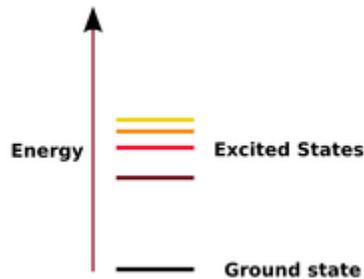# Quantum Mechanics_quantum mechanical system

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Energy levels for an <u>electron</u> in an <u>atom</u>: ground state and <u>excited states</u>. After absorbing <u>energy</u>, an electron may jump from the ground state to a higher energy excited state.

A <u>quantum mechanical</u> system or <u>particle</u> that is <u>bound</u>—that is, confined spatially—can only take on certain discrete values of energy. This contrasts with <u>classical</u>particles, which can have any energy. These discrete values are called **energy levels**. The term is commonly used for the energy levels of <u>electrons</u> in <u>atoms</u>, <u>ions</u>, or<u>molecules</u>, which are bound by the electric field of the<u>nucleus</u>, but can also refer to energy levels of nuclei or<u>vibrational</u> or rotational energy levels in molecules. The energy spectrum of a system with such discrete energy levels is said to be <u>quantized</u>.

If the <u>potential energy</u> is set to zero at <u>infinite</u> distance from the atomic nucleus or molecule, the usual convention, then <u>bound electron states</u> 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*<u>ground state</u>*. If it is at a higher energy level, it is said to be *<u>excited</u>*, or any electrons that have higher energy than the ground state are *excited*.

If more than one quantum mechanical <u>State</u> is at the same energy, the energy levels are "degenerate". They are then called <u>degenerate energy levels</u>.

Explanation

Quantized energy levels result from the relation between a particle's energy and its <u>wavelength</u>. For a confined particle such as an electron in an atom, the <u>Wave function</u> has the form of <u>standing waves</u>. Only <u>stationary states</u> with energies corresponding to integral numbers of wavelengths[*clarification needed*] can exist; for other states the waves interfere destructively[*clarification needed*], resulting in zero <u>probability density</u>. Elementary examples that show mathematically how energy levels come about are the <u>particle in a box</u> and the <u>quantum harmonic oscillator</u>.

History

The first evidence of quantization in atoms was the observation of <u>spectral lines</u> in light from the sun in the early 1800s by <u>Joseph von Fraunhofer</u> and <u>William Hyde Wollaston</u>. The notion of energy levels was proposed in 1913 by Danish physicist<u>Niels Bohr</u> in the <u>Bohr theory</u> of the atom. The modern quantum mechanical theory given an explanation of these energy levels in terms of the <u>Schrödinger equation</u> was advanced by <u>Erwin Schrödinger</u> and <u>Werner Heisenberg</u> in 1926.

Atoms
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 <u>principal quantum number</u> $n = \infty$. When the electron is bound to the atom in any closer value of n, the electron's energy is lower and is considered negative.

Orbital state energy level: atom/ion with nucleus + one electron

Assume there is one electron in a given <u>atomic orbital</u> in a <u>hydrogen-like atom (ion)</u>. 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 :

$$E_n = -hcR_\infty \frac{Z^2}{n^2}$$

(typically between 1 $\underline{eV}$ and 10^3 eV), where R_∞ is the $\underline{Rydberg\ constant}$, Z is the$\underline{atomic}$ $\underline{number}$, n is the $\underline{principal\ quantum\ number}$, h is $\underline{Planck's\ constant}$, and $c$is the $\underline{speed}$ $\underline{of\ light}$. For hydrogen-like atoms (ions) only, the Rydberg levels depend only on the principal quantum number n.

This equation is obtained from combining the $\underline{Rydberg\ formula\ for\ any\ hydrogen-like}$ $\underline{element}$ (shown below) with $E = h\nu = hc/\lambda$ assuming that the $\underline{principal\ quantum}$ $\underline{number}$ 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$\underline{photon}$). The $\underline{Rydberg}$ $\underline{formula}$ was derived from empirical $\underline{spectroscopic\ emission}$data.

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

An equivalent formula can be derived quantum mechanically from the time-independent $\underline{Schrödinger\ equation}$ with a kinetic energy $\underline{Hamiltonian\ operator}$using a $\underline{Wave\ function}$ as an $\underline{eigenfunction}$ to obtain the energy levels as$\underline{eigenvalues}$, 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 wavefunctions 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 $\underline{atomic\ number}$. A simple (though not complete) way to understand this is as a $\underline{shielding\ effect}$, 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 $\underline{effective\ nuclear}$ $\underline{charge}$ symbolized as Z_{eff} that depends strongly on the principal quantum number.

$$E_{n,l} = -hcR_\infty \frac{Z_{eff}^2}{n^2}$$

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

atom with electrons in the <u>ground state</u>, the lowest energy levels are filled first and consistent with the <u>Pauli exclusion principle</u>, the<u>Aufbau principle</u>, and <u>Hund's rule</u>.

