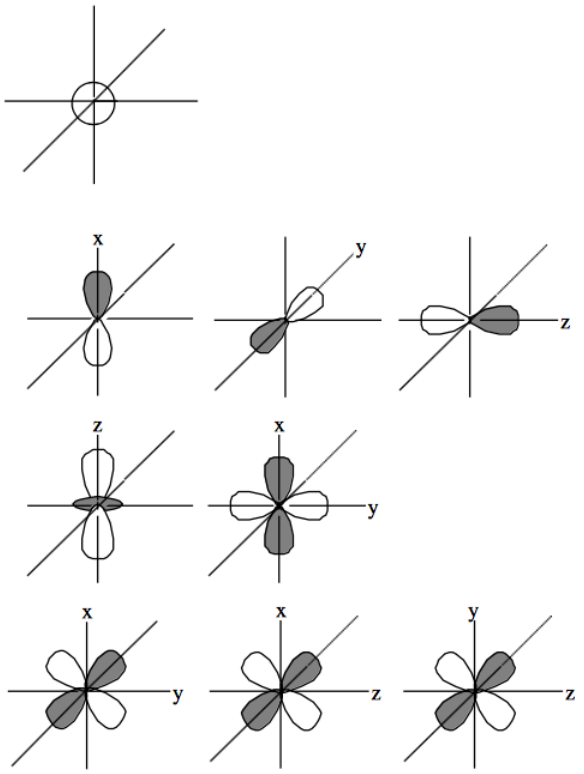
22.2.4: iv. Review Exercises Solutions

1.



2. i. In ammonia the only "core" orbital is the N 1s and this becomes an a1 orbital in C_{3v} symmetry. The N 2s orbitals and 3 H 1s orbitals become 2 a_1 and an e set of orbitals. The remaining N 2p orbitals also become 1 a_1 and a set of e orbitals. The total valence orbitals in C_{3v} symmetry are $3a_1$ and 2e orbitals.

   ii. In water the only core orbital is the O 1s and this becomes an a1 orbital in C_{2v} symmetry. Placing the molecule in the yz plane allows us to further analyze the remaining valence orbitals as: O $2p_z = a_1$, O $2p_y$ as b_2 , and O $2p_x$ as b_1 . The H 1s + H 1s combination is an a_1 whereas the H 1s - H 1s combination is a b_2.

   iii. Placing the oxygens of H_2O_2 in the yz plane (z bisecting the oxygens) and the (cis) hydrogens distorted slightly in +x and -x directions allows us to analyze the orbitals as follows. The core O 1s + O 1s combination is an a orbital whereas the O 1s - O 1s combination is aborbital. The valence orbitals are: O2s+O2s=a, O2s-O2s=b, O $2p_x$ + O $2p_x$ = b, O 2px - O 2px = a, O 2py + O 2py = a, O 2py - O 2py = b, O 2pz + O 2pz = b, O 2pz - O 2pz = a, H 1s + H 1s = a, and finally the H 1s - H 1s = b.

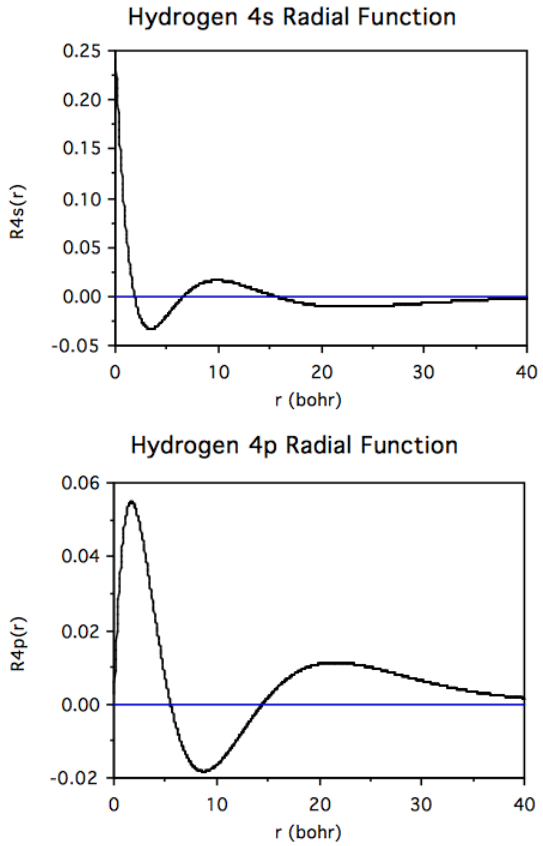
   iv. For the next two problems we will use the convention of choosing the z axis as principal axis for the $D_{\infty h}$, D_{2h}, and C_{2v} point groups and the xy plane as the horizontal reflection plane in C_s symmetry.

