Chapter 15. The Hydrogen Atom

The last chapters introduced you to quantum mechanical fundamentals starting from the de Broglie hypothesis. You learned about eigenvalue equations, operators and wavefunctions, and you tackled harder subjects like multidimensional Hamiltonians and rotational motion. Most important, the mathematics of probability and statistics have been shown to be essential for our interpretation of quantum mechanical principles. It is ironic that we wrap up this part of our learning exactly where Schrödinger began; he introduced the world to quantum mechanics by solving the energy levels of the hydrogen atom in the 1926 paper "Quantization as an Eigenvalue Problem." In it, the electron is described with a wavefunction that is centered over a stationary nucleus. And while there are plenty of quantum problems beyond the hydrogen atom, this is the last "pen-and-paper" example that we can solve for reasons you will see at the end of this chapter.

We begin with a historical note on the first explorations on the electronic structure of hydrogen starting with Johann Balmer in 1855. At this time it was known that excited hydrogen emits light over a few discrete wavelengths as shown in Figure 15.1A. Balmer and Johannes Rydberg demonstrated that the emission can be described by the equation:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

where λ is the emission wavelength, n_1 and n_2 are whole numbers, and $R = 1.097 \times 10^7\ m^{-1}$ is a constant named after Rydberg. This introduces the question, why would discrete emissions be observed, and what model for the hydrogen atom would have atomic energy levels that scale according to the square of a whole number? One of the first attempts to model hydrogen that correctly predicted this behavior was developed by Niels Bohr (Nobel Prize, 1922) as discussed below. This attempt also

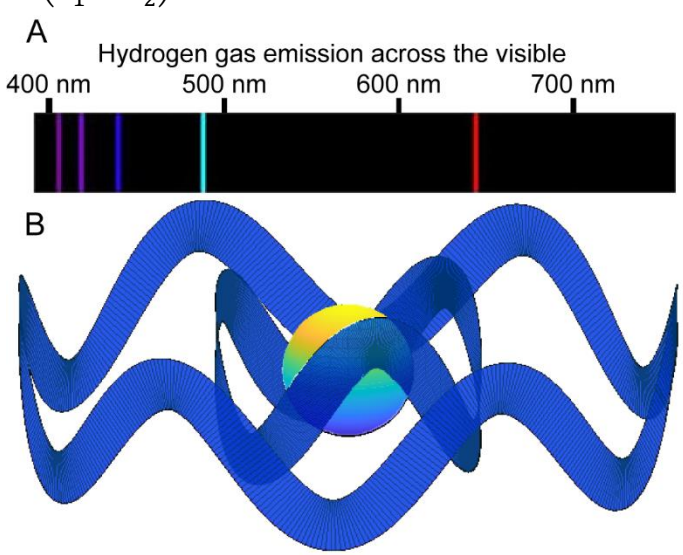


Figure 15.1. A. The emission spectrum of hydrogen gas reveals discrete lines as described by Balmer's formula. **B.** Early descriptions of the hydrogen atom incuded circulating electrons (Bohr) or wave-like electrons (Schrodinger).

reveals another aspect of science, which is that a scientific theory is either everything or it is nothing.

15.1 The Bohr Model

In 1913 Niels Bohr proposed a model for the hydrogen atom where the electron only exists in certain regions of space as it circulates around the nucleus (a single proton) as cartoonishly depicted in Figure 15.1B. He partially incorporated quantum theory by assumed that the orbiting electron can only have discrete values for the angular momentum. To model this behavior the angular momentum ($mv \cdot r$) was assumed to take integer values of $\hbar$, which is the reduced Planck constant ($h/2\pi$):

$$mv \cdot r = n \cdot \hbar$$

where n=1, 2, 3, etc. This means that velocity must be quantized: $v = \frac{n\hbar}{m \cdot r}$. Next, Bohr conjectured that the "outward" centripetal force: $\frac{mv^2}{r}$ matches the "inward" Coulomb attraction force:

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

According to the above $v = \sqrt{\frac{e^2}{4\pi\varepsilon_0 \cdot m \cdot r}}$, which must be equal to our previous expression velocity:

$$\frac{n\hbar}{m \cdot r} = \sqrt{\frac{e^2}{4\pi\varepsilon_0 \cdot m \cdot r}}$$

This allows us to solve for the electron's radius: $r = \frac{4\pi\varepsilon_0 \cdot n^2\hbar^2}{m \cdot e^2}$, which is a function of the integer n. If n = 1 the radius is: $r = \frac{4\pi\varepsilon_0\hbar^2}{m \cdot e^2}$, which is the famous Bohr unit of length $a_0 = 0.053\times10^{-9}$ m.

The energy can be calculated by adding the kinetic and potential from the electrostatic attraction: $\frac{1}{2}mv^2 - \frac{e^2}{4\pi\varepsilon_0 r}$, where the Coulomb energy is negative since the electron and proton have opposite charges. Since both velocity and radius are quantized, Bohr was able to show that the same is true for the energy levels:

$$E = -\frac{e^4 m}{32\pi^2\varepsilon_0^2 \cdot \hbar^2} \cdot \frac{1}{n^2}$$

Inserting n = 1 gives the ground state energy: $-\frac{m \cdot e^4}{32\pi^2\varepsilon_0^2 \cdot \hbar^2} = -13.6$ eV, which reveals how much energy has to be injected into the atom to fully remove the electron from the proton. And while this is the same value as measured experimentally, there are two problems with the model. For one, it doesn't explain the experimental observations that the spectra change under an applied magnetic field. Also, the model only works for atoms with one electron. More importantly, if an electron is circulating about a fixed point then it should emit electromagnetic waves; this is how a microwave oven heats your leftovers. If so, the electron eventually loses all its energy and crashes into the nucleus, and poof no more atom! Obviously, this doesn't happen. Consequently, the Bohr model was rejected which brings us to 1926 when Schrödinger formulated the hydrogen atom's Hamiltonian and used an eigenvalue equation approach to solve it.

15.2 The Hydrogen Schrödinger Equation

Concerning the energy of an atom, even a simple one as hydrogen, we must solve the wavefunction for both the electron and the proton. Afterall, light particle including protons may need to be described with wavefunctions. Electron must always be treated quantum mechanically due to their low mass. Thus, deriving a single wavefunction that describes both the electron and nucleus is unfortunately as complicated as it sounds. This problem can be circumvented using the concept of separability as described in Ch. 14. It was shown that a multidimensional wavefunction can be expressed as the product of smaller parts: $\psi_{total} = \psi_1\psi_2$, which is possible so long as the Hamiltonian can be separated into terms that do not contain the same quantum operators. As it applies to the hydrogen atom, we can achieve separability by dividing the coupled motion of the proton and electron into relative and center of mass components. The center of mass is defined almost entirely by the proton, which means that the other component is for the electron. The total wavefunction can now be separated into two:

$$\psi_{total} \approx \psi_{electron} \cdot \psi_{proton}$$

Since the proton is ~1800× heavier than the electron we can assume that it isn't moving, which allows us to simply ignore its wavefunction. The consequence for taking this approach is that the factor of mass in the electron's Hamiltonian is replaced with the proton / electron reduced mass:

$$\mu = \frac{m_p m_e}{m_p + m_e} \sim m_e$$

Due to the fact that a proton is ~1836× heavier than the electron, the reduced mass is only 0.05% different from the electron mass.

Now that we have decided to focus solely on the electron with its reduced mass, we must define the Hamiltonian and then solve the wavefunction. To this end we will start with the kinetic energy operator. It must be three dimensional and use spherical coordinates since the hydrogen atom (and indeed all atoms) are round. As a result we expect it to be similar to that encountered for the 3D rigid rotor model from Chapter 14, although there is one correction. The radial component of the rigid rotor problem is a fixed quantity, making the radius (r) a parameter as opposed to an operator. This is not true for the hydrogen atom since the electron can approach (or move away) from the nucleus as much as it wants. As a result the correct form of the kinetic energy operator is:

$$\frac{-\hbar^2}{2\mu \cdot r^2} \cdot \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right)$$

Here we will drop the accent mark on the $\hat{r}$, $\hat{\theta}$ and $\hat{\phi}$ operators for clarity. Next we must tack on the Coulombic potential operator that describes the attraction between the nucleus and the electron:

$$\hat{V}(r) = \frac{e^2}{4\pi\varepsilon_0 r}$$

With the addition of the electrostatic component we apply the wavefunction to the Hamiltonian operator into the standard eigenvalue form $\hat{H}\psi(r,\theta,\phi) = E \cdot \psi(r,\theta,\phi)$ as:

$$\frac{-\hbar^2}{2\mu} \left(\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2} \left\{ \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right\} \right) \psi(r,\theta,\phi) - \frac{e^2}{4\pi\varepsilon_0 r} \psi(r,\theta,\phi) = E \cdot \psi(r,\theta,\phi)$$

Real nightmare fuel, isn't it? Like Australian snakes, or pretty much any animal down under.

15.2.1. Separability. As with every multivariable quantum mechanical Hamiltonian the first thing to do is to check for separability, here between r, θ and ϕ. This is important because we can't solve the wavefunctions otherwise. Right out of the gate we can see that there may be a problem due to a single term with all three variables: $\frac{1}{r^2} \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2}$. However, we can make progress towards separability by first multiplying everything by $\frac{-2\mu}{\hbar^2} r^2$:

$$\left(r^2 \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \left\{ \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \sin(\theta) \frac{\partial}{\partial \theta} \right\} \right) \psi(r,\theta,\phi) + \frac{2\mu}{\hbar^2} \frac{e^2}{4\pi\varepsilon_0 r} r^2 \psi(r,\theta,\phi)$$
$$= -\frac{2\mu}{\hbar^2} r^2 \cdot E \cdot \psi(r,\theta,\phi)$$

The next step is to insert the separated solution: $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ and divide out the same on the left as: $\frac{1}{R(r)Y(\theta,\phi)}\hat{H}R(r)Y(\theta,\phi)$:

$$\frac{r^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}r^2 + \frac{1}{Y(\theta,\phi)}\left\{\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right\}Y(\theta,\phi)$$
$$= -\frac{2\mu}{\hbar^2}r^2E$$

Now we group all the r terms on one side and the angular θ and ϕ on the other:

$$\frac{r^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}r^2 + \frac{2\mu}{\hbar^2}r^2E$$
$$= \frac{1}{Y(\theta,\phi)}\left\{\frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta}\right\}Y(\theta,\phi)$$

We assume that the angular wavefunction $Y(\theta,\phi)$ is the same as encountered for the 3D rigid rotor, i.e. the spherical harmonics $Y_{l,m}$ discussed in Chapter 14, section 14.2.3. Based on the information derived from the 3D rigid rotor problem the right (angular) side of the expression $\frac{1}{Y_{l,m}}\hat{H}(\theta,\phi)Y_{l,m}$ is equal to $l(l+1)$, where the l quantum number is $l = 0, 1, 2$, etc. This leaves the radial part to solve as:

$$\frac{r^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) + \frac{2\mu}{\hbar^2}\frac{e^2}{4\pi\varepsilon_0 r}r^2 + \frac{2\mu}{\hbar^2}r^2E = l(l+1)$$

After some algebra and rearrangement we find:

$$\frac{-\hbar^2}{2\mu}\frac{r^2}{R(r)}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}R(r) - \frac{e^2}{4\pi\varepsilon_0 r}r^2 + \frac{\hbar^2}{2\mu}l(l+1) = r^2E$$

To return the above into an eigenvalue form we simply multiply by $\frac{R(r)}{r^2}$ to reveal the radial Schrödinger equation:

$$\frac{-\hbar^2}{2\mu}\left(\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{l(l+1)}{r^2}\right)R(r) - \frac{e^2}{4\pi\varepsilon_0 r}R(r) = E\cdot R(r)$$

This differential equation has to specify a value of the angular momentum quantum number l before solving it, which means that there will be an l dependence to the solutions as shown below. With the wavefunctions in hand the energy of the hydrogen atom can be determined:

$$E = -\frac{\mu\cdot e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2}$$

which is found to depend on a "principal" quantum number n = 1, 2, 3 etc. This quantum mechanical equation for energy is identical to that predicted by the Bohr model and conforms to the Balmer and Rydberg equation for spectroscopic transitions. The energies are negative due to the Coulomb potential as shown in Figure 15.2. As in all our previous examples the quantization occurs from a boundary condition, which for the hydrogen atom is that $R(r) \to 0$ as $r \to \infty$.

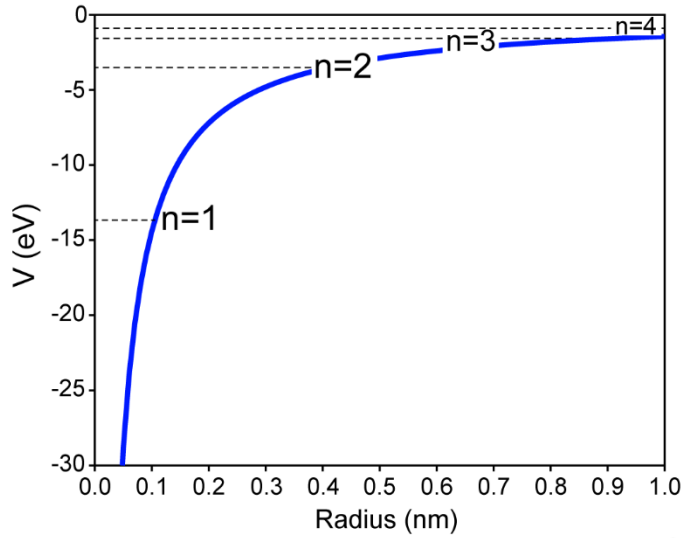


Figure 15.2. The hydrogen atom's Coulomb potential and eigenvalues of the n=1,2,3 and 4 states. An electron at an infinite distance from the nucleus has an energy of 0 eV.

