

7.11: Spin

The model described in section 7.10 describes the hydrogen spectrum quite well, and, though it is much heavier mathematically than the Bohr model, it is much more satisfying because it does not have the *ad hoc* assumptions of the Bohr model. It is still not good enough, though. It predicts that all of the n^2 wavefunctions with a given value of n have the same energy, because the expression for the energy included only the single quantum number n . Careful measurements show, however, that the Balmer lines have fine structure, and consequently the energy levels have some fine structure and hence the energy is not a function of n alone. The fine structure is much more obvious in more complex atoms, so the form of the Schrödinger equation we have seen so far is inadequate to explain this structure. At the theoretical level, we obviously used the nonrelativistic expression $p^2/(2m)$ for the kinetic energy. This is good enough except for precise measurements, when it is necessary to use the correct relativistic expression.

This short chapter is not a textbook or formal course in quantum mechanics, and its intention is little more than to introduce the various words and ideas that are used in spectroscopy. At this stage, then, although there is a strong temptation to delve deeper into quantum mechanics and pursue further the ideas that we have started, I am merely going to summarize some of the results and the ways in which spectra are described. Anyone who wants to pursue the quantum theory of spectra further and in detail will sooner or later come across some quite forbidding terms, such as Clebsch-Gordan coefficients, Racah algebra, 3- j and 6- j symbols, and tensorial harmonics. What these are concerned with is the algebra of combining the wavefunctions of two or more electrons and calculating the resulting angular momenta. The 3- j and 6- j symbols are parentheses or braces in which various quantum numbers are displayed, and they are manipulated according to certain rules as two or more wavefunctions are combined. It is in fact great fun to use them, and you can do stupendous calculations at enormous speed and with very little thought - but only after you have overcome the initial steep learning process and only if you keep in constant practice. If you programme the manipulations for a computer to deal with, not only are the calculations done even faster, but it doesn't matter if you are out of practice - the computer's memory will not lapse!

It is found that the complete wavefunction that describes an electron bound in an atom requires not just three, but four quantum numbers. There are the three quantum numbers that we are already familiar with - n , l and m , except that the third of these now bears a subscript and is written m_l . The energy of a wavefunction depends mostly on n , but there is a small dependence also on l . Orbital angular momentum, in units of \hbar , is $\sqrt{l(l+1)}$ and its z -component is m_l . The additional quantum number necessary to describe an electron bound to an atom is denoted by the symbol m_s , and it can take either of two values, $+1/2$ and $-1/2$. For a given value of n , therefore, there are now $2n^2$ combinations of the quantum numbers - i.e. $2n^2$ wavefunctions. (Recall that, before we introduced the concept of electron spin, we had predicted just n^2 wavefunctions for a given n . See the discussion immediately following equation 7.9.2.)

In terms of a mechanical model of the electron, it is convenient to associate the extra quantum number with a *spin* angular momentum of the electron. The spin angular momentum of an electron, in units of \hbar , is $\sqrt{s(s+1)}$, where s has the only value $1/2$. In other words, the spin angular momentum of an electron, in units of \hbar , is $3/2$. Its z -component is m_s ; that is, $+1/2$ or $-1/2$.

The concept that an electron has an intrinsic spin and that its z -component is $+1/2$ or $-1/2$ arose not only from a study of spectra (including especially the splitting of lines when the source is placed in a magnetic field, known as the Zeeman effect) but also from the famous experiment of Stern and Gerlach in 1922. The totality of evidence from spectroscopy plus the Stern-Gerlach experiment led Goudsmit and Uhlenbeck in 1925 to propose formally that an electron has an intrinsic magnetic moment, and certainly if we think of an electron as a spinning electric charge we would indeed expect it to have a magnetic moment. A magnetic dipole may experience a torque if it is placed in a uniform magnetic field, but it will experience no net force. However, if a magnetic dipole is placed in a nonuniform magnetic field - i.e. a field with a pronounced spatial gradient in its strength, then it will indeed experience a force, and this is important in understanding the Stern-Gerlach experiment. Stern and Gerlach directed a beam of "electrons" (I'll explain the quote marks shortly) between the poles of a strong magnet in which one of the pole pieces was specially shaped so that the "electrons" passed through a region in which there was not only a strong transverse magnetic field but also a large transverse magnetic field gradient. One might have expected the beam to become broadened as the many electrons were attracted one way or another and to varying degrees, depending on the orientation of their magnetic moments to the field gradient. In fact the beam was split into two, with one half being pulled in the direction of the field gradient, and the other half being pushed in the opposite direction. This is because there were only two possible directions of the magnetic moment vector. (As a matter of experimental detail it was not actually a beam of electrons that Stern and Gerlach used. This would have completely spoiled the experiment, because an electron is electrically charged and an electron beam would have been deflected by the Lorentz force far more than by the effect of the field gradient on the dipole moment. As far as I recall they actually used a beam of silver atoms. These were not

accelerated in a particle accelerator of any sort (after all, they are neutral) but were just vaporized in an oven, and a beam was selected by means of two small apertures between the oven and the magnet. The silver atom has a number of paired electrons (with no resultant magnetic moment) plus a lone, unpaired electron in the outer shell, and this was the electron that supplied the magnetic moment.)

In some atoms the orbital angular momentum \mathbf{l} and the spin angular momentum \mathbf{s} are more strongly coupled to each other than they are to the z -axis. In that case m_l and m_s are no longer "good quantum numbers". The total angular momentum of the electron (orbit and spin combined) is given the symbol \mathbf{j} . Its magnitude, in units of \hbar , is $\sqrt{j(j+1)}$ and its z -component is called m . In that case the four "good quantum numbers" that describe the electron are n, l, j and m rather than n, l, m_l, m_s . Intermediate cases are possible, but we'll worry about that later. In any case the wavefunction that describes an electron is described by four quantum numbers, and of course no two wavefunctions (and hence no two electrons bound in an atom) have the same set of four quantum numbers. (If we return briefly to the vibrating sphere, each mode of vibration is described by three quantum numbers. It makes no sense to talk about two different modes having the same set of three quantum numbers.) The truism that no two electrons bound in an atom have the same set of four quantum numbers is called *Pauli's Exclusion Principle*.

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