## Term symbols

If we know $(2S + 1)$, $L$ and $J$ for an energy state, we can write the full *term symbol*. This is done by writing the symbol of the value of $L$ (i.e. $S$, $P$, $D$ ...) with the value of $(2S + 1)$ as a left-superscript and the value of $J$ as a right-subscript. Thus, the electronic ground state of carbon is $^3P_0$ ('triplet P zero') denoting $L = 1$, $(2S + 1) = 3$ (i.e. $S = 1$) and $J = 0$. Different values of $J$ denote different

*levels* within the term, i.e. $^{(2S+1)}L_{J_1}$, $^{(2S+1)}L_{J_2}$..., the levels having different energies. Inorganic chemists often omit the value of $J$ and refer to a $^{(2S+1)}L$ term; we shall usually follow this practice in this book.

Now we look in detail at the electronic ground states of atoms with $Z = 1$ to 10.

The quantity $(2S + 1)$ is the *multiplicity* of the term where $S$ is the total spin quantum number. Terms for which $(2S + 1) = 1, 2, 3, 4 \ldots$ (corresponding to $S = 0, \frac{1}{2}, 1, \frac{3}{2} \ldots$) are called *singlets*, *doublets*, *triplets*, *quartets* $\ldots$

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

### Hydrogen (Z = 1)

A hydrogen atom has an electronic configuration of $1s^1$; for the electron, $l = 0$ so $L$ must be 0 and, therefore, we have an $S$ term. The total spin quantum number $S = \frac{1}{2}$ so $(2S + 1) = 2$ (a doublet term). The only possible value of $J$ is $\frac{1}{2}$, and so the term symbol for the hydrogen atom is $^2S_{1/2}$.

### Helium (Z = 2)

For helium ($1s^2$), both electrons have $l = 0$, so $L = 0$. Two electrons both with $n = 1$ and $l = 0$ must have $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$, so $S = 0$ and $(2S + 1) = 1$ (a singlet term). The only value of $J$ is 0, and so the term symbol is $^1S_0$. Thus, the $ns^2$ configuration, having $L = 0$, $S = 0$ and $J = 0$, will contribute nothing to the term symbol in lithium and later atoms. The same conclusion can be drawn for any $np^6$ configuration and the reader is left to confirm this statement.

