

Electronic structure methods

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Overview

Electron configuration

In atomic physics and quantum chemistry, the **electron configuration** is the distribution of electrons of an atom or molecule (or other physical structure) in atomic or molecular orbitals. For example, the electron configuration of the neon atom is $1s^2 2s^2 2p^6$.

Electronic configurations describe electrons as each moving independently in an orbital, in an average field created by all other orbitals.

Mathematically, configurations are described by Slater determinants or configuration state functions.

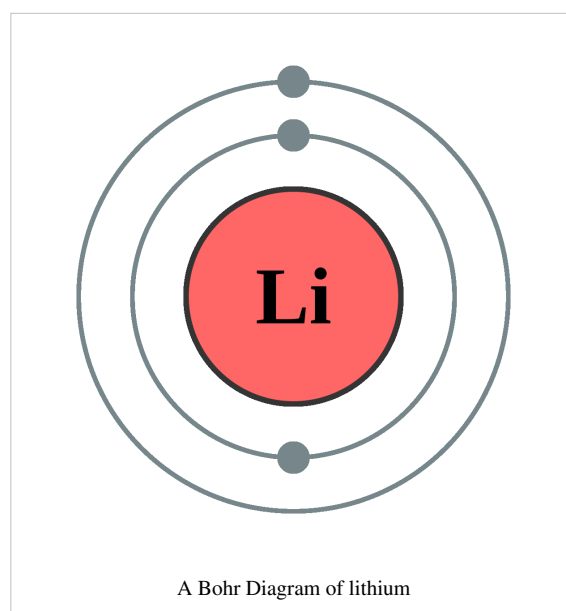
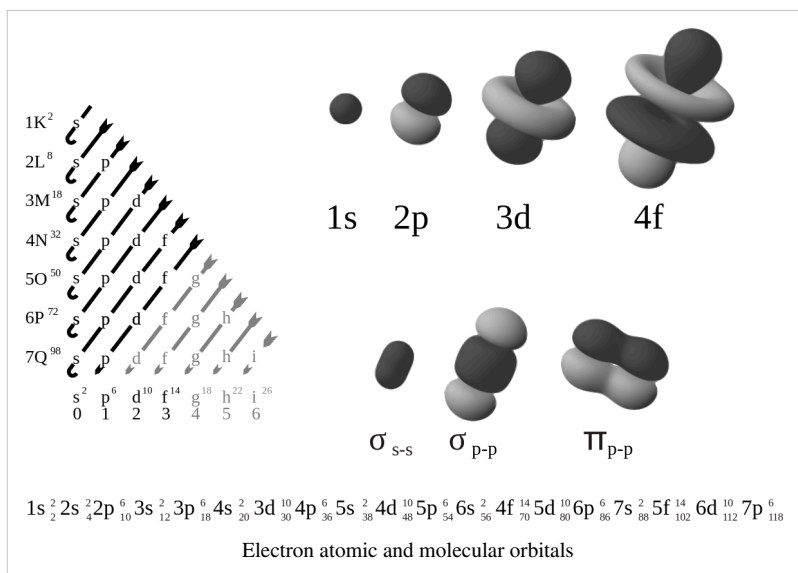
According to the laws of quantum mechanics, for systems with only one electron, an energy is associated with each electron configuration and, upon certain conditions, electrons are able to move from one configuration to another by emission or absorption of a quantum of energy, in the form of a photon.

For atoms or molecules with more than one electron, the motion of electrons are correlated and such a picture is no longer exact. A very large number of electronic configurations are needed to exactly describe any multi-electron

system, and no energy can be associated with one single configuration. However, the electronic wave function is usually dominated by a very small number of configurations and therefore the notion of electronic configuration remains essential for multi-electron systems.




Electronic configuration of polyatomic molecules can change without absorption or emission of photon through vibronic couplings.

Knowledge of the electron configuration of different atoms is useful in understanding the structure of the periodic table of elements. The concept is also useful for describing the chemical bonds that hold atoms together. In bulk



materials this same idea helps explain the peculiar properties of lasers and semiconductors.

Shells and subshells

| | s ($\ell=0$) | p ($\ell=1$) | | |
|-------|------------------|---|---|---|
| | $m=0$ | $m=0$ | $m=\pm 1$ | |
| | s | p_z | p_x | p_y |
| $n=1$ | • | | | |
| $n=2$ | • |  |  |  |

Electron configuration was first conceived of under the Bohr model of the atom, and it is still common to speak of shells and subshells despite the advances in understanding of the quantum-mechanical nature of electrons.

An electron shell is the set of allowed states electrons may occupy which share the same principal quantum number, n (the number before the letter in the orbital label). An atom's n th electron shell can accommodate $2n^2$ electrons, *e.g.* the first shell can accommodate 2 electrons, the second shell 8 electrons, and the third shell 18 electrons. The factor of two arises because the allowed states are doubled due to electron spin—each atomic orbital admits up to two otherwise identical electrons with opposite spin, one with a spin $+1/2$ (usually noted by an up-arrow) and one with a spin $-1/2$ (with a down-arrow).

A subshell is the set of states defined by a common azimuthal quantum number, ℓ , within a shell. The values $\ell = 0, 1, 2, 3$ correspond to the $s, p, d,$ and f labels, respectively. The maximum number of electrons which can be placed in a subshell is given by $2(2\ell + 1)$. This gives two electrons in an s subshell, six electrons in a p subshell, ten electrons in a d subshell and fourteen electrons in an f subshell.

The numbers of electrons that can occupy each shell and each subshell arise from the equations of quantum mechanics,^[1] in particular the Pauli exclusion principle, which states that no two electrons in the same atom can have the same values of the four quantum numbers.

Notation

Physicists and chemists use a standard notation to indicate the electron configurations of atoms and molecules. For atoms, the notation consists of a sequence of atomic orbital labels (*e.g.* for phosphorus the sequence $1s, 2s, 2p, 3s, 3p$) with the number of electrons assigned to each orbital (or set of orbitals sharing the same label) placed as a superscript. For example, hydrogen has one electron in the s -orbital of the first shell, so its configuration is written $1s^1$. Lithium has two electrons in the $1s$ -subshell and one in the (higher-energy) $2s$ -subshell, so its configuration is written $1s^2 2s^1$ (pronounced "one-s-two, two-s-one"). Phosphorus (atomic number 15) is as follows: $1s^2 2s^2 2p^6 3s^2 3p^3$.

For atoms with many electrons, this notation can become lengthy and so an abbreviated notation is used, since all but the last few subshells are identical to those of one or another of the noble gases. Phosphorus, for instance, differs from neon ($1s^2 2s^2 2p^6$) only by the presence of a third shell. Thus, the electron configuration of neon is pulled out, and phosphorus is written as follows: $[\text{Ne}] 3s^2 3p^3$. This convention is useful as it is the electrons in the outermost shell which most determine the chemistry of the element.

The order of writing the orbitals is not completely fixed: some sources group all orbitals with the same value of n together, while other sources (as here) follow the order given by Madelung's rule. Hence the electron configuration of iron can be written as $[\text{Ar}] 3d^6 4s^2$ (keeping the $3d$ -electrons with the $3s$ - and $3p$ -electrons which are implied by the configuration of argon) or as $[\text{Ar}] 4s^2 3d^6$ (following the Aufbau principle, see below).

The superscript 1 for a singly occupied orbital is not compulsory. It is quite common to see the letters of the orbital labels (s, p, d, f) written in an italic or slanting typeface, although the International Union of Pure and Applied Chemistry (IUPAC) recommends a normal typeface (as used here). The choice of letters originates from a now-obsolete system of categorizing spectral lines as "sharp", "principal", "diffuse" and "fundamental" (or "fine"), based on their observed fine structure: their modern usage indicates orbitals with an azimuthal quantum number, l , of 0, 1, 2 or 3 respectively. After "f", the sequence continues alphabetically "g", "h", "i"... ($l = 4, 5, 6...$), skipping "j", although orbitals of these types are rarely required.

The electron configurations of molecules are written in a similar way, except that molecular orbital labels are used instead of atomic orbital labels (see below).

Energy — ground state and excited states

The energy associated to an electron is that of its orbital. The energy of a configuration is often approximated as the sum of the energy of each electron, neglecting the electron-electron interactions. The configuration that corresponds to the lowest electronic energy is called the ground state. Any other configuration is an excited state.

As an example, the ground state configuration of the sodium atom is $1s^2 2s^2 2p^6 3s$, as deduced from the Aufbau principle (see below). The first excited state is obtained by promoting a 3s electron to the 3p orbital, to obtain the $1s^2 2s^2 2p^6 3p$ configuration, abbreviated as the 3p level. Atoms can move from one configuration to another by absorbing or emitting energy. In a sodium-vapor lamp for example, sodium atoms are excited to the 3p level by an electrical discharge, and return to the ground state by emitting yellow light of wavelength 589 nm.

Usually the excitation of valence electrons (such as 3s for sodium) involves energies corresponding to photons of visible or ultraviolet light. The excitation of core electrons is possible, but requires much higher energies generally corresponding to x-ray photons. This would be the case for example to excite a 2p electron to the 3s level and form the excited $1s^2 2s^2 2p^5 3s^2$ configuration.

The remainder of this article deals only with the ground-state configuration, often referred to as "the" configuration of an atom or molecule.

History

Niels Bohr (1923) was the first to propose that the periodicity in the properties of the elements might be explained by the electronic structure of the atom. His proposals were based on the then current Bohr model of the atom, in which the electron shells were orbits at a fixed distance from the nucleus. Bohr's original configurations would seem strange to a present-day chemist: sulfur was given as 2.4.4.6 instead of $1s^2 2s^2 2p^6 3s^2 3p^4$ (2.8.6).

The following year, E. C. Stoner incorporated Sommerfeld's third quantum number into the description of electron shells, and correctly predicted the shell structure of sulfur to be 2.8.6. However neither Bohr's system nor Stoner's could correctly describe the changes in atomic spectra in a magnetic field (the Zeeman effect).

Bohr was well aware of this shortcoming (and others), and had written to his friend Wolfgang Pauli to ask for his help in saving quantum theory (the system now known as "old quantum theory"). Pauli realized that the Zeeman effect must be due only to the outermost electrons of the atom, and was able to reproduce Stoner's shell structure, but with the correct structure of subshells, by his inclusion of a fourth quantum number and his exclusion principle (1925).^[2]

It should be forbidden for more than one electron with the same value of the main quantum number n to have the same value for the other three quantum numbers k [l], j [m_l] and m [m_s].

The Schrödinger equation, published in 1926, gave three of the four quantum numbers as a direct consequence of its solution for the hydrogen atom: this solution yields the atomic orbitals which are shown today in textbooks of chemistry (and above). The examination of atomic spectra allowed the electron configurations of atoms to be determined experimentally, and led to an empirical rule (known as Madelung's rule (1936), see below) for the order

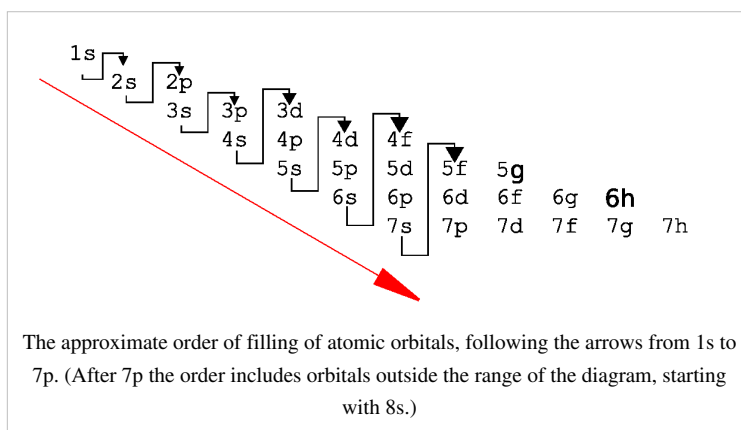
in which atomic orbitals are filled with electrons.

Aufbau principle and Madelung rule

The Aufbau principle (from the German *Aufbau*, "building up, construction") was an important part of Bohr's original concept of electron configuration. It may be stated as:

a maximum of two electrons are put into orbitals in the order of increasing orbital energy: the lowest-energy orbitals are filled before electrons are placed in higher-energy orbitals.

The principle works very well (for the ground states of the atoms) for the first 18 elements, then decreasingly well for the following 100 elements. The modern form of the Aufbau principle describes an order of orbital energies given by Madelung's rule (or Klechkowski's rule). This rule was first stated by Charles Janet in 1929, rediscovered by Erwin Madelung in 1936, and later given a theoretical justification by V.M. Klechkowski



1. Orbitals are filled in the order of increasing $n+l$;
2. Where two orbitals have the same value of $n+l$, they are filled in order of increasing n .

