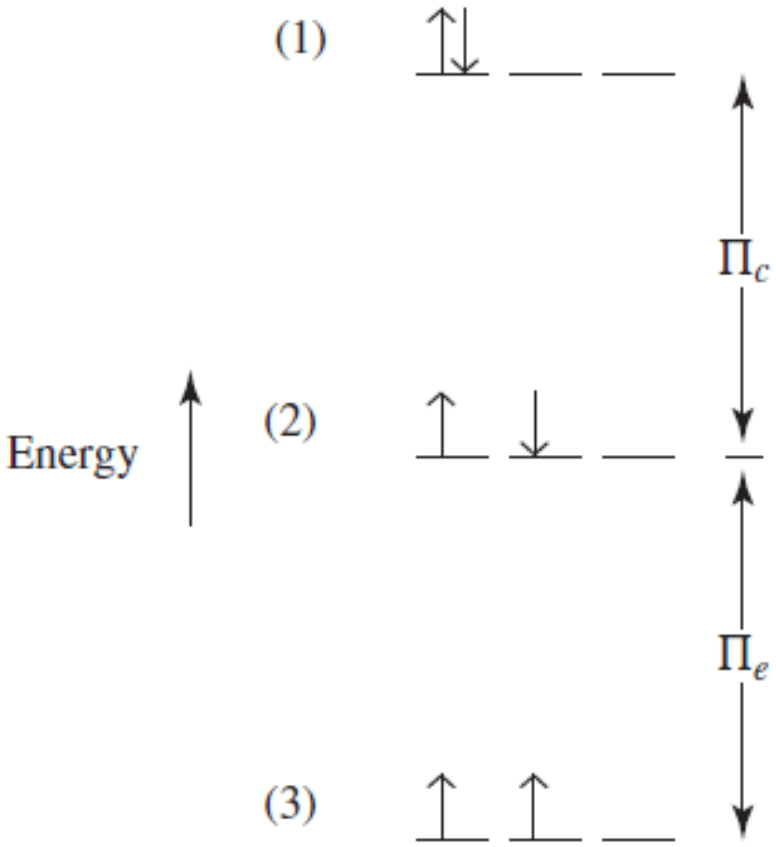
TABLE 2.6 Hund's Rule and Multiplicity

Number of Electrons	Arrangement	Unpaired e^-	Multiplicity
1	↑ _ _	1	2
2	↑ ↑ _	2	3
3	↑ ↑ ↑	3	4
4	↑↓ ↑ ↑	2	3
5	↑↓ ↑↓ ↑	1	2
6	↑↓ ↑↓ ↑↓	0	1


(1)
Π_c
Energy
(2)
Π_e
(3)

EXAMPLE 2.2

Oxygen

With four *p* electrons, oxygen could have two unpaired electrons (↑↓ ↑ ↑), or it could have no unpaired electrons (↑↓ ↑↓).

a. Determine the number of electrons that could be exchanged in each case, and find the Coulombic and exchange energies.

↑↓ ↑ ↑ This configuration has one pair, energy contribution Π_c.

↑↓ ↑ ↑ One electron with ↓ spin and no possibility of exchange.

↑↓ ↑ ↑ Four possible arrangements for electrons with ↑ spin; three exchange possibilities (1–2, 1–3, 2–3), shown below; energy contribution $3\Pi_e$.

