \frac{1}{\sqrt{2}}(1 - r/2)e^{-r/2} \quad (15)$$

$$2p : R_{21}(r) = \frac{1}{2\sqrt{6}}re^{-r/2} \quad (16)$$

$$3s : R_{30}(r) = \frac{2}{3\sqrt{3}}(1 - 2r/3 + 2r^2/27)e^{-r/3} \quad (17)$$

$$3p : R_{31}(r) = \frac{8}{27\sqrt{6}}(r - r^2/6)e^{-r/3} \quad (18)$$

$$3d : R_{32}(r) = \frac{4}{81\sqrt{30}}r^2e^{-r/3} \quad (19)$$

Some things to notice about these functions: (1) The factor $e^{-r/n}$ determines the orbital's size, which increases with the principal quantum number n , since the wavefunction goes to zero quickly for $r \gg na_0$. (2) For small r , the functions behave like r^l . (3) The number of nodes (zeros) is $n-l-1$. (4) For a given n , the functions with maximum l ($1s, 2p, 3d, \dots$) have no nodes, and correspond to the circular orbits in the Kepler theory; as l decreases, the Kepler ellipses become more eccentric (elongated).

2.2 Electron spin

Besides the wavefunction $\psi(\vec{r})$ of equation (6) which describes the electron's motion in space, we must have a quantum description of its spin. The wavefunction now has two components, one for a "spin up", the other for a "spin down" electron. A good first approximation is to factor this wavefunction into the product $\psi(\vec{r}) \chi$ where χ is a two-component vector called a Pauli *spinor*. A spin state with $m_s = +1/2$ is represented by the spinor χ_+ , while $m_s = -1/2$ is represented by χ_- , with

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad (20)$$

These are eigenfunctions of the spin operators $\mathbf{S}^2, \mathbf{S}_z$, in the standard representation using *Pauli spin matrices*:

$$\vec{\mathbf{S}} = \frac{\hbar}{2} \vec{\sigma} \quad (21)$$

where

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (22)$$

For example an electron in the hydrogen $2p$ orbital might be described by the wavefunction

$$\psi(n, l, m_l, m_s; \vec{r}) = R_{2p}(r) Y_{11}(\theta, \phi) \chi_-, \quad (23)$$

indicating it has $m_l = +1$, $m_s = -1/2$. Note this means that the z component of its total angular momentum would be $m_j = +1/2$. Also note that we soon get in the habit of saying that the angular momentum is m when it is really $m\hbar$!

While we usually discuss hydrogen states which are eigenstates of \mathbf{S}_z , that is not necessary. Suppose an electron is known to be in the state

$$\chi = \alpha \chi_+ + \beta \chi_- = \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \quad (24)$$

Now the probability of finding this electron with spin up is $|\alpha|^2$ and the expectation (mean) value of $\mathbf{S}_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ is found by ordinary matrix multiplication:

$$\langle \sigma_z \rangle = \langle \chi | \sigma_z | \chi \rangle = (\alpha^* \beta^*) \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = (\alpha^* \beta^*) \begin{pmatrix} \alpha \\ -\beta \end{pmatrix} = |\alpha|^2 - |\beta|^2 \quad (25)$$

2.3 Hydrogen: Relativistic

A proper description of spin requires use of the Dirac relativistic wave equation [3]. In the full Dirac theory, the electron wavefunction (Dirac spinor) has four components. We need four functions of \vec{r} , rather than just one (as in the spinless theory) or two (as in the Pauli theory), to describe the electron. This theory includes *antiparticles* as well as spin. Crudely speaking the four functions describe the distribution in space of the four possible kinds of particles: spin-up electrons, spin-down electrons, spin-up positrons, and spin-down positrons. An approximation due to Pauli, often used in atomic physics, reduces the number of components to two and gets rid of the positrons.