This gives the following order for filling the orbitals:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, (8s, 5g, 6f, 7d, 8p, and 9s)

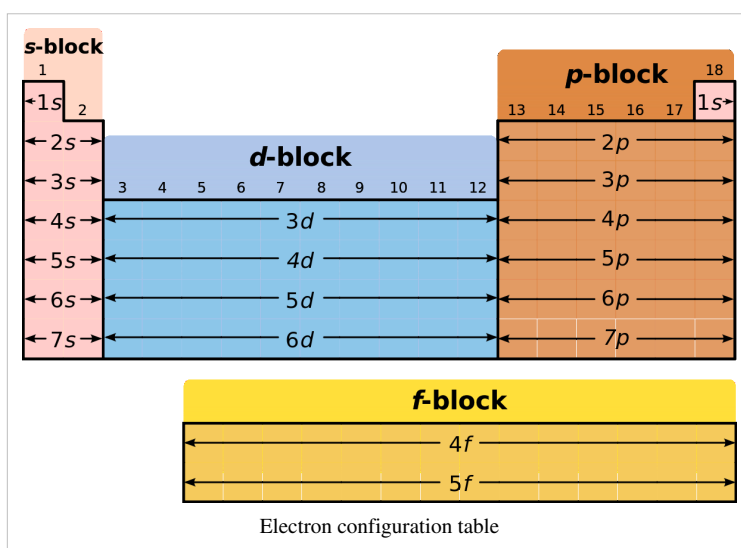
In this list the orbitals in parentheses are not occupied in the ground state of the heaviest atom now known (Uuo, $Z = 118$).

The Aufbau principle can be applied, in a modified form, to the protons and neutrons in the atomic nucleus, as in the shell model of nuclear physics and nuclear chemistry.

Periodic table

The form of the periodic table is closely related to the electron configuration of the atoms of the elements. For example, all the elements of group 2 have an electron configuration of $[E] ns^2$ (where $[E]$ is an inert gas configuration), and have notable similarities in their chemical properties. In general, the periodicity of the periodic table in terms of periodic table blocks is clearly due to the number of electrons (2, 6, 10, 14...) needed to fill s, p, d, and f subshells.

The outermost electron shell is often referred to as the "valence shell" and (to a first approximation) determines the



chemical properties. It should be remembered that the similarities in the chemical properties were remarked more than a century before the idea of electron configuration.^[3] It is not clear how far Madelung's rule *explains* (rather than simply describes) the periodic table, although some properties (such as the common +2 oxidation state in the first row of the transition metals) would obviously be different with a different order of orbital filling.

Shortcomings of the Aufbau principle

The Aufbau principle rests on a fundamental postulate that the order of orbital energies is fixed, both for a given element and between different elements; neither of these is true (although they are approximately true enough for the principle to be useful). It considers atomic orbitals as "boxes" of fixed energy into which can be placed two electrons and no more. However the energy of an electron "in" an atomic orbital depends on the energies of all the other electrons of the atom (or ion, or molecule, etc.). There are no "one-electron solutions" for systems of more than one electron, only a set of many-electron solutions which cannot be calculated exactly^[4] (although there are mathematical approximations available, such as the Hartree–Fock method).

The fact that the Aufbau principle is based on an approximation can be seen from the fact that there is an almost-fixed filling order at all, that, within a given shell, the s-orbital is always filled before the p-orbitals. In a hydrogen-like atom, which only has one electron, the s-orbital and the p-orbitals of the same shell have exactly the same energy, to a very good approximation in the absence of external electromagnetic fields. (However, in a real hydrogen atom, the energy levels are slightly split by the magnetic field of the nucleus, and by the quantum electrodynamic effects of the Lamb shift).

Ionization of the transition metals

The naive application of the Aufbau principle leads to a well-known paradox (or apparent paradox) in the basic chemistry of the transition metals. Potassium and calcium appear in the periodic table before the transition metals, and have electron configurations $[\text{Ar}] 4s^1$ and $[\text{Ar}] 4s^2$ respectively, i.e. the 4s-orbital is filled before the 3d-orbital. This is in line with Madelung's rule, as the 4s-orbital has $n+l = 4$ ($n = 4, l = 0$) while the 3d-orbital has $n+l = 5$ ($n = 3, l = 2$). However, chromium and copper have electron configurations $[\text{Ar}] 3d^5 4s^1$ and $[\text{Ar}] 3d^{10} 4s^1$ respectively, i.e. one electron has passed from the 4s-orbital to a 3d-orbital to generate a half-filled or filled subshell. In this case, the usual explanation is that "half-filled or completely filled subshells are particularly stable arrangements of electrons".

The apparent paradox arises when electrons are *removed* from the transition metal atoms to form ions. The first electrons to be ionized come not from the 3d-orbital, as one would expect if it were "higher in energy", but from the 4s-orbital. The same is true when chemical compounds are formed. Chromium hexacarbonyl can be described as a chromium atom (not ion, it is in the oxidation state 0) surrounded by six carbon monoxide ligands: it is diamagnetic, and the electron configuration of the central chromium atom is described as $3d^6$, i.e. the electron which was in the 4s-orbital in the free atom has passed into a 3d-orbital on forming the compound. This interchange of electrons between 4s and 3d is universal among the first series of the transition metals.^[5]

The phenomenon is only paradoxical if it is assumed that the energies of atomic orbitals are fixed and unaffected by the presence of electrons in other orbitals. If that were the case, the 3d-orbital would have the same energy as the 3p-orbital, as it does in hydrogen, yet it clearly doesn't. There is no special reason why the Fe^{2+} ion should have the same electron configuration as the chromium atom, given that iron has two more protons in its nucleus than chromium and that the chemistry of the two species is very different. When care is taken to compare "like with like", the paradox disappears.

Other exceptions to Madelung's rule

There are several more exceptions to Madelung's rule among the heavier elements, and it is more and more difficult to resort to simple explanations such as the stability of half-filled subshells. It is possible to predict most of the exceptions by Hartree–Fock calculations, which are an approximate method for taking account of the effect of the other electrons on orbital energies. For the heavier elements, it is also necessary to take account of the effects of Special Relativity on the energies of the atomic orbitals, as the inner-shell electrons are moving at speeds approaching the speed of light. In general, these relativistic effects tend to decrease the energy of the s-orbitals in relation to the other atomic orbitals.

Electron shells filled in violation of Madelung's rule (red)

| Period 4 | | | Period 5 | | | Period 6 | | | Period 7 | | |
|-----------|----|--------------------------------------|------------|----|--------------------------------------|--------------|----|---|---------------|-----|---|
| Element | Z | Electron Configuration | Element | Z | Electron Configuration | Element | Z | Electron Configuration | Element | Z | Electron Configuration |
| | | | | | | Lanthanum | 57 | [Xe] 6s ² 5d ¹ | Actinium | 89 | [Rn] 7s ² 6d ¹ |
| | | | | | | Cerium | 58 | [Xe] 6s ² 4f ¹ 5d ¹ | Thorium | 90 | [Rn] 7s ² 6d ² |
| | | | | | | Praseodymium | 59 | [Xe] 6s ² 4f ³ | Protactinium | 91 | [Rn] 7s ² 5f ² 6d ¹ |
| | | | | | | Neodymium | 60 | [Xe] 6s ² 4f ⁴ | Uranium | 92 | [Rn] 7s ² 5f ³ 6d ¹ |
| | | | | | | Promethium | 61 | [Xe] 6s ² 4f ⁵ | Neptunium | 93 | [Rn] 7s ² 5f ⁴ 6d ¹ |
| | | | | | | Samarium | 62 | [Xe] 6s ² 4f ⁶ | Plutonium | 94 | [Rn] 7s ² 5f ⁶ |
| | | | | | | Europium | 63 | [Xe] 6s ² 4f ⁷ | Americium | 95 | [Rn] 7s ² 5f ⁷ |
| | | | | | | Gadolinium | 64 | [Xe] 6s ² 4f ⁷ 5d ¹ | Curium | 96 | [Rn] 7s ² 5f ⁷ 6d ¹ |
| | | | | | | Terbium | 65 | [Xe] 6s ² 4f ⁹ | Berkelium | 97 | [Rn] 7s ² 5f ⁹ |
| Scandium | 21 | [Ar] 4s ² 3d ¹ | Yttrium | 39 | [Kr] 5s ² 4d ¹ | Lutetium | 71 | [Xe] 6s ² 4f ¹⁴ 5d ¹ | Lawrencium | 103 | [Rn] 7s ² 5f ¹⁴ 7p ¹ |
| Titanium | 22 | [Ar] 4s ² 3d ² | Zirconium | 40 | [Kr] 5s ² 4d ² | Hafnium | 72 | [Xe] 6s ² 4f ¹⁴ 5d ² | Rutherfordium | 104 | [Rn] 7s ² 5f ¹⁴ 6d ² |
| Vanadium | 23 | [Ar] 4s ² 3d ³ | Niobium | 41 | [Kr] 5s ¹ 4d ⁴ | Tantalum | 73 | [Xe] 6s ² 4f ¹⁴ 5d ³ | | | |
| Chromium | 24 | [Ar] 4s ¹ 3d ⁵ | Molybdenum | 42 | [Kr] 5s ¹ 4d ⁵ | Tungsten | 74 | [Xe] 6s ² 4f ¹⁴ 5d ⁴ | | | |
| Manganese | 25 | [Ar] 4s ² 3d ⁵ | Technetium | 43 | [Kr] 5s ² 4d ⁵ | Rhenium | 75 | [Xe] 6s ² 4f ¹⁴ 5d ⁵ | | | |
| Iron | 26 | [Ar] 4s ² 3d ⁶ | Ruthenium | 44 | [Kr] 5s ¹ 4d ⁷ | Osmium | 76 | [Xe] 6s ² 4f ¹⁴ 5d ⁶ | | | |
| Cobalt | 27 | [Ar] 4s ² 3d ⁷ | Rhodium | 45 | [Kr] 5s ¹ 4d ⁸ | Iridium | 77 | [Xe] 6s ² 4f ¹⁴ 5d ⁷ | | | |

| | | | | | | | | | |
|--------|----|---|-----------|----|---------------------------------------|----------|----|---|--|
| Nickel | 28 | [Ar] 4s ² 3d ⁸ or [Ar] 4s ¹ 3d ⁹ (disputed) | Palladium | 46 | [Kr] 4d ¹⁰ | Platinum | 78 | [Xe] 6s ¹ 4f ¹⁴ 5d ⁹ | |
| Copper | 29 | [Ar] 4s ¹ 3d ¹⁰ | Silver | 47 | [Kr] 5s ¹ 4d ¹⁰ | Gold | 79 | [Xe] 6s ¹ 4f ¹⁴ 5d ¹⁰ | |
| Zinc | 30 | [Ar] 4s ² 3d ¹⁰ | Cadmium | 48 | [Kr] 5s ² 4d ¹⁰ | Mercury | 80 | [Xe] 6s ² 4f ¹⁴ 5d ¹⁰ | |

The electron-shell configuration of elements beyond rutherfordium has not yet been empirically verified, but they are expected to follow Madelung's rule without exceptions until element 120.

Electron configuration in molecules

In molecules, the situation becomes more complex, as each molecule has a different orbital structure. The molecular orbitals are labelled according to their symmetry,^[6] rather than the atomic orbital labels used for atoms and monoatomic ions: hence, the electron configuration of the dioxygen molecule, O₂, is 1σ_g² 1σ_u² 2σ_g² 2σ_u² 1π_u⁴ 3σ_g² 1π_g². The term 1π_g² represents the two electrons in the two degenerate π*-orbitals (antibonding). From Hund's rules, these electrons have parallel spins in the ground state, and so dioxygen has a net magnetic moment (it is paramagnetic). The explanation of the paramagnetism of dioxygen was a major success for molecular orbital theory.

Electron configuration in solids

In a solid, the electron states become very numerous. They cease to be discrete, and effectively blend into continuous ranges of possible states (an electron band). The notion of electron configuration ceases to be relevant, and yields to band theory.

Applications

The most widespread application of electron configurations is in the rationalization of chemical properties, in both inorganic and organic chemistry. In effect, electron configurations, along with some simplified form of molecular orbital theory, have become the modern equivalent of the valence concept, describing the number and type of chemical bonds that an atom can be expected to form.

This approach is taken further in computational chemistry, which typically attempts to make quantitative estimates of chemical properties. For many years, most such calculations relied upon the "linear combination of atomic orbitals" (LCAO) approximation, using an ever larger and more complex basis set of atomic orbitals as the starting point. The last step in such a calculation is the assignment of electrons among the molecular orbitals according to the Aufbau principle. Not all methods in calculational chemistry rely on electron configuration: density functional theory (DFT) is an important example of a method which discards the model.

A fundamental application of electron configurations is in the interpretation of atomic spectra. In this case, it is necessary to convert the electron configuration into one or more term symbols, which describe the different energy levels available to an atom. Term symbols can be calculated for any electron configuration, not just the ground-state configuration listed in tables, although not all the energy levels are observed in practice. It is through the analysis of atomic spectra that the ground-state electron configurations of the elements were experimentally determined.

Notes

- [1] In formal terms, the quantum numbers n , l and m arise from the fact that the solutions to the time-independent Schrödinger equation for hydrogen-like atoms are based on spherical harmonics.
- [2] English translation from
- [3] The similarities in chemical properties and the numerical relationship between the atomic weights of calcium, strontium and barium was first noted by Johann Wolfgang Döbereiner in 1817.
- [4] Electrons are identical particles, a fact which is sometimes referred to as "indistinguishability of electrons". A one-electron solution to a many-electron system would imply that the electrons could be distinguished from one another, and there is strong experimental evidence that they can't be. The exact solution of a many-electron system is a n -body problem with $n \geq 3$ (the nucleus counts as one of the "bodies"): such problems have evaded analytical solution since at least the time of Euler.
- [5] There are some cases in the second and third series where the electron remains in an s-orbital.
- [6] The labels are written in lowercase to indicate that they correspond to one-electron functions. They are numbered consecutively for each symmetry type (irreducible representation in the character table of the point group for the molecule), starting from the orbital of lowest energy for that type.