Examination of the wavefunctions as discussed below reveal that n is related to the size of the orbital which we will now refer to as a "shell". Degeneracies may be observed because, for any given principal quantum number n, there are $l = 0, 1, 2 \ldots (n - 1)$ solutions to the radial equation. In fact there are even more degeneracies due to the angular part of the Hamiltonian, as for each l there are $2l$ +1 more states as defined by the $m_l = -l \ldots 0 \ldots l$ quantum number. Hence, it must be true that the first shell state (n = 1) has no angular momentum ($l = 0$) and is nondegenerate. In contrast, the n = 2 state has four degenerate wavefunctions characterized by $l = 0$ (2s orbitals) and $l = 1$ (2p orbitals). The 2p state has three wavefunctions that we know as p_x, p_y and p_z. The third and fourth shell can have l = 2 (d orbitals, describing transition metals) and l = 3 (f orbitals, characteristic of the actinides and lanthanides).

15.2.1. Quantum numbers and the periodic table. The dependencies of the various quantum numbers for the hydrogen atom are what give the periodic table its overall shape. Shown in Figure 15.3 is a representation based solely on quantum numbers; the rows are arranged according to the shell, which is the same thing as the principal quantum number n. The columns are arranged by the l quantum number, and each l block is $2l + 1$ wide due to the m_l states. However, the overall arrangement of elements in Figure 15.3 is very different than the periodic table as you know it, which is arranged with the l blocks starting from s, f (tucked underneath) d, and finally p. This arrangement is due to the phenomenon of shielding that causes

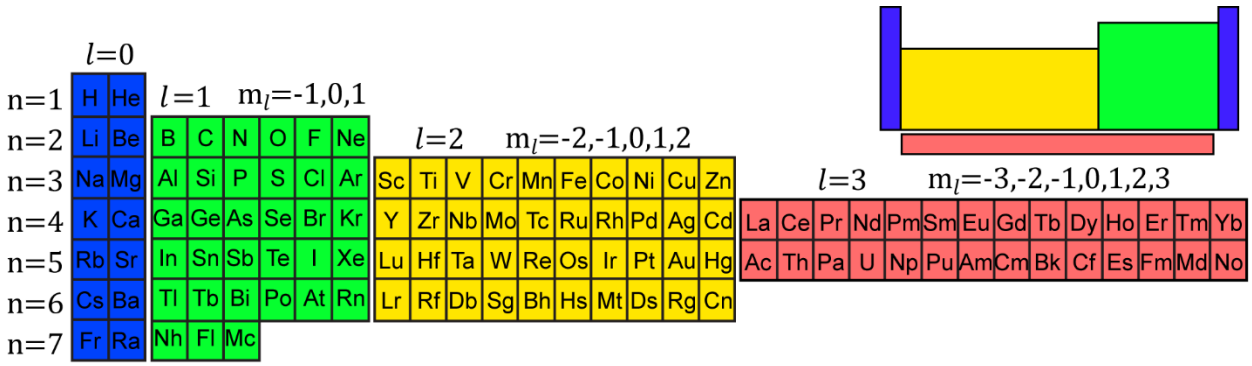


Figure 15.3. The periodic table of elements as arranged by l quantum number. The reason that the various blocks have 2, 6, 10 and 14 colums is due to the m_l quantum number. Inset shows the traditional arrangement of the periodic table which is the result of shielding.

electrons to fill into orbitals according to that arrangement rather than monotonically with l as the atomic number Z increases. Shielding is discussed further below.

15.3 Hydrogen Radial Wavefunctions.

Before we study the wavefunctions, we will first make some approximations to the Hamiltonian that simulate the electron's behavior at short and long distances. For example, what does the radial Schrödinger equation say about the electron if it is highly displaced from the nucleus (at large r)? First, we can use the product rule to show that the kinetic energy operator $\frac{1}{r}\frac{\partial^2}{\partial r^2}r$ is equivalent to $\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}$ (you might demonstrate this as a homework assignment). We make this substitution in the kinetic energy operator because, when the Hamiltonian is multiplied by r:

$$\frac{-\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial r^2}-\frac{l(l+1)}{r^2}-\frac{e^2}{4\pi\varepsilon_0 r}\right)r\cdot R(r)=E\cdot r\cdot R(r)$$

This shows us that, if $r\to\infty$ we can remove the potential energy terms: $\frac{l(l+1)}{r^2}-\frac{e^2}{4\pi\varepsilon_0 r}$ leaving:

$$\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}r\cdot R(r)=E\cdot r\cdot R(r)$$

At long distances we can also make the approximation: $\frac{\partial^2}{\partial r^2}r\cdot R(r)\to r\frac{\partial^2 R(r)}{\partial r^2}$. Next we simply divide by r to find:

$$\frac{\partial^2}{\partial r^2}R(r)=\frac{-2\mu}{\hbar^2}E\cdot R(r)$$

n	l	m	$R_{n,l}(r)$	$Y_{l,m}(\theta,\phi)$
1s	0		$\frac{2}{(a_0)^{3/2}}e^{-r/a_0}$	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2\pi}}$
2s	0		$\frac{1}{2\sqrt{2}(a_0)^{3/2}}\left(2-\frac{r}{a_0}\right)e^{-r/2a_0}$	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2\pi}}$
3s	0		$\frac{2}{81\sqrt{3}(a_0)^{3/2}}\left(27-\frac{18r}{a_0}+\frac{2r^2}{a_0^2}\right)e^{-r/3a_0}$	$\frac{1}{\sqrt{2}}\frac{1}{\sqrt{2\pi}}$
2p	1	m=0	$\frac{1}{2\sqrt{6}(a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{\sqrt{6}}{2}\cos(\theta)\frac{1}{\sqrt{2\pi}}$
		m=±1	$\frac{1}{2\sqrt{6}(a_0)^{3/2}}\frac{r}{a_0}e^{-r/2a_0}$	$\frac{\sqrt{3}}{2}\sin(\theta)\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
3p	1	m=0	$\frac{4}{81\sqrt{6}(a_0)^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{\sqrt{6}}{2}\cos(\theta)\frac{1}{\sqrt{2\pi}}$
		m=±1	$\frac{1}{81\sqrt{6}(a_0)^{3/2}}\left(6-\frac{r}{a_0}\right)\frac{r}{a_0}e^{-r/3a_0}$	$\frac{\sqrt{3}}{2}\sin(\theta)\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
3d	2	m=0	$\frac{4}{81\sqrt{30}(a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{\sqrt{10}}{4}(3\cos^2(\theta)-1)\frac{1}{\sqrt{2\pi}}$
		m=±1	$\frac{4}{81\sqrt{30}(a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{\sqrt{15}}{2}\sin(\theta)\cos(\theta)\frac{1}{\sqrt{2\pi}}e^{\pm i\phi}$
		m=±2	$\frac{4}{81\sqrt{30}(a_0)^{3/2}}\frac{r^2}{a_0^2}e^{-r/3a_0}$	$\frac{\sqrt{15}}{4}\sin^2(\theta)\frac{1}{\sqrt{2\pi}}e^{\pm i2\phi}$

Table 15.1 Hydrogen atom radial and angular wavefunctions.

The solution is $R(r) = e^{-c\cdot r}$, where $c = \sqrt{\frac{-2\mu E}{\hbar^2}}$ and has units of inverse length. It may appear that $\sqrt{\frac{-2\mu E}{\hbar^2}}$ should be imaginary; however, this isn't the case because the energies of the hydrogen atom are negative. What is important is that the wavefunction exponentially decays at large distance, which means that the electron very much wants to remain in proximity to the nucleus.

At short distances $(r \to 0)$ we remove the $\sim r^{-1}$ Coulombic potential energy while retaining the angular momentum term $\frac{-\hbar^2}{2\mu}\frac{l(l+1)}{r^2}$ due to its $\sim r^{-2}$ dependence. Likewise we also make the approximation $E \cdot r \cdot R(r) \to 0$ to yield:

$$\frac{\partial^2}{\partial r^2} r \cdot R(r) - \frac{l(l+1)}{r} R(r) = 0$$

Example Problem 15.1

Problem: Can you show that the eigenvalue equation can be used to calculate the energy of the hydrogen atom 1s ground state using the radial wavefunction $R_{1,0}(r) = 2(a_0)^{-3/2} \cdot e^{-r/a_0}$?

Answer: The Hamiltonian for the 1s is simplified as $l = 0$ and there is no rotational kinetic energy:

$$\frac{-\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} \cdot r \cdot 2(a_0)^{-3/2} \cdot e^{-r/a_0} + \frac{-e^2}{4\pi\varepsilon_0 r} \cdot r \cdot 2(a_0)^{-3/2} \cdot e^{-r/a_0} =$$

$$\frac{-2\hbar^2}{2\mu \cdot (a_0)^{3/2}} \cdot \frac{\partial^2}{\partial r^2}\left(r \cdot e^{-r/a_0}\right) + \frac{-2}{(a_0)^{3/2}}\frac{e^2}{4\pi\varepsilon_0} e^{-r/a_0} =$$

$$\frac{-\hbar^2}{\mu \cdot (a_0)^{3/2}}\frac{\partial}{\partial r}\left(e^{-r/a_0} - \frac{1}{a_0} \cdot r \cdot e^{-r/a_0}\right) + \frac{-1}{(a_0)^{3/2}}\frac{e^2}{2\pi\varepsilon_0} e^{-r/a_0} =$$

$$\frac{-\hbar^2}{\mu \cdot (a_0)^{3/2}}\left(-\frac{e^{-r/a_0}}{a_0} - \frac{e^{-r/a_0}}{a_0} + \frac{1}{a_0^2} \cdot r \cdot e^{-r/a_0}\right) + \frac{-1}{(a_0)^{3/2}}\frac{e^2}{2\pi\varepsilon_0} e^{-r/a_0} =$$

$$\frac{2\hbar^2}{\mu \cdot (a_0)^{5/2}} e^{-r/a_0} - \frac{\hbar^2}{\mu \cdot (a_0)^{7/2}} \cdot r \cdot e^{-r/a_0} + \frac{-1}{(a_0)^{3/2}}\frac{e^2}{2\pi\varepsilon_0} e^{-r/a_0}$$

Given $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu \cdot e^2}$, simple rearrangement reveals: $\frac{e^2}{2\pi\varepsilon_0} = \frac{2\hbar^2}{\mu \cdot a_0}$ and thus $\frac{-1}{(a_0)^{3/2}}\frac{e^2}{2\pi\varepsilon_0} = \frac{-1}{(a_0)^{3/2}}\frac{2\hbar^2}{\mu \cdot a_0} = \frac{-2\hbar^2}{\mu \cdot (a_0)^{5/2}}$. As a result, the 1st and 3rd term of the expression above cancel leaving:

$$-\frac{\hbar^2}{\mu \cdot (a_0)^{7/2}} \cdot r \cdot e^{-r/a_0} = -\frac{\hbar^2}{2\mu \cdot a_0^2} \cdot r \cdot 2(a_0)^{-3/2} \cdot e^{-r/a_0} = E \cdot r \cdot 2(a_0)^{-3/2} \cdot e^{-r/a_0}$$

Thus the energy is $E = -\frac{\hbar^2}{2\mu \cdot a_0^2}$. Inserting $a_0 = \frac{4\pi\varepsilon_0\hbar^2}{\mu \cdot e^2}$ reveals $E = -\frac{\mu \cdot e^4}{32\pi^2\varepsilon_0^2\hbar^2}$, exactly as derived by Bohr and Schrödinger.

A solution is $R(r) = r^l$ as verified below:

$$\frac{\partial^2}{\partial r^2} r \cdot r^l - \frac{l(l+1)}{r} r^l = \frac{\partial^2}{\partial r^2} r^{l+1} - l(l+1)r^{l-1} = l(l+1)r^{l-1} - l(l+1)r^{l-1} = 0$$

What this means is that the radial wavefunctions have different behavior as a function of angular momentum. This is due to the increase in rotational kinetic energy as the electron approaches the nucleus. In fact it would gain infinite kinetic energy at $r = 0$, although at small distances the fact that $R(r) \approx r^l \to 0$ prevents this from happening.

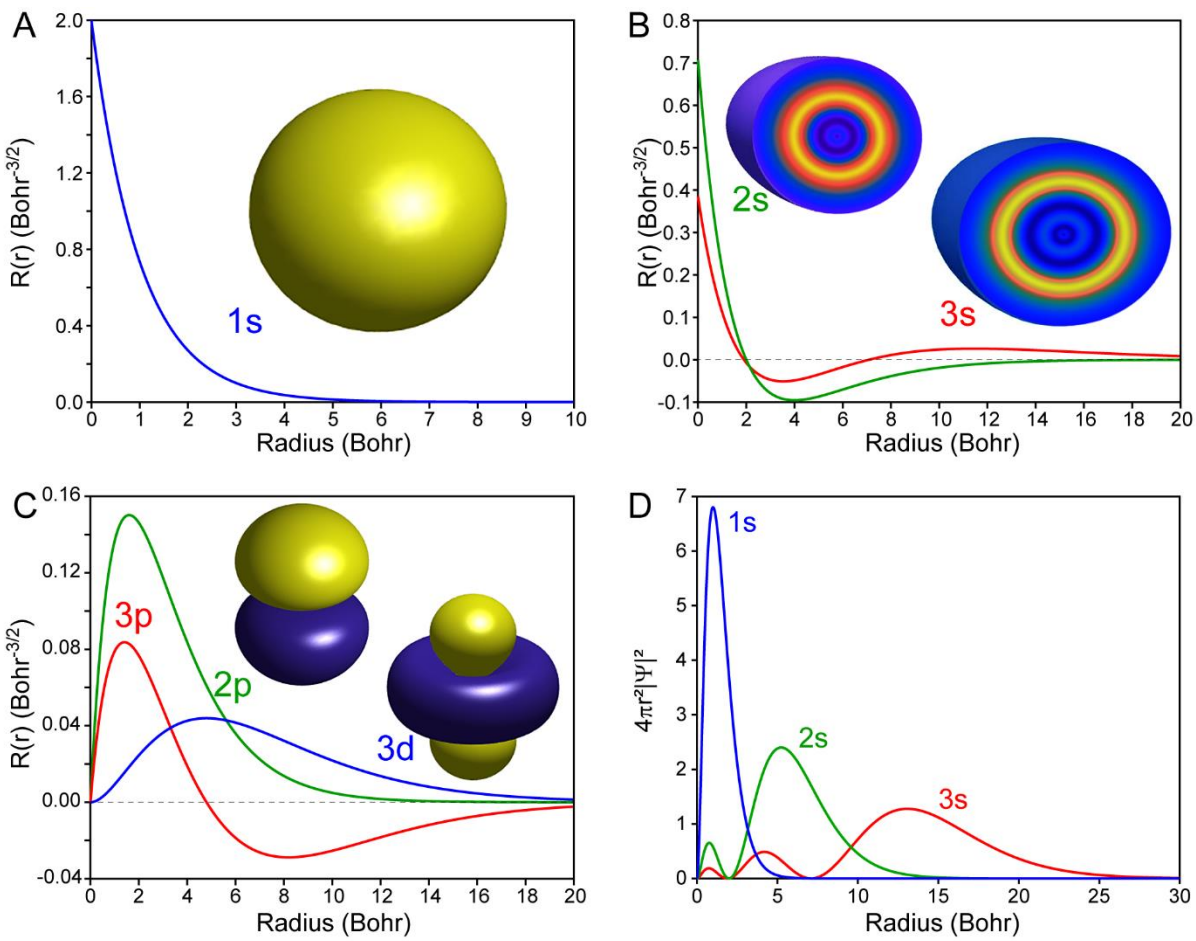


Figure 15.4. Radial wavefunctions for (A) the 1S state, (B) the 2S and 2P staes where the complex raidal nodes are observed in the solid rendering, (C) the 2P, 3P and 3D states. The $2P_Z$ and $3D_{Z^2}$ states are shown in space filling models. D. Radial distribution functions for hydrogenic 1s, 2s and 3s states.