So for a proper description of the hydrogen atom, we need a Dirac spinor wavefunction for each state, instead of the nonrelativistic wavefunctions given above. In practice this means two radial functions P and Q instead of the single R (or P) we used in the nonrelativistic theory. It also means two different spherical harmonics instead of just one. The reason for this important effect is that the orbital and spin angular momenta are mixed up together instead of being specified separately. So we must use the quantum numbers n, l, j, m instead of n, l, m_l, m_s . This means that different values of l, m_l are involved in a single state; for example $2p(j=1/2, m=1/2)$ is constructed as a combination of $2p(m_l = 0, m_s = +1/2)$, $2p(m_l = 1, m_s = -1/2)$, and $2s(m_l = 0, m_s = +1/2)$. So we find we need two radial functions $P(r), Q(r)$, and three angular functions $Y_{11}(\theta, \phi)$, $Y_{10}(\theta, \phi)$, and $Y_{00}(\theta, \phi)$ to take the place of the nonrelativistic wavefunction $P(r)Y_{lm}(\theta, \phi)$.

Consider the *energy level* E_{nlj} . (Actually for hydrogen the energy depends only on n, j , not on l , but for more complex atoms that's not true.) There are $(2j + 1)$ *states* with the same energy E_{nlj} , since the z component of the angular momentum, $m\hbar$, can have $(2j + 1)$ values, given by $m = -j, -j + 1, \dots, j - 1, j$. It is easy to understand physically that the

energy is the same for all values of m because the energy cannot depend on the *direction* of the angular momentum. We can use the **Dirac notation** $|n, l, j, m\rangle$, if we want to speak of the **quantum state** rather than the energy E_{nlj} or the wavefunction $\psi_{nljm}(\vec{r})$.

Now to finally write the wavefunctions for the state $|n, l, j, m\rangle$. The relations which are analogous to equation (6) above are

$$\psi_{nljm}^{(+)}(\vec{r}) = \frac{1}{r} P_{nlj}(r) C_+(ljm) Y_{l,m-1/2}(\theta, \phi) + \frac{i}{r} Q_{nlj}(r) C_+(l'jm) Y_{l',m-1/2}(\theta, \phi) \quad (26)$$

and

$$\psi_{nljm}^{(-)}(\vec{r}) = \frac{1}{r} P_{nlj}(r) C_-(ljm) Y_{l,m+1/2}(\theta, \phi) + \frac{i}{r} Q_{nlj}(r) C_-(l'jm) Y_{l',m+1/2}(\theta, \phi). \quad (27)$$

Here $l' = l \pm 1$ is the other value of l which can combine with the spin to form the given j . For $j = l + 1/2$, $l' = l + 1$; for $j = l - 1/2$, $l' = l - 1$. The quantities $C_{\pm}(ljm)$ are simple numerical “vector coupling coefficients” coming from the quantum version of the vector addition $\vec{l} + \vec{s} = \vec{j}$. For example

$$\psi_{np\frac{3}{2}\frac{3}{2}}^{(+)} = \frac{1}{r} P_{np\frac{3}{2}}(r) Y_{11} - \sqrt{\frac{1}{5}} \frac{i}{r} Q_{np\frac{3}{2}}(r) Y_{21}. \quad (28)$$

The (\pm) superscript on the wavefunction refers to the electron spin. The physical meaning of the wavefunction $\psi_{nljm}^{(\pm)}(\vec{r})$ is as follows: $|\psi_{nljm}^{(+)}(\vec{r})|^2$ is the probability density of finding a spin-up electron at \vec{r} . $|\psi_{nljm}^{(-)}(\vec{r})|^2$ is the probability density of finding a spin-down electron at \vec{r} . This is what we mean when we say that $\psi_{nljm}^{(\pm)}(\vec{r})$ is the **probability amplitude** for finding an electron at a certain place with a certain spin.

3 Angular momentum operators and eigenstates.

The hamiltonian \mathbf{H} of an isolated atom is isotropic (invariant under the rotation group R_3) and therefore commutes with the angular momentum operator.[4] The operators for the total angular momentum components \mathbf{J}_i ($i = x, y, z$), are the generators of R_3 , and have the corresponding commutation relations with each other (using $\hbar = 1$):

$$[\mathbf{J}_i, \mathbf{H}] = 0, \quad [\mathbf{J}_1, \mathbf{J}_2] = i\mathbf{J}_3 \text{ etc}, \quad [\mathbf{J}_i, \mathbf{J}^2] = 0. \quad (29)$$