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External links

- What does an atom look like? Configuration in 3D (http://www.hydrogenlab.de/elektronium/HTML/einleitung_hauptseite_uk.html)

Methods

Tight binding

| Electronic structure methods |
|---|
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| Generalized valence bond Modern valence bond |
| Molecular orbital theory |
| Hartree–Fock method Møller–Plesset perturbation theory Configuration interaction Coupled cluster Multi-configurational self-consistent field Quantum chemistry composite methods Quantum Monte Carlo Linear combination of atomic orbitals |
| Electronic band structure |
| Nearly free electron model Tight binding Muffin-tin approximation Density functional theory k-p perturbation theory Empty lattice approximation |
|  Book |

In solid-state physics, the **tight-binding model** (or **TB model**) is an approach to the calculation of electronic band structure using an approximate set of wave functions based upon superposition of wave functions for isolated atoms located at each atomic site. The method is closely related to the LCAO method used in chemistry. Tight-binding models are applied to a wide variety of solids. The model gives good qualitative results in many cases and can be combined with other models that give better results where the tight-binding model fails. Though the tight-binding model is a one-electron model, the model also provides a basis for more advanced calculations like the calculation of surface states and application to various kinds of many-body problem and quasiparticle calculations.

Introduction

The name "tight binding" of this electronic band structure model suggests that this quantum mechanical model describes the properties of tightly bound electrons in solids. The electrons in this model should be tightly bound to the atom to which they belong and they should have limited interaction with states and potentials on surrounding atoms of the solid. As a result the wave function of the electron will be rather similar to the atomic orbital of the free atom to which it belongs. The energy of the electron will also be rather close to the ionization energy of the electron in the free atom or ion because the interaction with potentials and states on neighboring atoms is limited.

Though the mathematical formulation of the one-particle tight-binding Hamiltonian may look complicated at first glance, the model is not complicated at all and can be understood intuitively quite easily. There are only three kinds of elements that play a significant role in the theory. Two of those three kinds of elements should be close to zero and can often be neglected. The most important elements in the model are the interatomic matrix elements, which would simply be called the bond energies by a chemist.

In general there are a number of atomic energy levels and atomic orbitals involved in the model. This can lead to complicated band structures because the orbitals belong to different point-group representations. The reciprocal lattice and the Brillouin zone often belong to a different space group than the crystal of the solid. High-symmetry points in the Brillouin zone belong to different point-group representations. When simple systems like the lattices of elements or simple compounds are studied it is often not very difficult to calculate eigenstates in high-symmetry points analytically. So the tight-binding model can provide nice examples for those who want to learn more about group theory.

The tight-binding model has a long history and has been applied in many ways and with many different purposes and different outcomes. The model doesn't stand on its own. Parts of the model can be filled in or extended by other kinds of calculations and models like the nearly-free electron model. The model itself, or parts of it, can serve as the basis for other calculations. In the study of conductive polymers, organic semiconductors and molecular electronics, for example, tight-binding-like models are applied in which the role of the atoms in the original concept is replaced by the molecular orbitals of conjugated systems and where the interatomic matrix elements are replaced by inter- or intramolecular hopping and tunneling parameters. These conductors nearly all have very anisotropic properties and sometimes are almost perfectly one-dimensional.

Historical background

By 1928, the idea of a molecular orbital had been advanced by Robert Mulliken, who was influenced considerably by the work of Friedrich Hund. The LCAO method for approximating molecular orbitals was introduced in 1928 by B. N. Finklestein and G. E. Horowitz, while the LCAO method for solids was developed by Felix Bloch, as part of his doctoral dissertation in 1928, concurrently with and independent of the LCAO-MO approach. A much simpler interpolation scheme for approximating the electronic band structure, especially for the d-bands of transition metals, is the parameterized tight-binding method conceived in 1954 by John Clarke Slater and George Fred Koster, sometimes referred to as the SK tight-binding method. With the SK tight-binding method, electronic band structure calculations on a solid need not be carried out with full rigor as in the original Bloch's theorem but, rather, first-principles calculations are carried out only at high-symmetry points and the band structure is interpolated over the remainder of the Brillouin zone between these points.

In this approach, interactions between different atomic sites are considered as perturbations. There exist several kinds of interactions we must consider. The crystal Hamiltonian is only approximately a sum of atomic Hamiltonians located at different sites and atomic wave functions overlap adjacent atomic sites in the crystal, and so are not accurate representations of the exact wave function. There are further explanations in the next section with some mathematical expressions.

Recently, in the research about strongly correlated material, the tight binding approach is basic approximation because highly localized electrons like 3-d transition metal electrons sometimes display strongly correlated behaviors. In this case, the role of electron-electron interaction must be considered using the many-body physics description.

The tight-binding model is typically used for calculations of electronic band structure and band gaps in the static regime. However, in combination with other methods such as the random phase approximation (RPA) model, the dynamic response of systems may also be studied.

Mathematical formulation

We introduce the atomic orbitals $\varphi_m(\mathbf{r})$, which are eigenfunctions of the Hamiltonian H_{at} of a single isolated atom. When the atom is placed in a crystal, this atomic wave function overlaps adjacent atomic sites, and so are not true eigenfunctions of the crystal Hamiltonian. The overlap is less when electrons are tightly bound, which is the source of the descriptor "tight-binding". Any corrections to the atomic potential ΔU required to obtain the true Hamiltonian H of the system, are assumed small:

$$H(\mathbf{r}) = \sum_{\mathbf{R}_n} H_{at}(\mathbf{r} - \mathbf{R}_n) + \Delta U(\mathbf{r}) .$$

A solution ψ_r to the time-independent single electron Schrödinger equation is then approximated as a linear combination of atomic orbitals $\varphi_m(\mathbf{r} - \mathbf{R}_n)$:

$$\psi(\mathbf{r}) = \sum_{m, \mathbf{R}_n} b_m(\mathbf{R}_n) \varphi_m(\mathbf{r} - \mathbf{R}_n) ,$$

where m refers to the m -th atomic energy level and \mathbf{R}_n locates an atomic site in the crystal lattice.

Translational symmetry and normalization

The Bloch theorem states that the wave function in crystal can change under translation only by a phase factor:

$$\psi(\mathbf{r} + \mathbf{R}_\ell) = e^{i\mathbf{k} \cdot \mathbf{R}_\ell} \psi(\mathbf{r}) ,$$

where \mathbf{k} is the wave vector of the wave function. Consequently, the coefficients satisfy

$$\sum_{m, \mathbf{R}_n} b_m(\mathbf{R}_n) \varphi_m(\mathbf{r} - \mathbf{R}_n + \mathbf{R}_\ell) = e^{i\mathbf{k} \cdot \mathbf{R}_\ell} \sum_{m, \mathbf{R}_n} b_m(\mathbf{R}_n) \varphi_m(\mathbf{r} - \mathbf{R}_n) .$$

By substituting $\mathbf{R}_p = \mathbf{R}_n - \mathbf{R}_\ell$, we find

$$b_m(\mathbf{R}_p + \mathbf{R}_\ell) = e^{i\mathbf{k} \cdot \mathbf{R}_\ell} b_m(\mathbf{R}_p) ,$$

or

$$b_m(\mathbf{R}_p) = e^{i\mathbf{k} \cdot \mathbf{R}_p} b_m(\mathbf{0}) .$$

Normalizing the wave function to unity:

$$\begin{aligned} \int d^3r \psi^*(\mathbf{r})\psi(\mathbf{r}) &= 1 \\ &= \sum_{\mathbf{R}_n} b^*(\mathbf{R}_n) \sum_{\mathbf{R}_\ell} b(\mathbf{R}_\ell) \int d^3r \varphi^*(\mathbf{r} - \mathbf{R}_n)\varphi(\mathbf{r} - \mathbf{R}_\ell) \\ &= b^*(\mathbf{0})b(\mathbf{0}) \sum_{\mathbf{R}_n} e^{-i\mathbf{k} \cdot \mathbf{R}_n} \sum_{\mathbf{R}_\ell} e^{i\mathbf{k} \cdot \mathbf{R}_\ell} \int d^3r \varphi^*(\mathbf{r} - \mathbf{R}_n)\varphi(\mathbf{r} - \mathbf{R}_\ell) \\ &= Nb^*(\mathbf{0})b(\mathbf{0}) \sum_{\mathbf{R}_p} e^{-i\mathbf{k} \cdot \mathbf{R}_p} \int d^3r \varphi^*(\mathbf{r} - \mathbf{R}_p)\varphi(\mathbf{r}) \\ &= Nb^*(\mathbf{0})b(\mathbf{0}) \sum_{\mathbf{R}_p} e^{i\mathbf{k} \cdot \mathbf{R}_p} \int d^3r \varphi^*(\mathbf{r})\varphi(\mathbf{r} - \mathbf{R}_p) , \end{aligned}$$

so the normalization sets $b(\mathbf{0})$ as

$$b^*(\mathbf{0})b(\mathbf{0}) = \frac{1}{N} \cdot \frac{1}{1 + \sum_{\mathbf{R}_p \neq \mathbf{0}} e^{-i\mathbf{k} \cdot \mathbf{R}_p} \alpha(\mathbf{R}_p)} ,$$

where $\alpha(\mathbf{R}_p)$ are the atomic overlap integrals, which frequently are neglected resulting in^[1]

$$b_n(\mathbf{0}) \approx \frac{1}{\sqrt{N}} ,$$

and

$$\psi(\mathbf{r}) \approx \frac{1}{\sqrt{N}} \sum_{m, \mathbf{R}_n} e^{i\mathbf{k} \cdot \mathbf{R}_n} \varphi_m(\mathbf{r} - \mathbf{R}_n) .$$

The tight binding Hamiltonian

Using the tight binding form for the wave function, and assuming only the m -th atomic energy level is important for the m -th energy band, the Bloch energies ε_m are of the form

$$\begin{aligned} \varepsilon_m &= \int d^3r \psi^*(\mathbf{r}) H(\mathbf{r}) \psi(\mathbf{r}) \\ &= \sum_{\mathbf{R}_n} b^*(\mathbf{R}_n) \int d^3r \varphi^*(\mathbf{r} - \mathbf{R}_n) H(\mathbf{r}) \psi(\mathbf{r}) \\ &= \sum_{\mathbf{R}_\ell} \sum_{\mathbf{R}_n} b^*(\mathbf{R}_n) \int d^3r \varphi^*(\mathbf{r} - \mathbf{R}_n) H_{\text{at}}(\mathbf{r} - \mathbf{R}_\ell) \psi(\mathbf{r}) + \sum_{\mathbf{R}_n} b^*(\mathbf{R}_n) \int d^3r \varphi^*(\mathbf{r} - \mathbf{R}_n) \Delta U(\mathbf{r}) \psi(\mathbf{r}) . \\ &\approx E_m + b^*(0) \sum_{\mathbf{R}_n} e^{-i\mathbf{k} \cdot \mathbf{R}_n} \int d^3r \varphi^*(\mathbf{r} - \mathbf{R}_n) \Delta U(\mathbf{r}) \psi(\mathbf{r}) . \end{aligned}$$

Here terms involving the atomic Hamiltonian at sites other than where it is centered are neglected. The energy then becomes

$$\begin{aligned} \varepsilon_m(\mathbf{k}) &= E_m - N |b(0)|^2 \left(\beta_m + \sum_{\mathbf{R}_n \neq 0} \sum_l \gamma_{m,l}(\mathbf{R}_n) e^{i\mathbf{k} \cdot \mathbf{R}_n} \right) , \\ &= E_m - \frac{\beta_m + \sum_{\mathbf{R}_n \neq 0} \sum_l e^{i\mathbf{k} \cdot \mathbf{R}_n} \gamma_{m,l}(\mathbf{R}_n)}{1 + \sum_{\mathbf{R}_n \neq 0} \sum_l e^{i\mathbf{k} \cdot \mathbf{R}_n} \alpha_{m,l}(\mathbf{R}_n)} , \end{aligned}$$

where E_m is the energy of the m -th atomic level, and $\alpha_{m,l}$, β_m and $\gamma_{m,l}$ are the tight binding matrix elements.

The tight binding matrix elements

The element

$$\beta_m = - \int \varphi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \varphi_m(\mathbf{r}) d^3r ,$$

is the atomic energy shift due to the potential on neighboring atoms. This term is relatively small in most cases. If it is large it means that potentials on neighboring atoms have a large influence on the energy of the central atom.

The next term

$$\gamma_{m,l}(\mathbf{R}_n) = - \int \varphi_m^*(\mathbf{r}) \Delta U(\mathbf{r}) \varphi_l(\mathbf{r} - \mathbf{R}_n) d^3r ,$$

is the inter atomic matrix element between the atomic orbitals m and l on adjacent atoms. It is also called the bond energy or two center integral and it is the **most important element** in the tight binding model.

The last terms

$$\alpha_{m,l}(\mathbf{R}_n) = \int \varphi_m^*(\mathbf{r}) \varphi_l(\mathbf{r} - \mathbf{R}_n) d^3r ,$$

denote the overlap integrals between the atomic orbitals m and l on adjacent atoms.

