

1.1 — ENERGETIC TRANSITION

A quantum mechanical system or particle that is bound can only take on certain discrete values of energy. These discrete values are called energy levels. The term is commonly used for the energy levels of electrons in atoms, ions, or molecules, which are bound by the electric field of the nucleus, but can also refer to energy levels of nuclei or vibrational or rotational energy levels in molecules. The energy spectrum of a system with such discrete energy levels is said to be quantized. If the potential energy is set to zero at infinite distance from the atomic nucleus or molecule, the usual convention, then bound electron states have negative potential energy.

If an atom, ion, or molecule is in the lowest possible energy level, if any, and its electrons are in the lowest possible energy level, it is said to be in the ground state. States with higher energy than the ground state are called excited states. In quantum mechanical state is the same energy, they are then called degenerate energy levels.

CHAPTER 1

Energy States

1.2 — ATOMS

1.2.1 — Intrinsic Energy Levels

In the formulas for energy of electrons at various levels given below for an atom, the zero point for energy is set when the electron in question has completely left the atom, i.e. when the electron's principal quantum number $n = \infty$. When the electron is bound to the atom in any other value of n , the electron's energy is lower and is considered negative. To state that there is one electron in a given atomic orbital in a hydrogen like atom (ion). The energy of its state is mainly determined by the electrostatic interaction of the negatively charged electron with the positively charged nucleus. The energy levels of an electron around a nucleus are given by

$$E_n = -hcR_\infty \frac{Z^2}{n^2} \quad (1.1)$$

Typically between 1 eV and 103 eV), where R_∞ is the Rydberg constant, Z is the atomic number, n is the principal quantum number, h is Planck's constant, and c is the speed of light. For hydrogen like atoms (ions) only, the hydrogen levels depend only on the principal quantum number n .

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A quantum mechanical system or particle that is bound can only take on certain discrete values of energy. These discrete values are called energy levels. The term is commonly used for the energy levels of electrons in atoms, ions, or molecules, which are bound by the electric field of the nucleus, but can also refer to energy levels of nuclei or vibrational or rotational energy levels in molecules. The energy spectrum of a system with such discrete energy levels is said to be quantized. If the potential energy is set to zero at infinite distance from the atomic nucleus or molecule, the usual convention, then bound electron states have negative potential energy.

If an atom, ion, or molecule is at the lowest possible energy level, it and its electrons are said to be in the ground state. If it is at a higher energy level, it is said to be excited, or any electrons that have higher energy than the ground state are excited. If more than one quantum mechanical state is at the same energy, the energy levels are 'degenerate' they are then called degenerate energy levels.

1.2 ATOMS

1.2.1 Intrinsic Energy Levels

In the formulas for energy of electrons at various levels given below in an atom, the zero point for energy is set when the electron in question has completely left the atom, i.e. when the electron's principal quantum number $n = \infty$. When the electron is bound to the atom in any closer value of n , the electron's energy is lower and is considered negative. Assume that, there is one electron in a given atomic orbital in a hydrogen-like atom (ion). The energy of its state is mainly determined by the electrostatic interaction of the (negative) electron with the (positive) nucleus. The energy levels of an electron around a nucleus are given by:

$$E_n = -hcR_\infty \frac{Z^2}{n^2} \quad (1.1)$$

(typically between 1 eV and 103 eV), where R_∞ is the Rydberg constant, Z is the atomic number, n is the principal quantum number, h is Planck's constant, and c is the speed of light. For hydrogen-like atoms (ions) only, the Rydberg levels depend only on the principal quantum number n .

This equation is obtained from combining the Rydberg formula for any hydrogen-like element (shown below) with $E = h\nu = hc/\lambda$ assuming that the principal quantum number n above = n_1 in the Rydberg formula and $n_2 = \infty$ (principal quantum number of the energy level the electron descends from, when emitting a photon). The Rydberg formula was derived from empirical spectroscopic emission data.

$$\frac{1}{\lambda} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1.2)$$

An equivalent formula can be derived quantum mechanically from the time-independent Schrödinger equation with a kinetic energy Hamiltonian operator using a wave function as an Eigen function to obtain the energy levels as eigenvalues, but the Rydberg constant would be replaced by other fundamental physics constants.

Multi-electron atoms include electrostatic interaction of an electron with other electrons. If there is more than one electron around the atom, electron-electron-interactions raise the energy level. These interactions are often neglected if the spatial overlap of the electron wave functions is low. For multi-electron atoms, interactions between electrons cause the preceding equation to be no longer accurate as stated simply with Z as the atomic number. A simple way to understand this is as a shielding effect, where the outer electrons see an effective nucleus of reduced charge, since the inner electrons are bound tightly to the nucleus and partially cancel its charge. This leads to an approximate correction where Z is substituted with an effective nuclear charge symbolized as Z_{eff} that depends strongly on the principal quantum number.

$$E_{n,l} = -hcR_{\infty} \frac{Z_{\text{eff}}^2}{n^2} \quad (1.3)$$

In such cases, the orbital types (determined by the azimuthal quantum number l) as well as their levels within the molecule affect Z_{eff} and therefore also affect the various atomic electron energy levels [1]. The Aufbau principle of filling an atom with electrons for an electron configuration takes these differing energy levels into account.

1.2.2 Fine Structure Splitting

Fine structure arises from relativistic kinetic energy corrections, spin-orbit coupling (an electrodynamic interaction between the electron's spin