8.E: Multielectron Atoms (Exercises)

Solutions to select questions can be found online.

8.4

Prove the speed of electron in first Bohr orbit is $e^2/4\pi\epsilon_0\hbar = 2.188 \times 10^6 m \bullet s^{-1}$. The speed is in atomic units.

Solution

Use following formula in order to make the calculations

$$v = \frac{\hbar}{m_e a_0}$$

$$v = \frac{\hbar}{m_e}\left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2}\right)$$

$$v = \frac{e^2}{4\pi\epsilon_0\hbar}$$

Substituting values get the following:

$$v = \frac{(1.6022\times 10^{-19}\ C)^2}{(1.1127\times 10^{-10}C^2\cdot J^{-1}\cdot m^{-1})(1.0546\times 10^{-34}\ J\cdot s)}$$

$$v = 2.1877\times 10^6\ m\cdot s^{-1}$$

This is the speed in atomic units. Are either of the two separate terms in the two term helium Hartree-Fock Orbital acceptable wavefunctions by themselves?

$$\psi(r) = 0.81839e^{-1.44608r} + 0.52072e^{-2.86222r}$$

8.15

Explain why:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1 dr_2 d\sigma_1 d\sigma_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1 dr_2 d\sigma_1 d\sigma_2}$$

can be rewritten as:

$$E = \frac{\int \Phi_2^*(1,2)\hat{H}\Phi_2(1,2)dr_1 dr_2}{\int \Phi_2^*(1,2)\Phi_2(1,2)dr_1 dr_2}$$

Solution

The Hamiltonian does not depend on spin, so the spin integral can be factored out.

8.16

Why must you distinguish the two electrons in separated hydrogen atoms?

Solution

They must be distinguished from one another because they each belong to a separate nucleus, not to an individual one.

8.17

In both the Hartree-Fock approximation and hydrogen atomic wavefunction, why is the angular dependence the same?

Solution

Since the Hamiltonian used in the approximation only depends on r, the angular dependence is not affected in the Hartree-Fock approximation. So both the Hartree-Fock approximation and hydrogen atom will have the same angular dependence.

8.20

Given the two electron determinate wavefunction below, determine if the spin component of the system is symmetric, anti-symmetric, or neither.

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\alpha(2) \end{vmatrix}$$

Solution

We have to solve the determinate.

$$1s1\alpha(2)1s2\beta(2) - 1s1\beta(2)1s1\alpha(2)$$

Now we have to factor out the spatial part from the spin part.

$$1s11s2[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

We are focused on the spin part and by observation, we can tell that the spin component is anti-symmetric.

8.23

Given $\hat{S}_z\alpha = \dfrac{\hbar}{2}\alpha$ and $\hat{S}_z\alpha = \dfrac{-\hbar}{2}\beta$, show that Ψ_{200} is an eigenfunction of $S_{z,total} = \hat{S}_{za} + \hat{S}_{zB}$.

Solution

Start with $\Psi_{200} = C(\psi_{2sa} + \psi_{2sB})$.

$$\hat{S}_{z.total}\Psi = C(\hat{S}_{za} + \hat{S}_{zB})[\psi_{2sa} + \psi_{2sB}]$$
$$= C\left(\frac{\hbar}{2} - \frac{\hbar}{2}\right)[\psi_{2sa} + \psi_{2sB}]$$
$$= 0$$

8.24

For the wavefunction:

$$\psi = \begin{vmatrix} \psi_A(1) & \psi_A(2) \\ \psi_B(1) & \psi_B(2) \end{vmatrix}$$

discuss the effect on the wavefunction of (a) swapping rows of the matrix and (b) swapping columns of the matrix.

Solution

Let's expand the determinant to inspect the complete multi-electron wavefunction:

$$\psi = \psi_A(1)\psi_B(2) - \psi_A(2)\psi_B(1)$$

If we swap rows:

$$\psi_{RowSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

If we swap columns:

$$\psi_{ColumSwap} = \psi_A(2)\psi_B(1) - \psi_A(1)\psi_B(2) = -\psi$$

Conclusion: swapping the either two rows or two columns of a Slater determinant changes the sign of the wavefunction.

8.27

What are the term symbols for carbon and oxygen atoms in the ground state?

Solution

Carbon: The electron configuration for carbon at ground state (lowest energy) is $1s^2 2s^2 2p^2$

Since the 1s and 2s orbitals are completely filled, they can be neglected when calculating for S. For the lowest energy, you need to use the highest values of S and L, therefore we find that S= 1/2 +1/2=1 and L=1 which corresponds to the letter P. Since the 2p orbital is less than half-way filled, we use J=|L-S|=|1-1|=0.

The term symbol is $^{2S+1}L_J$ which is $^3P_0$ for the ground-state of carbon atoms.