This means that we can use energy eigenstates which are also eigenstates of \mathbf{J}^2 and \mathbf{J}_z .

$$\begin{aligned} \mathbf{H} |E, J, M\rangle &= E |E, J, M\rangle \\ \mathbf{J}^2 |E, J, M\rangle &= J(J+1) |E, J, M\rangle \\ \mathbf{J}_z |E, J, M\rangle &= M |E, J, M\rangle \end{aligned} \quad (30)$$

It is often useful to use spherical components \mathbf{J}_m (with $m = -1, 0, +1$), rather than the cartesian components \mathbf{J}_i . These are defined by

$$\mathbf{J}_{\pm 1} = \mp \sqrt{1/2} (\mathbf{J}_x \pm i\mathbf{J}_y), \quad \mathbf{J}_0 = \mathbf{J}_z. \quad (31)$$

It is also convenient to form linear combinations called *shift operators*:

$$\mathbf{J}_{\pm} = \mathbf{J}_x \pm i\mathbf{J}_y. \quad (32)$$

In terms of these operators, the commutation relations can be written in the form

$$[\mathbf{J}_z, \mathbf{J}_m] = m\mathbf{J}_m, \quad [\mathbf{J}_{\pm}, \mathbf{J}_m] = C_{\pm}(1, m)\mathbf{J}_{m\pm 1}. \quad (33)$$

Also the action of the shift operators on the eigenstates can be written in the same form:

$$\mathbf{J}_z |E, J, M\rangle = M |E, J, M\rangle, \quad \mathbf{J}_{\pm} |E, J, M\rangle = C_{\pm}(J, M) |E, J, M \pm 1\rangle. \quad (34)$$

In both these equations the constant is given by

$$C_{\pm}(J, M) = \sqrt{J(J+1) - M(M \pm 1)}. \quad (35)$$

3.1 Spin-orbit coupling.

The atomic states can be specified further by using the *total orbital* and *total spin* angular momentum operators, the sum of which is the total angular momentum operator:

$$\mathbf{J}_i = \mathbf{L}_i + \mathbf{S}_i. \quad (36)$$

Of course \mathbf{L} and \mathbf{S} are themselves the vector sums of the orbital and spin angular momenta of all the electrons in the atom. We say that the individual l 's are *coupled* to form \mathbf{L} , the individual spins are coupled to form \mathbf{S} ; then \mathbf{L} and \mathbf{S} are coupled to form \mathbf{J} .

Note that the commutation relations among the components of \mathbf{L} , and separately among the components of \mathbf{S} , are the same as those among the components of \mathbf{J} (equation 29). However all commutators between a component of \mathbf{L} and a component of \mathbf{S} will be zero, because they act on completely different variables — one on the electrons' position coordinates, one on their spin coordinates. Therefore we can form state vectors which are simultaneous eigenstates of \mathbf{L}^2 , \mathbf{L}_z , \mathbf{S}^2 , and \mathbf{S}_z , which we denote by $|L, M_L, S, M_S\rangle$. However this is not an eigenstate of \mathbf{J}^2 and \mathbf{J}_z . Such eigenstates are linear combinations:

$$|L, S, J, M\rangle = \sum_{M_L, M_S} \langle L, M_L, S, M_S | L, S, J, M\rangle |L, M_L, S, M_S\rangle. \quad (37)$$

The vector-coupling (Clebsch-Gordan) coefficient is proportional to a three-j symbol:

$$\langle L, M_L, S, M_S | L, S, J, M\rangle = (-1)^{L-S+M} \sqrt{2J+1} \begin{pmatrix} L & S & J \\ M_L & M_S & -M_J \end{pmatrix}. \quad (38)$$

Note that \mathbf{L} and \mathbf{S} do *not* represent conserved quantities (“good quantum numbers”) because they do not commute with \mathbf{H} . Thus $|L, S, J, M\rangle$ is not an energy eigenstate. Nevertheless we can use the set of all such states $\{|L, S, J, M\rangle\}$ as a convenient orthonormal basis and write the energy eigenstates as linear combinations of them.