The analysis above demonstrates that the radial wavefunctions must have short and long-distance components, with a mathematical entity that bridges the two:

$$R(r) \approx r^l \cdot (?) \cdot e^{-r}$$

This behavior is borne out from the "generalized Laguerre polynomials"; these are solutions to a related differential equation that were derived in 1880. In fact, it is the Laguerre polynomials that are responsible for the quantization of energy because, if the principal quantum number n wasn't an integer, then the wavefunctions wouldn't go to 0 at large distances. The complete radial wavefunctions are listed in Table 15.1.

15.3.1 Properties of the radial wavefunctions. The hydrogen atom's radial Schrödinger equation "controls" the energy via the principal quantum number n. As a result we can examine various features of the radial wavefunctions as they reveal the inner energetic workings of the simplest atom. This information can then be used to build up our knowledge of more complex

Example Problem 15.2

Problem: Can you show that the average distance of the s-state electron from the nucleus increases with principal quantum number from n=1 to n=2?

Answer: While it is tempting to calculate $\langle r \rangle$ by integrating the radial wavefunction as

$$\langle r \rangle = \int_0^\infty R_{1,0}^*(r) \cdot r \cdot R_{1,0}(r)\, \partial r$$

this is a mistake since the normalization condition includes the angular wavefunctions and the volume-normalizing Jacobian factor. We should always double check that our wavefunctions are normalized, and we do so here for the $R_{1,0}(r)Y_{0,0}(\theta, \phi)$ from Table 15.1:

$$\int_0^\infty \left(2a_0^{-\frac{3}{2}} \cdot e^{-r/a_0}\right)^* \left(2a_0^{-\frac{3}{2}} \cdot e^{-r/a_0}\right) r^2 \cdot \partial r = \frac{4}{a_0^3} \int_0^\infty e^{-2r/a_0} \cdot r^2 \cdot \partial r$$

Using an integral identity reveals that the result is 1.0, which means the wavefunction is properly normalized and we may perform further calculations. For the 1s state:

$$\langle r \rangle = \int_0^\infty r^2 \cdot r \cdot \left(2a_0^{-\frac{3}{2}} \cdot e^{-r/a_0}\right)^2 \partial r = \frac{3}{2} a_0$$

while the average distance for the 2s state is:

$$\langle r \rangle = \int_0^\infty r^2 \cdot r \cdot \left(\frac{1}{2\sqrt{2}(a_0)^{3/2}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}\right)^2 \partial r = 6a_0$$

These results reveal that there is a significant increase in the average radial distance for electrons as a function of shell number as seen in Figure 15.4.

(multielectron) atoms and eventually molecules. The most sensible organization scheme on hydrogen's electronic properties is based on the shell and angular momentum as characterized by the n and l quantum numbers; in fact the radial wavefunctions are labeled as $R_{n,l}(r)$.

15.3.1.1 The $l = 0$ states. Atomic states with no angular momentum are of the "s" type, and the radial wavefunctions for the first three s-state shells are shown in Figure 15.4 A, B. The 1s wavefunction $R_{1,0}(r) = N \cdot e^{-r/a_0}$ is a simple exponential decay from the origin. The 2s and 3s states are similar, although they have an increasing number of nodes that raises the energy and maintains orthogonality between different eigenstates. The most important feature of the s-states wavefunctions is that they are finite at the origin (i.e. $R_{n,l=0} > 0$ at $r = 0$). The reason that this is

allowed is because there is no rotational kinetic energy: $\frac{\hbar^2}{2\mu \cdot r^2} l(l+1) = 0$ that would erstwhile become infinitely high as $r \to 0$. Most interesting is the fact that the s-states are ostensibly degenerate with their higher angular momentum siblings within the same shell; however, as discussed later the phenomenon of shielding energetically favors the s-states.

15.3.1.2 Radial distribution functions. According to Coulomb's Law if the electron "touches" the nucleus then an infinite amount of energy will be released that would destroy the Universe. The fact that the s-state wavefunctions are finite at $r = 0$ suggests this possibly; however, universal annihilation is thwarted because electron never "finds" the nucleus since it is a point particle. In more technical language, the probability that the electron resides exactly within the same volume as the nucleus is 0%. This fact reveals that it is desirable to represent this volume-probability relationship. To do so we simply multiply the volume-normalizing (Jacobian) $4\pi r^2$ factor times the absolute value of the radial wavefunctions $R_{n,l}^2$ as shown in Figure 15.4D. These are called radial distribution functions, and they provide a great way to communicate quantum information as one can now clearly see that the electron isn't going to be found at the nucleus for any state. Furthermore, the radial separation between the various s-states due to the n-dependence of the wavefunctions $\sim e^{-r/n \cdot a_0}$ is more visible.

15.3.1.3 The $l > 0$ states. The fact that $R_{n,l>0} = 0$ at the origin is the most distinguishing feature of the higher angular momentum orbitals as seen in the 2p, 3p and 3d functions shown in Figure 15.4C. This is due to the $R(r) \approx r^l$ short length scale behavior originating from the rotational energy that is proportional to $\sim \frac{1}{r^2}$. This radial dependence means that, if the electron approaches the origin it will be spinning with near infinite energy; however, the suppression of wavefunction amplitude as $r \to 0$ prevents this. As seen in Figure 15.4C increasing the principal quantum number from the 2p to the 3p shell imparts a radial node that steps up the kinetic energy and maintains orthogonality. And while the 2p and 3p radial functions are clearly distinguished from each other, it is interesting to note that the 2p and 3d are similar in their overall shape due to a lack of nodes. The 4f state is similarly nodeless.

15.3.1.4 Degeneracies and magnetism. Due to the dependence of energy on the principal quantum number n one might ask, how do we even know that there are three p, five d and seven f m_l states? It's because we can directly observe them, and to describe how we first note that an electron with angular momentum is a spinning charge. As such it creates its own magnetic field,

the direction of which is proportional to $-\mathrm{m}_l$ (the minus sign is a result of the negative charge of the electron). This is why m_l is often called the "magnetic quantum number". Let's analyze the 2p ($l = 1$) state's three $\mathrm{m}_l = -1, 0, 1$ sub-states. Since the $\mathrm{m}_l = 1$ and $\mathrm{m}_l = -1$ have opposing magnetic fields, an external field will interact to split their energies while the $\mathrm{m}_l = 0$ state isn't affected. As a result the m_l degeneracies are lifted which can be observed using fluorescence spectroscopy. Pieter Zeeman first did so in 1896 using sodium and lithium. The so-called Zeeman effect allowed Hendrik Lorentz to predict the properties electrons before the electron was even discovered, and as a result Lorentz and Zeeman won the Nobel Prize in 1902. Later m_l state splitting was observed due to the application of a strong electric field on hydrogen by Johannes Stark in 1913. This effect could only be accurately described using quantum theory which was considered one of the early validations of quantum mechanics, and Stark was awarded the Nobel Prize in 1919.

15.4 Spin-Orbit Coupling

A curious thing about the hydrogen atom is that the 2p states always appear split *even if no magnetic field has been applied!* This phenomenon originates from the fact that and any electron in a $l > 0$ state has orbital rotation that creates a magnetic field, just as discussed in the previous section. This field then acts upon the intrinsic magnetism of an electron, which exists due to its spin angular momentum. Essentially, they are like little bar magnets. Thus, the orbital and spin magnetic fields can either be aligned (higher energy) or not (lower energy). This effect is called spin-orbit coupling and is depicted in Figure 15.5.

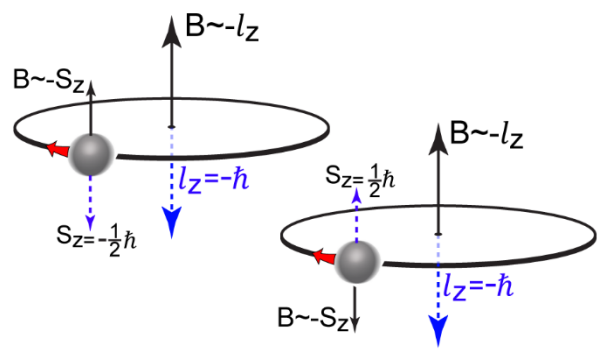


Figure 15.5. Spin orbit coupling affects the energy of $l > 0$ states due to alignment of the orbital and spin magentic (B) fields.

The Hamiltonian for this interaction can be derived from the Einstein's theory of relativity:

$$\hat{\mathrm{H}}_{\mathrm{SO}} = -\frac{\mu_{\mathrm{B}}}{\hbar \mathrm{m_e} \mathrm{e} c^2} \frac{1}{\mathrm{r}} \frac{\partial \hat{\mathrm{V}}}{\partial \mathrm{r}} \hat{\mathrm{L}} \cdot \hat{\mathrm{S}}$$

where $\mu_{\mathrm{B}} = 9.274\ \mathrm{J} \cdot \mathrm{T}^{-1}$ is the Bohr magneton that describes the magnetic moment of an electron due to orbital or spin angular momentum. The constants and gradient of the potential are generally lumped into a constant "A" such that $\hat{\mathrm{H}}_{\mathrm{SO}} \sim \mathrm{A} \cdot \hat{\mathrm{L}} \cdot \hat{\mathrm{S}}$. The dot product of the two

operators is defined as any standard vector: $\hat{L} \cdot \hat{S} = \hat{l}_x \cdot \hat{s}_x + \hat{l}_y \cdot \hat{s}_y + \hat{l}_z \cdot \hat{s}_z$. However, we cannot use this expression because the uncertainty principle dictates that we cannot know the x, y, and z components of angular momentum simultaneously. As a result, we employ an alternative strategy where we calculate the total angular momentum using the $\hat{J}$ operator, where $\hat{J} = \hat{L} + \hat{S}$. We encountered the issue of addition of angular momentum in Ch. 14, so you might want to review that section. Regardless, the operator $\hat{J}^2$ contains the $\hat{L} \cdot \hat{S}$ dot product:

$$\hat{J}^2 = \left(\hat{L} + \hat{S}\right)^2 = \hat{L}^2 + \hat{S}^2 + 2\hat{L} \cdot \hat{S}$$

We can rearrange the above to show that: $\hat{L} \cdot \hat{S} = \frac{1}{2}\{\hat{J}^2 - \hat{L}^2 - \hat{S}^2\}$, where the $\hat{J}$, $\hat{L}$, and $\hat{S}$ operators return their respective quantum numbers (j, l and s) such that the interaction is:

$$E_{SO} = \frac{A}{2} \cdot \{j(j+1) - l(l+1) - s(s+1)\}$$

This spin-orbit energy is a unique function of the electronic configuration of an atom or molecule. To understand exactly how this works we will provide an example for a hydrogen atom with a $2p^1$ electron configuration, i.e. $l = 1$ and $s = \frac{1}{2}$. As discussed in Ch. 14 the l and s angular momenta add to produce two possible j states:

$$j = |l + s| = \frac{3}{2} \quad \text{or} \quad j = |l - s| = \frac{1}{2}$$

Term symbols ($^{2S+1}L_j$) distinguish between the two as having $^2P_{3/2}$ and $^2P_{1/2}$ electronic configurations. Spin-orbit coupling raises the energy of the $^2P_{3/2}$ state:

$$E_{SO} = A \cdot \left\{\frac{3}{2}\left(\frac{3}{2} + 1\right) - 1(1+1) + \frac{1}{2}\left(\frac{1}{2} + 1\right)\right\} = \frac{A}{2} \cdot \left\{\frac{15}{4} - \frac{8}{4} - \frac{3}{4}\right\} = \frac{A}{2}$$

while the $^2P_{1/2}$ state is pushed downhill:

$$E_{SO} = A \cdot \left\{\frac{1}{2}\left(\frac{1}{2} + 1\right) - 1(1+1) - \frac{1}{2}\left(\frac{1}{2} + 1\right)\right\} = \frac{A}{2} \cdot \left\{\frac{3}{4} - \frac{8}{4} - \frac{3}{4}\right\} = -A$$

Consequently the otherwise degenerate $^2P_{3/2}$ and $^2P_{1/2}$ configurations are split as shown in Figure 15.6. Also shown is how the spin-orbit effect is observed from the H_α fluorescence which is the target of astronomers for charting the galaxy.