↑1 ↑2 ↑3 ↑2 ↑1 ↑3 ↑3 ↑2 ↑1 ↑1 ↑3 ↑2

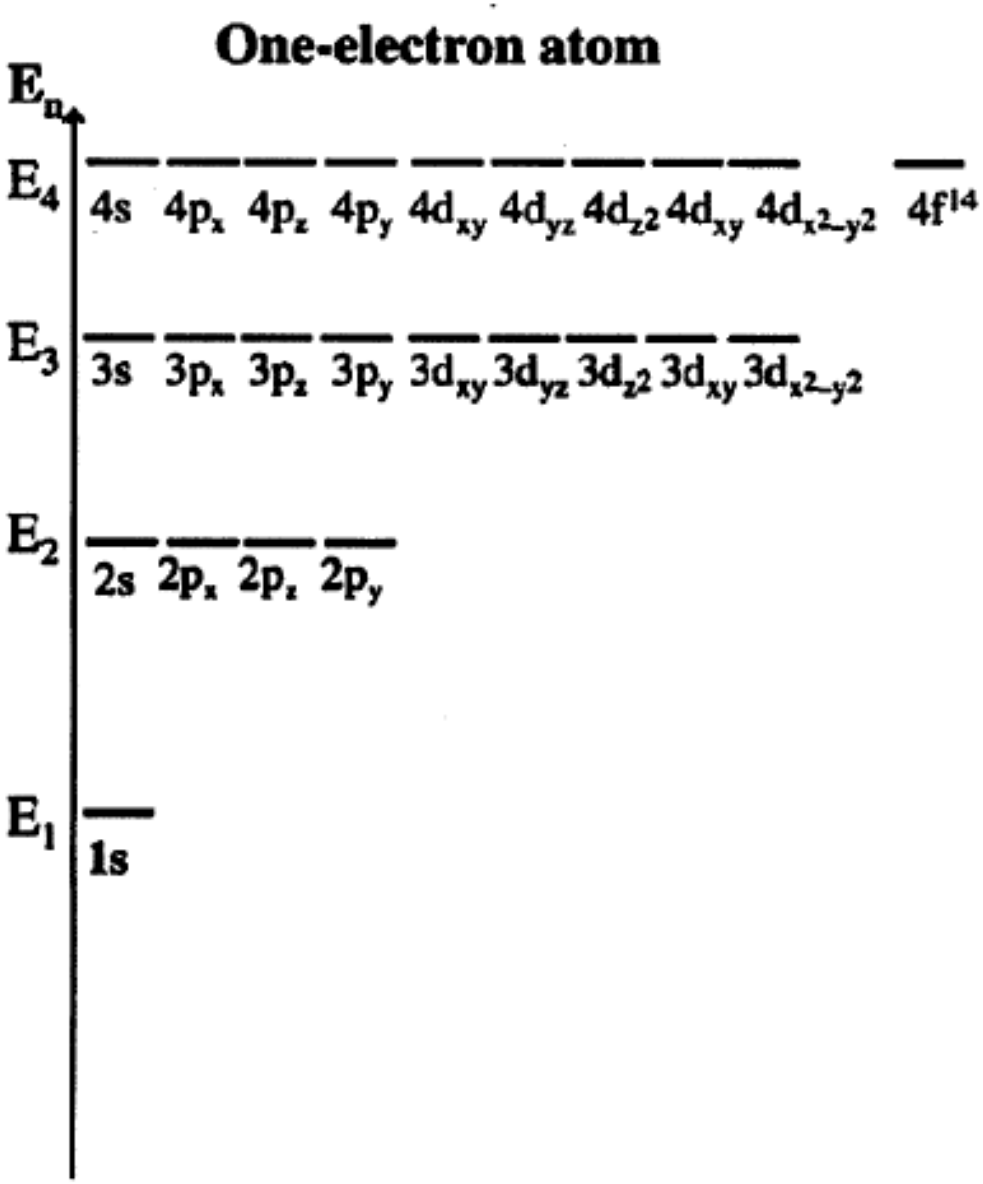
Overall, $3\Pi_e + \Pi_c$.

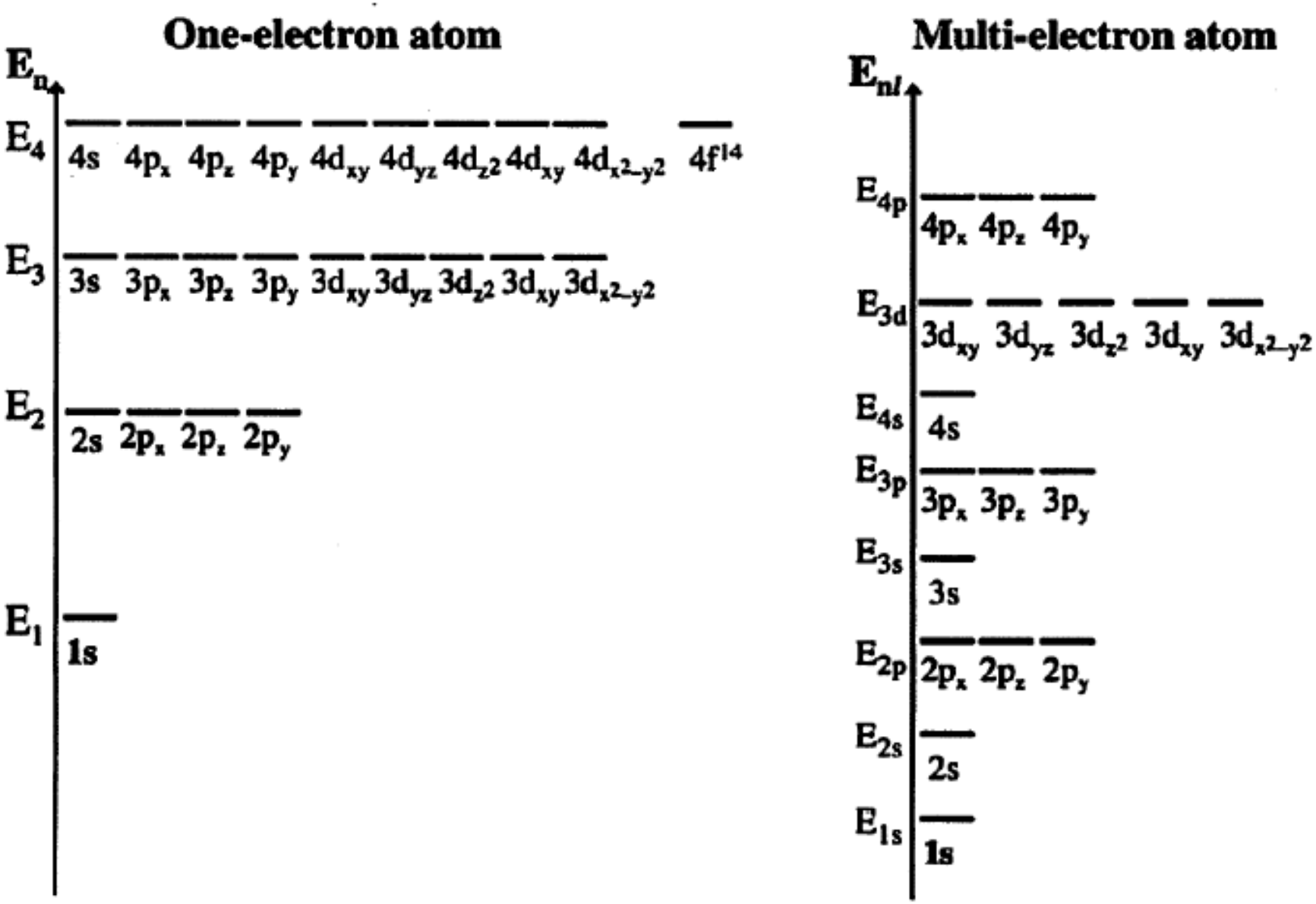
↑↓ ↑↓ has two pairs in the same orbitals and one exchange possibility for each spin pair.