## Lithium (Z = 3) and beryllium (Z = 4)

Atomic lithium has the electronic configuration $1s^2 2s^1$, and its term symbol is the same as that for hydrogen, $^2S_{1/2}$. Similarly, the term symbol for beryllium ($1s^2 2s^2$) is the same as that for helium, $^1S_0$.
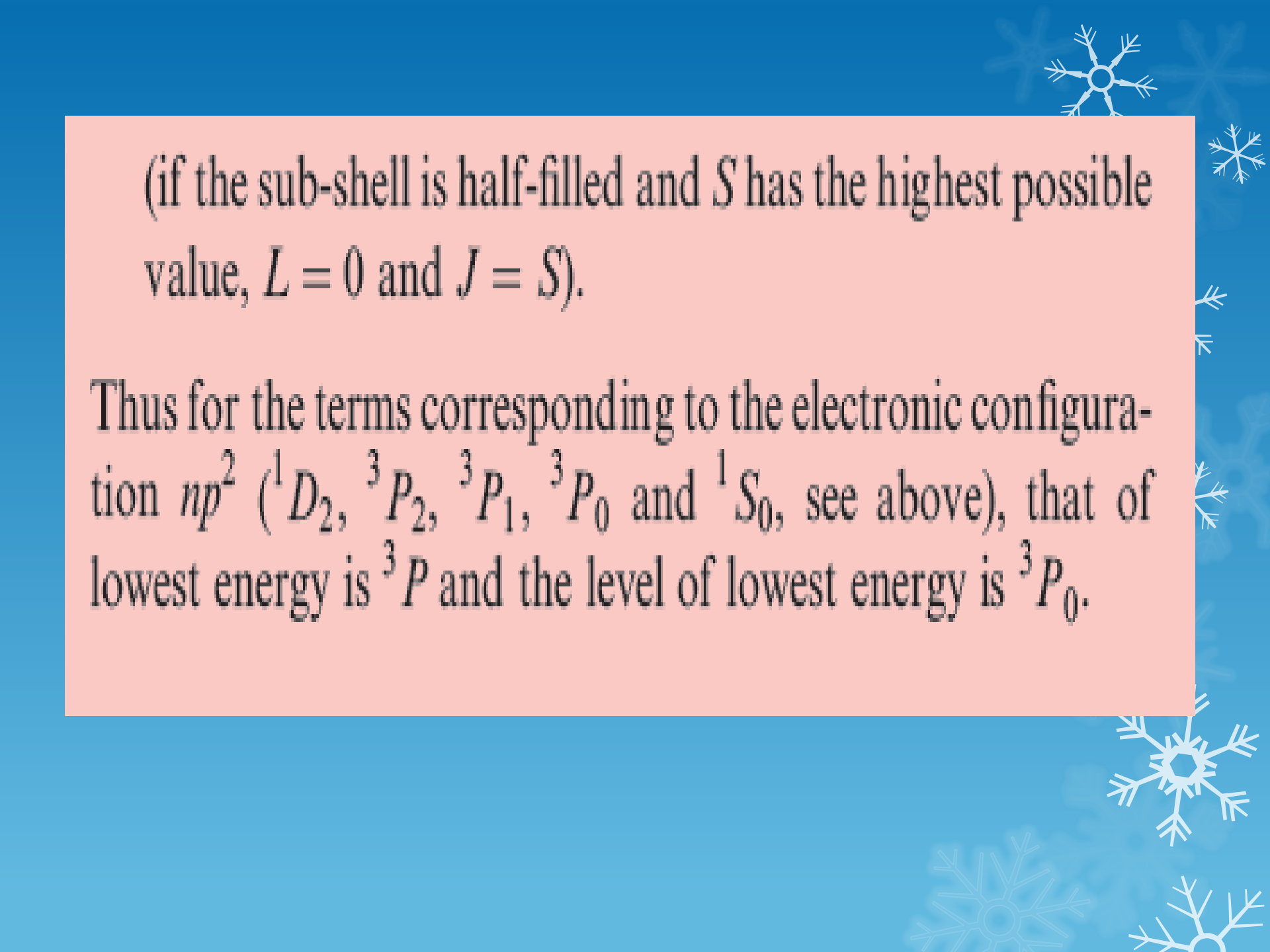
## Boron (Z = 5)

For boron ($1s^2 2s^2 2p^1$) we need only consider the $p$ electron for reasons outlined above. For this, $l = 1$ so $L = 1$ (a $P$ term); $S = \frac{1}{2}$ and so $(2S + 1) = 2$ (a doublet term). $J$ can take values $(L + S), (L + S - 1) \ldots |L - S|$, and so $J = \frac{3}{2}$ or $\frac{1}{2}$. The term symbol for boron may be $^2P_{3/2}$ or $^2P_{1/2}$.

# Relative energies of terms and levels

In regard to relative energies of terms, we state all of Hund's rules in a formal way. It is found from analysis of spectroscopic data that, provided that Russell–Saunders coupling holds:
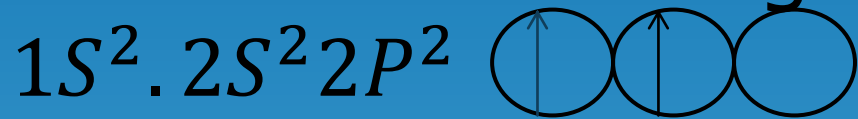
- the term having the highest spin multiplicity (highest value of $S$) is the most stable (lowest energy);
- if two or more terms have the same value of $S$, the term having the higher value of $L$ is the more stable;
- for all terms having the same values of $S$ and $L$, the level with the lowest value of $J$ is the most stable if the sub-shell is less than half-filled, and the level with the highest value of $J$ is most stable if the sub-shell is more than half-filled

(if the sub-shell is half-filled and $S$ has the highest possible value, $L = 0$ and $J = S$).

Thus for the terms corresponding to the electronic configuration $np^2$ ($^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$ and $^1S_0$, see above), that of lowest energy is $^3P$ and the level of lowest energy is $^3P_0$.