Moreover \mathbf{L} and \mathbf{S} are *approximately* conserved, and often this approximation is very good. The atomic hamiltonian can be written

$$H = H_0 + H_{es} + H_{so} + H_{rc}. \quad (39)$$

Here H_0 contains the electrons' kinetic energy and the electron-nucleus attraction terms; H_{es} is the sum of the electron-electron electrostatic repulsions; H_{so} is the spin-orbit interaction; H_{rc} represents relativistic corrections. For light atoms, which are not too highly ionized, we find that $H_0 + H_{es} \gg H_{so} \gg H_{rc}$. Since H_0 and H_{es} are spin-independent, they clearly commute with \mathbf{S} . But by rotational invariance they also commute with \mathbf{J} , and since $\mathbf{L} = \mathbf{J} - \mathbf{S}$, they must also commute with \mathbf{L} . So we see that $|L, S, J, M\rangle$ *can be* an energy eigenstate in the “nonrelativistic approximation” $H \rightarrow H_0 + H_{es}$. (In other words, the electrostatic interaction is diagonal in \mathbf{L} and \mathbf{S} .)

3.2 Tensor operators.

A set of $2k+1$ operators T^k_q ($q = -k, \dots, k$), is said to form a *tensor operator of rank k* if its commutation relations with the angular momentum operators are exactly analogous to equation (34), namely

$$[\mathbf{J}_z, T^k_q] = q T^k_q, \quad [\mathbf{J}_\pm, T^k_q] = C_\pm(k, q) T^k_{q\pm 1}. \quad (40)$$

Note that this means that the set of three angular momentum operators \mathbf{J}_q forms a tensor operator of rank one.

Now the matrix elements of tensor operators between angular momentum eigenstates can be partially evaluated *via* these equations.[5] The result is the celebrated **Wigner-Eckart theorem**:

$$\langle J, M | T^k_q | J', M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle J || T^k || J' \rangle. \quad (41)$$

The second factor on the right-hand side is called a three-j symbol; these are well-tabulated functions with well-known sum rules and other identities. The last factor is called the *reduced matrix element*; it contains all the dependence on the details of the states and the operators, for example integrals over radial wavefunctions.

The main point is that the dependence of the matrix element on M, M', q is completely determined by the fact that the operator is a tensor and the states are angular-momentum eigenstates.

4 Wavefunctions for coupled states

4.1 Two electrons

We have seen that it is convenient to describe 2-electron states using LS coupling. For example we saw that there are 12 states in the $1s2p$ configuration of helium, which are

grouped into 4 energy levels designated 3P_0 , 3P_1 , 3P_2 , 1P_1 . In general, each electron has $2(2l+1)$ possible states, so the configuration $n_1l_1n_2l_2$ has $4(2l_1+1)(2l_2+1)$ states. The energy levels are formed by using all integer values of L between $|l_1-l_2|$ and l_1+l_2 with $S = 1$ and $S = 0$ for each L , and finally all integer values of J between $|L-S|$ and $L+S$. For example for the $2p3d$ configuration we have 1P_1 , 1D_2 , 1F_3 , ${}^3P_{0,1,2}$, ${}^3D_{1,2,3}$, ${}^3F_{2,3,4}$.

In the *independent-particle model* we write approximate wavefunctions for these states by combining hydrogen-like single-particle wavefunctions with each other according to the rules of angular momentum algebra discussed above. The general form is the same as that of equation (37):

$$\Psi((n_1l_1, n_2l_2)L, M_L, S, M_S) = \sum_{m_1m_2\mu_1\mu_2} \langle l_1m_1, l_2m_2 | L, M_L \rangle \langle s_1\mu_1, s_2\mu_2 | S, M_S \rangle \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \quad (42)$$

Here for simplicity we have used m instead of m_l for the z-component of orbital angular momentum, and μ instead of m_s for the z-component of spin angular momentum. And of course $\psi(\vec{r})$ is short for

$$\psi(\vec{r}) = \psi_{nlm}(\vec{r}) \chi_\mu \quad (43)$$

But to get an eigenstate of \mathbf{J} we need to take a linear combination of these states, introducing one more summation:

$$\Psi((n_1l_1, n_2l_2)L, S, J, M) = \sum_{M_L M_S} \langle L, M_L, S, M_S | J, M \rangle \Psi((n_1l_1, n_2l_2)L, M_L, S, M_S) \quad (44)$$