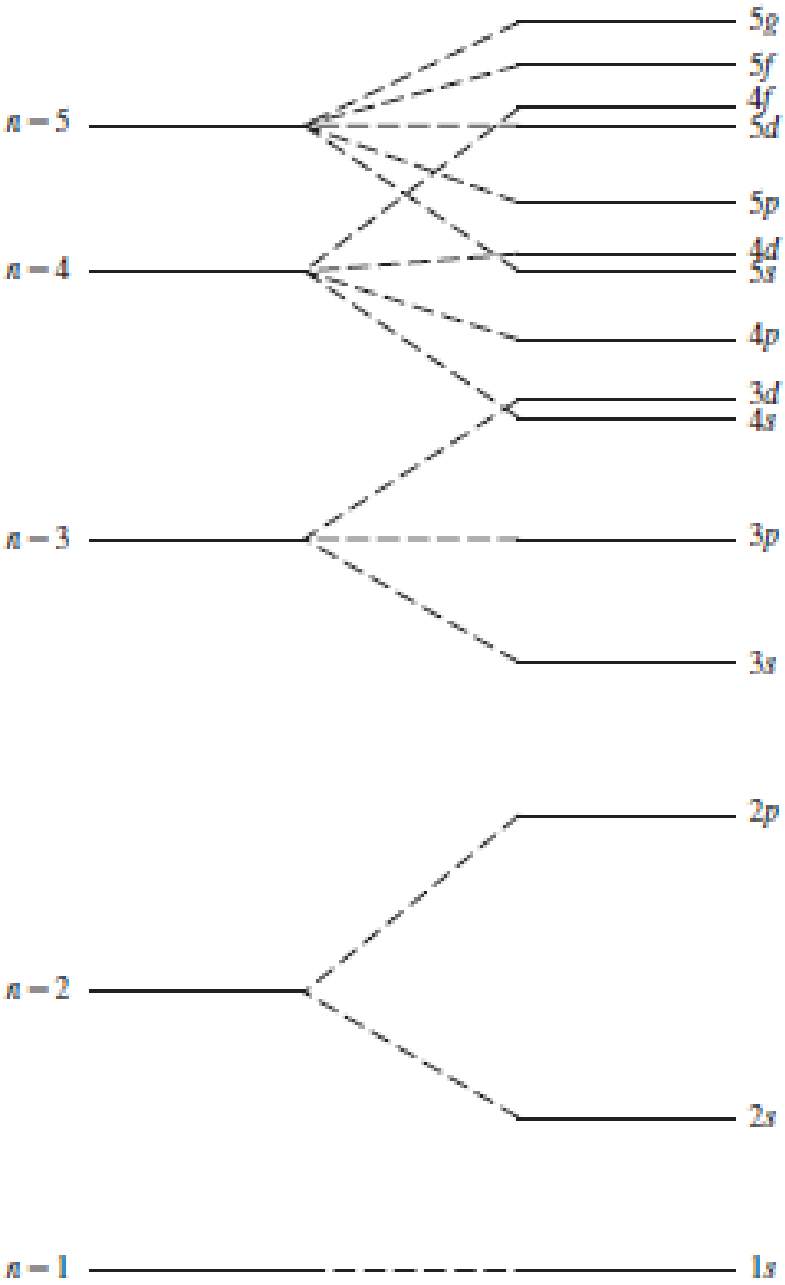
Overall, $2\Pi_e + 2\Pi_c$.

