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Many-Electron Atoms - Solutions

1. For an electron in the $4f$ state, $l = 3$ and $s = 1/2$. From Chapter 4, the possible quantum numbers are:

$$m_l = -3, -2, -1, 0, 1, 2, 3$$
$$m_s = -\frac{1}{2}, \ +\frac{1}{2}$$

Hence, there are thus 14 possible states in which to put the first electron. For the second electron, there are now 13 possible states. The order in which the electrons are placed does not matter, so divide the product by two:

$$\# \text{ of distinct states} = \frac{14 \cdot 13}{2} = 91$$

2. Interchanging the coordinates in Eq. (5.5):

$$\psi = \frac{1}{\sqrt{2}}[\phi_a(2)\phi_b(1) - \phi_a(1)\phi_b(2)]$$

which is the same as multiplying Eq. (5.5) by a minus sign.

3. Using Eq. (5.6), each row of the determinant is attributed to a particular state and each column to a particular electron. For a lithium atom, there are three electrons. Using the given notation, the wavefunction is:

$$\Phi = \sqrt{\frac{1}{3}} \begin{vmatrix} \psi_{10}\alpha(1) & \psi_{10}\alpha(2) & \psi_{10}\alpha(3) \\ \psi_{10}\beta(1) & \psi_{10}\beta(2) & \psi_{20}\beta(3) \\ \psi_{20}\alpha(1) & \psi_{20}\alpha(2) & \psi_{20}\alpha(3) \end{vmatrix}$$

4. From Figure 5.2, the shells fill in the following order: 1s, 2s, 2p, 3s, 3p, 4s, 4p, and so on. Using the atomic number Z of each element as the number of electrons:

$$\begin{array}{lll}
\text{Flourine}(Z=9) & : 1s^2\ 2s^2\ 2p^5 \\
\text{Magnesium}(Z=12) & : 1s^2\ 2s^2\ 2p^6\ 3s^2 & : [Ne]\ 3s^2 \\
\text{Silicon}(Z=14) & : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2 & : [Ne]\ 3s^2\ 3p^2 \\
\text{Potassium}(Z=19) & : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1 & : [Ar]\ 4s^1 \\
\text{Cobalt}(Z=27) & : 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7 & : [Ar]\ 4s^2\ 3d^7
\end{array}$$

Note that a shorter way to notate these, as done on the right above, is to use the symbol of the inert gas that occurs closest before a particular element to denote the filled shells.

5. a) All elements with a given ground configuration reside in the same column of the periodic table. For a p^4 configuration, this corresponds to the fourth column of the right-side block:

$$p^4\ :\ O,\ S,\ Se,\ Te,\ Po$$

b) For a d^5 configuration, this corresponds to the fifth column of the transition metals:

$$d^5\ :\ Mn,\ Te,\ Re,\ Ns$$

6. The ground state configuration of carbon $(Z=6)$ is: $1s^2 2s^2 2p^2$. The first excitation happens when one electron jumps from the $2p$ state to the next available orbit, with configuration: $1s^2 2s^2 2p^1 3s^1$. Because the $3s$ and $3p$ orbits have nearly the same energy, the configuration for the second excitation is: $1s^2 2s^2 2p^1 3s^1$.

7. The ground state configuration of nitrogen $(Z=7)$ is: $1s^2 2s^2 2p^3$. Similar to the solution of the previous problem, the next two excitations have configurations: $1s^2 2s^2 2p^2 3s^1$ and $1s^2 2s^2 2p^2 3p^1$.

8. ns^2: Both electrons have $l=0$, so $L=0$. The spins combine to give $S=0$ or $S=1$. By the Pauli Exclusion Principle, $L+S$ must be even for two electrons in the same shell, the only possibility is $^1S(S=0,\ L=0)$.

nd^2: Two electrons with $l=2$ can combine giving choices: $L=4,3,2,1,0$. Again, the two spins combine to give $S=0,1$ and $L+S$ must be even. The following configurations are possible: $^1G(L=4,\ S=0)$, $^3F(L=3,\ S=1)$, $^1D(L=2,\ S=0)$, $^3P(L=1,\ S=1)$, and $^1S(S=0,\ L=0)$.

$4f^2$: Two electrons with $l=3$ can combine giving the choices: $L=6,5,\ldots,0$. As before, $S=0,1$ and $L+S$ must be even. The following configurations are possible: $^1I(L=6,\ S=0)$, $^3H(L=5,\ S=1)$, $^1G(L=4,\ S=0)$, $^3F(L=3,\ S=1)$, $^1D(L=2,\ S=0)$, $^3P(L=1,\ S=1)$, and $^1S(S=0,\ L=0)$.

Applying Hund's rules to the $4f$ configurations, those corresponding to the maximum value of S are: ^3H, ^3F, and ^3P. Of these, the one with maximum value of L is the ^3H configuration. Hence, the ^3H configuration is the lowest.