Oxygen: The electron configuration for oxygen at ground state (lowest energy) is $1s^2 2s^2 2p^4$

Again, the 1s and 2s orbitals may be neglected when calculating for S.

$$S = 1/2 + 1/2 + 1/2 - 1/2 = 1$$

The last electron has a spin down due to the Pauli Exclusion Principle.

L=1 which corresponds to the letter P.

Since the 2p orbital for oxygen is more than half-filled,

$$J = L + S = 2$$

The term symbol for the ground-state oxygen atom is $^3P_2$

8.28

Show that the number of sets of magnetic quantum number (m_l) and spin quantum number (m_s) associated with any term symbol is equal to $(2L+1)(2S+1)$. Apply this result to the np^2 case and show that symbol ^1S, ^3P and ^1D account for all the possible sets of magnetic quantum numbers and spin quantum numbers

8.29

Calculate all possible numbers of term symbol for an np^1 electron configuration.

Solution

$$N = \frac{G!}{e!(G-e)!}$$

where G is the highest number of electrons that an orbital can hold and e is the highest number of electrons that a subshell can hold

$$N = \frac{6!}{2!(6-2)!} = 15$$

8.30

Determine the ground state term symbol for the electron configuration of the Halogens.

Solution

Halogens have the electron configuration np^5 we can determine the term symbols for this configuration by mapping out all possible configurations the electrons can fit into the six spin orbitals. To quickly determine how many possible combinations there are we can use a statistical method of $N_{Comb.} = \binom{spinorbitals}{electrons}$

$$N_{comb} = \binom{6}{5} = \frac{6!}{5!(6!-5!)} = 6$$

Now we know that there are 6 different configurations that we can map out to determine the term symbols. Since we are working with the p orbital we know $l = 1$ and $m_s = -1,\ 0,\ 1$. I will denote spin using α as spin up $+\dfrac{1}{2}$ and β as spin down $-\dfrac{1}{2}$. M_L is the sum of the m_s values corresponding to the number of electrons in that energy level. For example if you have $\alpha\beta$ in $m_s = +1$ only, you then have 2 electrons in $m_s = +1$ resulting in $M_L = +1+1 = 2$. M_s is the sum of the spin up and spin down values.

+1	0	-1	M_L	M_s
$\alpha\beta$	$\alpha\beta$	α	+1	$+\dfrac{1}{2}$
$\alpha\beta$	α	$\alpha\beta$	0	$+\dfrac{1}{2}$
α	$\alpha\beta$	$\alpha\beta$	-1	$+\dfrac{1}{2}$
$\alpha\beta$	$\alpha\beta$	β	+1	$-\dfrac{1}{2}$
$\alpha\beta$	β	$\alpha\beta$	0	$-\dfrac{1}{2}$
β	$\alpha\beta$	$\alpha\beta$	-1	$-\dfrac{1}{2}$

Now we need to determine the maximum value of M_L and M_s. Looking at the table we see that

$$max\ M_L = 1$$
$$max\ M_s = \frac{1}{2}$$

From this we know our maximum value of L and S

$$L_{max} = 1$$
$$S_{max} = \frac{1}{2}$$

Our possible values for L and S are

$$L = 1,\ 0$$
$$S = \frac{1}{2}$$

Since S is only $\dfrac{1}{2}$ we know we can only have doublet term symbols since $2\left(\dfrac{1}{2}\right)+1 = 2$. L ranges from 1 to 0 so our possible corresponding symbols will be P and S. This leaves us with the possibility of having

$$^2P,\ ^2S$$

To figure out what is there we start with the term symbol that has the largest L value, with is the P. We see that for P, $L = 1$ and $S = \frac{1}{2}$. For a value of $L = 1$ our m_l can be $+1,\ 0,\ -1$ and for an $S = \frac{1}{2}$ our $m_s = +\frac{1}{2},\ -\frac{1}{2}$. In the table above all rows that contain these possible combination include every row. Therefore all of the configurations are contained in this doublet P term symbol. Including values of J we know that $L + S \geq J \geq |L - S|$. Since $L = 1$ and $S = \frac{1}{2}$ our final term symbols are

$$^2P_{\frac{3}{2}},\ ^2P_{\frac{1}{2}}$$

Hund's rules say that when L and S are the same with a subshell more than half filled, you look to the largest J value to be the most stable. Therefore our final answer and the ground state term symbol for halogens is

$$\boxed{^2P_{\frac{3}{2}}}$$

8.33

^2P, ^2D, and ^4S are the term symbols for an atom with the np^3 electron configuration. Using the term symbols for the np^3 electron configuration, calculate the J values associated with each of the term symbol. Then find out which term symbol represent the ground state.

