

CHM 3411 - Physical Chemistry II
Chapter 9 - Supplementary Material

1. Constuction of orbitals from the spherical harmonics

The wavefunctions that are solutions to the time independent Schrodinger equation for the hydrogen atom may be written as

$$\Psi_{n,\ell,m_\ell}(r,\theta,\phi) = R_{n,\ell}(r) Y_{\ell,m_\ell}(\theta,\phi) \quad (9.1.1)$$

where $R_{n,\ell}(r)$ is the radial wavefunction and $Y_{\ell,m_\ell}(\theta,\phi)$, a spherical harmonic, is the angular wavefunction.

One difficulty with working with the wavefunction given in eq 9.1.1 is that in general the spherical harmonics are imaginary functions (the only exception is the $m_\ell = 0$ spherical harmonics, which are real functions). Having an imaginary wavefunction makes it difficult to visualize what the wavefunction looks like.

As a means of finding real wavefunctions that are solutions to the TISE for the hydrogen atom, we often take combinations of the wavefunctions in eq 9.1.1 to give functions that are real and still solutions to the TISE. One such set of functions for the $\ell = 1$ spherical harmonics is the following

$$Y_{1,0}(\theta,\phi) = Y_z(\theta,\phi) \quad (9.1.2)$$

$$Y_-(\theta,\phi) = (-1/2^{1/2}) [Y_{1,1}(\theta,\phi) - Y_{1,-1}(\theta,\phi)] = Y_x(\theta,\phi) \quad (9.1.3)$$

$$Y_+(\theta,\phi) = (i/2^{1/2}) [Y_{1,1}(\theta,\phi) + Y_{1,-1}(\theta,\phi)] = Y_y(\theta,\phi) \quad (9.1.4)$$

The three angular wavefunctions given in eq 9.1.2 - 9.1.4 correspond to the p_z , p_x , and p_y orbitals. For example, if we substitute into the relationships in eq 9.1.3 and 9.1.4 we get

$$Y_-(\theta,\phi) = Y_x(\theta,\phi) = (3/4\pi)^{1/2} \sin\theta \cos\phi \quad (9.1.5)$$

$$Y_+(\theta,\phi) = Y_y(\theta,\phi) = (3/4\pi)^{1/2} \sin\theta \sin\phi \quad (9.1.6)$$

$Y_x(\theta,\phi)$ is a wavefunction that takes its maximum value in the x-y plane at $\phi = 0$ or $\phi = \pi$, and so has its maximum probability along the x-axis. Similarly $Y_y(\theta,\phi)$ is a wavefunction that takes its maximum value in the x-y plane at $\phi = \pi/2$ or $\phi = 3\pi/2$, and so has maximum probability along the y-axis.

The advantage of using these rewritten wavefunctions, called orbitals, to describe an electron in a hydrogen atom (or a multi-electron atom) is that the orbitals are real and therefore easy to visualize. Note however that $Y_x(\theta,\phi)$ and $Y_y(\theta,\phi)$ are no longer eigenfunctions of L_z , although they remain eigenfunctions of L^2 .

The above procedure can be repeated for larger values of ℓ to give d-orbitals, f-orbitals, and so forth.

2. The Pauli exclusion principle

A fundamental property that applies to atoms, molecules, and ions is the Pauli exclusion principle. This principle is usually given as the statement that no two electrons in a system can have the same set of quantum numbers. The principle itself arises from a more fundamental property, as discussed below.

Consider a system containing N identical particles, which we will label 1, 2, ...N. Let $\Psi(1,2,..N)$ be a function that is a solution to the TISE for the system. Since the particles are identical, exchange of any two particles should leave us with a solution to the TISE whose properties are identical with those of the original solution.

Let us define the operator that exchanges particle 1 with particle 2 $P(1,2)$ (with a corresponding operator for the exchange of any other pairs of particles). Since the particles are identical, we require that operating on the wavefunction with $P(1,2)$ must have one of the following two effects

$$P(1,2) \Psi(1,2,\dots,N) = \Psi(2,1,\dots,N) = (+1) \Psi(1,2,\dots,N) \quad (9.2.1)$$

where we say that the wavefunction is symmetric with respect to exchange of two particles, or

$$P(1,2) \Psi(1,2,\dots,N) = \Psi(2,1,\dots,N) = (-1) \Psi(1,2,\dots,N) \quad (9.2.2)$$

where we say that the wavefunction is antisymmetric with respect to exchange of two particles. Since properties such as the probability depend on the square of the wavefunction, both symmetric and antisymmetric behavior with respect to the exchange operation are acceptable.