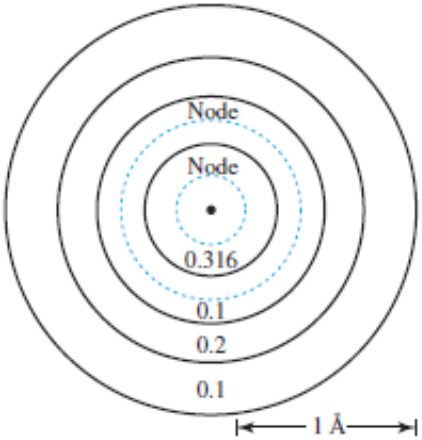
b. Which state, ↑↓ ↑ ↑, or ↑↓ ↑↓ , is lower in energy?

The state ↑↓ ↑ ↑ is lower in energy because it has less Coulombic energy of repulsion (Π_c in comparison with $2\Pi_c$) and is stabilized by a greater number of exchanges ($3\Pi_e$ in comparison with $2\Pi_e$).

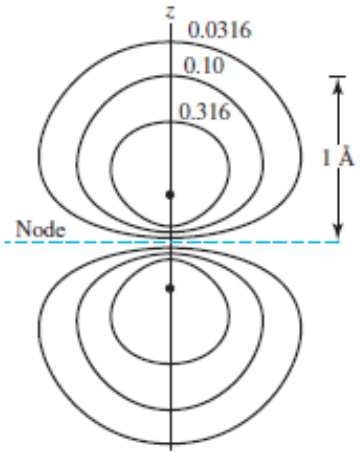

One-electron atom
E_n
E_4
4s 4p_x 4p_z 4p_y 4d_xy 4d_yz 4d_z2 4d_xy 4d_x2-y2 4f^14
E_3
3s 3p_x 3p_z 3p_y 3d_xy 3d_yz 3d_z2 3d_xy 3d_x2-y2
E_2
2s 2p_x 2p_z 2p_y
E_1
1s


One-electron atom
E_n
E_4
4s 4p$_x$ 4p$_z$ 4p$_y$ 4d$_{xy}$ 4d$_{yz}$ 4d$_{z2}$ 4d$_{xy}$ 4d$_{x2-y2}$ 4f^{14}
E_3
3s 3p$_x$ 3p$_z$ 3p$_y$ 3d$_{xy}$ 3d$_{yz}$ 3d$_{z2}$ 3d$_{xy}$ 3d$_{x2-y2}$
E_2
2s 2p$_x$ 2p$_z$ 2p$_y$
E_1
1s
Multi-electron atom
E_{nl}
E_{4p}
4p$_x$ 4p$_z$ 4p$_y$
E_{3d}
3d$_{xy}$ 3d$_{yz}$ 3d$_{z2}$ 3d$_{xy}$ 3d$_{x2-y2}$
E_{4s}
4s
E_{3p}
3p$_x$ 3p$_z$ 3p$_y$
E_{3s}
3s
E_{2p}
2p$_x$ 2p$_z$ 2p$_y$
E_{2s}
2s
E_{1s}
1s