Hydrogen's spin-orbit coupling is very small and can only be observed with a fine spectrometer. However, the spin-orbit Hamiltonian's A constant is a function of the gradient of the Coulombic potential energy: $\frac{\partial \hat{V}}{\partial r}$, which in turn is proportional to the atomic number (Z) of an element as Z^4. This has two effects; one is that the spin-orbit energy becomes overwhelmingly

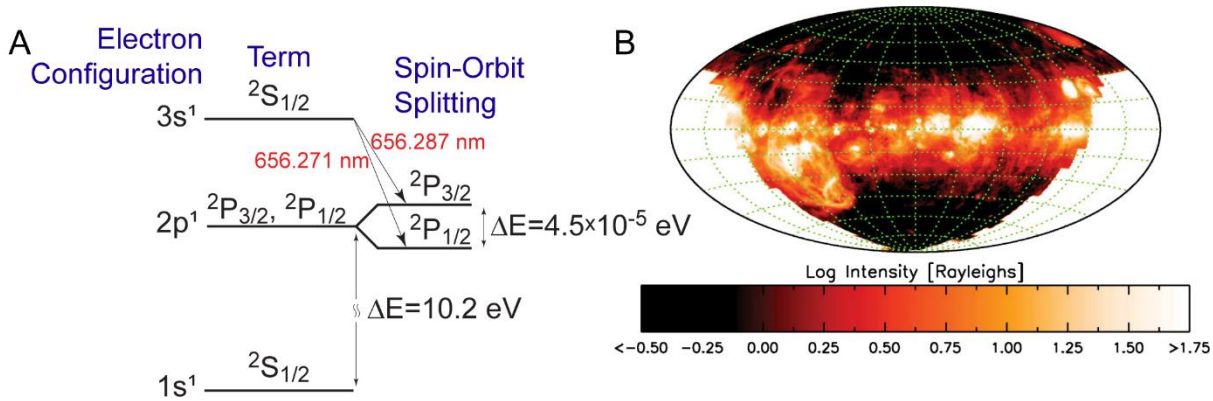


Figure 15.6 A. Energy levels for the hydrogen atom reveal splitting of the 2p state due to the spin-orbit effect. Emission from an excited 3s to 2p state results in red wavelength fluorescence called the hydrogen Hα line. **B.** Image of the Milkey Way galaxy taken at the Hα wavelength (1).

strong for high Z elements. Second, the spin-orbit effect means that the total wavefunction cannot have the orbital and spin wavefunctions separated as: $\psi_{\text{total}} \neq \psi_{\text{space}} \cdot \psi_{\text{spin}}$. This introduces significant problems when trying to classify these atoms using term symbols and order their energy levels. Unfortunately this is very difficult to deal with, and the development of theoretical calculations that incorporate spin-orbit effects is a topic of current research.

15.5 Spectroscopy

Spectroscopy is the most common method of characterizing chemical and biological compounds. While the absorption of light can be attributed to dynamics such as electronic (visible), vibrational (infrared), or rotational (microwave) excitation, one must apply quantum mechanics connect a spectrum to molecular physical properties. We are especially concerned with what makes an atom or molecule absorb light at all! As shown here, such information necessitates knowledge of the ground and excited state wavefunctions of a molecule's Hamiltonian as solved by the Schrödinger equation.

One of the central tenets of quantum mechanics is that all observables have associated operators. Absorption of light is (mostly) due to the interaction of the photon's electric field with the dipole moment of an atom or molecule. To absorb light there must be a change in the dipole moment, which is defined from classical electromechanics as $\vec{\mu} = q_1 q_2 \vec{r}$. Here, q_1 and q_2 are the charges (for hydrogen, and electron and proton) and $\vec{r}$ is the distance between. The quantum mechanical analog is the dipole operator, which for the hydrogen atom is:

$$\hat{\mu} = -e \cdot \hat{r}$$

We can calculate the expectation value of the dipole operator as it applied to a transition across energy states:

$$\langle\hat{\mu}\rangle = -e \cdot \langle\psi_f|\hat{r}|\psi_i\rangle = \int\int\int \psi_f^*(r,\theta,\phi) \cdot r \cdot \psi_i(r,\theta,\phi) \cdot r^2\, \partial r \cdot \sin(\theta)\, \partial\theta \cdot \partial\phi$$

This expression isn't quite the same as our previous examples of expectation values because different states are to the right and left of the operator. Here, ψ_i is the initial state of the atom or molecule; most likely this is the ground state. The "go-to" state is ψ_f, which must have a higher energy such that the difference in energy from the excited to the ground state matches the energy of the light absorbed:

$$\lambda = \frac{hc}{\Delta E}$$

The transition dipole moment $\langle\hat{\mu}\rangle$, sometimes called the difference dipole moment, is related to the strength of the absorption. A large $\langle\hat{\mu}\rangle$ means that the atom or molecule has a large Beer's Law (ε) constant, although it should be noted that the absolute strength of the transition dipole moment is not very quantitative. Mostly, $\langle\hat{\mu}\rangle$ tells us whether absorption of light occurs or not. If $\langle\hat{\mu}\rangle = 0$ then we say that the excited state is "optically silent". Otherwise, $\langle\hat{\mu}\rangle > 0$ means that the transition between ground and excited states can occur through light absorption. We can also determine what molecular properties and dynamics allow for a non-zero $\langle\hat{\mu}\rangle$; these are called selection rules.

The fact that light is polarized is an important detail when calculating the transition dipole moment. As shown in Figure 15.7, the oscillation of the photon's electric field must be represented in the dipole operator. To demonstrate we study the case of x-polarized light impinging on the 1s ground state of a hydrogen atom. To describe this correctly the dipole operator must align in the x direction, requiring a modification of the dipole operator as:

$$\hat{\mu} = -e \cdot \hat{x}$$

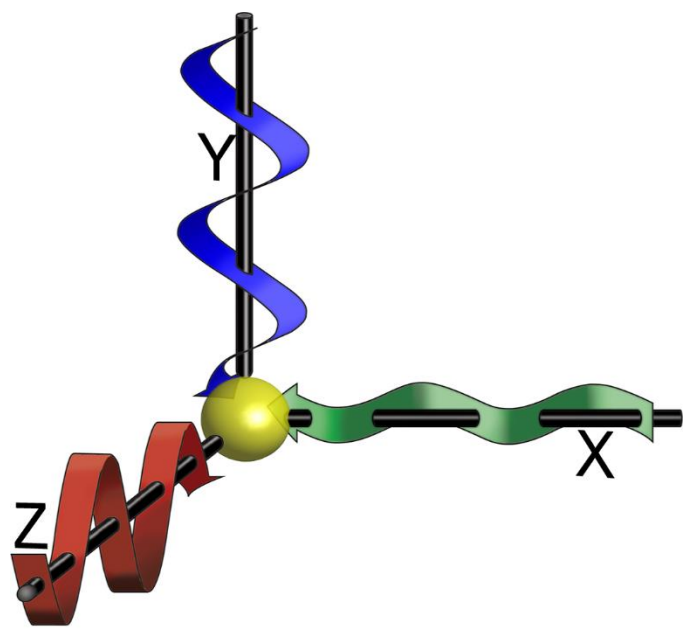


Figure 15.7. Different polarizations of light striking a ground state hydrogen atom results in angular dependence to the transition dipole moment.

Since atoms are round and we are working in spherical coordinates, we have to substitute the x coordinate in the spherical form as: $\hat{\mu} = -e^2 \cdot r \cdot \sin(\theta)\cos(\phi)$. Inserting this into the expression for calculating difference dipole moment yields:

$$\langle\hat{\mu}\rangle = \int_0^{\infty} \psi_f^*(r) \cdot r \cdot \psi_i(r) \cdot r^2 \, \partial r \cdot \int_0^{\pi} \psi_f^*(\theta)\psi_i(\theta) \cdot \sin^2(\theta) \cdot \partial\theta \cdot \int_0^{2\pi} \psi_f^*(\phi)\psi_i(\phi) \cdot \cos(\phi) \cdot \partial\phi$$

An interesting fact of this expression is that, while we think of the radial component as being overwhelmingly important, here it isn't so. The radial integral is non-zero for any combination of initial and final states, yet, we know from experiment that hydrogen is selective as to what transitions are optically allowed. In fact, the difference dipole moment is dependent on the angular integrals, as $\langle\hat{\mu}\rangle \neq 0$ *if and only if the change in angular momentum quantum number from the ground to excited state is* $\Delta l = \pm 1$. This spectroscopic selection rule is consistent with the fact that a photon has an angular momentum of $l = 1$, which conserves angular momentum upon absorption of light. Thus, the ground 1s state of hydrogen can only transition to a 2p state (x, y or z) depending on the polarization of light. Likewise if a hydrogen atom is in an excited 2p state it can transition only to the 3s or one of the 3d states. There are also selection rules about Δm_l depending on the light polarization and the initial and final states. Last, the process of fluorescence is analogous to absorption in reverse, where a drop from an excited state to the ground state creates a photon. The same $\Delta l = \pm 1$ selection rule applies.

15.6 Multielectron Atoms and Exchange

Having exhausted our investigations into hydrogen, we now study helium as the next element on the periodic table. This atom has two electrons to balance out the nuclear charge of Z = +2. Due to the extra electron we now must solve a larger Schrödinger equation with a Hamiltonian that more than doubles in size:

$$\hat{H}(1,2) = \frac{-\hbar^2}{2\mu r^2}\nabla_1 + \frac{-\hbar^2}{2\mu r^2}\nabla_2 - \frac{e^2}{4\pi\varepsilon_0 r_1} - \frac{e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |r_1 - r_2|}$$

where ∇ is called the "Laplacian" operator that returns all the kinetic energy including rotational. The reason that the Hamiltonian more than doubles is because there is an electron-electron repulsive (energy raising) term: $\frac{+e^2}{4\pi\varepsilon_0|r_1-r_2|}$, which unfortunately creates a problem for solving the wavefunctions. To explain, note that without this part the Hamiltonian can be separated into

terms for either electron 1 or 2 only. Thus, the total wavefunction is separable into the product of two individual states:

$$\psi_{total}(1,2) = \psi_1(1)\psi_2(2)$$

where the "(1)" and "(2)" are labels for the first and second electron and the subscripts on $\boldsymbol{\psi_1}$ and $\boldsymbol{\psi_2}$ refers to what type of orbital (1s, $2p_x$ etc.) that the electron resides. We expect that the individual electron states are the same as the hydrogen atom albeit with a higher nuclear charge of Z=+2. The He wavefunction for the ground state $1s^2$ configuration should be $\psi_{1S}(1)\psi_{1S}(2)$.

However, none of this is true because the $\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$ term completely negates the ability to separate the Hamiltonian into "mini" Schrödinger equations for electrons 1 and 2. Maybe you are expecting us to introduce a clever math trick that allows us to derive the real wavefunctions- actually there isn't one. *We don't know what the real wavefunctions are for any atom or molecule with more than one electron.*

Even though the separation solution $\psi_{total}(1,2) \approx \psi_1(1)\psi_2(2)$ isn't correct, we use it anyways due to the fact that we are confronted with a problem with no simple solution. This approximation requires us to employ a variety of different approaches for developing a quantum-based understanding of multielectron atoms. For example, since a separated solution is not an eigenstate of the multielectron Hamiltonian:

$$\hat{H}\psi_1(1)\psi_2(2) \neq E \cdot \psi_1(1)\psi_2(2)$$

we cannot use the eigenvalue way of solving the energy. However, we can employ the expectation value approach: $\langle E \rangle = \int \psi^* \hat{H} \psi$. While it is comforting that we have some mathematical tools at our disposal, the expectation value nonetheless is not real energy of the atom because the separated wavefunctions allow the two electrons to partially overlap each other in the same space at the same time. This energy raising mistake is called the "correlation error", and it causes $\langle E \rangle$ to be higher than the real energy. Methods to mitigate the correlation error can be complex and are usually introduced in graduate-level courses in quantum mechanics.

15.6.1 The Variational Principle. The use of an approximate ψ solution to the multielectron Hamiltonian causes the $\langle E \rangle$ expectation value to always be greater than the true energy:

$$\int \psi^* \hat{H} \psi > E_{exact}$$

This provides an interesting approach to create better wavefunctions for multielectron atoms and molecules using what is called the Variational Principle. What we do is alter and adjust our "best guess" separated wavefunctions to achieve the lowest ⟨E⟩ possible, as any change that results in a lower energy is better. Here is an example; if we are trying to optimize a quantum mechanical description for the helium atom ground state using a separated solution: $\psi_{total}(1,2) \approx \psi_{1S}(1)\psi_{1S}(2)$, we first re-derive the hydrogen ψ_{1S} using the variable Z for the atomic number. These are called "hydrogen-like" wavefunctions, which for the 1s state is:

$$\psi_{1,0}(r,Z) = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Z\cdot r/a_0}$$

(recall that Z = +1 for hydrogen). Next, we insert this function for electrons 1 and 2 and apply it to calculate the ⟨E⟩ expectation value for the helium atom. The result is a function of Z, which we then adjust to achieve the lowest energy possible. To do so we find the best ⟨E⟩ by applying standard calculus definition of the minimum of a function:

$$\frac{\partial}{\partial Z}\int \psi_{1S}(1)^*\psi_{1S}(2)^*\hat{H}\psi_{1S}(1)\psi_{1S}(2) = 0 \text{ @ } Z_{opt}$$

While Z = +2 for helium, applying the above method we find that Z_{opt}= +1.7. While the lower atomic charge may seem arbitrary, in fact one can understand why such alterations make sense based on physical grounds. In this example, reducing the effect of the nuclear charge in the helium atom wavefunction means that the electrons screen each other from the nucleus. This has a substantial effect on atomic energies as discussed below. And while changing the apparent nuclear charge improves our description of the multielectron wavefunction, it's not a perfect solution and further optimizations are necessary. In fact, this is one of the most active areas of research in chemical theory.

15.6.2 Shielding. An electron's attraction to the nucleus is offset by repulsive interactions with other electrons. This is easy to imagine for electrons in different shells because one electron is closer to the nucleus than the other. As a result, one can say that the higher shell electron is "shielded" from the positive nuclear charge. The shielding effect also operates within the l states (s, p, d etc.) of the same n shell, which results in a loss of their degeneracy. The reason for this can be seen in the 2s and 2p wavefunctions in Figure 15.4, where the 2s has amplitude near r = 0 while the 2p doesn't. As a result, in a multielectron atom the 2s electron's energy is lowered at the expense of the 2p.