Fine structure splitting

<u>Fine structure</u> arises from relativistic kinetic energy corrections, <u>spin–orbit coupling</u> (an electrodynamic interaction between the electron's <u>spin</u> and motion and the nucleus's electric field) and the Darwin term (contact term interaction of sshell[_which?_] electrons inside the nucleus). These affect the levels by a typical order of magnitude of 10^{-3} eV.

Hyperfine structure

This even finer structure is due to electron–nucleus <u>spin–spin interaction</u>, resulting in a typical change in the energy levels by a typical order of magnitude of 10^{-4} eV.

Energy levels due to external fields
Zeeman effect

Main article: <u>Zeeman effect</u>

There is an interaction energy associated with the magnetic dipole moment, $\boldsymbol{\mu}_L$, arising from the electronic orbital angular momentum, L, given by

$$U = -\boldsymbol{\mu}_L \cdot \mathbf{B}$$

with

$$-\boldsymbol{\mu}_L = \frac{e\hbar}{2m}\mathbf{L} = \mu_B\mathbf{L}$$
.

Additionally taking into account the magnetic momentum arising from the electron spin.

Due to relativistic effects (<u>Dirac equation</u>), there is a magnetic momentum, $\boldsymbol{\mu}_S$, arising from the electron spin

$$-\boldsymbol{\mu}_S = -\mu_B g_S \mathbf{S}$$
,

with g_S the electron–spin <u>g–factor</u> (about 2), resulting in a total magnetic moment,$\boldsymbol{\mu}$,

$$\boldsymbol{\mu} = \boldsymbol{\mu}_L + \boldsymbol{\mu}_S$$
.

The interaction energy therefore becomes

$$U_B = -\boldsymbol{\mu} \cdot \mathbf{B} = \mu_B B(M_L + g_S M_S)$$
.

Stark effect
Molecules

Chemical bonds between atoms in a molecule form because they make the situation more stable for the involved atoms, which generally means the sum energy level for the involved atoms in the molecule is lower than if the atoms were not so bonded. As separate atoms approach each other to covalently bond, their orbitals affect each other's energy levels to form bonding and antibondingmolecular orbitals. The energy level of the bonding orbitals is lower, and the energy level of the antibonding orbitals is higher. For the bond in the molecule to be stable, the covalent bonding electrons occupy the lower energy bonding orbital, which may be signified by such symbols as σ or π depending on the situation. Corresponding anti-bonding orbitals can be signified by adding an asterisk to get σ* or π* orbitals. A non-bonding orbital in a molecule is an orbital with electrons in outer shells which do not participate in bonding and its energy level is the same as that of the constituent atom. Such orbitals can be designated as **n** orbitals. The electrons in an n orbital are typically lone pairs. [1] In polyatomic molecules, different vibrational and rotational energy levels are also involved.

Roughly speaking, a **molecular energy state**, i.e. an eigenstate of the molecular Hamiltonian, is the sum of the electronic, vibrational, rotational, nuclear, and translational components, such that:

$$E = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}} + E_{\text{nuclear}} + E_{\text{translational}}$$

where $E_{\text{electronic}}$ is an eigenvalue of the electronic molecular Hamiltonian (the value of the potential energy surface) at the equilibrium geometry of the molecule.

The molecular energy levels are labelled by the molecular term symbols.

The specific energies of these components vary with the specific energy state and the substance.

In molecular physics and quantum chemistry, an **energy level** is a quantized energy of a bound quantum mechanical state.
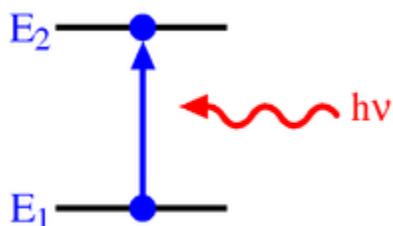
Energy level diagrams

There are various types of energy level diagrams for bonds between atoms in a molecule.
Examples

, *Jablonski diagrams*, and *Franck–Condon* diagrams.