Evaluation of the matrix elements

As mentioned before the values of the β_{mn} -matrix elements are not so large in comparison with the ionization energy because the potentials of neighboring atoms on the central atom are limited. If β_{mn} is not relatively small it means that the potential of the neighboring atom on the central atom is not small either. In that case it is an indication that the tight binding model is not a very good model for the description of the band structure for some reason. The inter atomic distances can be too small or the charges on the atoms or ions in the lattice is wrong for example.

The inter atomic matrix elements $\gamma_{mn,l}$ can be calculated directly if the atomic wave functions and the potentials are known in detail. Most often this is not the case. There are numerous ways to get parameters for these matrix elements. Parameters can be obtained from chemical bond energy data. Energies and eigenstates on some high symmetry points in the Brillouin zone can be evaluated and values integrals in the matrix elements can be matched with band structure data from other sources.

The inter atomic overlap matrix elements $\alpha_{mn,l}$ should be rather small or neglectable. If they are large it is again an indication that the tight binding model is of limited value for some purposes. Large overlap is an indication for too short inter atomic distance for example. In metals and transition metals the broad s-band or sp-band can be fitted better to an existing band structure calculation by the introduction of next-nearest-neighbor matrix elements and overlap integrals but fits like that don't yield a very useful model for the electronic wave function of a metal. Broad bands in dense materials are better described by a nearly free electron model.

The tight binding model works particularly well in cases where the band width is small and the electrons are strongly localized, like in the case of d-bands and f-bands. The model also gives good results in the case of open crystal structures, like diamond or silicon, where the number of neighbors is small. The model can easily be combined with a nearly free electron model in a hybrid NFE-TB model.

Connection to Wannier functions

Bloch wave functions describe the electronic states in a periodic crystal lattice. Bloch functions can be represented as a Fourier series^[2]

$$\psi_m(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_n a_m(\mathbf{R}_n, \mathbf{r}) e^{i\mathbf{k} \cdot \mathbf{R}_n},$$

where \mathbf{R}_n denotes an atomic site in a periodic crystal lattice, \mathbf{k} is the wave vector of the Bloch wave, \mathbf{r} is the electron position, m is the band index, and the sum is over all N atomic sites. The Bloch wave is an exact eigensolution for the wave function of an electron in a periodic crystal potential corresponding to an energy $E_m(\mathbf{k})$, and is spread over the entire crystal volume.

Using the Fourier transform analysis, a spatially localized wave function for the m -th energy band can be constructed from multiple Bloch waves:

$$a_m(\mathbf{R}_n, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{R}_n} \psi_m(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r} - \mathbf{R}_n)} u_m(\mathbf{k}, \mathbf{r}).$$

These real space wave functions $a_m(\mathbf{R}_n, \mathbf{r})$ are called Wannier functions, and are fairly closely localized to the atomic site \mathbf{R}_n . Of course, if we have exact Wannier functions, the exact Bloch functions can be derived using the inverse Fourier transform.

However it is not easy to calculate directly either Bloch functions or Wannier functions. An approximate approach is necessary in the calculation of electronic structures of solids. If we consider the extreme case of isolated atoms, the Wannier function would become an isolated atomic orbital. That limit suggests the choice of an atomic wave function as an approximate form for the Wannier function, the so-called tight binding approximation.

Second quantization

Modern explanations of electronic structure like t-J model and Hubbard model are based on tight binding model. If we introduce second quantization formalism, it is clear to understand the concept of tight binding model.

Using the atomic orbital as a basis state, we can establish the second quantization Hamiltonian operator in tight binding model.

$$H = -t \sum_{\langle i,j \rangle, \sigma} (c_{i,\sigma}^\dagger c_{j,\sigma} + h.c.),$$

$c_{i,\sigma}^\dagger, c_{j,\sigma}$ - creation and annihilation operators

σ - spin polarization

t - hopping integral

$\langle i, j \rangle$ -nearest neighbor index

Here, hopping integral t corresponds to the transfer integral γ in tight binding model. Considering extreme cases of $t \rightarrow 0$, it is impossible for electron to hop into neighboring sites. This case is the isolated atomic system. If the hopping term is turned on ($t > 0$) electrons can stay in both sites lowering their kinetic energy.

In the strongly correlated electron system, it is necessary to consider the electron-electron interaction. This term can be written in

$$H_{ee} = \frac{1}{2} \sum_{n, n', \sigma} \langle n_1 m_1, n_2 m_2 | \frac{e^2}{|r_1 - r_2|} | n_3 m_3, n_4 m_4 \rangle c_{n_1 m_1 \sigma_1}^\dagger c_{n_2 m_2 \sigma_2}^\dagger c_{n_4 m_4 \sigma_2} c_{n_3 m_3 \sigma_1}$$

This interaction Hamiltonian includes direct Coulomb interaction energy and exchange interaction energy between electrons. There are several novel physics induced from this electron-electron interaction energy, such as metal-insulator transitions (MIT), high-temperature superconductivity, and several quantum phase transitions.

Example: one-dimensional s-band

Here the tight binding model is illustrated with a **s-band model** for a string of atoms with a single s-orbital in a straight line with spacing a and σ bonds between atomic sites.

To find approximate eigenstates of the Hamiltonian, we can use a linear combination of the atomic orbitals

$$|k\rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{inka} |n\rangle$$

where N = total number of sites and k is a real parameter with $-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$. (This wave function is normalized to unity by the leading factor $1/\sqrt{N}$ provided overlap of atomic wave functions is ignored.) Assuming only nearest neighbor overlap, the only non-zero matrix elements of the Hamiltonian can be expressed as

$$\langle n | H | n \rangle = E_0 = E_i - U .$$

$$\langle n \pm 1 | H | n \rangle = -\Delta$$

$$\langle n | n \rangle = 1 ; \langle n \pm 1 | n \rangle = S .$$

The energy E_i is the ionization energy corresponding to the chosen atomic orbital and U is the energy shift of the orbital as a result of the potential of neighboring atoms. The $\langle n \pm 1 | H | n \rangle = -\Delta$ elements, which are the Slater and Koster interatomic matrix elements, are the bond energies $E_{i,j}$. In this one dimensional s-band model we only have σ -bonds between the s-orbitals with bond energy $E_{s,s} = V_{ss\sigma}$. The overlap between states on neighboring atoms is S . We can derive the energy of the state $|k\rangle$ using the above equation:

$$H|k\rangle = \frac{1}{\sqrt{N}} \sum_n e^{inka} H|n\rangle$$

$$\langle k|H|k\rangle = \frac{1}{N} \sum_{n, m} e^{i(n-m)ka} \langle m|H|n\rangle = \frac{1}{N} \sum_n \langle n|H|n\rangle + \frac{1}{N} \sum_n \langle n-1|H|n\rangle e^{+ika} + \frac{1}{N} \sum_n \langle n+1|H|n\rangle e^{-ika}$$

where, for example,

$$\frac{1}{N} \sum_n \langle n|H|n\rangle = E_0 \frac{1}{N} \sum_n 1 = E_0 ,$$

and

$$\frac{1}{N} \sum_n \langle n-1|H|n\rangle e^{+ika} = -\Delta e^{ika} \frac{1}{N} \sum_n 1 = -\Delta e^{ika} .$$

$$\frac{1}{N} \sum_n \langle n-1|H|n\rangle e^{-ika} = S e^{ika} \frac{1}{N} \sum_n 1 = S e^{ika} .$$

Thus the energy of this state $|k\rangle$ can be represented in the familiar form of the energy dispersion:

$$E(k) = \frac{E_0 - 2\Delta \cos(ka)}{1 + 2S \cos(ka)} .$$

- For $k = 0$ the energy is $E = (E_0 - 2\Delta)/(1 + 2S)$ and the state consists of a sum of all atomic orbitals. This state can be viewed as a chain of bonding orbitals.
- For $k = \pi/(2a)$ the energy is $E = E_0$ and the state consists of a sum of atomic orbitals which are a factor $e^{i\pi/2}$ out of phase. This state can be viewed as a chain of non-bonding orbitals.
- Finally for $k = \pi/a$ the energy is $E = (E_0 + 2\Delta)/(1 - 2S)$ and the state consists of an alternating sum of atomic orbitals. This state can be viewed as a chain of anti-bonding orbitals.

This example is readily extended to three dimensions, for example, to a body-centered cubic or face-centered cubic lattice by introducing the nearest neighbor vector locations in place of simply $n a$. Likewise, the method can be extended to multiple bands using multiple different atomic orbitals at each site. The general formulation above shows how these extensions can be accomplished.

Table of interatomic matrix elements

In 1954 J.C. Slater and F.G. Koster published, mainly for the calculation of transition metal d-bands, a table of interatomic matrix elements

$$E_{i,j}(\vec{r}_{n,n'}) = \langle n, i|H|n', j\rangle$$

which, with a little patience and effort, can also be derived from the cubic harmonic orbitals straightforwardly. The table expresses the matrix elements as functions of LCAO two-centre bond integrals between two cubic harmonic orbitals, i and j , on adjacent atoms. The bond integrals are for example the $V_{ss\sigma}$, $V_{pp\pi}$ and $V_{dd\delta}$ for sigma, pi and delta bonds.

The interatomic vector is expressed as

$$\vec{r}_{n,n'} = (r_x, r_y, r_z) = d(l, m, n)$$

where d is the distance between the atoms and l, m and n are the direction cosines to the neighboring atom.

$$E_{s,s} = V_{ss\sigma}$$

$$E_{s,x} = lV_{sp\sigma}$$

$$E_{x,x} = l^2V_{pp\sigma} + (1 - l^2)V_{pp\pi}$$

$$E_{x,y} = lmV_{pp\sigma} - lmV_{pp\pi}$$

$$E_{x,z} = lnV_{pp\sigma} - lnV_{pp\pi}$$

$$E_{s,xy} = \sqrt{3}lmV_{sd\sigma}$$

$$E_{s,x^2-y^2} = \frac{\sqrt{3}}{2}(l^2 - m^2)V_{sd\sigma}$$

$$\begin{aligned}
E_{s,3z^2-r^2} &= [n^2 - (l^2 + m^2)/2]V_{sd\sigma} \\
E_{x,xy} &= \sqrt{3}l^2mV_{pd\sigma} + m(1 - 2l^2)V_{pd\pi} \\
E_{x,yz} &= \sqrt{3}lmnV_{pd\sigma} - 2lmnV_{pd\pi} \\
E_{x,zx} &= \sqrt{3}l^2nV_{pd\sigma} + n(1 - 2l^2)V_{pd\pi} \\
E_{x,x^2-y^2} &= \frac{\sqrt{3}}{2}l(l^2 - m^2)V_{pd\sigma} + l(1 - l^2 + m^2)V_{pd\pi} \\
E_{y,x^2-y^2} &= \frac{\sqrt{3}}{2}m(l^2 - m^2)V_{pd\sigma} - m(1 + l^2 - m^2)V_{pd\pi} \\
E_{z,x^2-y^2} &= \frac{\sqrt{3}}{2}n(l^2 - m^2)V_{pd\sigma} - n(l^2 - m^2)V_{pd\pi} \\
E_{x,3z^2-r^2} &= l[n^2 - (l^2 + m^2)/2]V_{pd\sigma} - \sqrt{3}ln^2V_{pd\pi} \\
E_{y,3z^2-r^2} &= m[n^2 - (l^2 + m^2)/2]V_{pd\sigma} - \sqrt{3}mn^2V_{pd\pi} \\
E_{z,3z^2-r^2} &= n[n^2 - (l^2 + m^2)/2]V_{pd\sigma} + \sqrt{3}n(l^2 + m^2)V_{pd\pi} \\
E_{xy,xy} &= 3l^2m^2V_{dd\sigma} + (l^2 + m^2 - 4l^2m^2)V_{dd\pi} + (n^2 + l^2m^2)V_{dd\delta} \\
E_{xy,yz} &= 3lm^2nV_{dd\sigma} + ln(1 - 4m^2)V_{dd\pi} + ln(m^2 - 1)V_{dd\delta} \\
E_{xy,zx} &= 3l^2mnV_{dd\sigma} + mn(1 - 4l^2)V_{dd\pi} + mn(l^2 - 1)V_{dd\delta} \\
E_{xy,x^2-y^2} &= \frac{3}{2}lm(l^2 - m^2)V_{dd\sigma} + 2lm(m^2 - l^2)V_{dd\pi} + lm(l^2 - m^2)/2V_{dd\delta} \\
E_{yz,x^2-y^2} &= \frac{3}{2}mn(l^2 - m^2)V_{dd\sigma} - mn[1 + 2(l^2 - m^2)]V_{dd\pi} + mn[1 + (l^2 - m^2)/2]V_{dd\delta} \\
E_{zx,x^2-y^2} &= \frac{3}{2}nl(l^2 - m^2)V_{dd\sigma} + nl[1 - 2(l^2 - m^2)]V_{dd\pi} - nl[1 - (l^2 - m^2)/2]V_{dd\delta} \\
E_{xy,3z^2-r^2} &= \sqrt{3} \left[lm(n^2 - (l^2 + m^2)/2)V_{dd\sigma} - 2lmn^2V_{dd\pi} + lm(1 + n^2)/2V_{dd\delta} \right] \\
E_{yz,3z^2-r^2} &= \sqrt{3} \left[mn(n^2 - (l^2 + m^2)/2)V_{dd\sigma} + mn(l^2 + m^2 - n^2)V_{dd\pi} - mn(l^2 + m^2)/2V_{dd\delta} \right] \\
E_{zx,3z^2-r^2} &= \sqrt{3} \left[ln(n^2 - (l^2 + m^2)/2)V_{dd\sigma} + ln(l^2 + m^2 - n^2)V_{dd\pi} - ln(l^2 + m^2)/2V_{dd\delta} \right] \\
E_{x^2-y^2,x^2-y^2} &= \frac{3}{4}(l^2 - m^2)^2V_{dd\sigma} + [l^2 + m^2 - (l^2 - m^2)^2]V_{dd\pi} + [n^2 + (l^2 - m^2)^2/4]V_{dd\delta} \\
E_{x^2-y^2,3z^2-r^2} &= \sqrt{3} \left[(l^2 - m^2)[n^2 - (l^2 + m^2)/2]V_{dd\sigma}/2 + n^2(m^2 - l^2)V_{dd\pi} + (1 + n^2)(l^2 - m^2)/4V_{dd\delta} \right] \\
E_{3z^2-r^2,3z^2-r^2} &= [n^2 - (l^2 + m^2)/2]^2V_{dd\sigma} + 3n^2(l^2 + m^2)V_{dd\pi} + \frac{3}{4}(l^2 + m^2)^2V_{dd\delta}
\end{aligned}$$

Not all interatomic matrix elements are listed explicitly. Matrix elements that are not listed in this table can be constructed by permutation of indices and cosine directions of other matrix elements in the table.