This trend continues across states of increasing angular momentum, and as a result the 3s state is lower in energy than the 3p, which in turn is lower in energy than the 3d. In fact, the effect of shielding is so substantial the 4s state is lower in energy than the 3d! Let's use radial wavefunctions to demonstrate. At first, the reordering of 4s < 3d appears incorrect because the average electron-nuclear distance of a hydrogenic 4s state is $\langle r\rangle_{4s} = \int_0^\infty R_{4s}^* \cdot r \cdot R_{4s}(r) \cdot r^2\, \partial r = 24 \cdot a_0$, which is much longer than $\langle r\rangle_{3d} = 10.5 \cdot a_0$ of a 3d electron. The 4s electron's greater $\langle r\rangle$ implies that it is higher in energy than the 3d. However, the shielding effect occurs close to the nucleus. Thus we must alter our approach by calculating $|R_{4s}(r)|^2$ and $|R_{3d}(r)|^2$over the shorter distance range of $0 \rightarrow a_0$. Integral of the absolute value of the 4s wavefunction yields:

$\int_0^{a_0} R_{4s}^* \cdot R_{4s}(r) \cdot r^2\, \partial r =$

$$\frac{1}{96^2 \cdot {a_0}^3} \int_0^{a_0} \left\{ \left(24 - 18\frac{r}{a_0} + 3\frac{r^2}{a_0^2} - \frac{r^3}{8 \cdot a_0^3} \right) \cdot e^{-r/4a_0} \right\}^2 \cdot r^2\, \partial r = 4.1 \times 10^{-3}$$

When we perform the same calculation using the 3d radial wavefunction we find:

$$\int_0^{a_0} {\Psi_{3d}}^* \cdot \Psi_{3d} \cdot r^2\, \partial r = 6.5 \times 10^{-6}$$

As a result, the 4s electron is more likely to be within $0 \rightarrow a_0$ of the nucleus by a factor of ~630× compared to the 3d. In turn the 4s electron soaks up more Coulombic energy by ~1000×, which is why a multielectron atom has a lower energy 4s orbital compared to 3d. Don't forget, however, that 4s is higher in energy that the 3d in a 1-electron hydrogenic atom as shielding only occurs if there are multiple electrons.

When applied across all elements shielding reorders the periodic table into its familiar form shown in Figure 15.8. A diagram to

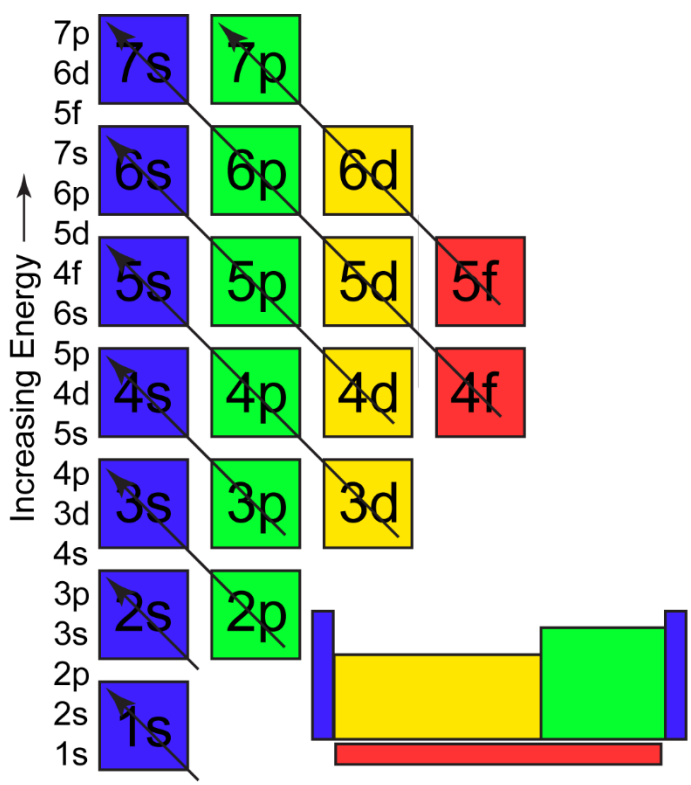


Figure 15.8. Shielding in multielectron atoms results in a reorganizational of atomic energy levels. This in turn affects the overall structure of the periodic table.

remember the state ordering is also presented. We conclude this section with one last effect on atomic structure due to the effects of relativity. For very heavy elements such as gold (Z=79), the 1s electrons experience an extremely high positive nuclear charge that considerably increases the electrons' kinetic energy. Thus, the velocities approach that of light, which causes an increase in mass and a contraction of the 1s orbital's radius. This is consistent with the fact that the Bohr unit of length is inversely proportional to mass. This relativistic effect causes gold and other heavy elements of the 6th and 7th row to reverse erstwhile normal trends of the periodic table concerning electron binding energies and oxidation states. The relativistic effect has also been used to explain why the periodic table appears to come to an end. If the atomic number Z becomes too high then 1s electrons simply become too unstable such that the element can't exist.

15.6.3 The Pauli exclusion principle and Slater determinants. In Ch. 14 it was discussed how spin is an angular momentum-like property of an electron. The spin wavefunctions are $\psi_{\text{spin}} = \alpha$ (the "up" ↑ state) and $\psi_{\text{spin}} = \beta$ (the "down" ↓ state). The $\hat{S}_z$ operator acts upon them as:

$$\hat{S}_z\alpha = s_z \cdot \alpha = ½\hbar \cdot \alpha \quad \text{and} \quad \hat{S}_z \cdot \beta = s_z \cdot \beta = -½\hbar \cdot \beta$$

Likewise $\hat{S}\alpha = \sqrt{s(s+1)}\hbar \cdot \alpha$ and $\hat{S}\beta = \sqrt{s(s+1)}\hbar \cdot \beta$. Last, we note that the spin states are orthonormal:

$$\int \alpha^*\alpha = \int \beta^*\beta = 1 \quad \text{and} \quad \int \alpha^*\beta = \int \beta^*\alpha = 0$$

Electrons are assigned spin wavefunctions by labeling them as such; for example, $\psi_{\text{spin}} = \alpha(1)\beta(2)$ for an orbital with an up and down electron (↑↓).

One "rule" of the Universe is that particles with ½$\hbar$ spin angular momentum cannot occupy the same quantum state at the same time. This is called the Pauli exclusion principle, and it is the reason why you can't have an atomic orbital hold two electrons of the same spin: ↑↑ = $\alpha(1)\alpha(2)$. Rather they must have opposite s_z as: ↑↓ = $\alpha(1)\beta(2)$. To include spin into our multielectron wavefunction we simply express it as the product of space and spin. Consequently, it would appear that the multielectron wavefunction for helium's $1s^2$ ↑↓ configuration is:

$$\psi(1,2) = \psi_{\text{space}}(1,2)\psi_{\text{spin}}(1,2) = \psi_{1S}(1)\alpha(1) \cdot \psi_{1S}(2)\beta(2)$$

However, this approach easily allows us to create a wavefunction for a $1s^2$ ↑↑ configuration that violates the Pauli principle: $\psi_{1S}(1)\alpha(1) \cdot \psi_{1S}(2)\alpha(2)$. This cannot be correct, which causes us

to enforce the Pauli principle by imparting a mathematical property called "inversion to interchange" defined by:

$$\psi(1,2) = -\psi(2,1)$$

This means that, upon exchanging the labels on an electron pair, the wavefunction should become the opposite of its former self. Any multielectron wavefunction that has this property satisfies the Pauli exclusion principle as shown below.

15.6.3.1 Singlet States. A singlet state is one with an even number of electrons that are equally split between up and down spins. This is called a "low spin" configuration and is diamagnetic; most chemical compounds have low spin electronic ground states. We will demonstrate the effects of the Pauli exclusion principle by developing an appropriate singlet $1s^2$ ↑↓ ground state helium wavefunction. While it appears that the inversion to interchange property: $\psi(1,2) = -\psi(2,1)$ might be mathematically intractable, in fact this is trivial to engineer. Beginning with the total wavefunction divided into space and spin components as:

$$\psi_{\text{total}}(1,2) = \psi_{\text{space}}(1,2) \cdot \psi_{\text{spin}}(1,2)$$

We create the inversion to interchange property within the spin manifold as:

$$\psi_{\text{spin}}(1,2) = \alpha(1)\beta(2) - \alpha(2)\beta(1)$$

To verify, we exchange the electron's labels to find:

$$\alpha(2)\beta(1) - \alpha(1)\beta(2) = -\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

This is antisymmetry property we are looking for. The total singlet ground state wavefunction with space and spin is therefore:

$$^1\Psi(1,2) = \psi_{\text{space}}\psi_{\text{spin}} \approx \psi_1(1)\psi_2(2)\left\{\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right\}$$

where the $\frac{1}{\sqrt{2}}$ is a normalization factor. It is now evident how the creation of an "illegal" $1s^2$ ↑↑ configuration for helium is avoided:

$$\psi_1(1)\psi_2(2)\left\{\frac{\alpha(1)\alpha(2) - \alpha(2)\alpha(1)}{\sqrt{2}}\right\} = 0$$

due cancellation of the spin wavefunctions. There is one more property that is required, which is that it shouldn't be possible to distinguish between the two electrons. This is accomplished by altering the real space orbital manifold as:

$$^1\Psi(1,2) = \left\{\frac{\psi_1(1)\psi_2(2) + \psi_1(2)\psi_2(1)}{\sqrt{2}}\right\}\left\{\frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}\right\}$$

This works because electron 1 can be in either the first or second spatial orbital, and the same is true for the 2nd electron. As a result they are not identifiably different.

15.6.3.2 Triplet states. A high spin electronic configuration has an unbalanced number of up and down electrons. The triplet is the most common example and occurs when the number of spin up and down electrons differ by 2. In Chapter 14 we discussed how spin angular momenta add to create three possible triplet spin wavefunctions:

$$\psi_{\text{spin}} = \alpha(1)\alpha(2) \qquad \psi_{\text{spin}} = \beta(1)\beta(2) \qquad \psi_{\text{spin}} = \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\}$$

The above are symmetric with respect to interchange of the electron's labels, we must impart antisymmetry to the spatial wavefunctions as follows:

$$^{3}\Psi(1,2) = \left\{\frac{\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)}{\sqrt{2}}\right\}\left\{\begin{matrix} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}}\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\} \end{matrix}\right\}$$

It is very uncommon to observe molecules with triplet ground states as the Pauli principle forbids two up or down spins from occupying the same space orbital. However, it is more frequently observed in excited electronic states, especially as a high spin configuration can be lower in energy compared to an equivalent singlet state as discussed below. An exception is molecular oxygen that is a ground state triplet. This fact dictates much about O_2's reactivity with organics, which has important implications for oxidation of biological molecules and materials.

15.6.3.3 Slater Determinants. While the ability to write antisymmetrized wavefunctions for two electrons isn't particularly difficult, one runs into greater complexity when trying to do the same for more electron rich systems. For example, in the case of a three electron atom, the principle of antisymmetry requires the permutation of any pair of electrons result in a negative wavefunction:

$$\psi(1,2,3) = -\psi(2,1,3) = -\psi(1,3,2) = -\psi(3,2,1)$$

It isn't clear how to mathematically engineer these relationships into a single wavefunction. In 1929 John Slater developed a method to do so using matrices, where the orbital identity change down the column while the electron identity moves to the right across the row. The wavefunction is the normalized determinant of this configuration. Let's practice by creating a helium two electron $1s^1\ 2s^1$ triplet state the wavefunction:

$$^{3}\Psi = \det\frac{1}{\sqrt{2}}\begin{vmatrix} \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(2)\alpha(2) \\ \Psi_{2s}(1)\alpha(1) & \Psi_{2s}(2)\alpha(2) \end{vmatrix}$$

Expanding the determinant reveals:

$$^{3}\Psi = \frac{1}{\sqrt{2}}\{\Psi_{1s}(1)\alpha(1)\Psi_{2s}(2)\alpha(2) - \Psi_{2s}(1)\alpha(1)\Psi_{1s}(2)\alpha(2)\}$$

This expression is equal to: $\frac{1}{\sqrt{2}}\{\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)\}\alpha(1)\alpha(2)$, exactly as we determined previously. The singlet $1s^2$ ↑↓ ground state configuration of helium requires two determinants:

$$^{1}\Psi = det\frac{1}{2}\left(\begin{vmatrix}\Psi_{1s}(1)\alpha(1) & \Psi_{1s}(2)\alpha(2)\\ \Psi_{1s}(1)\beta(1) & \Psi_{1s}(2)\beta(2)\end{vmatrix} - \begin{vmatrix}\Psi_{1s}(1)\beta(1) & \Psi_{1s}(2)\beta(2)\\ \Psi_{1s}(1)\alpha(1) & \Psi_{1s}(2)\alpha(2)\end{vmatrix}\right)$$

Simplification yields:

$$\frac{1}{2}\{\Psi_{1s}(1)\Psi_{1s}(2) + \Psi_{1s}(1)\Psi_{1s}(2)\}\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}$$

which is identical to the expression derived earlier.

Next on the periodic table is lithium, which has a $1s^2\ 2s^1$ configuration for its three electrons. The wavefunction in the determinant form is:

$$\Psi = \det\frac{1}{\sqrt{3}}\begin{vmatrix}\Psi_{1s}(r_1)\alpha(1) & \Psi_{1s}(r_2)\alpha(2) & \Psi_{1s}(r_3)\alpha(3)\\ \Psi_{1s}(r_1)\alpha(1) & \Psi_{1s}(r_2)\alpha(2) & \Psi_{1s}(r_3)\alpha(3)\\ \Psi_{2s}(r_1)\alpha(1) & \Psi_{2s}(r_2)\alpha(2) & \Psi_{2s}(r_3)\alpha(3)\end{vmatrix}$$

We won't expand the determinant here; however, if we did so and switched any two electron labels, we would find that the resulting total wavefunction has picked up a "-" sign as required by the Pauli principle. The addition of more electrons creates an even more complex state, which is why one needs supercomputers to model large molecules such as proteins using quantum mechanics.