For example, consider the simple configuration $1s2p$. There are 1P_1 , 3P_0 , 3P_1 , 3P_2 energy levels. The corresponding coupled quantum states can be constructed from the equations above, giving:

$$\begin{aligned} \Psi(1s2p {}^1P_1, M = +1) &= \psi_{1,1}^{(+)}(\vec{r}_1, \vec{r}_2) \chi_{0,0}(1, 2) \\ \Psi(1s2p {}^3P_2, M = +2) &= \psi_{1,1}^{(-)}(\vec{r}_1, \vec{r}_2) \chi_{1,1}(1, 2) \\ \Psi(1s2p {}^3P_1, M = +1) &= \sqrt{1/2} \psi_{1,1}^{(-)}(\vec{r}_1, \vec{r}_2) \chi_{1,0}(1, 2) - \sqrt{1/2} \psi_{1,0}^{(-)}(\vec{r}_1, \vec{r}_2) \chi_{1,1}(1, 2) \end{aligned} \quad (45)$$

where $\chi_{S,M_S}(1, 2)$ is the total spin eigenstate, coupling the two spins to give either the triplet ($S = 1$) or singlet ($S = 0$) spin state:

$$\begin{aligned} \chi_{0,0}(1, 2) &= \sqrt{1/2} \chi_+(1)\chi_-(2) - \sqrt{1/2} \chi_-(1)\chi_+(2) \\ \chi_{1,1}(1, 2) &= \chi_+(1)\chi_+(2) \\ \chi_{1,0}(1, 2) &= \sqrt{1/2} \chi_+(1)\chi_-(2) + \sqrt{1/2} \chi_-(1)\chi_+(2) \end{aligned} \quad (46)$$

and $\psi_{L,M_L}^{(\pm)}(\vec{r}_1, \vec{r}_2)$ is the total space wave function, coupling the two orbital angular momenta to give eigenstates of L, M_L , with the symmetric or antisymmetric combination chosen to make the total wavefunction (state vector) antisymmetric under interchange of electron labels as required by Fermi-Dirac statistics:

$$\begin{aligned} \psi_{1,1}^{(+)}(\vec{r}_1, \vec{r}_2) &= \sqrt{1/2} \psi_{1s}(\vec{r}_1) \psi_{2p1}(\vec{r}_2) + \sqrt{1/2} \psi_{2p1}(\vec{r}_1) \psi_{1s}(\vec{r}_2) \\ \psi_{1,1}^{(-)}(\vec{r}_1, \vec{r}_2) &= \sqrt{1/2} \psi_{1s}(\vec{r}_1) \psi_{2p1}(\vec{r}_2) - \sqrt{1/2} \psi_{2p1}(\vec{r}_1) \psi_{1s}(\vec{r}_2) \\ \psi_{1,0}^{(-)}(\vec{r}_1, \vec{r}_2) &= \sqrt{1/2} \psi_{1s}(\vec{r}_1) \psi_{2p0}(\vec{r}_2) - \sqrt{1/2} \psi_{2p0}(\vec{r}_1) \psi_{1s}(\vec{r}_2) \end{aligned} \quad (47)$$

The 3P_2 states with smaller values of M can be constructed by applying the lowering operator (Eq. 34) $J_- = L_- + S_-$ to the ${}^3P_2, M = 2$ state. In the same way the ${}^3P_1, M = 0, -1$ states can be constructed from the ${}^3P_1, M = 1$ state. Finally the 3P_0 state is constructed by defining it to be orthogonal to ${}^3P_1, M = 0$ and ${}^3P_2, M = 0$.

Exercise 1 Derive equations (45)–(47) from equations (42)–(44) using explicit values of the required vector-coupling coefficients, for example from [2] or [4].

Exercise 2 Derive the needed vector coupling coefficients, using the lowering-operator method (equation 34) above (or see for example reference [2]).