References

- [1] As an alternative to neglecting overlap, one may choose as a basis instead of atomic orbitals a set of orbitals based upon atomic orbitals but arranged to be orthogonal to orbitals on other atomic sites, the so-called Löwdin orbitals. See
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External links

- Crystal-field Theory, Tight-binding Method, and Jahn-Teller Effect (<http://www.cond-mat.de/events/correl12/manuscripts/pavarini.pdf>) in E. Pavarini, E. Koch, F. Anders, and M. Jarrell (eds.): *Correlated Electrons: From Models to Materials*, Jülich 2012, ISBN 978-3-89336-796-2

Nearly free electron model

| |
|---|
| Electronic structure methods |
| Valence bond theory |
| Generalized valence bond Modern valence bond |
| Molecular orbital theory |
| Hartree–Fock method Møller–Plesset perturbation theory Configuration interaction Coupled cluster Multi-configurational self-consistent field Quantum chemistry composite methods Quantum Monte Carlo Linear combination of atomic orbitals |
| Electronic band structure |
| Nearly free electron model Tight binding Muffin-tin approximation Density functional theory k·p perturbation theory Empty lattice approximation |
|  Book |

In solid-state physics, the **nearly free electron model** (or **NFE model**) is a quantum mechanical model of physical properties of electrons that can move almost freely through the crystal lattice of a solid. The model is closely related to the more conceptual Empty Lattice Approximation. The model enables understanding and calculating the electronic band structure of especially metals.

Introduction

Free electrons are traveling plane waves. Generally the time independent part of their wave function is expressed as

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_r}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

These plane wave solutions have an energy of

$$E_k = \frac{\hbar^2 k^2}{2m}$$

The expression of the plane wave as a complex exponential function can also be written as the sum of two periodic functions which are mutually shifted a quarter of a period.

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega_r}} [\cos(\mathbf{k} \cdot \mathbf{r}) + i \sin(\mathbf{k} \cdot \mathbf{r})]$$

In this light the wave function of a free electron can be viewed as an aggregate of two plane waves. Sine and cosine functions can also be expressed as sums or differences of plane waves moving in opposite directions

$$\cos(\mathbf{k} \cdot \mathbf{r}) = \frac{1}{2} [e^{i\mathbf{k}\cdot\mathbf{r}} + e^{-i\mathbf{k}\cdot\mathbf{r}}]$$

Assume that there is only one kind of atom present in the lattice and that the atoms are located at the origin of the unit cells of the lattice. The potential of the atoms is attractive and limited to a relatively small part of the volume of the unit cell of the lattice. In the remainder of the cell the potential is zero.

The Hamiltonian is expressed as

$$H = T + V$$

in which T is the kinetic and V is the potential energy. From this expression the energy expectation value, or the statistical average, of the energy of the electron can be calculated with

$$E = \langle H \rangle = \int_{\Omega_r} \psi_{\mathbf{k}}^*(\mathbf{r}) [T + V] \psi_{\mathbf{k}}(\mathbf{r}) d\mathbf{r}$$

If we assume that the electron still has a free electron plane wave wave function the energy of the electron is:

$$E_{\mathbf{k}} = \frac{1}{\Omega_r} \int_{\Omega_r} e^{-i\mathbf{k}\cdot\mathbf{r}} \left[\frac{\hbar^2 k^2}{2m} + V(\mathbf{r}) \right] e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}$$

Let's assume further that at an arbitrary \mathbf{k} -point in the Brillouin zone we can integrate the \mathbf{r} over a single lattice cell, then for an arbitrary \mathbf{k} -point the energy becomes

$$E_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} + \langle V \rangle$$

This means that at an arbitrary point the energy is lowered by the lowered average of the potential in the unit cell due to the presence of the attractive potential of the atom. If the potential is very small we get the Empty Lattice Approximation. This isn't a very sensational result and it doesn't say anything about what happens when we get close to the Brillouin zone boundary. We will look at those regions in \mathbf{k} -space now.

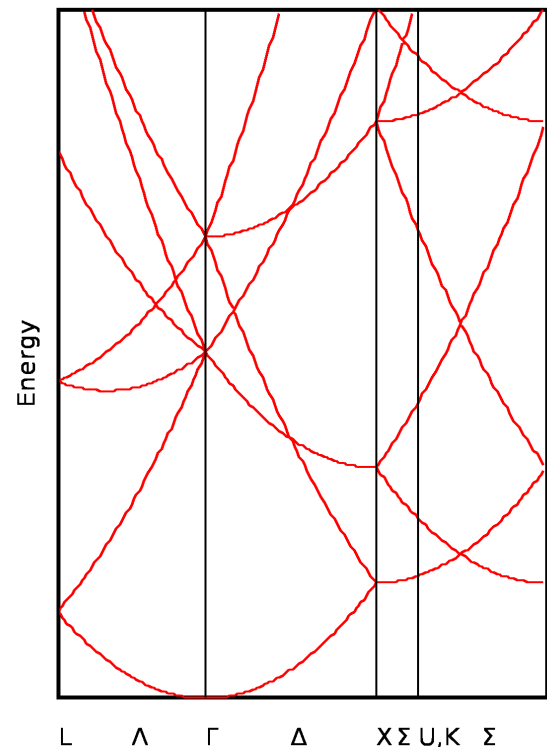
Let's assume that we look at the problem from the origin, at position $\mathbf{r} = 0$. If $\mathbf{k} = 0$ only the cosine part is present and the sine part is moved to ∞ . If we let the length of the wave vector \mathbf{k} grow, then the central maximum of the cosine part stays at $\mathbf{r} = 0$. The first maximum and minimum of the sine part are at $\mathbf{r} = \pm\pi/(2\mathbf{k})$. They come nearer as \mathbf{k} grows. Let's assume that \mathbf{k} is close to the Brillouin zone boundary for the analysis in the next part of this introduction.

The atomic positions coincide with the maximum of the $\cos(\mathbf{k} \cdot \mathbf{r})$ -component of the wave function. The interaction of the $\cos(\mathbf{k} \cdot \mathbf{r})$ -component of the wave function with the potential will be different than the interaction of the $\sin(\mathbf{k} \cdot \mathbf{r})$ -component of the wave

function with the potential because their phases are shifted. The charge density is proportional to the absolute square of the wave function. For the $\cos(\mathbf{k} \cdot \mathbf{r})$ -component it is

$$\rho_{\mathbf{k}}^c(\mathbf{r}) = \frac{1}{2\Omega} [1 + \cos(2\mathbf{k} \cdot \mathbf{r})]$$

and for the $\sin(\mathbf{k} \cdot \mathbf{r})$ -component it is



Some free electron bands in a FCC crystal structure according to the Empty Lattice Approximation

$$\rho_{\mathbf{k}}^s(\mathbf{r}) = \frac{1}{2\Omega} [1 - \cos(2\mathbf{k} \cdot \mathbf{r})]$$

For values of \mathbf{k} close to the Brillouin zone boundary, the length of the two waves and the period of the two different charge density distributions almost coincide with the periodic potential of the lattice. As a result the charge densities of the two components have a different energy because the maximum of the charge density of the $\cos(\mathbf{k} \cdot \mathbf{r})$ -component coincides with the attractive potential of the atoms while the maximum of the charge density of the $\sin(\mathbf{k} \cdot \mathbf{r})$ -component lies in the regions with a higher electrostatic potential between the atoms.

As a result the aggregate will be split in high and low energy components when the kinetic energy increases and the wave vector approaches the length of the reciprocal lattice vectors. The potentials of the atomic cores can be decomposed into Fourier components to meet the requirements of a description in terms of reciprocal space parameters.

Mathematical formulation

The nearly free electron model is a modification of the free-electron gas model which includes a *weak* periodic perturbation meant to model the interaction between the conduction electrons and the ions in a crystalline solid. This model, like the free-electron model, does not take into account electron-electron interactions; that is, the independent-electron approximation is still in effect.

As shown by Bloch's theorem, introducing a periodic potential into the Schrödinger equation results in a wave function of the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k} \cdot \mathbf{r}}$$

where the function u has the same periodicity as the lattice:

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$$

(where T is a lattice translation vector.)

Because it is a *nearly* free electron approximation we can assume that

$$u_{\mathbf{k}}(\mathbf{r}) \approx \frac{1}{\sqrt{\Omega_r}}$$

A solution of this form can be plugged into the Schrödinger equation, resulting in the **central equation**:

$$(\lambda_{\mathbf{k}} - \epsilon)C_{\mathbf{k}} + \sum_{\mathbf{G}} U_{\mathbf{G}}C_{\mathbf{k}-\mathbf{G}} = 0$$

where the kinetic energy $\lambda_{\mathbf{k}}$ is given by

$$\lambda_{\mathbf{k}}\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi_{\mathbf{k}}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2(u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k} \cdot \mathbf{r}})$$

which, after dividing by $\psi_{\mathbf{k}}(\mathbf{r})$, reduces to

$$\lambda_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m}$$

if we assume that $u_{\mathbf{k}}(\mathbf{r})$ is almost constant and $\nabla^2 u_{\mathbf{k}}(\mathbf{r}) \ll k^2$.

The reciprocal parameters C_k and U_G are the Fourier coefficients of the wave function $\psi(r)$ and the screened potential energy $U(r)$, respectively:

$$U(\mathbf{r}) = \sum_{\mathbf{G}} U_{\mathbf{G}}e^{i\mathbf{G} \cdot \mathbf{r}}$$

$$\psi(\mathbf{r}) = \sum_{\mathbf{k}} C_{\mathbf{k}}e^{i\mathbf{k} \cdot \mathbf{r}}$$

The vectors G are the reciprocal lattice vectors, and the discrete values of k are determined by the boundary conditions of the lattice under consideration.

In any perturbation analysis, one must consider the base case to which the perturbation is applied. Here, the base case is with $U(x) = 0$, and therefore all the Fourier coefficients of the potential are also zero. In this case the central equation reduces to the form

$$(\lambda_{\mathbf{k}} - \epsilon)C_{\mathbf{k}} = 0$$

This identity means that for each k , one of the two following cases must hold:

1. $C_{\mathbf{k}} = 0$,
2. $\lambda_{\mathbf{k}} = \epsilon$

If the values of $\lambda_{\mathbf{k}}$ are non-degenerate, then the second case occurs for only one value of k , while for the rest, the Fourier expansion coefficient $C_{\mathbf{k}}$ must be zero. In this non-degenerate case, the standard free electron gas result is retrieved:

$$\psi_{\mathbf{k}} \propto e^{i\mathbf{k}\cdot\mathbf{r}}$$

In the degenerate case, however, there will be a set of lattice vectors k_1, \dots, k_m with $\lambda_1 = \dots = \lambda_m$. When the energy ϵ is equal to this value of λ , there will be m independent plane wave solutions of which any linear combination is also a solution:

$$\psi \propto \sum_{i=1}^m A_i e^{i\mathbf{k}_i \cdot \mathbf{r}}$$

Non-degenerate and degenerate perturbation theory can be applied in these two cases to solve for the Fourier coefficients $C_{\mathbf{k}}$ of the wavefunction (correct to first order in U) and the energy eigenvalue (correct to second order in U). An important result of this derivation is that there is no first-order shift in the energy ϵ in the case of no degeneracy, while there is in the case of near-degeneracy, implying that the latter case is more important in this analysis. Particularly, at the Brillouin zone boundary (or, equivalently, at any point on a Bragg plane), one finds a twofold energy degeneracy that results in a shift in energy given by:

$$\epsilon = \lambda_{\mathbf{k}} \pm |U_{\mathbf{k}}|$$

This **energy gap** between Brillouin zones is known as the band gap, with a magnitude of $2|U_{\mathbf{k}}|$.