Particles can be divided into two categories based on their spin properties and behavior with respect to the exchange operation. Bosons are particles with integer spin ($s = 0, 1, 2, \dots$), and have wavefunctions that are symmetric with respect to the exchange operation. Fermions are particles with half-integer spin ($s = 1/2, 3/2, \dots$) and have wavefunctions that are antisymmetric with respect to the exchange operations. Since electrons have a spin quantum number $s = 1/2$, they are fermions.

Consider the total wavefunction for the ground state of the helium atom in the orbital approximation. For each electron there will be a space wavefunction (corresponding to motion in space, and to the quantum numbers n , ℓ , and m_ℓ) and a spin wavefunction (corresponding to electron spin, and to the quantum numbers s and m_s). If we let α and β represent the normalized spin wavefunctions corresponding to $m_s = +1/2$ and $m_s = -1/2$, then for two electrons the possible combinations of spin wavefunctions are

$$\alpha(1)\alpha(2) \quad \alpha(1)\beta(2) \quad \beta(1)\alpha(2) \quad \beta(1)\beta(2) \quad (9.2.3)$$

If we operate on the the above space wavefunctions with the exchange operator $P(1,2)$ we get the following results

$$P(1,2) \alpha(1)\alpha(2) = \alpha(2)\alpha(1) = (+1) \alpha(1)\alpha(2) \quad \text{symmetric} \quad (9.2.4)$$

$$P(1,2) \alpha(1)\beta(2) = \alpha(2)\beta(1) \neq \pm \alpha(1)\beta(2) \quad (9.2.5)$$

$$P(1,2) \beta(1)\alpha(2) = \beta(2)\alpha(1) \neq \pm \beta(1)\alpha(2) \quad (9.2.6)$$

$$P(1,2) \beta(1)\beta(2) = \beta(2)\beta(1) = (+1) \beta(1)\beta(2) \quad \text{symmetric} \quad (9.2.7)$$

Notice that two of the combinations of spin wavefunctions are symmetric with respect to the exchange operator, while the other two combinations are, as written, neither symmetric nor antisymmetric with respect to the exchange operator (technically speaking, these two combinations are not eigenfunctions of $P(1,2)$).

We can form combinations of the mixed spin wavefunctions that are eigenfunctions of $P(1,2)$. Define the new functions

$$\sigma_+ = (1/2)^{1/2} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \quad (9.2.8)$$

$$\sigma_- = (1/2)^{1/2} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \quad (9.2.9)$$

It is easy to show that these two new functions are eigenfunctions of $P(1,2)$, with

$$P(1,2) \sigma_+ = (+1) \sigma_+ \quad \text{symmetric} \quad (9.2.10)$$

$$P(1,2) \sigma_- = (-1) \sigma_- \quad \text{antisymmetric} \quad (9.2.11)$$

Returning now to the wavefunction for the ground state of a helium atom, we may write the wavefunction in one of four ways

$$\Psi(1,2) = \psi_{1s}(1)\psi_{1s}(2)\alpha(1)\alpha(2) \quad (9.2.12)$$

$$\psi_{1s}(1)\psi_{1s}(2)\beta(1)\beta(2) \quad (9.2.13)$$

$$\psi_{1s}(1)\psi_{1s}(2)\sigma_+ \quad (9.2.14)$$

$$\psi_{1s}(1)\psi_{1s}(2)\sigma_- \quad (9.2.15)$$

Since the space wavefunctions are both 1s orbitals they are symmetric with respect to the exchange operator. Therefore, the first three wavefunctions given above are overall symmetric with respect to P(1,2), and are therefore not acceptable solutions. The last wavefunction, however, is antisymmetric with respect to P(1,2), as expected for a system composed of identical fermions. Since σ_- corresponds to a state where electron 1 and electron 2 have different spins, the two electrons have a different set of spin quantum numbers, and the Pauli principle is satisfied.

The above demonstrates that the Pauli principle applies for the specific case of two electrons with the same spacial wavefunction. The argument presented here can be generalized. The conclusion that may be drawn from the general argument is that no two electrons in the same system (atom, molecule, or ion) have the same set of quantum numbers, the usual way in which the Pauli principle is stated.