15.6.4 Exchange energy and magnetism. The effects of Pauli principle are substantial due to the antisymmetry of wavefunctions. This in turn affects energetic ordering of excites states as a function of spin. To demonstrate we will study the dynamics of excitation of the helium atom shown in Figure 15.9A. The singlet $1s^2$ ground state transitions into the singlet $1s^1\ 2p_z^1$ excited state of helium after absorption of z-polarized light due to the angular momentum selection rule. While a spin selection rule stipulates $\langle\hat{\mu}\rangle = 0$ for excitation to the triplet state, the excited singlet may intersystem cross into a high spin $1s^1\ 2p_z^1$ configuration nonetheless. As a result we will study the difference in the singlet and triplet state energies by applying the antisymmetrized wavefunction to the electron-electron Coulomb operator:

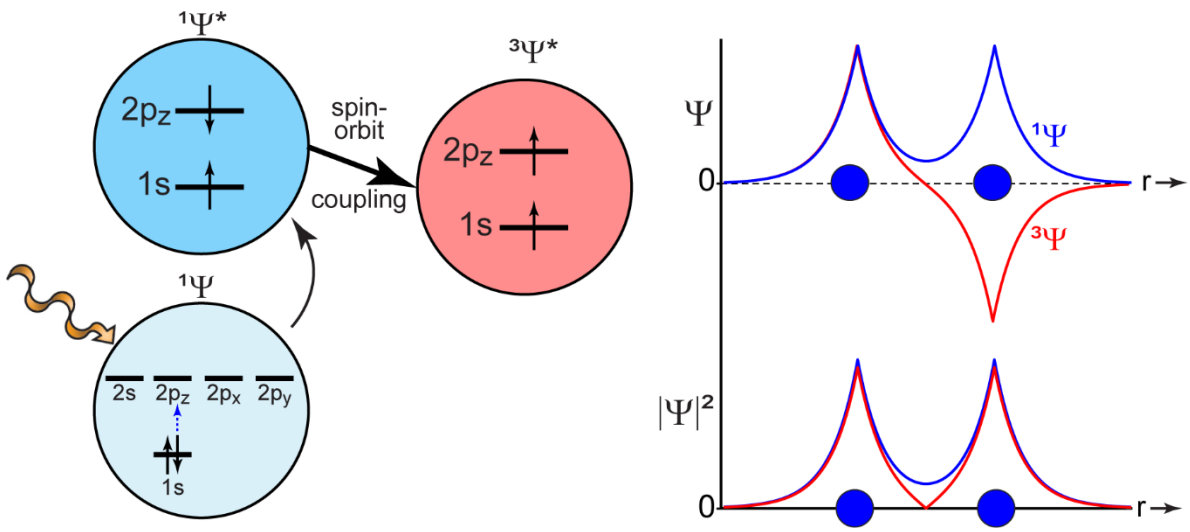


Figure 15.9. A. Excitation of the He atom creates an exicted singlet state due to the spin selection rule. Spin-orbit coupling allows for intersystem crossing into the lower energy triplet. **B.** Triplet states are lower in energy because of their antisymmetric space wavefunctions prevent electrons from crowding too close together as observed in singlet states.

$$\int \Psi^1(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}\Psi^1(1,2)\cdot\partial\tau \quad \int \Psi^3(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}\Psi^3(1,2)\cdot\partial\tau$$

These integrals are evaluated in full in the Appendix, where we demonstrate that the many terms collapse into the form K + J, where the term K is the Coulomb integral:

$$K = \int \psi_1^*(1)\psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}\psi_1(1)\psi_2(2)\cdot\partial\tau = \int |\psi_1(1)|^2 \frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}|\psi_2(2)|^2\cdot\partial\tau$$

This describes the probability density of the first electron in the first orbital, $|\psi_1(1)|^2$, electrostatically interacting with the same for the second electron $|\psi_2(2)|^2$. This is essentially identical to what was taught to you in Physics II Electromagnetism. Where this story gets more complex is that there is a second term found in the Coulombic interaction. It is called the exchange term and is usually abbreviated J:

$$J = \pm\int \psi_1^*(1)\psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}\psi_2^*(2)\psi_2(1)\cdot\partial\tau$$

where + is for the singlet and – is for the triplet. Consequently, the excited triplet state of helium is slightly lower in energy as shown in Figure 15.9.

The exchange term describes electrons as being in two places at once. While this is hard to understand, the effect is very much real as the fact that the excited triplet state is lower in energy than the singlet has been verified experimentally. One reason for this is the “odd” space

symmetry of the triplet state. Take for example diatomic H_2 that shares two electrons as shown in Figure 15.9B. The even symmetry of the singlet allows the electrons to become closer together while the triplet does the opposite, which would energetically favor the triplet. It should be noted that wavefunctions become increasingly complex as atoms gain more electrons and form molecules. As a result there is no simple rule about the ordering of the energies of excited states although one often hears "triplets are lower in energy than singlets". While this is often the case, especially for organics, in reality nothing is assured pending a full quantum chemical analysis.

Tipping the energy balance between high spin triplet states and low spin singlets due to the exchange interaction has many significant effects. For one, if an excited organic molecule intersystem crosses into a triplet state it will vigorously react with oxygen as O_2 is also triplet. Furthermore, the unpaired electron configuration of a high spin state imparts magnetic properties such as ferromagnetism. This phenomenon occurs when the constituent atoms of a solid piece of metal align their magnetic moments in parallel, which massively augments the high spin magnetic character. This is due to the strength of the exchange interaction, which is a function of atomic geometry because of the unusual nature of the exchange integral. This is why some metals are magnetic and some are not; the crystal structure and interatomic distances of some materials don't allow for enough exchange to impart a net magnetic field.

15.6.4 Spin-orbit mixing, intersystem crossing and phosphorescence. Any molecular dynamics that require a change of the overall spin state is formally not allowed, and such processes are usually referred to as "spin forbidden". However, the spin-orbit effect relaxes this prohibition. For example, most molecules have singlet ground states, and as such upon absorption of light the final state must also be a singlet due to the spin selection rule. This is also consistent with the fact that a photon does not have any spin-type angular momentum. Once an excited state singlet is created, however, the spin-orbit effect allows that state to intersystem cross into the lower energy triplet as shown in Figure 15.10A. This is because the forbidden nature of the transition is lifted by spin-orbit coupling, which mixes the spin states together as shown in Figure 15.10B. Here, spin-orbit coupling rotates a triplet state eigenvector into the singlet electronic state space causing it to gain some singlet character. The same is true for the singlet, and as a result an excited singlet state can become a triplet given that it already has some

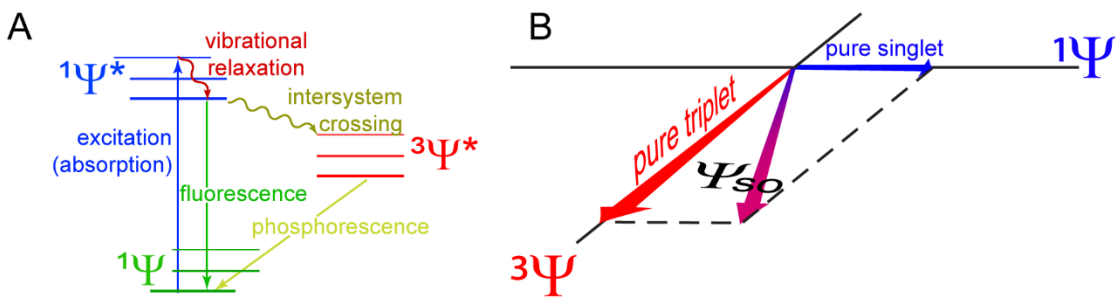


Figure 15.10. A. A Jablonski diagram of excited state dynamics. **B.** Spin-orbit coupling results in a mixing of singlet and triplet states. This allows for intersystem crossing and phosphorescece from the excited states of atoms and molecules.

triplet character. Phosphorescence, which is the emission of light from an excited triplet state back to a ground singlet state, is also allowed due to the spin-orbit effect.

Conclusions.

References.

1. L. M. Haffner *et al* 2003 *ApJS* **149** 405.

Appendix. Coulomb and exchange integrals of singlet and triplet states.

Triplets. A triplet wavefunction is defined by the Slater determinate: $\Psi^3(1,2) =$

$$\det\frac{1}{\sqrt{2}}\begin{vmatrix}\Psi_1(1)\alpha(1) & \Psi_1(2)\alpha(2)\\ \Psi_2(1)\alpha(1) & \Psi_2(2)\alpha(2)\end{vmatrix} = \frac{1}{\sqrt{2}}\Psi_1(1)\alpha(1)\Psi_2(2)\alpha(2) - \frac{1}{\sqrt{2}}\Psi_2(1)\alpha(1)\Psi_1(2)\alpha(2)$$

We now apply this to the electron-electron repulsion operator $\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$ as follows:

$$\int \Psi^3(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^3(1,2)\cdot\partial\tau =$$

$$\int\{\psi_1^*(1)\alpha^*(1)\psi_2^*(2)\alpha^*(2) - \psi_2^*(1)\alpha^*(1)\psi_1^*(2)\alpha^*(2)\}\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\{\Psi_1(1)\alpha(1)\Psi_2(2)\alpha(2) - \Psi_2(1)\alpha(1)\Psi_1(2)\alpha(2)\}\cdot\partial\tau$$

Next the expression is FOIL'ed out and the spin wavefunctions are factored out:

$$\begin{aligned}\frac{1}{2}\int \psi_1^*(1)\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\psi_2^*(2)\Psi_2(2)\cdot\partial\tau\int\alpha^*(1)\,\alpha(1)\int\alpha^*(2)\,\alpha(2)\\ +\frac{1}{2}\int \Psi_1^*(2)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(1)\Psi_2(1)\cdot\partial\tau\int\alpha^*(1)\,\alpha(1)\int\alpha^*(2)\,\alpha(2)\\ -\frac{1}{2}\int \Psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\Psi_2(1)\cdot\partial\tau\int\alpha^*(1)\,\alpha(1)\int\alpha^*(2)\,\alpha(2)\\ -\frac{1}{2}\int \Psi_1^*(2)\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(1)\Psi_2(2)\cdot\partial\tau\int\alpha^*(1)\,\alpha(1)\int\alpha^*(2)\,\alpha(2)\end{aligned}$$

Since $\int\alpha^*\,\alpha = 1$ and $\Psi_1^*(1)\Psi_1(1) = |\Psi_1(1)|^2$ etc., the above can be factored into:

$$\frac{1}{2}\left(\int|\Psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int|\Psi_1(2)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(1)|^2\cdot\partial\tau\right)$$

$$-\frac{1}{2}\left(\int \Psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\Psi_2(1)\cdot\partial\tau + \int \Psi_1^*(2)\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(1)\Psi_2(2)\cdot\partial\tau\right)$$

The terms in parentheses are equal because the labels "1" and "2" are arbitrary, and the integral results are the same. The result is the Coulomb integral minus the exchange integral:

$$\int \Psi^3(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^3(1,2)\cdot\partial\tau =$$

$$\int|\Psi_1(1)|^2\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}|\Psi_2(2)|^2\cdot\partial\tau - \int \Psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2^*(2)\Psi_2(1)\cdot\partial\tau$$

Singlets: A singlet wavefunction is defined by two Slater determinates:

$$det\frac{1}{2}\left(\begin{vmatrix}\Psi_1(1)\alpha(1) & \Psi_1(2)\alpha(2)\\ \Psi_2(1)\beta(1) & \Psi_2(2)\beta(2)\end{vmatrix} - \begin{vmatrix}\Psi_1(1)\beta(1) & \Psi_1(2)\beta(2)\\ \Psi_2(1)\alpha(1) & \Psi_2(2)\alpha(2)\end{vmatrix}\right)$$

$$= \frac{1}{2}\Psi_1(1)\alpha(1)\Psi_2(2)\beta(2) - \frac{1}{2}\Psi_2(1)\beta(1)\Psi_1(2)\alpha(2) - \frac{1}{2}\Psi_1(1)\beta(1)\Psi_2(2)\alpha(2) + \frac{1}{2}\Psi_2(1)\alpha(1)\Psi_1(2)\beta(2)$$

We now apply this to the electron-electron repulsion operator $\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}$ as:

$$\int \Psi^1(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}\Psi^1(1,2)\cdot\partial\tau$$

The expression is FOIL'ed and the spin wavefunctions are factored out on the following page. Since $\int \alpha^* \alpha = 1$, $\int \alpha^* \beta = \int \beta^* \alpha = 0$ and $\psi_1^*(1)\Psi_1(1) = |\Psi_1(1)|^2$ etc., half the terms can be removed, and the remainder factored into:

$$\frac{1}{2}\left(\int |\Psi_1(1)|^2 \frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int |\Psi_1(2)|^2 \frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}|\Psi_2(1)|^2\cdot\partial\tau\right)$$

$$+\frac{1}{2}\left(\int \psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}\psi_2^*(2)\Psi_2(1)\cdot\partial\tau + \int \psi_1^*(2)\Psi_1(1)\frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}\psi_2^*(1)\Psi_2(2)\cdot\partial\tau\right)$$

The terms in parentheses are equal because the labels "1" and "2" are arbitrary. Thus, we have the Coulomb integral plus the exchange integral:

$$\int \Psi^1(1,2)^* \frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi^1(1,2)\cdot\partial\tau =$$

$$\int |\Psi_1(1)|^2 \frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}|\Psi_2(2)|^2\cdot\partial\tau + \int \Psi_1^*(1)\Psi_1(2)\frac{e^2}{4\pi\varepsilon_0|r_1 - r_2|}\Psi_2^*(2)\Psi_2(1)\cdot\partial\tau$$

which proves that the paramagnetic triplet state is lower in energy than the singlet.