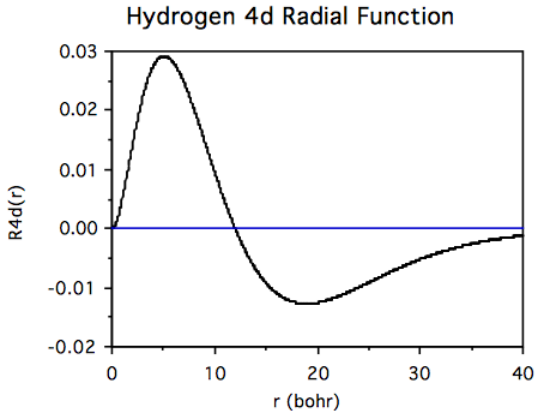
	$D_{\infty h}$	D_{2h}	C_{2v}	C_s	
$N1s$	σ_g	a_g	a_1	a'	(22.2.4.2)
$N2s$	σ_g	a_g	a_1	a'	(22.2.4.3)
$N2p_x$	π_{xu}	b_{3u}	b_1	a'	(22.2.4.4)
$N2p_y$	π_{yu}	b_{2u}	b_2	a'	(22.2.4.5)
$N2p_z$	σ_u	b_{1u}	a_1	a''	(22.2.4.6)

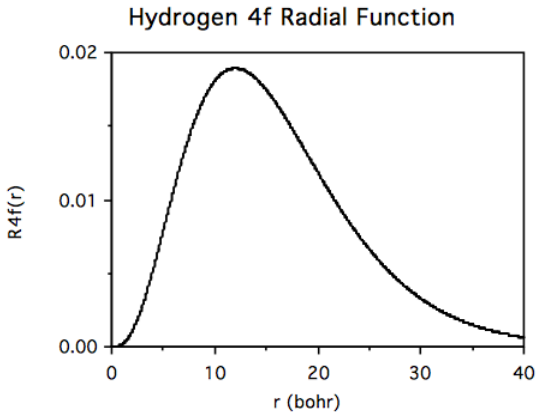
v. The Nitrogen molecule is in the yz plane for all point groups except the Cs in which case it is placed in the xy plane.

	$D_{\infty h}$	D_{2h}	C_{2v}	C_s	
$N1s+N1s$	σ_g	a_g	a_1	a'	(22.2.4.8)
$N1s-N1s$	σ_u	b_{1u}	b_2	a'	(22.2.4.9)
$N2s+N2s$	σ_g	a_g	a_1	a'	(22.2.4.10)
$N2s-N2s$	σ_u	b_{1u}	b_2	a'	(22.2.4.11)
$N2p_x+N2p_x$	π_{xu}	b_{3u}	b_1	a'	(22.2.4.12)
$N2p_x-N2p_x$	π_{xg}	b_{2g}	a_2	a'	(22.2.4.13)
$N2p_y+N2p_y$	π_{yu}	b_{2u}	a_1	a'	(22.2.4.14)
$N2p_y-N2p_y$	π_{yg}	b_{3g}	b_2	a'	(22.2.4.15)
$N2p_z+N2p_z$	σ_u	b_{1u}	b_2	a''	(22.2.4.16)
$N2p_z-N2p_z$	σ_g	a_g	a_1	a''	(22.2.4.17)

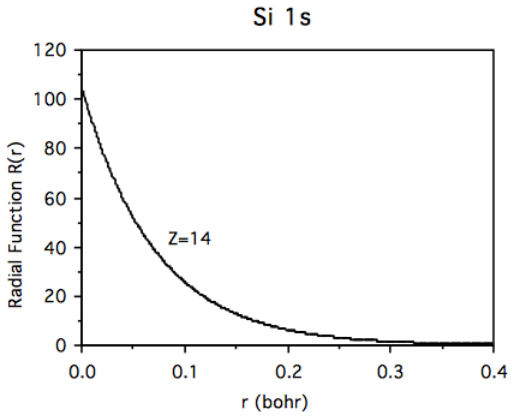
3.