9. The number of M_L and M_S states will combine to give the total for each configuration:

Configuration	# of M_L	# of M_S	Total
$^1I(L=6, S=0)$	13	1	13
$^3H(L=5, S=1)$	11	3	33
$^1G(L=4, S=0)$	9	1	9
$^3F(L=3, S=1)$	7	3	21
$^1D(L=2, S=0)$	5	1	5
$^3P(L=1, S=1)$	3	3	9
$^1S(L=0, S=0)$	1	1	1

Adding up the Total column the number of possible state is 91, in agreement with Problem 1.

10. Ignoring the filled $1s$ and $2s$ shells, the $2p$ electron with $l=1$ and the $3d$ electron with $l=2$, give the possible values of $L=1, 2, 3$. These two electrons can combine to give $S=0, 1$. The possible configurations are:

$$^1P, \ ^3P, \ ^1D, \ ^3D, \ ^1F, \ ^3F$$

11. Here, we have two different situations: 1) case of non-equvalent electrons for the $[Xe]\ 4f\ 5d$ configuration, and 2) equivalent electrons for the $[Xe]\ 4f^2$ configuration.

$[Xe]\ 4f\ 5d$: One electron has $l=3$ and the other $l=2$. So the allowed values are $L=5, 4, 3, 2, 1$ and $S=0, 1$ in any combinations.

$[Xe]4f^2$: Now we impose the condition that $L+S$ be even. The two $1=3$ electrons allow the choices $L=6, 5, 4, 3, 2, 1, 0$ and $S=0, 1$. The allowed LS terms are: $(L=6, \ S=0)$, $(L=5, \ S=1)$, $(L=4, \ S=0)$, $(L=3, \ S=1)$, $(L=2, \ S=2)$, $(L=1, \ S=1)$, and $(L=0, S=0)$.

12. For the $4f^2$ configuration of $Ce^{2}+$, the allowed values of L and S are given by the previous problem. The allowed values of J are given by the vector sum of $L+S$:

$$J = 6, 5, 4, 3, 2, 1, 0$$

As for Problem 8, using Hund's rule, the lowest state is for the case $(L=5, \ S=1)$. Since the $4f$ shell is less than half full, the lowest state has the minimum J, which in this case is $J=4$.

13. From section 5.5.2, the nuclear charge increases going across a row in the periodic table. Increasing Z has the effect of decreasing the electron's average

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radius from the nucleus. This causes an increase in the Coulomb interaction, so sulfur (S) should have the greatest Coulomb interaction of the given choices.

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15. From Chapter 4, the spin-orbit interaction is proportional to $Z^4 e^2$, as shown in Eq. (4.51) and below. As in the above problem, suffer (S) has the largest Z and should have the largest spin-orbit splitting. This was also shown numerically in Problem 24 of Chapter 4.

16.* Using the Hartree-Fock applet, the values are:

$$Si : \langle \frac{1}{r^3} \rangle = 2.05a_0, \ \zeta = 130.2 \ cm^{-1}$$

$$P : \langle \frac{1}{r^3} \rangle = 3.31a_0, \ \zeta = 229.5 \ cm^{-1}$$

$$S : \langle \frac{1}{r^3} \rangle = 4.84a_0, \ \zeta = 364.0 \ cm^{-1}$$

The decreasing distance of the electrons with increasing Z makes for less screening of the magnetic field, which increases the spin-orbit splitting.

17. From Eq. (4.51), the strength of the spin-orbit interaction increases with atomic number as Z^4. The spin-orbit interaction is mainly responsible for the breakdown of LS coupling. Oxygen has the smallest spin-orbit interaction and hence the states of O are the closest to pure LS coupling.

18.* Using the Hartree-Fock applet, the average values of $\langle r \rangle$ for the electrons are:

$$La^+ \ 4f : \ 1.14a_0, \ 5d : \ 2.88a_0$$
$$Ce^{2+} \ 4f : \ 1.00a_0, \ 5d : \ 2.34a_0$$
$$Pr^{3+} \ 4f : \ 0.94a_0, \ 5d : \ 2.08a_0$$

The average distances for the $4f$ are clearly smaller than for the $5d$ in all cases.

19.* Using the Hartree-Fock applet, the total energy for the ground state of Ne is $-128.55 \ eV$. Removing a $2p$ electron, the configuration should now read $1s^2 2s^2 2p^5$. Running the applet again gives the total energy as $127.82 \ eV$. The binding energy is the difference of these two values:

$$|-128.55 - (-127.82)| \approx 0.73 \ eV$$

For the neutral neon atom, the $2p$ state has a single-electron energy of $0.85\ eV$. This is close to the binding energy found above.

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22. The following transitions are permitted:

$$[Xe]\ 4f\ 5d\ :\ {}^3H \rightarrow\ {}^3G,\ {}^3G \rightarrow\ {}^3F,\ {}^3F \rightarrow\ {}^3D,\ {}^3D \rightarrow\ {}^3P,\ {}^3P \rightarrow\ {}^3S$$

and the reverse of these transitions. No transitions are allowed for the $[Xe]4f^2$ configuration due to the selection rules.