Energy level transitions

Further information: <u>atomic electron transition</u> and <u>molecular electron transition</u>

An increase in energy level from E_1 to E_2 resulting from absorption of a photon represented by the red squiggly arrow, and whose energy is *hν*
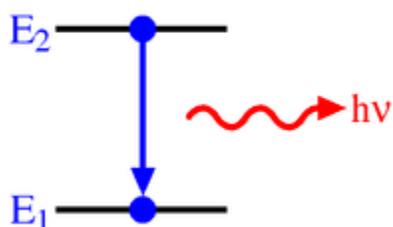
A decrease in energy level from E_2 to E_1 resulting in emission of a photon represented by the red squiggly arrow, and whose energy is *hν*

Electrons in atoms and molecules can change (make *transitions* in) energy levels by emitting or absorbing a <u>photon</u> (of <u>electromagnetic radiation</u>) whose energy must be exactly equal to the energy difference between the two levels. Electrons can also be completely removed from a chemical species such as an atom, molecule, or <u>ion</u>. Complete removal of an electron from an atom can be a form of <u>ionization</u>, which is effectively moving the electron out to an <u>orbital</u> with an infinite <u>principal quantum number</u>, in effect so far away so as to have practically no more effect on the remaining atom (ion). For various types of atoms, there are 1st, 2nd, 3rd, etc. <u>ionization energies</u> for removing the 1st, then the 2nd, then the 3rd, etc. of the highest energy electrons, respectively, from the atom originally in the <u>ground state</u>. Energy in corresponding opposite quantities can also be released, sometimes in the form of photon energy, when electrons are added to positively charged ions or sometimes atoms. Molecules can also undergo transitions in their <u>vibrational</u> or rotational energy

levels. Energy level transitions can also be nonradiative, meaning emission or absorption of a photon is not involved.

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_. Such a species can be excited to a higher energy level by absorbing a photon whose energy is equal to the energy difference between the levels. Conversely, an excited species can go to a lower energy level by spontaneously emitting a photon equal to the energy difference. A photon's energy is equal to Planck's constant (h) times its frequency (ν) and thus is proportional to its frequency, or inversely to its wavelength (λ).[1]

$$\Delta E = h\nu = hc/\lambda,$$

since c, the speed of light, equals to $\nu\lambda$[1]

Correspondingly, many kinds of spectroscopy are based on detecting the frequency or wavelength of the emitted or absorbed photons to provide information on the material analyzed, including information on the energy levels and electronic structure of materials obtained by analyzing the spectrum.

An asterisk is commonly used to designate an excited state. An electron transition in a molecule's bond from a ground state to an excited state may have a designation such as σ → σ*, π → π*, or n → π* meaning excitation of an electron from a σ bonding to a σ antibonding orbital, from a π bonding to a π antibonding orbital, or from an n non-bonding to a π antibonding orbital. [1] [2] Reverse electron transitions for all these types of excited molecules are also possible to return to their ground states, which can be designated as σ* → σ, π* → π, or π* → n.

A transition in an energy level of an electron in a molecule may be combined with a vibrational transition and called a vibronic transition. A vibrational and rotational transition may be combined by rovibrational coupling. In rovibronic coupling, electron transitions are simultaneously combined with both vibrational and rotational transitions. Photons involved in transitions may have energy of various ranges in the electromagnetic spectrum, such as X-ray, ultraviolet, visible light, infrared,

or microwave radiation, depending on the type of transition. In a very general way, energy level differences between electronic states are larger, differences between vibrational levels are intermediate, and differences between rotational levels are smaller, although there can be overlap. Translational energy levels are practically continuous and can be calculated as kinetic energy usingClassical mechanics.

Higher temperature causes fluid atoms and molecules to move faster increasing their translational energy, and thermally excites molecules to higher average amplitudes of vibrational and rotational modes (excites the molecules to higher internal energy levels). This means that as temperature rises, translational, vibrational, and rotational contributions to molecular heat capacity let molecules absorb heat and hold more internal energy. Conduction of heat typically occurs as molecules or atoms collide transferring the heat between each other. At even higher temperatures, electrons can be thermally excited to higher energy orbitals in atoms or molecules. A subsequent drop of an electron to a lower energy level can release a photon, causing a possibly colored glow.

An electron farther from the nucleus has higher potential energy than an electron closer to the nucleus, thus it becomes less bound to the nucleus, since its potential energy is negative and inversely dependent on its distance from the nucleus.[3]

Crystalline materials

Crystalline solids are found to have energy bands, instead of or in addition to energy levels. Electrons can take on any energy within an unfilled band. At first this appears to be an exception to the requirement for energy levels. However, as shown in band theory, energy bands are actually made up of many discrete energy levels which are too close together to resolve. Within a band the number of levels is of the order of the number of atoms in the crystal, so although electrons are actually restricted to these energies, they appear to be able to take on a continuum of values. The important energy levels in a crystal are the top of thevalence band, the bottom of the conduction band, the Fermi level, the vacuum level, and the energy levels of any defect states in the crystal.

References

1. ^ *a* *b* *c* *d* UV–Visible Absorption Spectra

2. **^** [Theory of Ultraviolet-Visible (UV-Vis) Spectroscopy](#)
3. **^** [http://chemed.chem.wisc.edu/chempaths/GenChem-Textbook/Electron-Density-and-Potential-Energy-899.html](#)

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