Results

Introducing this weak perturbation has significant effects on the solution to the Schrödinger equation, most significantly resulting in a band gap between wave vectors in different Brillouin zones.

Justifications


In this model, the assumption is made that the interaction between the conduction electrons and the ion cores can be modeled through the use of a "weak" perturbing potential. This may seem like a severe approximation, for the Coulomb attraction between these two particles of opposite charge can be quite significant at short distances. It can be partially justified, however, by noting two important properties of the quantum mechanical system:

1. The force between the ions and the electrons is greatest at very small distances. However, the conduction electrons are not "allowed" to get this close to the ion cores due to the Pauli exclusion principle: the orbitals closest to the ion core are already occupied by the core electrons. Therefore, the conduction electrons never get close enough to the ion cores to feel their full force.
2. Furthermore, the core electrons shield the ion charge magnitude "seen" by the conduction electrons. The result is an *effective nuclear charge* experienced by the conduction electrons which is significantly reduced from the actual nuclear charge.

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Hartree–Fock method

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| Electronic structure methods |
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| Molecular orbital theory |
| Hartree–Fock method Møller–Plesset perturbation theory Configuration interaction Coupled cluster Multi-configurational self-consistent field Quantum chemistry composite methods Quantum Monte Carlo Linear combination of atomic orbitals |
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In computational physics and chemistry, the **Hartree–Fock (HF)** method is a method of approximation for the determination of the wave function and the energy of a quantum many-body system in a stationary state.

The Hartree–Fock method often assumes that the exact, N -body wave function of the system can be approximated by a single Slater determinant (in the case where the particles are fermions) or by a single permanent (in the case of bosons) of N spin-orbitals. By invoking the variational method, one can derive a set of N -coupled equations for the N spin orbitals. A solution of these equations yields the Hartree–Fock wave function and energy of the system.

Especially in the older literature, the Hartree–Fock method is also called the **self-consistent field method (SCF)**. In deriving what is now called the Hartree equation as an approximate solution of the Schrödinger equation, Hartree required the final field as computed from the charge distribution to be "self-consistent" with the assumed initial field. Thus, self-consistency was a requirement of the solution. The solutions to the non-linear Hartree–Fock equations also behave as if each particle is subjected to the mean field created by all other particles (see the Fock operator below) and hence the terminology continued. The equations are almost universally solved by means of an iterative method, although the fixed-point iteration algorithm does not always converge. This solution scheme is not the only one possible and is not an essential feature of the Hartree–Fock method.

The Hartree–Fock method finds its typical application in the solution of the Schrödinger equation for atoms, molecules, nanostructures and solids but it has also found widespread use in nuclear physics. (See Hartree–Fock–Bogoliubov method for a discussion of its application in nuclear structure theory). In atomic structure theory, calculations may be for a spectrum with many excited energy levels and consequently the Hartree–Fock method for atoms assumes the wave function is a single configuration state function with well-defined quantum numbers and that the energy level is not necessarily the ground state.

For both atoms and molecules, the Hartree–Fock solution is the central starting point for most methods that describe the many-electron system more accurately.

The rest of this article will focus on applications in electronic structure theory suitable for molecules with the atom as a special case. The discussion here is only for the Restricted Hartree–Fock method, where the atom or molecule is a closed-shell system with all orbitals (atomic or molecular) doubly occupied. Open-shell systems, where some of the electrons are not paired, can be dealt with by one of two Hartree–Fock methods:

- Restricted open-shell Hartree–Fock (ROHF)
- Unrestricted Hartree–Fock (UHF)

Brief history

The origin of the Hartree–Fock method dates back to the end of the 1920s, soon after the discovery of the Schrödinger equation in 1926. In 1927 D. R. Hartree introduced a procedure, which he called the self-consistent field method, to calculate approximate wave functions and energies for atoms and ions. Hartree was guided by some earlier, semi-empirical methods of the early 1920s (by E. Fues, R. B. Lindsay, and himself) set in the old quantum theory of Bohr.

In the Bohr model of the atom, the energy of a state with principal quantum number n is given in atomic units as $E = -1/n^2$. It was observed from atomic spectra that the energy levels of many-electron atoms are well described by applying a modified version of Bohr's formula. By introducing the quantum defect d as an empirical parameter, the energy levels of a generic atom were well approximated by the formula $E = -1/(n + d)^2$, in the sense that one could reproduce fairly well the observed transitions levels observed in the X-ray region (for example, see the empirical discussion and derivation in Moseley's law). The existence of a non-zero quantum defect was attributed to electron–electron repulsion, which clearly does not exist in the isolated hydrogen atom. This repulsion resulted in partial screening of the bare nuclear charge. These early researchers later introduced other potentials containing additional empirical parameters with the hope of better reproducing the experimental data.

Hartree sought to do away with empirical parameters and solve the many-body time-independent Schrödinger equation from fundamental physical principles, i.e., *ab initio*. His first proposed method of solution became known as the **Hartree method**. However, many of Hartree's contemporaries did not understand the physical reasoning behind the Hartree method: it appeared to many people to contain empirical elements, and its connection to the solution of the many-body Schrödinger equation was unclear. However, in 1928 J. C. Slater and J. A. Gaunt independently showed that the Hartree method could be couched on a sounder theoretical basis by applying the variational principle to an ansatz (trial wave function) as a product of single-particle functions.

In 1930 Slater and V. A. Fock independently pointed out that the Hartree method did not respect the principle of antisymmetry of the wave function. The Hartree method used the Pauli exclusion principle in its older formulation, forbidding the presence of two electrons in the same quantum state. However, this was shown to be fundamentally incomplete in its neglect of quantum statistics.

It was then shown that a Slater determinant, a determinant of one-particle orbitals first used by Heisenberg and Dirac in 1926, trivially satisfies the antisymmetric property of the exact solution and hence is a suitable ansatz for applying the variational principle. The original Hartree method can then be viewed as an approximation to the Hartree–Fock method by neglecting exchange. Fock's original method relied heavily on group theory and was too abstract for

contemporary physicists to understand and implement. In 1935 Hartree reformulated the method more suitably for the purposes of calculation.

The Hartree–Fock method, despite its physically more accurate picture, was little used until the advent of electronic computers in the 1950s due to the much greater computational demands over the early Hartree method and empirical models. Initially, both the Hartree method and the Hartree–Fock method were applied exclusively to atoms, where the spherical symmetry of the system allowed one to greatly simplify the problem. These approximate methods were (and are) often used together with the central field approximation, to impose that electrons in the same shell have the same radial part, and to restrict the variational solution to be a spin eigenfunction. Even so, solution by hand of the Hartree–Fock equations for a medium sized atom were laborious; small molecules required computational resources far beyond what was available before 1950.

Hartree–Fock algorithm

The Hartree–Fock method is typically used to solve the time-independent Schrödinger equation for a multi-electron atom or molecule as described in the Born–Oppenheimer approximation. Since there are no known solutions for many-electron systems (hydrogenic atoms and the diatomic hydrogen cation being notable one-electron exceptions), the problem is solved numerically. Due to the nonlinearities introduced by the Hartree–Fock approximation, the equations are solved using a nonlinear method such as iteration, which gives rise to the name "self-consistent field method."

Approximations

The Hartree–Fock method makes five major simplifications in order to deal with this task:

- The Born–Oppenheimer approximation is inherently assumed. The full molecular wave function is actually a function of the coordinates of each of the nuclei, in addition to those of the electrons.
- Typically, relativistic effects are completely neglected. The momentum operator is assumed to be completely non-relativistic.
- The variational solution is assumed to be a linear combination of a finite number of basis functions, which are usually (but not always) chosen to be orthogonal. The finite basis set is assumed to be approximately complete.
- Each energy eigenfunction is assumed to be describable by a single Slater determinant, an antisymmetrized product of one-electron wave functions (i.e., orbitals).
- The mean field approximation is implied. Effects arising from deviations from this assumption, known as electron correlation, are completely neglected for the electrons of opposite spin, but are taken into account for electrons of parallel spin. (Electron correlation should not be confused with electron exchange, which is fully accounted for in the Hartree–Fock method.)

Relaxation of the last two approximations give rise to many so-called post-Hartree–Fock methods.

Variational optimization of orbitals

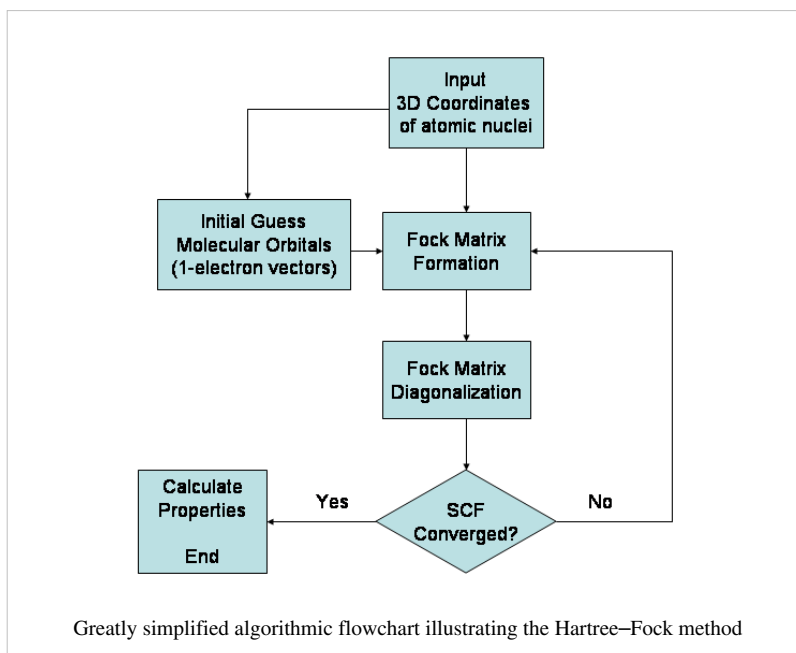
The variational theorem states that for a time-independent Hamiltonian operator, any trial wave function will have an energy expectation value that is greater than or equal to the true ground state wave function corresponding to the given Hamiltonian. Because of this, the Hartree–Fock energy is an upper bound to the true ground state energy of a given molecule. In the context of the Hartree–Fock method, the best possible solution is at the *Hartree–Fock limit*; i.e., the limit of the Hartree–Fock energy as the basis

set approaches completeness. (The other is the *full-CI limit*, where the last two approximations of the Hartree–Fock theory as described above are completely undone. It is only when both limits are attained that the exact solution, up to the Born–Oppenheimer approximation, is obtained.) The Hartree–Fock energy is the minimal energy for a single Slater determinant.

The starting point for the Hartree–Fock method is a set of approximate one-electron wave functions known as *spin-orbitals*. For an atomic orbital calculation, these are typically the orbitals for a hydrogenic atom (an atom with only one electron, but the appropriate nuclear charge). For a molecular orbital or crystalline calculation, the initial approximate one-electron wave functions are typically a linear combination of atomic orbitals (LCAO).

The orbitals above only account for the presence of other electrons in an average manner. In the Hartree–Fock method, the effect of other electrons are accounted for in a mean-field theory context. The orbitals are optimized by requiring them to minimize the energy of the respective Slater determinant. The resultant variational conditions on the orbitals lead to a new one-electron operator, the Fock operator. At the minimum, the occupied orbitals are eigensolutions to the Fock operator via a unitary transformation between themselves. The Fock operator is an effective one-electron Hamiltonian operator being the sum of two terms. The first is a sum of kinetic energy operators for each electron, the internuclear repulsion energy, and a sum of nuclear-electronic Coulombic attraction terms. The second are Coulombic repulsion terms between electrons in a mean-field theory description; a net repulsion energy for each electron in the system, which is calculated by treating all of the other electrons within the molecule as a smooth distribution of negative charge. This is the major simplification inherent in the Hartree–Fock method, and is equivalent to the fifth simplification in the above list.

Since the Fock operator depends on the orbitals used to construct the corresponding Fock matrix, the eigenfunctions of the Fock operator are in turn new orbitals which can be used to construct a new Fock operator. In this way, the Hartree–Fock orbitals are optimized iteratively until the change in total electronic energy falls below a predefined threshold. In this way, a set of self-consistent one-electron orbitals are calculated. The Hartree–Fock electronic wave function is then the Slater determinant constructed out of these orbitals. Following the basic postulates of quantum mechanics, the Hartree–Fock wave function can then be used to compute any desired chemical or physical property within the framework of the Hartree–Fock method and the approximations employed.



Mathematical formulation

The Fock operator

Because the electron-electron repulsion term of the electronic molecular Hamiltonian involves the coordinates of two different electrons, it is necessary to reformulate it in an approximate way. Under this approximation, (outlined under Hartree–Fock algorithm), all of the terms of the exact Hamiltonian except the nuclear-nuclear repulsion term are re-expressed as the sum of one-electron operators outlined below, for closed-shell atoms or molecules (with two electrons in each spatial orbital).^[1] The "(1)" following each operator symbol simply indicates that the operator is 1-electron in nature.

$$\hat{F}[\{\phi_j\}](1) = \hat{H}^{\text{core}}(1) + \sum_{j=1}^{N/2} [2\hat{J}_j(1) - \hat{K}_j(1)]$$

where

$$\hat{F}[\{\phi_j\}](1)$$

is the one-electron Fock operator generated by the orbitals ϕ_j , and

$$\hat{H}^{\text{core}}(1) = -\frac{1}{2}\nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}}$$

is the one-electron core Hamiltonian. Also

$$\hat{J}_j(1)$$

is the Coulomb operator, defining the electron-electron repulsion energy due to each of the two electrons in the j th orbital. Finally

$$\hat{K}_j(1)$$

is the exchange operator, defining the electron exchange energy due to the antisymmetry of the total n -electron wave function. Finding the Hartree–Fock one-electron wave functions is now equivalent to solving the eigenfunction equation:

$$\hat{F}(1)\phi_i(1) = \epsilon_i\phi_i(1)$$

where $\phi_i(1)$ are a set of one-electron wave functions, called the Hartree–Fock molecular orbitals.