5 The Coulomb interaction

The most important two-body operator in the hamiltonian for an atom with N electrons is the electrostatic (Coulomb) interaction energy

$$\begin{aligned} H_{es} &= \sum_{a<b}^N \frac{e^2}{4\pi\epsilon_0 r_{ab}} && \text{(SI units)} \\ &= \sum_{a<b}^N 1/r_{ab} && \text{(atomic units)} \end{aligned} \quad (48)$$

where a, b are electron labels, so the sum runs over all pairs of electrons, with $1 \leq a < b \leq N$, and of course $r_{ab} = |\vec{r}_a - \vec{r}_b|$.

We have already seen that this operator commutes with $\mathbf{L}, \mathbf{S}, \mathbf{J}, \mathbf{J}_z$ so that it is diagonal in all these quantum numbers. However, it does not separate into a product of one-electron operators: it involves electron correlation in an essential way. In calculating the matrix elements of the operator H_{es} , the usual method is to expand it in a sum of terms, each of which is a product of operators on the individual electrons. From the point of view of rotational symmetry, this corresponds to an expansion of a scalar two-body operator in terms of tensor one-body operators [4, 5]. From a more elementary point of view, this is just an expansion in Legendre polynomials, followed by use of the addition theorem of the spherical harmonics.

$$\begin{aligned} \frac{1}{r_{ab}} &= \sum_{k=0}^{\infty} \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \theta_{ab}) \\ &= \sum_{k,q} \frac{4\pi}{2l+1} \frac{r_{<}^k}{r_{>}^{k+1}} Y_{k,q}^*(\theta_a, \phi_a) Y_{k,q}(\theta_b, \phi_b) \end{aligned} \quad (49)$$

Here of course $r_{<}$ stands for the smaller of r_a, r_b , and $r_{>}$ for the larger.

So now we have written the Coulomb energy in terms of one-electron coordinates so we can more easily work out integrals involving this operator. This approach leads to the direct and exchange Slater integrals F_k and G_k [5].

6 Electric dipole radiation.

The electromagnetic radiation emitted by any finite-sized source in which there are charged particles moving nonrelativistically, can be calculated in the electric dipole (E1) approximation. This nonrelativistic condition is equivalent to the usual criterion that the size of the source must be small compared to the wavelength of the emitted radiation. For “optical” (including infrared, ultraviolet) radiation emitted by atoms this is clearly a good approximation.

The correct relation between emission probability and dipole matrix element can be written down by starting from the classical expression for the emitted power in terms of the source’s time-dependent electric dipole moment. In the classical expression for emission at a certain frequency, there occurs the Fourier amplitude of the time-dependent dipole moment at that frequency. To obtain the quantum result, simply replace that Fourier amplitude by the matrix element of the dipole moment operator between the desired initial and final states (the “transition moment”). For the rate of emission of radiation polarized in the z direction, the result is

$$A(i \rightarrow f) = \frac{4k^3}{3\hbar} |\langle i | D_z | f \rangle|^2. \quad (50)$$

Here \vec{D} is the electric dipole moment of the atom, i.e. the sum of the dipole moment vectors of all the electrons. **Note that since the physical quantity is a vector, the dipole operator is a tensor operator of rank one.** Note that $k = \omega/c = 2\pi/\lambda$.

The simplest way to derive this result is to consider an atom in the lower level, subjected to an electric field in the z direction, oscillating in resonance with the transition frequency. Then standard Schrödinger time-dependent perturbation theory, with the electric-dipole interaction $\vec{E} \cdot \vec{D}$ as perturbation, will give the absorption probability per unit time. Then the Einstein analysis which relates stimulated and spontaneous emission to absorption, gives the above result.

For the rate of emission without regard to polarization, we simply sum over the components of \vec{D} :

$$A(J, M \rightarrow J', M') = \frac{4k^3}{3\hbar} \sum_{q=-1}^{+1} |\langle J, M | D_q^1 | J', M' \rangle|^2. \quad (51)$$

Since, in the absence of applied fields, the states of different M all have the same energy, we usually want to sum over M' and average over M . (Actually the latter operation is not needed, since the result of the former is independent of M .) This gives the transition probability (Einstein A value) for a particular spectrum line:

$$\begin{aligned} A(J \rightarrow J') &= \frac{4k^3}{3\hbar} \sum_{M', q} |\langle J, M | D_q^1 | J', M' \rangle|^2, \\ &= \frac{4k^3}{3\hbar} \mathbf{S}(J, J'). \end{aligned} \quad (52)$$