For example, $_6C$
the electron configuration is
$1S^2 . 2S^2 2P^2$ ⬆◯ ⬆◯ ◯
$2S + 1 = 3$

$$L = +1 + 0 = 1$$
$$J = |1 + 1| \ldots \ldots |1 - 1|$$
$$= 2,1,0$$

the term symbol is $^3P_0$

For Nitrogen 7
The term symbol is
$$^4S_{3/2}$$

How?

**Shielding Electrons**
Shielding electrons are the electrons in the energy levels **between** the nucleus and the valence electrons. They are called "shielding" electrons because they "shield" the valence electrons from the force of attraction exerted by the positive charge in the nucleus.

In fluorine there are 9 protons in the nucleus and there are 2 shielding electrons in the first level between the nucleus and the outer shell. They shield some of the charge of the nucleus from the electrons that are in the outermost energy level. (Also look at example 5b in your workbook.)

|  | nuclear charge | shielding electrons | valence electrons |
|---|---|---|---|
| F | +9 | $1s^2$ | $2s^2 2p^5$ |
|  |  | 2 | 7 |

Next, neon also has 2 shielding electrons along with 8 valence electrons.

|  | nuclear charge | shielding electrons | valence electrons |
|---|---|---|---|
| Ne | +10 | $1s^2$ | $2s^2 2p^6$ |
|  |  | 2 | 8 |

With sodium, we have 3 energy levels. There is one valence electron in the third level and all the electrons between that one valence electron and the nucleus are shielding electrons. In this case there are 2 in the first energy level and 8 in the second for a total of 10 shielding electrons.

|  | nuclear charge | shielding electrons | valence electrons |
|---|---|---|---|
| Na | +11 | $1s^2 2s^2 2p^6$ | $3s^1$ |
|  |  | 10 | 1 |

So notice that the number of shielding electrons increases when you reach the end of the periodic table and go on to the next period.

Now look at carbon, nitrogen, and oxygen to see that within a period there is no change in the number of shielding electrons. Even though the valence electrons increase in number from 4 to 5 to 6, the number of shielding electrons stays the same-- two shielding electrons for each of those elements.

|  | C | N | O |
|---|---|---|---|
| shielding electrons | 2 | 2 | 2 |
| valence electrons | 4 | 5 | 6 |

Now consider an atom of helium containing two protons (there are neutrons in the nucleus, too, but they are not pertinent to this topic) surrounded by two electrons both occupying the 1$s$ orbital. In this case, and for all other many electron atoms, we need to consider not just the proton - electron attractions, but also the electron - electron repulsions. Because of this repulsion, each electron experiences a nuclear charge that is somewhat less than the actual nuclear charge. Essentially, one electron **shields**, or screens the other electron from the nucleus. The positive charge that an electron actually experiences is called the **effective nuclear charge**, $Z_{eff}$, and $Z_{eff}$ is always somewhat less than the actual nuclear charge.

