9.9.9B: Orbital Energies

Orbital energies are not physical properties. They are constructs that arise from our approximate approach to a true multi-electron wavefunction using products of single-electron wavefunctions called atomic orbitals. Nevertheless, a great deal can be learned by considering orbital energies.

Our use of orbital energy level diagrams and the Aufbau principle to create electron configurations is based on the idea that the electrons fill the orbitals in order of increasing orbital energy. The implicit assumption is that the sum of the atomic orbital energies represents the total energy of the molecule. This assumption ignores electron correlation effects that arise when two electrons are in the same orbital. For example, electron configurations exhibit periodic trends in the number of electrons present in the atomic orbitals with the highest principal quantum number, n. These electrons are called valence electrons. The periodic table is arranged so that atoms with the same distributions of valence electrons are arranged in columns. Trends in physical properties track the trends in valence electron configurations and thus are called periodic properties.

We know how to calculate orbital energies from first principles. A single table or orbital energy level diagram that is valid for all elements does not suffice because the orbital energies depend on the electron-electron interactions that in turn depend on the number of electrons in the atom and the orbitals they occupy. Consequently, the orbital energies need to be specified for each element, which can be done most conveniently in graphical form.

The diagram/table reveals general trends as well as exceptions to these trends. A careful examination of the diagram reveals the basis for the electron configuration mnemonics or guides given in most introductory chemistry courses:

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$$

For example the 1s orbital is always lowest in energy, followed by the 2s, 2p and 3s orbitals. The 4s is lower than the 3d orbital between elements 7 and 20, so the potassium and calcium electron configurations (Z = 19 and 20, respectively) have electrons in the 4s orbital rather than the 3d, and scandium (Z = 21) has the expected configuration $[Ar]4s^23d^1$. For elements with very small and very large atomic numbers, the energies of all orbitals of a given n tend to converge.

> ### Exercise $9.9.9B.1B$
>
> Predict the configurations of K, Sc, Ni, Sb, I and Xe.

The ground-state electron configurations of the elements are listed in Table $9.9.9B.1$. The "exceptions" to the simple mnemonic noted in general chemistry texts are partly a consequence of the inadequacy of a "one-orbital order-fits-all" model. For example, copper has an electron configuration of $[Ar]4s^1d^{10}$. This configuration, which is at odds with the simple mnemonic, would be predicted successfully by the orbital ordering for copper given in an orbital energy diagram.

Table $9.9.9B.1$: The ground-state electron configurations of the elements.

Atomic Symbol	Atomic Number	Configuration
H	1	$1s^1$
He	2	$1s^2$
Li	3	$1s2\,2s^1$
Be	4	$1s^2\,2s^2$
B	5	$1s^2\,2s^2\,2p^1$
C	6	$1s^2\,2s^2\,2p^2$
N	7	$1s^2\,2s^2\,2p^3$
O	8	$1s2\,2s2\,2p4$
F	9	$1s2\,2s2\,2p5$
Ne	10	$1s2\,2s2\,2p6$
Na	11	$[Ne]\,3s^1$

Atomic Symbol	Atomic Number	Configuration
Mg	12	[Ne] $3s^2$
Al	13	[Ne] $3s^2\ 3p^1$
Si	14	[Ne] $3s^2\ 3p^2$
P	15	[Ne] $3s^2\ 3p^3$
S	16	[Ne] $3s^2\ 3p^4$
Cl	17	[Ne] $3s^2\ 3p^5$
Ar	18	[Ne] $3s^2\ 3p^6$
K	19	[Ar] $4s^1$
Ca	20	[Ar] $4s^2$
Sc	21	[Ar] $3d^1\ 4s^2$
Ti	22	[Ar] $3d^2\ 4s^2$
V	23	[Ar] $3d^3\ 4s^2$
Cr	24	[Ar] $3d^5\ 4s^1$
Mn	25	[Ar] $3d^5\ 4s^2$
Fe	26	[Ar] $3d^6\ 4s^2$
Co	27	[Ar] $3d^7\ 4s^2$
Ni	28	[Ar] $3d^8\ 4s^2$
Cu	29	[Ar] $3d^{10}\ 4s^1$
Zn	30	[Ar] $3d^{10}\ 4s^2$
Ga	31	[Ar] $3d^{10}\ 4s^2\ 4p^1$
Ge	32	[Ar] $3d^{10}\ 4s^2\ 4p^2$
As	33	[Ar] $3d^{10}\ 4s^2\ 4p^3$
Se	34	[Ar] $3d^{10}\ 4s^2\ 4p^4$
Br	35	[Ar] $3d^{10}\ 4s^2\ 4p^5$
Kr	36	[Ar] $3d^{10}\ 4s^2\ 4p^6$

Even with our best calculations, however, we can't successfully predict electron configurations for all elements using the ordering of orbital energies. For instance, orbital energy diagrams show that the 3d orbital energies are lower than the 4s orbital energies for all known elements with Z > 20. However, most of the elements in the first transition series have electron configurations with one or two electrons in the 4s orbital. The reason is that the sum of the orbital energies does not adequately describe the total energy of a multielectron system. Configuration interaction produces our best calculated values for the total energies of multi-electron systems, but the cost is that it wipes out the familiar conceptual picture of atomic orbitals and orbital energies.