Solution

To calculate J we use this equation

$$J = L + S$$

This equation can be further expanded to be

$$J = L + S, L + S - 1, L + S - 2, \ldots |L - S|$$

Term Symbol	L	S	J	Full Term Symbol
^2P	1	$\frac{1}{2}$	$\frac{3}{2}, \frac{1}{2}$	$^2P_{3/2}$ and $^2P_{1/2}$
^2D	2	$\frac{1}{2}$	$\frac{5}{2}\ \frac{3}{2}$	$^4D_{5/2}$ and $^4D_{3/2}$
^4S	0	$\frac{3}{2}$	$\frac{3}{2}$	$^4S_{3/2}$

8.34

What are the ground state electron configuration and term symbol for Calcium?

Solution

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

or

$$[Ar]4s^2$$
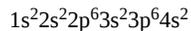
For the term symbol:

Spin Multiplicity: S = 0 (all electrons paired)

$$J = S + L = 0$$

There is only one valid value of J, so the term symbol for this configuration is

$$^{2S+1}L_J = {}^1S_0$$

$$2S + 1 = 1$$

Orbital Angular Multiplicity: L = 0 because we consider an s orbital. This corresponds to S.

8.34

Find the ground state term symbol for Ca.

Solution

ns^2 electron configurations have the term symbol $^1S_0$, so the term symbol for Ca in the ground state is $^1S_0$.

8.36

Write the electron configuration for vanadium and use this information to find the ground-state term symbol for V.

Solution

The electron configuration for vanadium is $[Ar]3d^3 4s^3$

Spin Multiplicity: The electron configuration predicts three unpaired electrons, so

$$S = 1/2 + 1/2 + 1/2 = 3/2$$

and the multiplicity of $2S + 1$ predicts that this will be a quartet. Orbital Angular Momentum: The electron configuration predicts three electrons with $l = 2$ and the rest so not contribute, so $L = 1 + 1 + 1 = 3$, which is an F state

The ground-state term symbol for vanadium is $^4F_{3/2}$ since vanadium has a half-filled 3d subshell.

- Total Angular Momentum: The shell is half full

8.36

What is the ground-state term symbol for Ne.

Solution

The term symbol is $^{2S+1}L_J$

where

S is the total electron spin L is the total orbital angular momentum

so $2S+1 = 2 \cdot 0 + 1 = 1$ and $J = 0 + 0 = 0$. So the term symbol for Ne is $^1S_0$.

and

$$J = L + S$$

The electron configuration for: Ne is $1s^2 2s^2 2p^6$ since Ne has spherical symmetry, we get:

$$L = 0 + 0 = S$$

$$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} - \frac{1}{2} = 0$$

8.37

Looking at the $1s2p$ electron configuration for He. Solve for the term symbols (states) of the Helium configuration and the degeneracies. If electron spin orbit coupling is included, what effect will this have?

Solution

There are two possible sets of m_l and m_s for the ns electron and six possible sets of m_l and m_s for the np electron, so there are $2 \times 6 = 12$ possible sets of m_l and m_s for the system. We can denote values for the electron in the ns orbital as m_{1j} and those for the electron in the np orbital as m_{2j}. The allowed values are given below:

Microstate	$m_l(1)$	$m_s(1)$	$m_l(2)$	$m_s(2)$	M_L	M_S	M_J
	Electron 1 in 1s orbital		*Electron 2 in 2p orbital*		*Combined Angular Momenta of both Electrons*		
1	0	+ 1/2	1	+ 1/2	1	1	2
2	0	- 1/2	1	+ 1/2	1	0	0
3	0	+ 1/2	1	- 1/2	1	0	0
4	0	- 1/2	1	- 1/2	1	-1	1
5	0	+ 1/2	0	+ 1/2	0	1	0
6	0	- 1/2	0	+ 1/2	0	0	1
7	0	+ 1/2	0	- 1/2	0	0	0
8	0	- 1/2	0	- 1/2	0	-1	0
9	0	+ 1/2	-1	+ 1/2	-1	1	0
10	0	- 1/2	-1	+ 1/2	-1	0	-1
11	0	+ 1/2	-1	- 1/2	-1	0	-2
12	0	- 1/2	-1	- 1/2	-1	-1	-2

Entries 1, 2, 4, 5, 6, 8, 9, 10, and 12 correspond to $L = 1$ and $S = 1$, or ^{3}P term symbol, and entries 3, 7, and 11 correspond to $L = 1$ and $S = 0$, which is a ^{1}P term symbol. The values of J can be derived from the table or by using

$$J = (L + S), (L + S - 1), (L + S - 2), \ldots\ldots, (|L + S|),$$

The final results given the term symbols below:
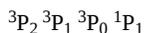
$^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

$(L + S)$ $(L + S - 1)$ $(|L - S|)$ $(|L + S|)$

The states corresponding to this electron configuration and their degeneracies are:

Term symbol: $^3P_2$ $^3P_1$ $^3P_0$ $^1P_1$

Degeneracy: 5 3 1 3

According to Hund's rule, the ground state $^3P_0$. Including the effect of spin-orbit coupling removes the degeneracy of the electronic states, and no spin orbit coupling splits the lines in an atomic spectra.

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