$Z_{eff}$ = Z - S, where S is the shielding constant

**⊢ EFFECTIVE NUCLEAR CHARGE** $Z_{eff} = Z_{actual} -$ Electron shielding
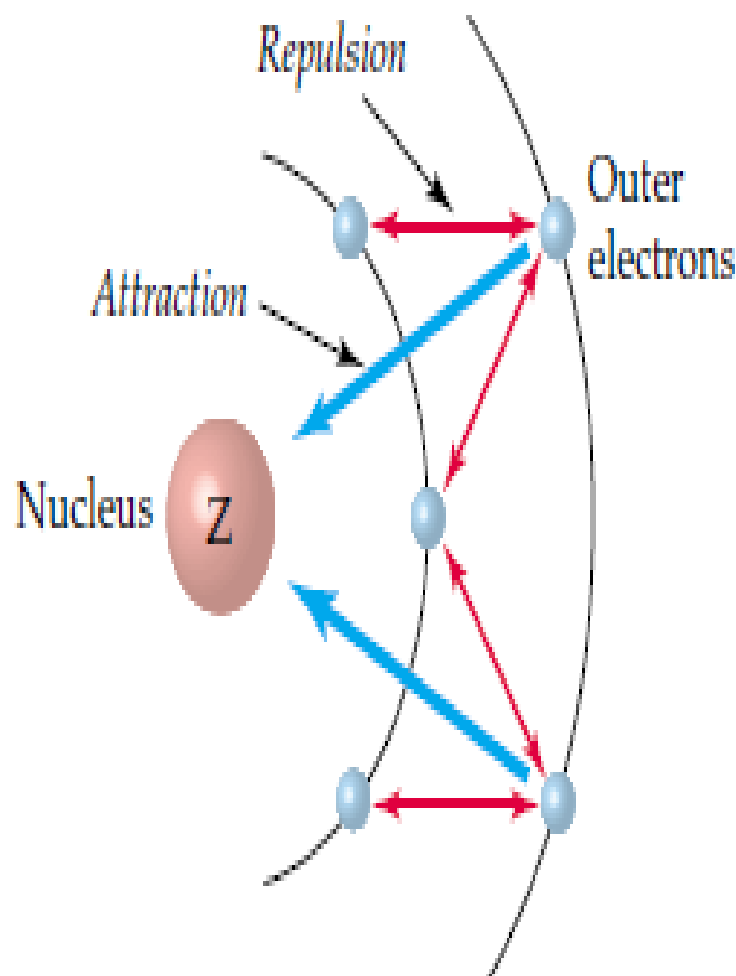


◀ **FIGURE 5.16** The origin of electron shielding and $Z_{eff}$. Outer electrons are attracted toward the nucleus by the nuclear charge but are pushed away by the repulsion of inner electrons. As a result, the nuclear attraction actually felt by outer electrons is diminished, and we say that the outer electrons are *shielded* from the full charge of the nucleus by the inner electrons.

Now let us consider the arrangement of the electrons in Li ($Z = 3$). In the ground state, the $1s$ atomic orbital is fully occupied and the third electron could occupy either a $2s$ or $2p$ orbital. Which arrangement will possess the lower energy? An electron in a $2s$ or $2p$ atomic orbital experiences the *effective charge*, $Z_{eff}$, of a nucleus partly *shielded* by the $1s$ electrons. Since the $2p$ orbital penetrates the $1s$ orbital less than a $2s$ orbital does, a $2p$ electron is shielded more than a $2s$ electron. Thus, occupation of the $2s$ rather than the $2p$ atomic orbital gives a lower energy system. Although we should consider the energies of the *electrons* in atomic orbitals, it is common practice to think in terms of the orbital energies themselves: $E(2s) < E(2p)$. ▮

Similar arguments lead to the sequence $E(3s) < E(3p) < E(3d)$ and $E(4s) < E(4p) < E(4d) < E(4f)$. As we move to atoms of elements of higher atomic number, the energy differences between orbitals with the same value of $n$ become smaller, the validity of assuming hydrogen-like wavefunctions becomes more doubtful, and predictions of ground states become less reliable. The treatment above also ignores electron–electron interactions within the same principal quantum shell.

## Slater's rules

Effective nuclear charges, $Z_{eff}$, experienced by electrons in different atomic orbitals may be estimated using *Slater's rules*. These rules are based on experimental data for electron promotion and ionization energies, and $Z_{eff}$ is determined from the equation:

$$Z_{eff} = Z - S$$

where $Z$ = nuclear charge, $Z_{eff}$ = effective nuclear charge, $S$ = screening (or shielding) constant.

Values of $S$ may be estimated as follows:

1. Write out the electronic configuration of the element in the following order and groupings: $(1s)$, $(2s, 2p)$, $(3s, 3p)$, $(3d)$, $(4s, 4p)$, $(4d)$, $(4f)$, $(5s, 5p)$ etc.
2. Electrons in any group higher in this sequence than the electron under consideration contribute nothing to $S$.
3. Consider a particular electron in an $ns$ or $np$ orbital:
   (i) Each of the other electrons in the $(ns, np)$ group contributes $S = 0.35$.
   (ii) Each of the electrons in the $(n-1)$ shell contributes $S = 0.85$.
   (iii) Each of the electrons in the $(n-2)$ or lower shells contributes $S = 1.00$.
4. Consider a particular electron in an $nd$ or $nf$ orbital:
   (i) Each of the other electrons in the $(nd, nf)$ group contributes $S = 0.35$.
   (ii) Each of the electrons in a lower group than the one being considered contributes $S = 1.00$.