3. Determination of electronic states (term symbols) for atoms

The Pauli principle, aufbau principle, and Hund's rules can be used to find the electron configuration for the lowest energy arrangement of electrons in an atom. It is of course possible to have electron configurations corresponding to excited (higher energy states) for atoms. In addition, there are often several different electronic states that arise from the same electron configuration. This is because the energy of an electronic state depends not only on the electron configuration but also on the total orbital angular momentum vector (\mathbf{L}) and total spin angular momentum vector (\mathbf{S}) (recall that by convention we use boldface to indicate vectors).

For a collection of N electrons in an atom the total orbital and total spin angular momentum vector are given by the expressions

$$\mathbf{L} = \ell_1 + \ell_2 + \dots + \ell_N \quad (9.3.1)$$

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \dots + \mathbf{s}_N \quad (9.3.2)$$

where ℓ_i and \mathbf{s}_i are the orbital and spin angular momentum vectors for the i th electron. There are a large number of possible ways in which these individual angular momentum vectors can combine. Fortunately, however, both the total orbital and spin angular momenta and the z-components of these angular momenta are quantized in a manner similar to the quantization of the individual angular momenta. As a result

$$|\mathbf{L}| = [L(L+1)]^{1/2}\hbar \quad L_z = M_L \hbar \quad M_L = L, L-1, \dots, -L \quad (9.3.3)$$

and

$$|\mathbf{S}| = [S(S+1)]^{1/2}\hbar \quad S_z = M_S \hbar \quad M_S = S, S-1, \dots, -S \quad (9.3.4)$$

where L and M_L are the quantum numbers for the total orbital angular momentum and S and M_S are the quantum numbers for the total spin angular momentum. The z-component of \mathbf{L} and \mathbf{S} can be found using the relationships

$$\begin{aligned} L_z &= \ell_{z1} + \ell_{z2} + \dots + \ell_{zN} = m_{\ell 1}\hbar + m_{\ell 2}\hbar + \dots + m_{\ell N}\hbar \\ &= (m_{\ell 1} + m_{\ell 2} + \dots + m_{\ell N})\hbar = M_L \hbar \end{aligned} \quad (9.3.5)$$

and

$$\begin{aligned} S_z &= s_{z1} + s_{z2} + \dots + s_{zN} = m_{s1}\hbar + m_{s2}\hbar + \dots + m_{sN}\hbar \\ &= (m_{s1} + m_{s2} + \dots + m_{sN})\hbar = M_S\hbar \end{aligned} \quad (9.3.6)$$

from which it follows that

$$M_L = m_{l1} + m_{l2} + \dots + m_{lN} \quad (9.3.7)$$

and

$$M_S = m_{s1} + m_{s2} + \dots + m_{sN} \quad (9.3.8)$$

Equations 9.3.7 and 9.3.8 provide a means for determining the possible values for L and S for a particular electron configuration by working backwards from the possible values for M_L and M_S .

The procedure we will use to find the possible values for L and S for a particular electron configuration can be outlined as follows:

1) Find all of the possible combinations M_L, M_S for a particular electron configuration. Note that the Pauli principle applies to electrons, which may limit the total number of possible combinations that can occur. Also note that $\sum m_l = \sum m_s = 0$ for a completely filled orbital or for an empty orbital.

2) Arrange the results from the first step into a table of M_L, M_S values. Note that the table will have a symmetric appearance.

3) Find the largest value of M_L in the table.

4) Find the largest value of M_S in the table that has a value of M_L equal to that found in step 3.

5) There will be one electronic state with a value of L and S equal to the values of M_L and M_S found in steps 3 and 4 above. Eliminate one entry from the table for each combination of M_L and M_S corresponding to the values of L and S you have found.

6) Go to step 3, and repeat this procedure until all of the M_L, M_S combinations have been eliminated. The values of L and S that you have found represent to different electronic states corresponding to this particular electron configuration.

Since this is a fairly involved procedure it will help to consider a specific example. Consider an atom whose only unfilled orbital has a configuration np^2 . The possible values for M_L and M_S corresponding to different arrangements of electrons are indicated below. (NOTE: The electronic states one obtains for a partially filled orbital with k electrons is the same as that obtained for an orbital that is k electrons short of being completely filled. Therefore, one obtains the same electronic states for p^1 and p^5 , for p^2 and p^4 , for d^2 and d^8 , and so forth.)