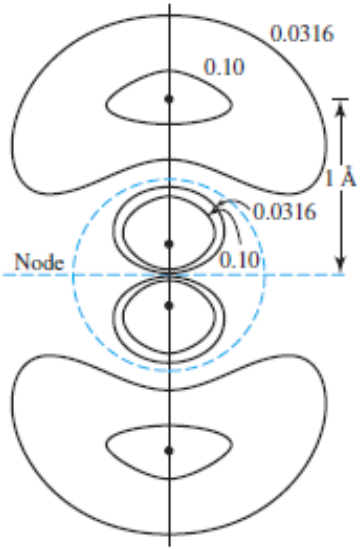

n = 5
n = 4
n = 3
n = 2
n = 1
5g
5f
4f
5d
5p
4d
5s
4p
3d
4s
3p
3s
2p
2s
1s



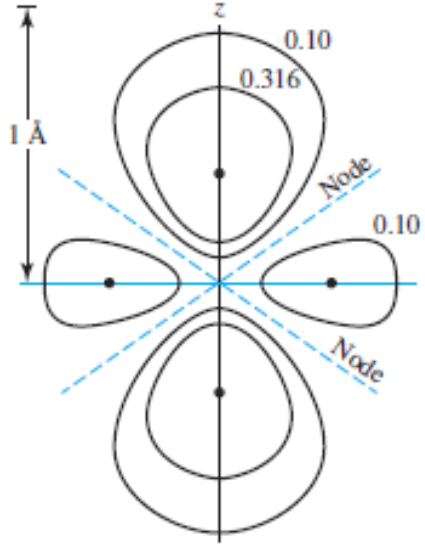
(a) Cl:3*s*



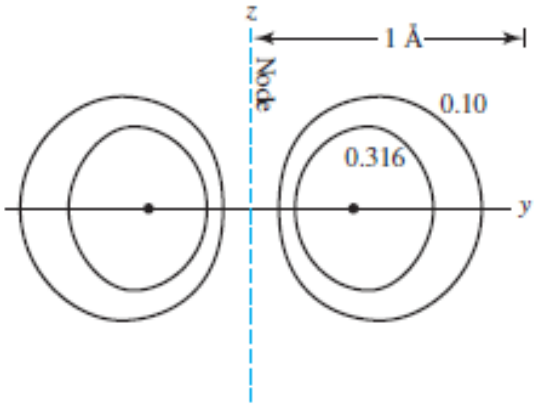
(b) C:2p_z



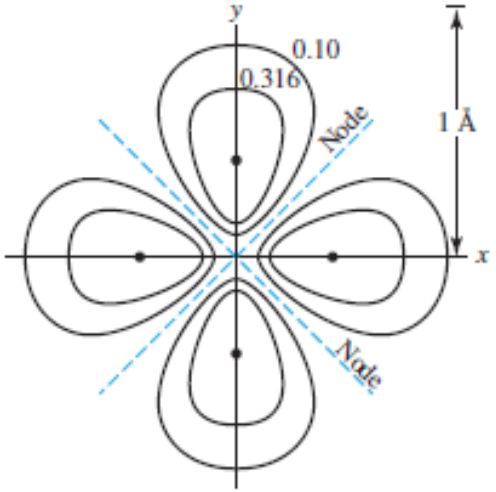
(c) Cl:3p_z



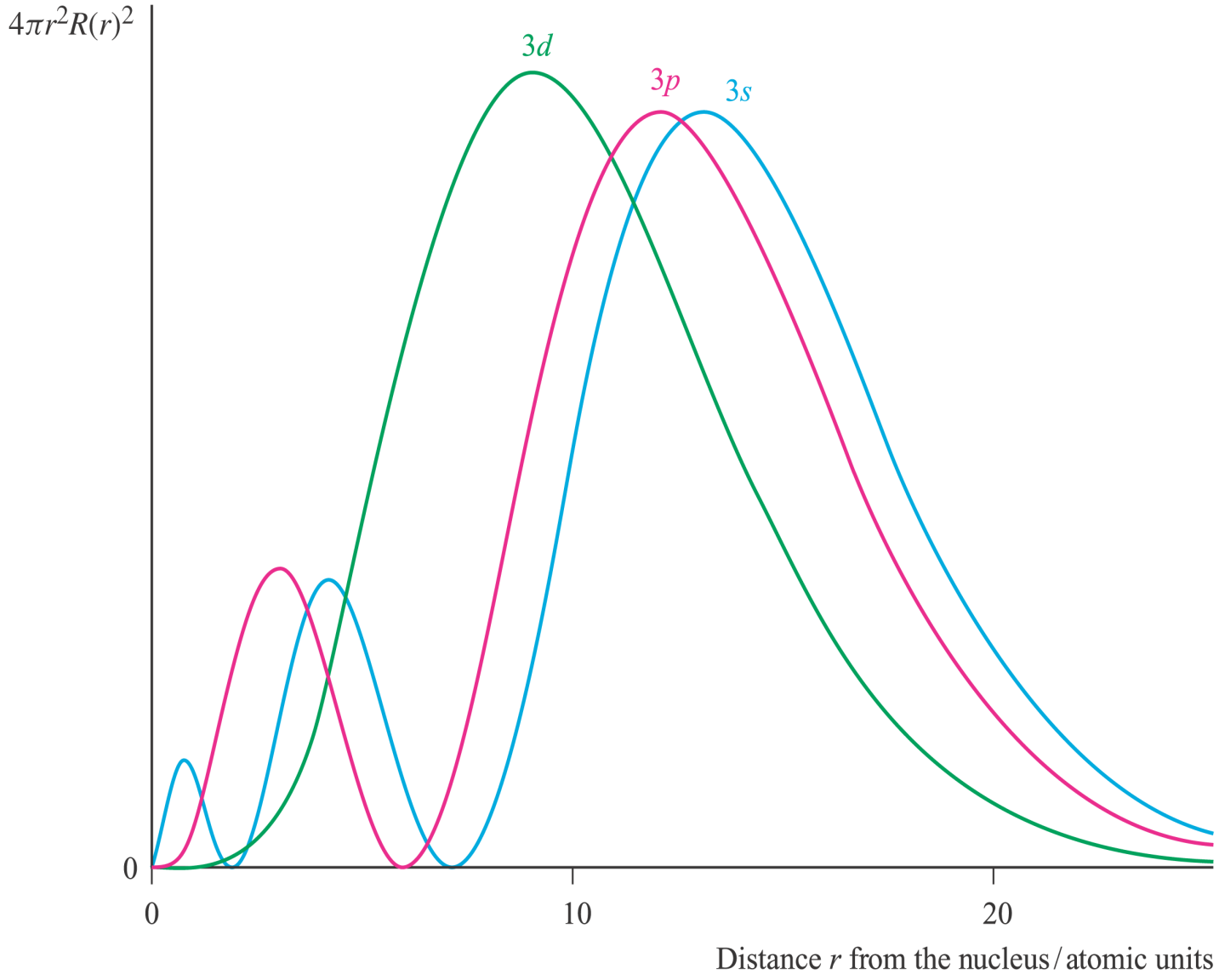
(d) Ti^{3+}:3d_{z^2}

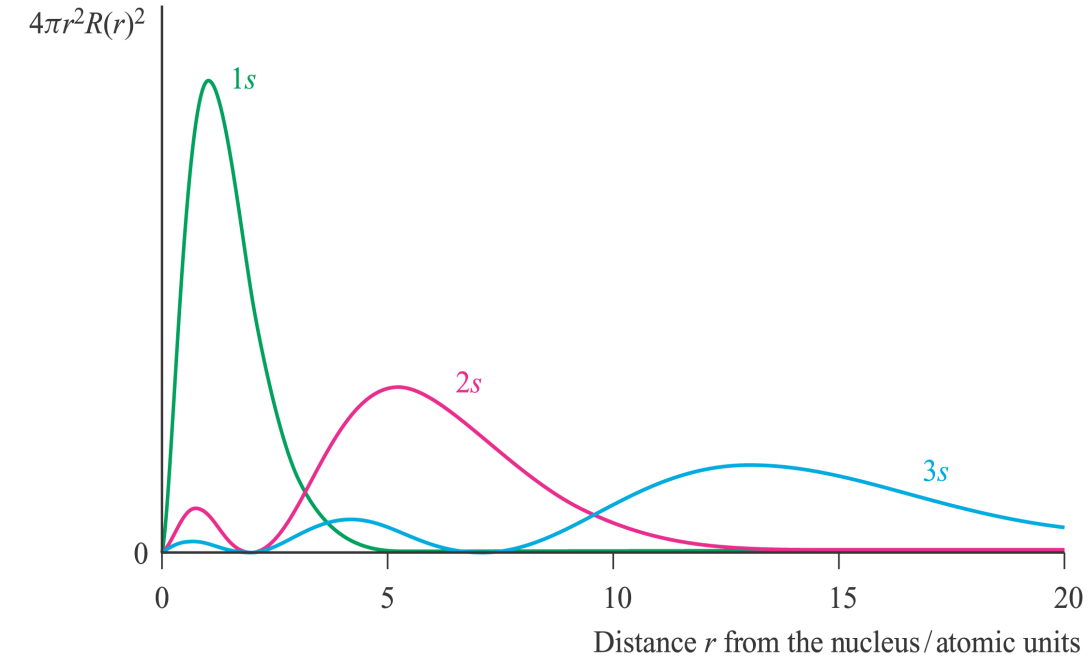