# An example of how to apply Slater's rules

Question: Confirm that the experimentally observed electronic configuration of K, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, is energetically more stable than the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$.

For K, $Z = 19$.

Applying Slater's rules, the effective nuclear charge experienced by the 4s electron for the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ is:

$$Z_{eff} = Z - S$$
$$= 19 - [(8 \times 0.85) + (10 \times 1.00)]$$
$$= 2.20$$

The effective nuclear charge experienced by the 3d electron for the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$ is:

$$Z_{eff} = Z - S$$
$$= 19 - (18 \times 1.00)$$
$$= 1.00$$

Thus, an electron in the 4s (rather than the 3d) atomic orbital is under the influence of a greater effective nuclear charge and in the ground state of potassium, it is the 4s atomic orbital that is occupied.

## Self-study exercises

1. Show that Slater's rules give a value of $Z_{eff} = 1.95$ for a 2s electron in a Be atom.

2. Show that Slater's rules give a value of $Z_{eff} = 5.20$ for a 2p electron of F.

3. Use Slater's rules to estimate values of $Z_{eff}$ for (a) a 4s and (b) a 3d electron in a V atom.

[*Ans.* (a) 3.30; (b) 4.30]

4. Using your answer to question 3, explain why the valence configuration of the ground state of a $V^+$ ion is likely to be $3d^3 4s^1$ rather than $3d^2 4s^2$.

**Oxygen**   The electron configuration is $(1s^2)(2s^2\,2p^4)$.

For the outermost electron,

$$Z^* = Z - S$$

$$= 8 - [2 \times (0.85)] - [5 \times (0.35)] = 4.55$$

$$(1s) \qquad\qquad (2s, 2p)$$

The two $1s$ electrons each contribute 0.85, and the five $2s$ and $2p$ electrons (the last electron is not counted, as we are finding $Z^*$ for it) each contribute 0.35, for a total shielding constant $S = 3.45$. The net effective nuclear charge is then $Z^* = 4.55$. Therefore, the last electron is held with about 57% of the force expected for a +8 nucleus and a −1 electron.

**Nickel**  The electron configuration is $(1s^2)\,(2s^2\,2p^6)\,(3s^2\,3p^6)\,(3d^8)\,(4s^2)$.

For a 3d electron,

$$Z^* = Z - S$$

$$= 28 - [18 \times (1.00)] - [7 \times (0.35)] = 7.55$$

$$(1s, 2s, 2p, 3s, 3p) \qquad (3d)$$

The 18 electrons in the $1s$, $2s$, $2p$, $3s$, and $3p$ levels contribute 1.00 each, the other 7 in $3d$ contribute 0.35, and the $4s$ contribute nothing. The total shielding constant is $S = 20.45$ and $Z^* = 7.55$ for the last $3d$ electron.

For the 4s electron,

$$Z^* = Z - S$$

$$= 28 - [10 \times (1.00)] - [16 \times (0.85)] - [1 \times (0.35)] = 4.05$$

$$(1s, 2s, 2p) \qquad (3s, 3p, 3d) \qquad (4s)$$

The ten $1s$, $2s$, and $2p$ electrons each contribute 1.00, the sixteen $3s$, $3p$, and $3d$ electrons each contribute 0.85, and the other $4s$ electron contributes 0.35, for a total $S = 23.95$ and $Z^* = 4.05$, considerably smaller than the value for the $3d$ electron above. The $4s$ electron is held less tightly than the $3d$ and should therefore be the first removed in ionization. This is consistent with experimental observations on nickel compounds. $Ni^{2+}$, the most common oxidation state of nickel, has an electron configuration of $[Ar]3d^8$ (rather than $[Ar]3d^6 4s^2$), corresponding to loss of the $4s$ electrons from nickel atoms. All the transition metals follow this same pattern of losing $ns$ electrons more readily than $(n - 1)d$ electrons.

## EXERCISE

Calculate the effective nuclear charge on a $5s$, a $5p$, and a $4d$ electron in a tin atom.

## EXERCISE

Calculate the effective nuclear charge on a $7s$, a $5f$, and a $6d$ electron in a uranium atom.