$$
\begin{aligned}
\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \alpha^*(1)\,\alpha(1)\int \beta^*(2)\,\beta(2)\\
-\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \alpha^*(1)\,\beta(1)\int \beta^*(2)\,\alpha(2)\\
-\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \alpha^*(1)\,\beta(1)\int \beta^*(2)\,\alpha(2)\\
+\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \alpha^*(1)\,\alpha(1)\int \beta^*(2)\,\beta(2)\\
-\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \beta^*(1)\,\alpha(1)\int \alpha^*(2)\,\beta(2)\\
+\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \beta^*(1)\,\beta(1)\int \alpha^*(2)\,\alpha(2)\\
+\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \beta^*(1)\,\beta(1)\int \alpha^*(2)\,\alpha(2)\\
-\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \beta^*(1)\,\alpha(1)\int \alpha^*(2)\,\beta(2)\\
-\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \beta^*(1)\,\alpha(1)\int \alpha^*(2)\,\beta(2)\\
+\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \beta^*(1)\,\beta(1)\int \alpha^*(2)\,\alpha(2)\\
+\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \beta^*(1)\,\beta(1)\int \alpha^*(2)\,\alpha(2)\\
-\frac{1}{4}\int \Psi_1^*(1)\Psi_2^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \beta^*(1)\,\alpha(1)\int \alpha^*(2)\,\beta(2)\\
+\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \alpha^*(1)\,\alpha(1)\int \beta^*(2)\,\beta(2)\\
-\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \alpha^*(1)\,\beta(1)\int \beta^*(2)\,\alpha(2)\\
-\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_1(1)\Psi_2(2)\cdot\partial\tau\int \alpha^*(1)\,\beta(1)\int \beta^*(2)\,\alpha(2)\\
+\frac{1}{4}\int \Psi_2^*(1)\Psi_1^*(2)\frac{e^2}{4\pi\varepsilon_0|r_1-r_2|}\Psi_2(1)\Psi_1(2)\cdot\partial\tau\int \alpha^*(1)\,\alpha(1)\int \beta^*(2)\,\beta(2)
\end{aligned}
$$

Problems: Numerical

1. Shielding. While I once calculated $\langle r \rangle_{2s} = 6a_0$ and $\langle r \rangle_{2p} = 5a_0$ for a *1-electron* hydrogen atom, it is still true that the 2s electron is much closer to the nucleus, such that in a *multielectron* atom the 2s orbital is at a lower energy than a 2p orbital. Let's confirm that this is the case.

a. Calculate $|\psi(r)|^2$ over a shorter range of distance, say $0 \rightarrow a_0$. First, start with the 2s wavefunction:

$$\psi_{2s}(r) = \frac{1}{(2 \cdot a_0)^{3/2}}\left(2 - \frac{r}{a_0}\right) \cdot e^{-r/2a_0}$$

and evaluate $\int_0^{a_0} \psi_{2s}^* \cdot \psi_{2s} \cdot 4\pi r^2 \cdot \partial r$ using Mathematica online:

http://www.wolframalpha.com/widgets/gallery/view.jsp?id=8ab70731b1553f17c11a3bbc87e0b605

Note that it is sometimes hard to write an equation such that Mathematica "likes" it: try this: x*x*(2-x/a)*(2-x/a)*exp(-x/a) dx. Use the limits 0 to a; note that $a = a_0$. And if you see the letter "e", that's exp(1)=2.71828… ***Hint:*** your answer should be a finite number like 0.4312, so don't forget all the constants especially the normalizer! Also if the website hangs just hit that equal sign to the lower right side of the box.

(8 pts)

b. Now do the same for the 2p wavefunction:

$$\psi_{2p}(r) = \frac{1}{\sqrt{24} \cdot a_0^{5/2}} r \cdot e^{-r/2a_0}$$

to find: $\int_0^{a_0} \psi_{2p}^* \cdot \psi_{2p} \cdot 4\pi r^2 \cdot \partial r$. **(8 pts)**

c. So, you see that in fact the 2s electron is more likely to be within $0 \rightarrow a_0$ of the nucleus by a factor of ~9.4× compared to the 2p, which is why multielectron atoms have lower energy 2s orbitals despite the fact that 2s and 2p are degenerate in 1-electron hydrogen atoms. Did you notice how this isn't a question?

( **pts)**

2. The Advanced Photon Source at Argonne National Lab is a huge facility that produces X-rays via Bremsstrahlung. It must generate a lot of X-ray power, right? For example, a nuclear power plant generates ~500 MW (megaWatts, or 500 Joules per second).

a. Let's say that the electrons circulate at a current of 1 nC ($= 1 \times 10^{-9}$C). How many electrons is that? **(4 pts)**

b. Now if the electrons (charge of an electron $= 1.6 \times 10^{-19}$ C) are accelerated to the speed of light ($= 3 \times 10^8$m/s) in 1.5 ps ($= 1.5 \times 10^{-12}$s), how much X-ray power is generated by the APS's electron beam? ***Hint:*** you need to use the Larmor formula for the power generated by a single, accelerating charge: $P = \frac{e^2 a^2}{6\pi\varepsilon_0 \cdot c^3}$, where e is the charge of an electron, a is the acceleration, and the permittivity of free space is: $\varepsilon_0 = 8.85 \times 10^{-12} \frac{s^4 A^2}{kgm^3}$.

(6 pts)

c. A typical result is ~1 mW power. Did you get a much smaller value? In that case you may have forgotten to multiply the Larmor formula by the number of electrons. **(**

 **pts)**

3. Absorption of light is not instantaneous- if it was, then there would be no conservation of energy or momentum. The timescale of absorption can be estimated from the time-energy uncertainty principal: $\Delta t \cdot \Delta E = \frac{1}{2}\hbar$. Try to calculate how much time it takes to absorb radiation for the following wavelength ranges (wavelengths given in parentheses):

a. Microwave (rotational, 10^{-1} m) **b.** Infra-Red (vibrational, 5×10^{-6} m)

c. Visible (electronic, 5×10^{-7} m) **d.** X-ray (core electronic, 1×10^{-9} m) **(8 pts)**

Hint: Estimate the uncertainty in the energy of the transition as being the same as the energy of light driving the transition itself.

Problems: Theoretical or Explain in Words

1. a. There is a branch of quantum mechanics called matrix mechanics. This is due to the fact that you can have eigenvalue equations in matrix form. Let's say that we have an operator: $\hat{\Omega} = \begin{bmatrix} 1 & 0.1 \\ 0.1 & 1 \end{bmatrix}$ and an eigenfunction of that operator: $\Phi = \begin{bmatrix} -1 \\ 1 \end{bmatrix}$. Can you show that:

$$\hat{\Omega}\Phi = \omega\Phi$$

where $\omega = 0.9$? ***Hint:*** you might have to look up how to multiply a matrix by a column vector in Google. Also here is a useful identity: $\begin{bmatrix} -\omega \cdot a \\ \omega \cdot a \end{bmatrix} = \omega \begin{bmatrix} -a \\ a \end{bmatrix}$. **(3 pts)**

b. The eigenvalue equation $\hat{\Omega}\Phi = \omega\Phi$ can be expressed as:

$$(\hat{\Omega} - \omega)\Phi = 0$$

Such that, as in the previous example:

$$\hat{\Omega} - \omega = \begin{bmatrix} 1-\omega & 0.1 \\ 0.1 & 1-\omega \end{bmatrix}$$

There is a theorem in mathematics that the eigenvalues ω of $\hat{\Omega}\Phi = \omega\Phi$ can be found by:

$$det(\hat{\Omega} - \omega) = 0$$

where det is the determinant. Can you show that solving:

$$det \begin{bmatrix} 1-\omega & 0.1 \\ 0.1 & 1-\omega \end{bmatrix} = 0$$

for ω provides a quadratic equation for ω? ***Hint:*** $det \begin{bmatrix} a & b \\ c & d \end{bmatrix} = ad - cb$. **(5 pts)**

c. Now if you solve the quadratic equation for ω in pt. b yields two eigenvalues, one of which is 0.9 as in pt. a. What is the other one? Hint: the roots of a quadratic equation: $ax^2 + bc + c = 0$ are $\frac{-b\pm\sqrt{b^2-4ac}}{2a}$. **(5 pts)**

d. Can you show that the eigenfunction $\Phi = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$ of $\hat{\Omega} = \begin{bmatrix} 1 & 0.1 \\ 0.1 & 1 \end{bmatrix}$ has an eigenvalue $\omega = 1.1$? **(3 pts)**

2. a. In the previous problem set you found that a hydrogen atom in the 1s ground state has a turning point, just like the harmonic oscillator (in case you forgot the turning point is where the potential energy is equal to the kinetic energy, and beyond the turning point you must technically have negative kinetic energy).

a. Now let's calculate r_{tp} for the 2p state. We start with the following expression:

$$\frac{h^2}{8\pi^2 m \cdot {r_{tp}}^2} l(l+1) - \frac{e^2}{4\pi\varepsilon_0 \cdot r_{tp}} = -\frac{m \cdot e^4}{32\varepsilon_0^2 \cdot h^2}$$

Hint: The Wolfram website has a facility to solve for a variable:

https://www.wolframalpha.com/widgets/view.jsp?id=c778a2d8bf30ef1d3c2d6bc5696defad

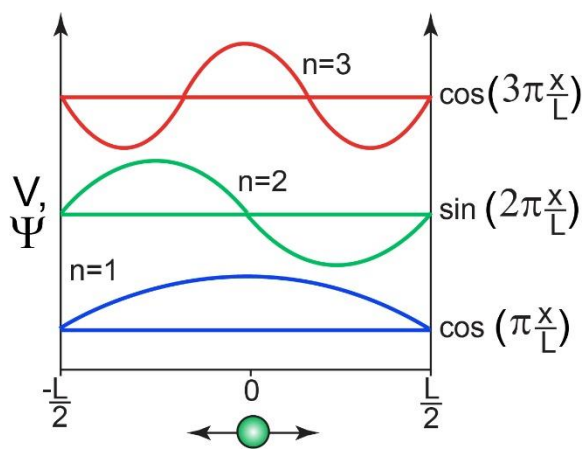
You need to input something that Wolfram understands, so I had to use some codes like:

f= e, h= h, o=ε_0, and pi= π. I then input: h^2/4/pi^2/m/x^2-f^2/4/pi/o/x=-m*f^4/32/o^2/h^2. **(5 pts)**

b. In pt. a you got two answers. One, at a large distance, is slightly less than the 2s value. This makes sense because the 2p has a small amount of angular kinetic energy, so it has less total energy to use to stretch further from the nucleus compared to the 2s.

However, you found another turning point at a shorter distance: $\left(\frac{1.17}{\pi}\right)\frac{\varepsilon_0 h^2}{m \cdot e^2}$. Can you explain this one? ***Hint:*** Do you recall why p- and d- orbitals have an $\psi \sim r^l$ term in the wavefunctions? Something about not getting to close to the nucleus? Maybe this will help: https://www.youtube.com/watch?v=0RVyhd3E9hY **(4 pts)**

3. Let's do some model calculations on spectroscopic transition moments using particle in a box wavefunctions instead of the H-atom, mostly because that is way easier. In this problem we will use the centered box form as shown here:



a. Let's evaluate some transition moments. Assuming particle-in-a-box wavefunctions as shown in the figure, what is the correct expression to calculate the transition moment for the ground state to the 1st excited state? For the 2nd excited state? **(2 pts)**

b. Now use the Wolfram symbolic integrator to evaluate: **(6 pts)**

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi x}{L}\right) \cdot (-e \cdot \hat{x}) \cdot \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right) \cdot \partial x$$

and:

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} \sqrt{\frac{2}{L}} \cos\left(\frac{3\pi x}{L}\right) \cdot (-e \cdot \hat{x}) \cdot \sqrt{\frac{2}{L}} \cos\left(\frac{\pi x}{L}\right) \cdot \partial x$$

c. Based from the results in pt. a, can you designate a □n transition rule, where n is the quantum number for the particle in a box? Hint: n=1 for the ground state, n=2 for the 1st excited state, … **(2 pts)**

4. a. You can often see spectroscopic transitions from the ground state to highly excited states. For example, for the particle in a box, can you show that the transition moment of the ground → 3th excited state is not 0 but is much weaker than for the ground → 1st excited state? **(4 pts)**

b. How much weaker is the ground → 3th excited state and ground → 5th excited state transition comparted to ground to 1st from question 4b? **(4 pts)**

5. Let's repeat the exercises of question 4 with vibrational wavefunctions!

Assuming the ground state is: $\psi_{\upsilon=0} = \left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2} \cdot e^{-x^2/2\alpha^2}$ and excited state is:

$\psi_{\upsilon=1} = \left(\frac{1}{2\alpha\pi^{1/2}}\right)^{1/2} \left(\frac{2x}{\alpha}\right) \cdot e^{-x^2/2\alpha^2}$. As a result, the transition moment is:

$$\int_{-\infty}^{\infty} \left(\frac{1}{2\alpha\pi^{1/2}}\right)^{1/2} \left(\frac{2x}{\alpha}\right) \cdot e^{-x^2/2\alpha^2} \cdot (-e \cdot \hat{x}) \cdot \left(\frac{1}{\alpha\pi^{1/2}}\right)^{1/2} \cdot e^{-x^2/2\alpha^2}\, \partial x$$

a. Note that I haven't asked a question yet- here it is- can you simplify the above expression into the simplest form and then evaluate whether the integral is 0 or not? Basically, just factor out constants and see what you have left, and then evaluate by any means whether the integral is 0 or not (don't worry about determining a value, just answer if it is 0 or not). **(4 pts)**

b. Now try the same thing with the ground to 2nd excited state:

$\psi_{\upsilon=2} = \left(\frac{1}{4\alpha\pi^{1/2}}\right)^{1/2} \left(\frac{4x^2}{\alpha^2} - 2\right) e^{-x^2/2\alpha^2}$ **(4 pts)**

Hint: You should be able to simplify the expressions a lot and find the proper identities at the beginning of this problem set.

6. a. Let's start simple- what do you get when you integrate the absolute value of a normalized radial wavefunction $\left|\Psi_{n=1,l=0}(r)\right|^2$ for a hydrogen atom with a single electron ($1s^1$ state)?