Linear combination of atomic orbitals

Typically, in modern Hartree–Fock calculations, the one-electron wave functions are approximated by a linear combination of atomic orbitals. These atomic orbitals are called Slater-type orbitals. Furthermore, it is very common for the "atomic orbitals" in use to actually be composed of a linear combination of one or more Gaussian-type orbitals, rather than Slater-type orbitals, in the interests of saving large amounts of computation time.

Various basis sets are used in practice, most of which are composed of Gaussian functions. In some applications, an orthogonalization method such as the Gram–Schmidt process is performed in order to produce a set of orthogonal basis functions. This can in principle save computational time when the computer is solving the Roothaan–Hall equations by converting the overlap matrix effectively to an identity matrix. However, in most modern computer programs for molecular Hartree–Fock calculations this procedure is not followed due to the high numerical cost of orthogonalization and the advent of more efficient, often sparse, algorithms for solving the generalized eigenvalue problem, of which the Roothaan–Hall equations are an example.

Numerical stability

Numerical stability can be a problem with this procedure and there are various ways of combating this instability. One of the most basic and generally applicable is called *F-mixing* or damping. With F-mixing, once a single electron wave function is calculated it is not used directly. Instead, some combination of that calculated wave function and the previous wave functions for that electron is used—the most common being a simple linear combination of the calculated and immediately preceding wave function. A clever dodge, employed by Hartree, for atomic calculations was to increase the nuclear charge, thus pulling all the electrons closer together. As the system stabilised, this was gradually reduced to the correct charge. In molecular calculations a similar approach is sometimes used by first calculating the wave function for a positive ion and then to use these orbitals as the starting point for the neutral molecule. Modern molecular Hartree–Fock computer programs use a variety of methods to ensure convergence of the Roothaan–Hall equations.

Weaknesses, extensions, and alternatives

Of the five simplifications outlined in the section "Hartree–Fock algorithm", the fifth is typically the most important. Neglecting electron correlation can lead to large deviations from experimental results. A number of approaches to this weakness, collectively called post-Hartree–Fock methods, have been devised to include electron correlation to the multi-electron wave function. One of these approaches, Møller–Plesset perturbation theory, treats correlation as a perturbation of the Fock operator. Others expand the true multi-electron wave function in terms of a linear combination of Slater determinants—such as multi-configurational self-consistent field, configuration interaction, quadratic configuration interaction, and complete active space SCF (CASSCF). Still others (such as variational quantum Monte Carlo) modify the Hartree–Fock wave function by multiplying it by a correlation function ("Jastrow" factor), a term which is explicitly a function of multiple electrons that cannot be decomposed into independent single-particle functions.

An alternative to Hartree–Fock calculations used in some cases is density functional theory, which treats both exchange and correlation energies, albeit approximately. Indeed, it is common to use calculations that are a hybrid of the two methods—the popular B3LYP scheme is one such hybrid functional method. Another option is to use modern valence bond methods.

Software packages

For a list of software packages known to handle Hartree–Fock calculations, particularly for molecules and solids, see the list of quantum chemistry and solid state physics software.

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External links

- Introduction by C. David Sherrill (<http://vergil.chemistry.gatech.edu/notes/hf-intro/hf-intro.html>)

Modern valence bond

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Modern valence bond theory is the application of valence bond theory, with computer programs that are competitive in accuracy and economy with programs for the Hartree-Fock method and other molecular orbital based methods. The latter methods dominated quantum chemistry from the advent of digital computers because they were easier to program. The early popularity of valence bond methods thus declined. It is only recently that the programming of valence bond methods has improved. These developments are due to and described by Gerratt, Cooper, Karadakov and Raimondi (1997); Li and McWeeny (2002); Joop H. van Lenthe and co-workers (2002);^[1] Song, Mo, Zhang and Wu (2005); and Shaik and Hiberty (2004).^[2]

In its simplest form the overlapping atomic orbitals are replaced by orbitals which are expanded as linear combinations of the atom-based basis functions, forming linear combinations of atomic orbitals (LCAO). This expansion is optimized to give the lowest energy. This procedure gives good energies without including ionic structures.

For example, in the hydrogen molecule, classic valence bond theory uses two 1s atomic orbitals (a and b) on the two hydrogen atoms respectively and then constructs a covalent structure:-

$$\Phi_C = (a(1)b(2) + b(1)a(2)) (\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

and then an ionic structure:-

$$\Phi_I = (a(1)a(2) + b(1)b(2)) (\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

The final wave function is a linear combination of these two functions. Coulson and Fischer^[3] pointed out that a completely equivalent function is:-

$$\Phi_{CF} = ((a+kb)(1)(b+ka)(2) + (b+ka)(1)(a+kb)(2)) ((\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

as expanding this out gives a linear combination of the covalent and ionic structures. Modern valence bond theory replaces the simple linear combination of the two atomic orbitals with a linear combination of all orbitals in a larger basis set. The two resulting valence bond orbitals look like an atomic orbital on one hydrogen atom slightly distorted towards the other hydrogen atom. Modern valence bond theory is thus an extension of this Coulson-Fischer method.

Spin-coupled theory

There are a large number of different valence bond methods. Most use n valence bond orbitals for n electrons. If a single set of these orbitals is combined with all linear independent combinations of the spin functions, we have **spin-coupled valence bond theory**. The total wave function is optimized using the variational method by varying the coefficients of the basis functions in the valence bond orbitals and the coefficients of the different spin functions. In other cases only a sub-set of all possible spin functions is used. Many valence bond methods use several sets of the valence bond orbitals. Be warned that different authors use different names for these different valence bond methods.

Valence bond programs

Several groups have produced computer programs for modern valence bond calculations that are freely available.


References

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- [2] See further reading section.
- [3] C. A. Coulson and I. Fischer, *Phil. Mag.* vol 40, p. 386 (1949)

Further reading

- J. Gerratt, D. L. Cooper, P. B. Karadakov and M. Raimondi, "Modern Valence Bond Theory", *Chemical Society Reviews*, **26**, 87, 1997, and several others by the same authors.
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Generalized valence bond

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The **generalized valence bond** (GVB) method is one of the simplest and oldest valence bond method that uses flexible orbitals in the general way used by modern valence bond theory. The method was developed by the group of William A. Goddard, III around 1970.

Theory


The generalized Coulson-Fisher theory for the hydrogen molecule, discussed in Modern valence bond theory, is used to describe every electron pair in a molecule. The orbitals for each electron pair are expanded in terms of the full basis set and are non-orthogonal. Orbitals from different pairs are forced to be orthogonal - the strong orthogonality condition. This condition simplifies the calculation but can lead to some difficulties.

Calculations

GVB code in some programs, particularly GAMESS (US), can also be used to do a variety of restricted open-shell Hartree-Fock calculations, such as those with one or three electrons in two pi-electron molecular orbitals while retaining the degeneracy of the orbitals. This wave function is essentially a two-determinant function, rather than the one-determinant function of the restricted Hartree-Fock method.

References

Møller–Plesset perturbation theory

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Møller–Plesset perturbation theory (MP) is one of several quantum chemistry post-Hartree–Fock ab initio methods in the field of computational chemistry. It improves on the Hartree–Fock method by adding electron correlation effects by means of Rayleigh–Schrödinger perturbation theory (RS-PT), usually to second (MP2), third (MP3) or fourth (MP4) order. Its main idea was published as early as 1934 by Christian Møller and Milton S. Plesset.

Rayleigh–Schrödinger perturbation theory

The MP perturbation theory is a special case of RS perturbation theory. In RS theory one considers an unperturbed Hamiltonian operator \hat{H}_0 , to which a small (often external) perturbation \hat{V} is added:

$$\hat{H} = \hat{H}_0 + \lambda\hat{V}.$$

Here, λ is an arbitrary real parameter that controls the size of the perturbation. In MP theory the zeroth-order wave function is an exact eigenfunction of the Fock operator, which thus serves as the unperturbed operator. The perturbation is the correlation potential. In RS-PT the perturbed wave function and perturbed energy are expressed as a power series in λ :

$$\Psi = \lim_{m \rightarrow \infty} \sum_{i=0}^m \lambda^i \Psi^{(i)},$$

$$E = \lim_{m \rightarrow \infty} \sum_{i=0}^m \lambda^i E^{(i)}.$$

Substitution of these series into the time-independent Schrödinger equation gives a new equation as $m \rightarrow \infty$:

$$\left(\hat{H}_0 + \lambda V \right) \left(\sum_{i=0}^m \lambda^i \Psi^{(i)} \right) = \left(\sum_{i=0}^m \lambda^i E^{(i)} \right) \left(\sum_{i=0}^m \lambda^i \Psi^{(i)} \right).$$

Equating the factors of λ^k in this equation gives a k th-order perturbation equation, where $k = 0, 1, 2, \dots, m$. See perturbation theory for more details.

Møller–Plesset perturbation

Original formulation

The MP-energy corrections are obtained from Rayleigh–Schrödinger (RS) perturbation theory with the unperturbed Hamiltonian defined as the *shifted* Fock operator,

$$\hat{H}_0 \equiv F + \langle \Phi_0 | (\hat{H} - \hat{F}) | \Phi_0 \rangle$$

and the perturbation defined as the *correlation potential*,

$$\hat{V} \equiv \hat{H} - \left(\hat{F} + \langle \Phi_0 | (\hat{H} - \hat{F}) | \Phi_0 \rangle \right),$$

where the normalized Slater determinant Φ_0 is the lowest eigenstate of the Fock operator:

$$\hat{F}\Phi_0 \equiv \sum_{k=1}^N \hat{f}(k)\Phi_0 = 2 \sum_{i=1}^{N/2} \varepsilon_i \Phi_0.$$

Here N is the number of electrons in the molecule under consideration (a factor of 2 in the energy arises from the fact that each orbital is occupied by a pair of electrons with opposite spin), \hat{H} is the usual electronic Hamiltonian, $\hat{f}(k)$ is the one-electron Fock operator, and ε_i is the orbital energy belonging to the doubly occupied spatial orbital φ_i . The interaction operator \hat{v} is assumed to couple up to two particles (electrons) at a time. A typical interaction would be the Coulomb repulsion (in atomic units), as defined by:

$$\langle \psi_p \psi_q | \hat{v} | \psi_r \psi_s \rangle = \int \psi_p^*(1) \psi_q^*(2) \frac{1}{r_{12}} \psi_r(1) \psi_s(2) d\tau_1 d\tau_2,$$

where ψ represents an arbitrary single-electron wavefunction and r_{12} is the distance between electrons 1 and 2.

For convenience, the exchange interaction can be included to produce an antisymmetric interaction operator $\hat{\tilde{v}}$, defined as:

$$\langle \psi_p \psi_q | \hat{\tilde{v}} | \psi_r \psi_s \rangle = \langle \psi_p \psi_q | \hat{v} | \psi_r \psi_s \rangle - \langle \psi_p \psi_q | \hat{v} | \psi_s \psi_r \rangle.$$

Since the Slater determinant Φ_0 is an eigenstate of \hat{F} , it follows readily that

$$\hat{F}\Phi_0 - \langle \Phi_0 | \hat{F} | \Phi_0 \rangle \Phi_0 = 0 \implies \hat{H}_0 \Phi_0 = \langle \Phi_0 | \hat{H} | \Phi_0 \rangle \Phi_0,$$

so that the zeroth-order energy is the expectation value of \hat{H} with respect to Φ_0 , *i.e.*, the Hartree–Fock energy:

$$E_{\text{MP0}} \equiv E_{\text{HF}} = \langle \Phi_0 | H | \Phi_0 \rangle.$$

Since the first-order MP energy

$$E_{\text{MP1}} \equiv \langle \Phi_0 | \hat{V} | \Phi_0 \rangle = 0$$

is obviously zero, the lowest-order MP correlation energy appears in second order. This result is the **Møller–Plesset theorem**: *the correlation potential does not contribute in first-order to the exact electronic energy.*

In order to obtain the MP2 formula for a closed-shell molecule, the second order RS-PT formula is written on basis of doubly excited Slater determinants. (Singly excited Slater determinants do not contribute because of the Brillouin theorem). After application of the Slater–Condon rules for the simplification of N -electron matrix elements with

Slater determinants in bra and ket and integrating out spin, it becomes

$$\begin{aligned} E_{\text{MP2}} &= \frac{1}{4} \sum_{i,j,a,b} \frac{\langle \varphi_i \varphi_j | \hat{v} | \varphi_a \varphi_b \rangle \langle \varphi_a \varphi_b | \hat{v} | \varphi_i \varphi_j \rangle}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b} \\ &= \sum_{i < j, a < b} \frac{2 \langle \varphi_i \varphi_j | \hat{v} | \varphi_a \varphi_b \rangle (\langle \varphi_a \varphi_b | \hat{v} | \varphi_i \varphi_j \rangle - \langle \varphi_a \varphi_b | \hat{v} | \varphi_j \varphi_i \rangle)}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}, \end{aligned}$$

where φ_i and φ_j are canonical occupied orbitals and φ_a and φ_b are canonical virtual (or unoccupied) orbitals. The quantities ε_i , ε_j , ε_a , and ε_b are the corresponding orbital energies. Clearly, through second-order in the correlation potential, the total electronic energy is given by the Hartree–Fock energy plus second-order MP correction: $E \approx E_{\text{HF}} + E_{\text{MP2}}$. The solution of the zeroth-order MP equation (which by definition is the Hartree–Fock equation) gives the Hartree–Fock energy. The first non-vanishing perturbation correction beyond the Hartree–Fock treatment is the second-order energy.