$m_l=+1$	$m_l=0$	$m_l=-1$	M_L	M_S
↑ ↓			+2	0
↑	↑		+1	+1
↑	↓		+1	0
↑		↑	0	+1
↑		↓	0	0
↓	↑		+1	0
↓	↓		+1	-1
↓		↑	0	0
↓		↓	0	-1
	↑ ↓		0	0
	↑	↑	-1	+1
	↑	↓	-1	0
	↓	↑	-1	0
	↓	↓	-1	-1
		↑ ↓	-2	0

Note that there are 15 different possible combinations of electrons that appear. We now organize the results into a table of M_L , M_S values:

M_L	2	1	0	-1	-2
M_S					
+1		1	1	1	
0	1	2	3	2	1
-1		1	1	1	

We now proceed with finding the possible combination of values for L and S . The largest value for M_L in the above table is $M_L = 2$. The largest value for M_S with $M_L = 2$ is $M_S = 0$. Therefore one electronic state is the state with $L = 2$, $S = 0$. The possible combinations of M_L , M_S corresponding to this combination of values for L and S are M_L , $M_S = 2,0; 1,0; 0,0; -1,0; \text{ and } -2,0$. We therefore eliminate one state for each of these combinations. After this is done, our table now has the following appearance:

	M_L	2	1	0	-1	-2
M_S						
+1			1	1	1	
0			1	2	1	
-1			1	1	1	

The largest value for M_L that remains is $M_L = 1$. The largest value for M_S with $M_L = 1$ is $M_S = 1$. Therefore, there is a second electronic state with $L = 1$ and $S = 1$. Possible combinations of M_L, M_S for this state are 1,1; 1,0; 1,-1; 0,1; 0,0; 0,-1; -1,1; -1,0; and -1,-1. Eliminating these combinations from the table leaves the following:

	M_L	2	1	0	-1	-2
M_S						
+1						
0				1		
-1						

There is only one state left in the table, with $M_L = 0$ and $M_S = 0$. This indicates a third electronic state, with $L = 0$ and $S = 0$. The only combination of M_L, M_S for this state is 0,0. Eliminating this combination leaves us with an empty table. Therefore, there are three electronic states for this particular electron configuration

L	S	term symbol
2	0	1D
1	1	3P
0	0	1S

These electronic states may be placed in order from lowest to highest energy by using the following rules (note that these rules apply for ordering of different electronic states arising from the same electron configuration, and so cannot be used to determine the relative energies of states arising from different electron configurations).

- 1) For a set of electronic states, the lowest energy state is the one having the largest value for S.
- 2) For states with the same value for S, the lowest energy state is the one with the largest value for L.

Based on these rules, the states arising from the np^2 electron configuration are in the order $^1S > ^1D > ^3P$.

Finally, if we are interested only in the ground state electron configuration, we may obtain that as follows. Place electrons in orbitals in such a way that the maximum value for M_S is obtained, and a maximum value for M_L subject to the condition of maximizing M_S . The value for M_L and M_S for the state so obtained is equal to the value for L and S for the ground electronic state of the atom

4. Selection rules for atomic spectroscopy

The following selection rules apply for allowed transitions in atoms:

1) Orbital angular momentum selection rule.

$$\Delta L = 0, \pm 1 \text{ (except that } L = 0 \rightarrow L = 0 \text{ is forbidden).}$$

2) Spin angular momentum selection rule.

$$\Delta S = 0$$

3) Parity selection rule. The parity of a configuration is defined as even if $\sum_i \ell_i =$ an even number, and odd if $\sum_i \ell_i =$ an odd number. The selection rule is

allowed

forbidden

even \rightarrow odd

even \rightarrow even

odd \rightarrow even

odd \rightarrow odd

4) Total angular momentum selection rule. Recall that possible values of J are $J = |L+S|, |L+S-1|, \dots, |L-S|$.

$$\Delta J = 0, \pm 1 \text{ (except that } J = 0 \rightarrow J = 0 \text{ is forbidden).}$$

A transition is allowed only if it satisfies all of the above selection rules, and forbidden if it violates one or more selection rule.