Hint: solve this:

$$\int |\Psi|^2 = \int_0^{\infty} \Psi^*(r) \cdot \Psi(r) \cdot \partial\tau = \int_0^{\infty} \left(\frac{2}{(a_0)^{3/2}} e^{-r/a_0}\right)^* \cdot \frac{2}{(a_0)^{3/2}} e^{-r/a_0} \cdot r^2 \cdot \partial r$$

You should know the answer, ***you don't have to do any math if you explain yourself***. **(2 pts)**

b. Now we will try to construct a multielectron wavefunction- let's work on a negative hydrogen with two electrons in the 1s state (the $1s^2$ configuration). Our first try for writing the wavefunction is:

$$\Psi = \Psi_{1s}(r_1) \cdot \Psi_{1s}(r_2)$$

We will now calculate the integrated absolute value:

$$\int |\Psi|^2 = \int_0^{\infty} \int_0^{\infty} \Psi_{1s}^*(r_1)\Psi_{1s}^*(r_2) \cdot \Psi_{1s}(r_1) \cdot \Psi_{1s}(r_2) \cdot r_1^2 \cdot \partial r_1 \cdot r_2^2 \cdot \partial r_2 =$$

$$\int_0^{\infty} \int_0^{\infty} \frac{4}{a_0^3} r_1^2 \cdot e^{-2r_1/a_0} \cdot \frac{4}{a_0^3} r_2^2 \cdot e^{-2r_2/a_0} \cdot \partial r_1 \cdot \partial r_2$$

Tell me what this double integral is equal to. Hint: you can evaluate them separately and then multiply the results ala: $\left(\int_0^{\infty} \frac{4r_1^2}{a_0^3} \cdot e^{-2r_1/a_0} \cdot \partial r_1\right) \cdot \left(\int_0^{\infty} \frac{4r_2^2}{a_0^3} \cdot e^{-2r_2/a_0} \cdot \partial r_2\right)$ **(4 pts)**

c. In actuality the result of "1.0" in pt. b is bad. While it appears that the wavefunction is properly normalized (good), it is also true that the two electrons are in the same state at the same time if they have the same spin. In this Universe this is impossible!

It must be true that, for two electrons in the same state: $\int |\Psi|^2 = 0$!

Here is our first attempt to fix this problem- we introduce spin wavefunctions α and β.

The spin wavefunctions only have the following properties:

$\int \alpha^* \cdot \alpha = \int \beta^* \cdot \beta = 1$ and $\int \alpha^* \cdot \beta = \int \beta^* \cdot \alpha = 0$ and $\alpha = \alpha^*, \beta = \beta^*$

Now for our example of a hydrogen anion $1s^2$ state Let's make both electrons spin up:

$$\Psi = \Psi_{1s}(r_1)\alpha(1) \cdot \Psi_{1s}(r_2)\alpha(2)$$

Now the integrated absolute value is:

$$\int |\Psi|^2 = \int_0^\infty \int_0^\infty \Psi_1^*(r_1)\Psi_1^*(r_2) \cdot \Psi_1(r_1)\Psi_1(r_2) \cdot 4\pi r_1^2 \cdot \partial r_1 \cdot 4\pi r_2^2 \cdot \partial r_2 \cdot \{\int \alpha^*(1)\alpha(1) \cdot \int \alpha^*(2)\alpha(2)\}$$

What does $\int |\Psi|^2$ above equal to (and explain your answer!)? **(2 pts)**

Hint: You have to evaluate two integrals of spin, and you still don't get 0!

7. Question 6c was screwed up- the wavefunction integrated to 1.0 even though the electrons were in the same state! This should not have happened!

Now here is the fix- you make the ***multielectron wavefunction itself equal to 0*** if both electrons are in the same state. The proper way to make this happen is to have the wavefunction be antisymmetric to interchange:

$$\Psi(1,2) = -\Psi(2,1)$$

Now how do you do this? Here is an example- first we start with a not-quite-right $1s^2$ spinup-spindown wavefunction: $\Psi = \Psi_{1s}(r_2)\beta(2) \cdot \Psi_{1s}(r_1)\alpha(1)$ and transform it into the proper antisymmetric form that you saw in class:

$$\Psi = \left\{\frac{\Psi_{1s}(r_1) \cdot \Psi_{1s}(r_2) + \Psi_{1s}(r_2) \cdot \Psi_{1s}(r_1)}{\sqrt{2}}\right\}\left\{\frac{\beta(1)\alpha(2) - \beta(2)\alpha(1)}{\sqrt{2}}\right\}$$

a. Can you show that $\Psi(1,2) = -\Psi(2,1)$? Hint, it happens in the "spin" part. **(4 pts)**

b. Can you now show that $\int |\Psi|^2 = 1$? You can just do the spin part, the space part:

$\iint \left|\frac{\Psi_{1s}(r_1)\cdot\Psi_{1s}(r_2)+\Psi_{1s}(r_2)\cdot\Psi_{1s}(r_1)}{\sqrt{2}}\right|^2 \cdot \partial\tau_1\partial\tau_2 = 1.0$. So you just have to do the spin part:

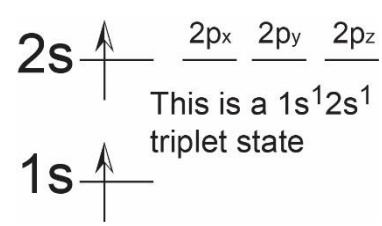
$$\frac{1}{2}\iint \{\beta(1)\alpha(2) - \beta(2)\alpha(1)\}^* \cdot \{\beta(1)\alpha(2) - \beta(2)\alpha(1)\}$$

Recall that spin identities are at the top of this page. **(8 pts)**

Hint: if you need to integrate something like this: $\iint \beta^2(2)\alpha^2(1)$, you divvy up the integrals between electrons 1 and 2 as so: $\int \beta^2(2) \cdot \int \alpha^2(1)$. This is $1 \cdot 1 = 1$.

c. If the system had both electrons spin up, can you show that $\Psi = 0$? **(2 pts)**

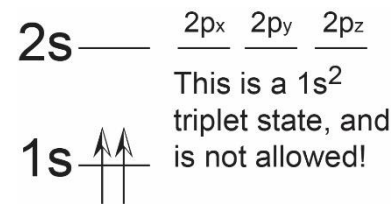
8. The example in question 9 was for a singlet state, which use spin wavefunctions to impart the antisymmetry property. For triplets, the "space" wavefunctions are used to enforce the antisymmetry property. For example, the proper antisymmetric wavefunction for a $1s^1 2s^1$ spinup-spinup configuration is:



$$\Psi(1,2) = \left\{\frac{\Psi_{2s}(r_1)\Psi_{1s}(r_2) - \Psi_{2s}(r_2)\Psi_{1s}(r_1)}{\sqrt{2}}\right\}\alpha(1)\alpha(2)$$

a. Let's see what happens if the two electrons are in the same state as shown here (a $1s^2$ triplet, which is impossible). Please write out the correct wavefunction and show that $\Psi = 0$. Hint: just write out $\Psi(1,2)$ above and make every "Ψ_{2s}" a "Ψ_{1s}".

(4 pts)



b. We can't make the spin wavefunctions symmetric if the space part is. As a result, there are three potential spin wavefunctions: $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$ and a weird one: $\frac{\beta(1)\alpha(2)+\beta(2)\alpha(1)}{\sqrt{2}}$. **(6 pts)**

Can you show that the spin parts of $\int|\Psi_{spin}|^2$ for $\frac{\beta(1)\alpha(2)+\beta(2)\alpha(1)}{\sqrt{2}}$ integrates to 1.0? To assist you, I have done an example for $\alpha(2)\alpha(1)$:

$$\int|\Psi_{spin}|^2 = \int\int\{\alpha(2)\alpha(1)\}^* \cdot \alpha(2)\alpha(1) = \{\int \alpha^*(2)\alpha(2)\} \cdot \{\int \alpha^*(1)\alpha(1)\} = 1.0 \cdot 1.0 = 1.0$$

2. Recall from the last problem set that you learned a bit about quantum mechanics and matrices. Here we will see how molecular orbitals are calculated from the matrix method.

a. If a H atom in its $1s^1$ ground state is infinitely far away from another ground state H atom, then there is no interaction, and the Hamiltonian matrix is:

$$\hat{H} = \begin{array}{c} \\ H(1)_{1s} \\ H(2)_{1s} \end{array} \begin{array}{c} \begin{array}{cc} H(1)_{1s} & H(2)_{1s} \end{array} \\ \begin{bmatrix} E_{1s} & 0 \\ 0 & E_{1s} \end{bmatrix} \end{array}$$

where $H(1)_{1s}$ represents the first H atom 1s state, $H(2)_{1s}$ represents the second H atom's 1s state, and E_{1s} is the energy of an H atom's 1s orbital. Please determine the eigenvalues of $\hat{H}$ using the on-line eigenvalue calculator from Wolfram. The input for a matrix such as $\begin{bmatrix} a & -b \\ 0 & c \end{bmatrix}$ would be {{a,-b},{0,c}}, and it calls the eigenvalues l. You also have to use letters for the matrix or the website won't work, so you should insert "E_{1s}" as "a". **(3 pts)**

b. Now if the H atoms get closer together they will have an interaction energy ϵ. Thus the Hamiltonian matrix is now:

$$\hat{H} = \begin{array}{c} \\ H(1)_{1s} \\ H(2)_{1s} \end{array} \begin{array}{c} \begin{array}{cc} H(1)_{1s} & H(2)_{1s} \end{array} \\ \begin{bmatrix} E_{1s} & -\epsilon \\ -\epsilon & E_{1s} \end{bmatrix} \end{array}$$

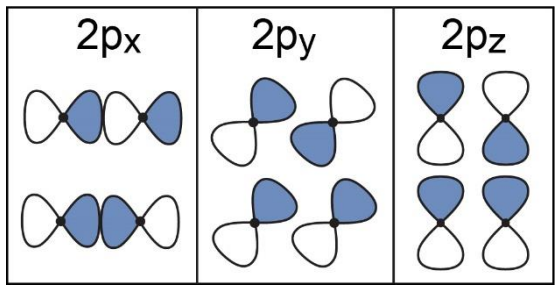
There is a negative sign in: $-\epsilon$ is because the interaction energy is attractive or "downhill". What are the eigenvalues of this matrix, and how do you interpret the results? **(5 pts)**

Answer: a. You plug into the website something like this: {{a,0},{0,a}}. The resulting eigenvalues are both $l_{1,2}$="a"=E_{1s}, meaning that there is no interaction and the energies of the H atoms haven't changed at all.

b. You plug into the website something like this: {{a,-b},{-b,a}}, and the resulting eigenvalues are:

l_1="a-b"=E_{1s}- ϵ, which is the bonding s-s orbital.

l_2="a+b"=E_{2p}+ϵ, which is the antibonding s-s orbital.



3. Now we will create the Hamiltonian matrix for an oxygen atom's p-orbitals when interacting with another O atom's p orbitals. Shown here are the bonding and antibonding configurations of the p_x, p_y and p_z orbitals between two oxygen atoms. You should note that the p_x orbital's interactions are different than the p_y and p_z, as the p_xs' appears "stronger" due to the greater overlap (i.e. the two p_x interact "head-to-head", forming s-type bonds, whereas the others appear "side-to-side" and form p-type bonds).

The Hamiltonian matrix is:

$$\hat{H} = \begin{array}{c} \\ H(1)_{2px} \\ H(1)_{2py} \\ H(1)_{2pz} \\ H(2)_{2px} \\ H(2)_{2py} \\ H(2)_{2pz} \end{array} \begin{array}{c} \begin{array}{cccccc} H(1)_{2px} & H(1)_{2py} & H(1)_{2pz} & H(2)_{2px} & H(2)_{2py} & H(2)_{2pz} \end{array} \\ \begin{bmatrix} E_{2p} & 0 & 0 & -\epsilon_2 & 0 & 0 \\ 0 & E_{2p} & 0 & 0 & -\epsilon_1 & 0 \\ 0 & 0 & E_{2p} & 0 & 0 & -\epsilon_1 \\ -\epsilon_2 & 0 & 0 & E_{2p} & 0 & 0 \\ 0 & -\epsilon_1 & 0 & 0 & E_{2p} & 0 \\ 0 & 0 & -\epsilon_1 & 0 & 0 & E_{2p} \end{bmatrix} \end{array}$$

a. Using the Wolfram website, what are the eigenvalues of this matrix? How do you interpret each one? ***Hint:*** obviously, there are 6 of them. Likely they represent boding and antibonding orbitals comprised of p_x, p_y and p_z orbitals. **(8 pts)**

b. Can you draw a MO diagram from the results? Also, please occupy the molecular orbitals with the 8 total electrons. Is oxygen a singlet or triplet? ***Hint:*** ϵ_2 is greater than ϵ_1.

(8 pts)

Answer: a. You plug into the website something like this:

{{a,0,0,-b,0,0},{0,a,0,0,-c,0},{0,0,a,0,0,-c},{-b,0,0,a,0,0},{0,-c,0,0,a,0},{0,0,-c,0,0,a}}

And the eigenvalues are:

l_1 E_{2p}-ϵ_2, which is the bonding p_x-p_x orbital.

l_2 E_{2p}+ϵ_2, which is the antibonding p_x-p_x orbital.

l_3 E_{2p}-ϵ_1, which is the bonding p_y-p_y or p_z-p_z orbital.

l_4 E_{2p}-ϵ_1, which is the bonding p_y-p_y or p_z-p_z orbital.

l_5 E_{2p}+ϵ_1, which is the antibonding p_y-p_y or p_z-p_z orbital.

l_6 E_{2p}+ϵ_1, which is the antibonding p_y-p_y or p_z-p_z orbital.

$\lambda_1 = a - b$

$\lambda_2 = a + b$

$\lambda_3 = a - c$

$\lambda_4 = a - c$

$\lambda_5 = a + c$

$\lambda_6 = a + c$

b. The eigenvalues are such that the bonding p_x-p_x bonding orbital is on bottom, followed by degenerate p_y-p_y and p_z-p_z bonding, and next p_y-p_y and p_z-p_z antibonding and p_x-p_x antibonding on top. Since there are 8 total electrons you get the following configuration which is clearly a triplet.