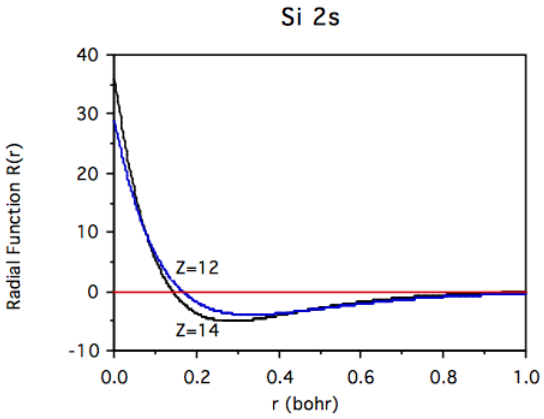


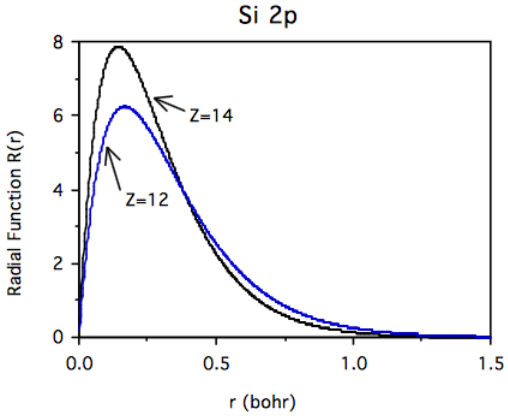

Hydrogen 4d Radial Function
R4d(r)
0.03
0.02
0.01
0.00
-0.01
-0.02
0
10
20
30
40
r (bohr)

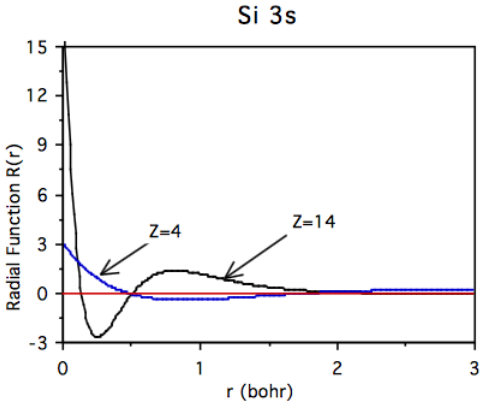

Hydrogen 4f Radial Function
R4f(r)
0.02
0.01
0.00
0
10
20
30
40
r (bohr)

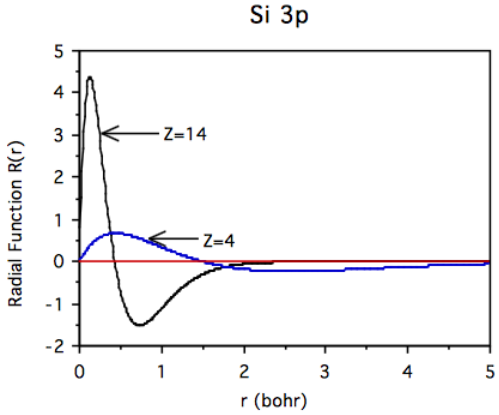
4.


Si 1s
Radial Function R(r)
120
100
80
60
40
20
0
Z=14
0.0
0.1
0.2
0.3
0.4
r (bohr)


Si 2s
Radial Function R(r)
r (bohr)
Z=12
Z=14


Si 2p
Radial Function R(r)
r (bohr)
Z=14
Z=12


Si 3s
Radial Function R(r)
r (bohr)
Z=4
Z=14


Si 3p
Radial Function R(r)
r (bohr)
Z=14
Z=4