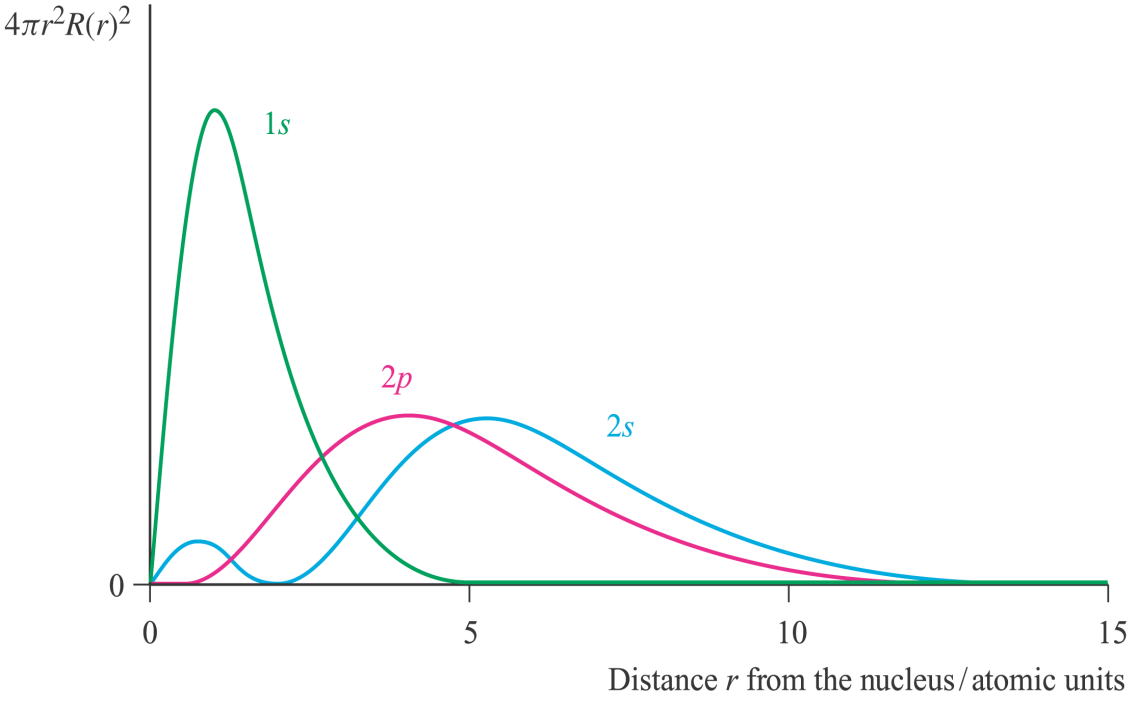
(e) Ti^{3+}:3$d_{x^2-y^2}$

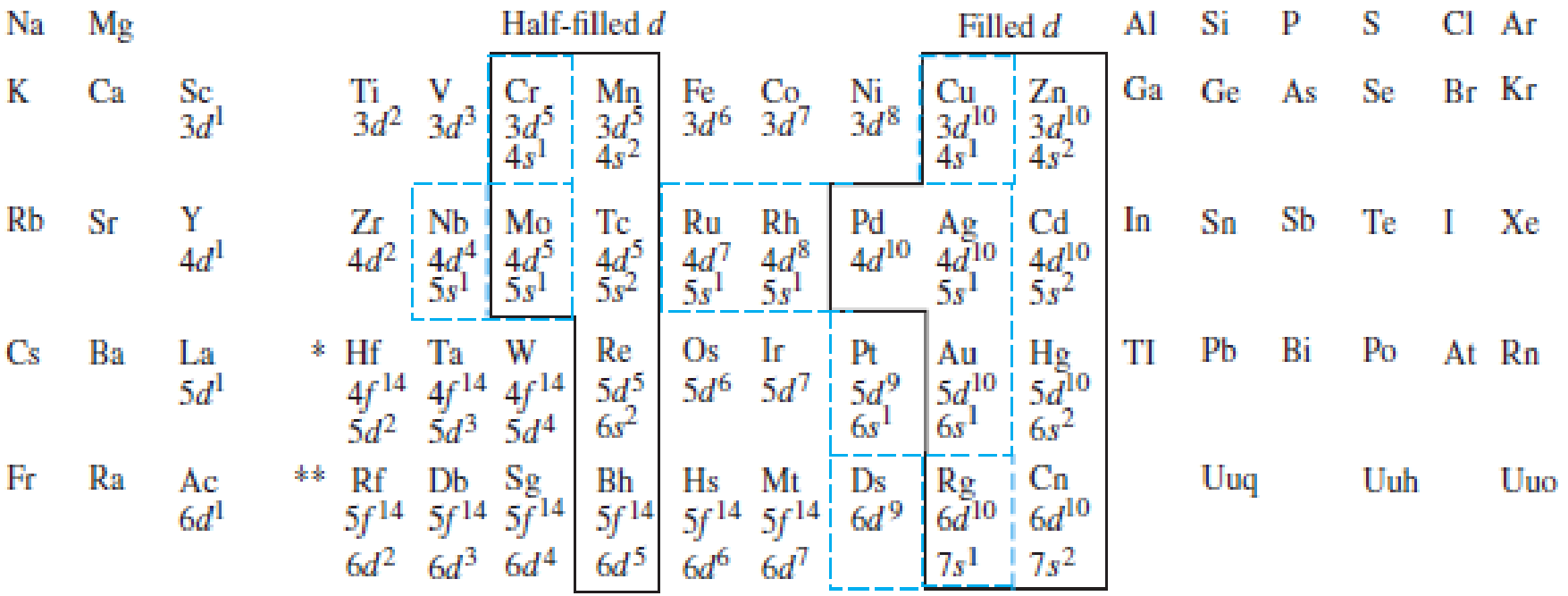


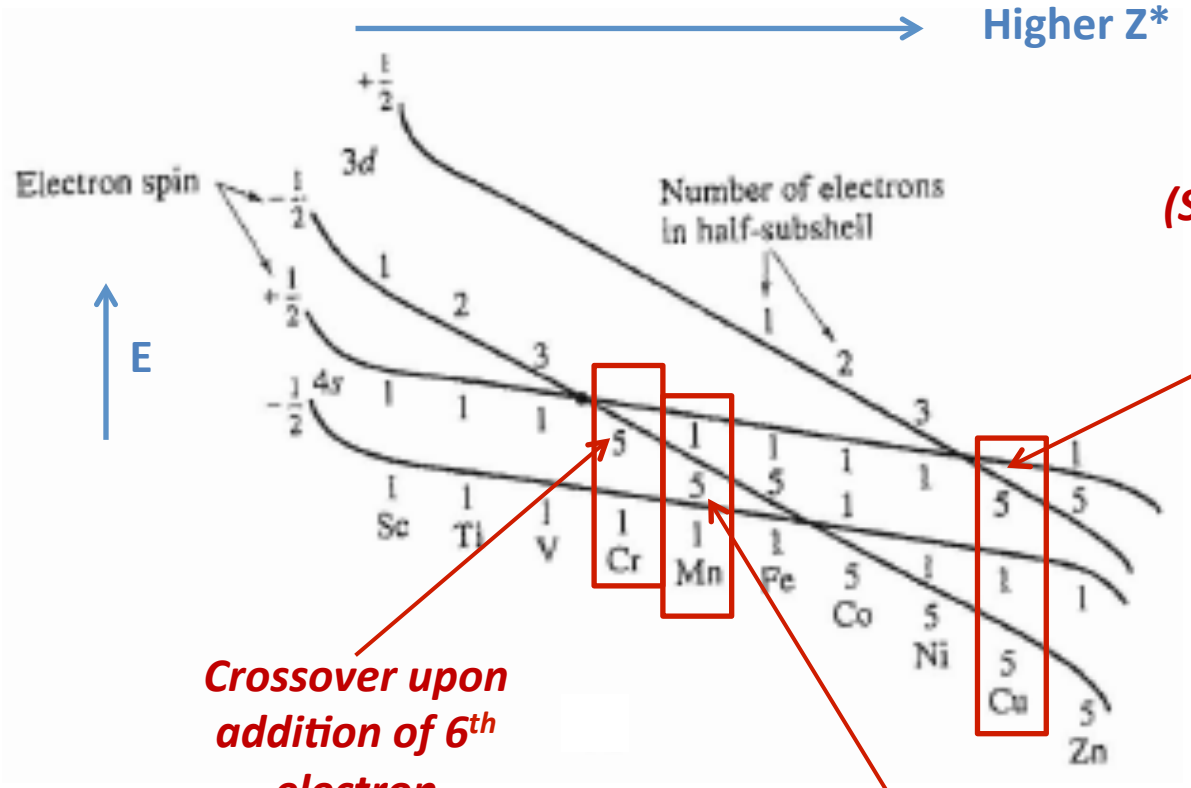
(f) Ti^{3+}:3$d_{x^2-y^2}$


$4\pi r^2 R(r)^2$
3d
3p
3s
0
0
10
20
Distance r from the nucleus / atomic units


$4\pi r^2 R(r)^2$
1s
2s
3s
0
0
5
10
15
20
Distance r from the nucleus / atomic units


$4\pi r^2 R(r)^2$
1s
2p
2s
0
0
5
10
15
Distance r from the nucleus / atomic units


Half-filled d
Filled d
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
3d1 3d2 3d3 3d5 4s1 3d5 4s2 3d6 3d7 3d8 3d10 4s1 3d10 4s2
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
4d1 4d2 4d4 5s1 4d5 5s1 4d5 5s2 4d7 5s1 4d8 5s1 4d10 4d10 5s1 4d10 5s2
Cs Ba La * Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
5d1 4f14 5d2 4f14 5d3 4f14 5d4 5d5 6s2 5d6 5d7 5d9 6s1 5d10 6s1 5d10 6s2
Fr Ra Ac ** Rf Db Sg Bh Hs Mt Ds Rg Cn Uuq Uuh Uuo
6d1 5f14 6d2 5f14 6d3 5f14 6d4 5f14 6d5 5f14 6d6 5f14 6d7 6d9 6d10 7s1 6d10 7s2



11th electron into 3d not 4s
(Shielding is less for d than for s)

Crossover upon addition of 6th electron

7th electron goes into 4s to maximize Πe from the 3d set