Here we have defined the *line strength* \mathbf{S} as follows:

$$\begin{aligned}\mathbf{S}(J, J') &= \sum_{M, M', q} \left| \langle J, M | D^1_q | J', M' \rangle \right|^2, \\ &= \left| \langle J || D^1 || J' \rangle \right|^2.\end{aligned}\tag{53}$$

The last equation can be derived easily using the Wigner-Eckart theorem and the sum rule for the three-j symbols.

Note that if, in the initial state, all M values are equally populated, then the total photon emission rate (“strength”) in the line $J \rightarrow J'$ is proportional to $(2J + 1)A(J \rightarrow J')$ and so is simply proportional to the line strength \mathbf{S} hence the name.

6.1 Dipole transitions in spin-orbit coupling.

Suppose we have a tensor operator T^k_q which we know is spin-independent — that is, it does not act on the spin coordinates of the electrons, and so commutes with \mathbf{S} . We can combine the above equations, do some “Racah algebra”, and prove the following important theorem:

$$\langle L, S, J || T^k || L', S', J' \rangle = \delta_{S'S} (-1)^{L+S+J'+1} \sqrt{(2J+1)(2J'+1)} \left\{ \begin{matrix} J' & 1 & J \\ L & S & L' \end{matrix} \right\} \langle L || T^k || L' \rangle\tag{54}$$

The six-j symbol, like the three-j, is a standard tabulated quantity. The significance of this result is that it gives explicitly the dependence of the original matrix element on S, S', J, J' . The essential quantity is the final reduced matrix element, which is independent of these four quantum numbers.

Now the electric dipole operator is clearly an example of a spin-independent tensor operator. Thus we can apply (54) to its matrix elements between states given in spin-orbit coupling. In particular, combining (54) and (53) gives the desired result for the transition probability in spin-orbit coupling:

$$\begin{aligned}A(L, S, J \rightarrow L', S', J') &= \frac{4k^3}{3\hbar} \frac{|\langle L, S, J || D^1 || L', S', J' \rangle|^2}{(2J+1)} \\ &= \delta_{S'S} \frac{4k^3}{3\hbar} (2J'+1) \left\{ \begin{matrix} J' & 1 & J \\ L & S & L' \end{matrix} \right\}^2 \left| \langle L || D^1 || L' \rangle \right|^2.\end{aligned}\tag{55}$$

The reduced matrix element $\langle L || D^1 || L' \rangle$ contains all the dynamics of the transition, *i.e.* the dependence on the radial wavefunctions. Here $|L\rangle$ is shorthand for all the quantities required to specify the state except for the quantum numbers S, J , which appear only in the six-j symbol.

6.2 Calculating dipole transitions

If we have theoretical wavefunctions for the initial and final states, we can now compute a theoretical transition probability. From equation (55) we see that the key quantity is the reduced matrix element $\langle L || D^1 || L' \rangle$. Recall that \vec{D} is the electric dipole operator: for an atom or ion with N electrons

$$\vec{D} = -e \sum_{i=1}^N \vec{r}_i \quad (56)$$

In general the reduced matrix element is computed in terms of integrals over the radial wavefunctions of the initial and final states, of the form

$$\mathbf{R}(nl, n'l') = \int_0^\infty P_{nl}(r) r P_{n'l'} dr \quad (57)$$

General formulas connecting the reduced matrix element to such radial integrals may be found for example in sections 14.7 – 14.11 of Cowan's book. [5]

For a hydrogen-like (one-electron) atom or ion, the connection is simple, namely:

$$\langle nl || D^1 || n'l' \rangle = \delta_{l', l \pm 1} (-1)^{l+l'} \sqrt{l_>} \mathbf{R}(nl, n'l') \quad (58)$$

Here $l_>$ is the larger of the two orbital quantum numbers l, l' . Note the selection rule that l must increase or decrease by 1; this follows from angular momentum conservation and the requirement that the parity must change, since the dipole operator has odd parity.

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