

1.3.1: Orbital Energies

Orbital Energies for the H Atom

The Schrödinger equation does not only allow to calculate the orbitals of the hydrogen atom, but also their energies. The energies of Bohr and Schrödinger model match: $E = \text{constant}/n^2$. This means that orbitals with the same quantum number n have the same energies. The energies are **not** a function of the quantum numbers l and m . The energies are negative because they are binding energies. In other words: Adding an electron to a proton is an exothermic process. The binding energy for the energy increases as the orbital energy decreases (Fig. 1.2.37).

shell	n	orbitals				
		s l = 0	p l = 1	d l = 2	f l = 3	
N	4	<div>↑</div> <div>4s</div>	<div>↑↑↑</div> <div>4p</div>	<div>↑↑↑↑</div> <div>4d</div>	<div>↑↑↑↑↑↑</div> <div>4f</div>	1/16 E ₁
M	3	<div>↑</div> <div>3s</div>	<div>↑↑↑</div> <div>3p</div>	<div>↑↑↑↑</div> <div>3d</div>	1/9 E ₁	
L	2	<div>↑</div> <div>2s</div>	<div>↑↑↑</div> <div>2p</div>	1/4 E ₁ = -13.6 eV/4 = -3.4 eV		
K	1	<div>↑</div> <div>1s</div>	E ₁ = -13.6 eV			

Figure 1.2.37 Orbital energies from the 1s orbital to 4f orbital. K, L, M, N indicate the shells associated with a quantum number n .

For the 1s orbital of H the energy is -13.6 eV, the energy of the 2s and the 2p orbitals are $1/4$ of that, the energy of the 3s, 3p, and 3d orbitals are $1/9$ of the energy of the 1s orbital and so forth. Note at $1/4$ and $1/9$ th of -13.6 eV is more than -13.6 eV due to the negative algebraic sign. The electron volt is a unit of energy. It is the amount of kinetic energy gained by a single unbound electron when it passes through an electrostatic potential difference of one volt, in vacuum.

$$1 \text{ eV} = 1.602176 \text{ } 53(14) \times 10^{-19} \text{ J.}$$

Equation 1.2.23 The electron volt to joule unit conversion.

In other words, it is equal to one volt (1 volt = 1 joule per coulomb) times the charge of a single electron (in coulombs). It is a very small unit of energy which is practical for orbital energy calculations because the orbital energies are very small (Eq. 1.2.23).

Multi-electron Atoms

Thus far we have only considered the orbitals for the hydrogen atom which contains only one electron. Can we also solve the Schrödinger equation for atoms that have more than one electron and get the exact energies of the orbitals? The answer is no, this mathematically not possible. The process is just already too complex even for only two electrons. The Schrödinger equation can only be solved for one electron systems. Therefore, the description of the atomic structure of all other atoms must work with approximations. Let us first consider the He atom. It has only one more electron than hydrogen. It is a useful approach to approximate multi-electron atoms as one-electron systems first, and then approximate the electron-electron interactions. Electron energies in an atom with more than one proton should follow the equation $E_n = -Z^2 \times 13.6 \text{ eV}/n^2$, whereby Z is the number of protons.

$$E_n = - \frac{Z^2 \text{ } 13.6 \text{ eV}}{n^2}$$

Equation 1.2.24 The orbital energies for atoms with more than one proton

The binding energy of the electron increases proportionally to the square of the number of protons because the attractive Coulomb forces that act on the negatively charged electrons increases with the number of positively charged protons in the nucleus. One can experimentally measure the orbital energies via ionization energies. The energy required to remove an electron in a particular orbital from the atom is equal to the binding energy for the electron in that orbital. Therefore the ionization energy $IE = -E_n$ ($E_n =$

orbital energy). According to the Schrödinger model the orbital energy for a helium electron in a 1s orbital should be $E_{1s} = -(2^2 \times 13.6 \text{ eV})/1^1 = -54.4 \text{ eV}$ (Eq. 1.2.25).

$$E_{1s} = -\frac{2^2 \times 13.6 \text{ eV}}{1^1} = -54.4 \text{ eV}$$

Equation 1.2.25 Energy for a helium electron in a 1s orbital.

However, the experimentally measured ionization energy of the electron is +24.6 eV, which means that the real orbital energy is -24.6 eV, and not -54.4 eV. On the other hand, the ionization of a He^+ ion is +54.4 eV which is exactly what we would expect. We can explain this phenomenon by the fact that the Schrödinger model works for a single electron only and must neglect electron interactions. In a He^+ ion there is only one electron, therefore the Schrödinger model correctly predicts the energy of the electron. However, in a helium atom there are two electrons, and the Schrödinger model cannot account for the electron-electron interactions. Therefore, it does not give the correct energy for the electrons in a Helium atom. The electron-electron interactions can be viewed as shielding effects. This means that the first electron shields part of the nuclear charge from the second electron. Therefore, the second electron experiences a reduced Coulomb force from the nucleus. Because of the reduced Coulomb force, the binding energy is smaller. It is reduced from -54.4 eV to -24.6 eV. It should be pointed out that the two electrons in the 1s orbital of the He atom are indistinguishable, that means they both have the reduced binding energy. The binding energy only increases to -54.4 eV after one of the two electrons has been removed.

The net positive charge from the nucleus after accounting for shielding effects is called the effective nuclear charge. For the helium atom the effective nuclear charge is 1.34. We can calculate the effective nuclear charge from the experimentally measured first ionization energy. Solving the equation for Z_{eff} gives $Z_{\text{eff}} = 1.34$ (Eq. 1.2.26).

$$E = -\frac{Z_{\text{eff}}^2}{n^2} \times 13.6 \text{ eV} = -24.6 \text{ eV} \quad \text{b/c } IE(\text{He}) = 24.6 \text{ eV}$$

$$Z_{\text{eff}} = \sqrt{n^2 \times \frac{24.6 \text{ eV}}{13.6 \text{ eV}}} = \sqrt{1^2 \times \frac{24.6 \text{ eV}}{13.6 \text{ eV}}} = 1.34$$

Equation 1.2.26 Calculation of Z_{eff} in the Helium atom from first ionization energies.

Dr. Kai Landskron ([Lehigh University](#)). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: [Click Here to Donate](#).

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