Alternative formulation

Equivalent expressions are obtained by a slightly different partitioning of the Hamiltonian, which results in a different division of energy terms over zeroth- and first-order contributions, while for second- and higher-order energy corrections the two partitionings give identical results. The formulation is commonly used by chemists, who are now large users of these methods.^[1] This difference is due to the fact, well known in Hartree–Fock theory, that

$$\langle \Phi_0 | (\hat{H} - \hat{F}) | \Phi_0 \rangle \neq 0 \iff E_{\text{HF}} \neq 2 \sum_{i=1}^{N/2} \varepsilon_i.$$

(The Hartree–Fock energy is *not* equal to the sum of occupied-orbital energies). In the alternative partitioning, one defines

$$\hat{H}_0 \equiv \hat{F}, \quad \hat{V} \equiv \hat{H} - \hat{F}.$$

Clearly, in this partitioning,

$$E_{\text{MP0}} = 2 \sum_{i=1}^{N/2} \varepsilon_i, \quad E_{\text{MP1}} = E_{\text{HF}} - 2 \sum_{i=1}^{N/2} \varepsilon_i.$$

Obviously, with this alternative formulation, the Møller–Plesset theorem does not hold in the literal sense that $E_{\text{MP1}} \neq 0$. The solution of the zeroth-order MP equation is the sum of orbital energies. The zeroth plus first-order correction yields the Hartree–Fock energy. As with the original formulation, the first non-vanishing perturbation correction beyond the Hartree–Fock treatment is the second-order energy. To reiterate, the second- and higher-order corrections are the same in both formulations.

Use of Møller–Plesset perturbation methods

Second (MP2), third (MP3), and fourth (MP4) order Møller–Plesset calculations are standard levels used in calculating small systems and are implemented in many computational chemistry codes. Higher level MP calculations, generally only MP5, are possible in some codes. However, they are rarely used because of their cost.

Systematic studies of MP perturbation theory have shown that it is not necessarily a convergent theory at high orders. Convergence can be slow, rapid, oscillatory, regular, highly erratic or simply non-existent, depending on the precise chemical system or basis set. The density matrix for the first-order and higher MP2 wavefunction is of the type known as *response density*, which differs from the more usual *expectation value density*. The eigenvalues of the response density matrix (which are the occupation numbers of the MP2 natural orbitals) can therefore be greater than 2 or negative. Unphysical numbers are a sign of a divergent perturbation expansion.

Additionally, various important molecular properties calculated at MP3 and MP4 level are no better than their MP2 counterparts, even for small molecules.

For open shell molecules, MPn-theory can directly be applied only to unrestricted Hartree–Fock reference functions (since ROHF states are not in general eigenvectors of the Fock operator). However, the resulting energies often suffer from severe spin contamination, leading to large errors. A possible better alternative is to use one of the MP2-like methods based on restricted open-shell Hartree–Fock (ROHF). Unfortunately, there are many ROHF based MP2-like methods because of arbitrariness in the ROHF wavefunction (for example HCPT, ROMP, RMP (also called ROHF-MBPT2), OPT1 and OPT2, ZAPT, IOPT, etc.). Some of the ROHF based MP2-like theories suffer from spin-contamination in their perturbed density and energies beyond second-order.

These methods, Hartree–Fock, unrestricted Hartree–Fock and restricted Hartree–Fock use a single determinant wave function. Multi-configurational self-consistent field (MCSCF) methods use several determinants and can be used for the unperturbed operator, although not uniquely, so many methods, such as complete active space perturbation theory (CASPT2), and Multi-Configuration Quasi-Degenerate Perturbation Theory (MCQDPT), have been developed. Unfortunately, MCSCF based methods are not without perturbation series divergences.


References

[1] See all volumes under #Further reading.

Further reading

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Configuration interaction

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Configuration interaction (CI) is a post-Hartree–Fock linear variational method for solving the nonrelativistic Schrödinger equation within the Born–Oppenheimer approximation for a quantum chemical multi-electron system. Mathematically, *configuration* simply describes the linear combination of Slater determinants used for the wave function. In terms of a specification of orbital occupation (for instance, $(1s)^2(2s)^2(2p)^1\dots$), *interaction* means the mixing (interaction) of different electronic configurations (states). Due to the long CPU time and immense hardware required for CI calculations, the method is limited to relatively small systems.

In contrast to the Hartree–Fock method, in order to account for electron correlation, CI uses a variational wave function that is a linear combination of configuration state functions (CSFs) built from spin orbitals (denoted by the superscript SO),

$$\Psi = \sum_{I=0} c_I \Phi_I^{SO} = c_0 \Phi_0^{SO} + c_1 \Phi_1^{SO} + \dots$$

where Ψ is usually the electronic ground state of the system. If the expansion includes all possible CSFs of the appropriate symmetry, then this is a full configuration interaction procedure which exactly solves the electronic Schrödinger equation within the space spanned by the one-particle basis set. The first term in the above expansion is normally the Hartree–Fock determinant. The other CSFs can be characterised by the number of spin orbitals that are swapped with virtual orbitals from the Hartree–Fock determinant. If only one spin orbital differs, we describe this as a single excitation determinant. If two spin orbitals differ it is a double excitation determinant and so on. This is used to limit the number of determinants in the expansion which is called the CI-space.

Truncating the CI-space is important to save computational time. For example, the method CID is limited to double excitations only. The method CISD is limited to single and double excitations. Single excitations on their own do not mix with the Hartree–Fock determinant. These methods, CID and CISD, are in many standard programs. The

Davidson correction can be used to estimate a correction to the CISD energy to account for higher excitations. An important problem of truncated CI methods is their size-inconsistency which means the energy of two infinitely separated particles is not double the energy of the single particle.

The CI procedure leads to a general matrix eigenvalue equation:

$$\mathbb{H}\mathbf{c} = \mathbf{e}\mathbb{S}\mathbf{c},$$

where \mathbf{c} is the coefficient vector, \mathbf{e} is the eigenvalue matrix, and the elements of the hamiltonian and overlap matrices are, respectively,

$$\begin{aligned} \mathbb{H}_{ij} &= \langle \Phi_i^{SO} | \mathbf{H}^{el} | \Phi_j^{SO} \rangle, \\ \mathbb{S}_{ij} &= \langle \Phi_i^{SO} | \Phi_j^{SO} \rangle. \end{aligned}$$

Slater determinants are constructed from sets of orthonormal spin orbitals, so that $\langle \Phi_i^{SO} | \Phi_j^{SO} \rangle = \delta_{ij}$, making \mathbb{S} the identity matrix and simplifying the above matrix equation.

The solution of the CI procedure are some eigenvalues \mathbf{E}^j and their corresponding eigenvectors \mathbf{c}_I^j .

The eigenvalues are the energies of the ground and some electronically excited states. By this it is possible to calculate energy differences (excitation energies) with CI methods. Excitation energies of truncated CI methods are generally too high, because the excited states are not that well correlated as the ground state is. For equally (balanced) correlation of ground and excited states (better excitation energies) one can use more than one reference determinant from which all singly, doubly, ... excited determinants are included (multireference configuration interaction). MRCI also gives better correlation of the ground state which is important if it has more than one dominant determinant. This can be easily understood because some higher excited determinants are also taken into the CI-space.

For nearly degenerate determinants which build the ground state one should use the multi-configurational self-consistent field (MCSCF) method because the Hartree–Fock determinant is qualitatively wrong and so are the CI wave functions and energies.


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Coupled cluster

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Coupled cluster (CC) is a numerical technique used for describing many-body systems. Its most common use is as one of several post-Hartree–Fock ab initio quantum chemistry methods in the field of computational chemistry. It essentially takes the basic Hartree–Fock molecular orbital method and constructs multi-electron wavefunctions using the exponential cluster operator to account for electron correlation. Some of the most accurate calculations for small to medium sized molecules use this method.

The method was initially developed by Fritz Coester and Hermann Kümmel in the 1950s for studying nuclear physics phenomena, but became more frequently used when in 1966 Jiří Čížek (and later together with Josef Paldus) reformulated the method for electron correlation in atoms and molecules. It is now one of the most prevalent methods in quantum chemistry that includes electronic correlation. CC theory is simply the perturbative variant of the Many Electron Theory (MET) of Oktay Sinanoğlu, which is the exact (and variational) solution of the many electron problem, so it was also called "Coupled Pair MET (CPMET)". J. Čížek used the correlation function of MET and used Goldstone type perturbation theory to get the energy expression while original MET was completely variational. Čížek first developed the Linear-CPMET and then generalized it to full CPMET in the same paper in 1966. He then also performed an application of it on benzene molecule with O. Sinanoğlu in the same year. Because MET is somewhat difficult to perform computationally, CC is simpler and thus, in today's computational chemistry, CC is the best variant of MET and gives highly accurate results in comparison to experiments.^[1]

Wavefunction ansatz

Coupled-cluster theory provides the exact solution to the time-independent Schrödinger equation

$$H|\Psi\rangle = E|\Psi\rangle$$

where H is the Hamiltonian of the system, $|\Psi\rangle$ the exact wavefunction, and E the exact energy of the ground state. Coupled-cluster theory can also be used to obtain solutions for excited states using, for example, linear-response, equation-of-motion, state-universal multi-reference coupled cluster, or valence-universal multi-reference coupled cluster approaches.

The wavefunction of the coupled-cluster theory is written as an exponential ansatz:

$$|\Psi\rangle = e^T|\Phi_0\rangle,$$

where $|\Phi_0\rangle$, the reference wave function, which is typically a Slater determinant constructed from Hartree–Fock molecular orbitals, though other wave functions such as Configuration interaction, Multi-configurational self-consistent field, or Brueckner orbitals can also be used. T is the cluster operator which, when acting on $|\Phi_0\rangle$, produces a linear combination of excited determinants from the reference wave function (see section below for greater detail).

The choice of the exponential ansatz is opportune because (unlike other ansätze, for example, configuration interaction) it guarantees the size extensivity of the solution. Size consistency in CC theory, however, depends on the size consistency of the reference wave function.

A criticism of the method is that the conventional implementation employing the similarity-transformed Hamiltonian (see below) is not variational, though there are bi-variational and quasi-variational approaches that have been developed since the first implementations of the theory. While the above ansatz for the wave function itself has no natural truncation, for other properties, such as energy, there is a natural truncation when examining expectation values, which has its basis in the linked- and connected-cluster theorems, and thus does not suffer from issues such as lack of size extensivity, like the variational configuration interaction.

Cluster operator

The cluster operator is written in the form,

$$T = T_1 + T_2 + T_3 + \dots,$$

where T_1 is the operator of all single excitations, T_2 is the operator of all double excitations and so forth. In the formalism of second quantization these excitation operators are expressed as

$$T_1 = \sum_i \sum_a t_a^i \hat{a}^a \hat{a}_i,$$

$$T_2 = \frac{1}{4} \sum_{i,j} \sum_{a,b} t_{ab}^{ij} \hat{a}^a \hat{a}^b \hat{a}_j \hat{a}_i,$$

and for the general n-fold cluster operator

$$T_n = \frac{1}{(n!)^2} \sum_{i_1, i_2, \dots, i_n} \sum_{a_1, a_2, \dots, a_n} t_{a_1, a_2, \dots, a_n}^{i_1, i_2, \dots, i_n} \hat{a}^{a_1} \hat{a}^{a_2} \dots \hat{a}^{a_n} \hat{a}_{i_n} \dots \hat{a}_{i_2} \hat{a}_{i_1}.$$

In the above formulae ($\hat{a}_a^\dagger = \hat{a}^\dagger$) and \hat{a}_i denote the creation and annihilation operators respectively and i, j stand for occupied (hole) and a, b for unoccupied (particle) orbitals (states). The creation and annihilation operators in the coupled cluster terms above are written in canonical form, where each term is in the normal order form, with respect to the Fermi vacuum, $|\Phi_0\rangle$. Being the one-particle cluster operator and the two-particle cluster operator, T_1 and T_2 convert the reference function $|\Phi_0\rangle$ into a linear combination of the singly and doubly excited Slater determinants, respectively, if applied without the exponential (such as in CI where a linear excitation operator is applied to the wave function). Applying the exponential cluster operator to the wave function, one can then generate more than doubly excited determinants due to the various powers of T_1 and T_2 that appear in the resulting

expressions (see below). Solving for the unknown coefficients t_a^i and t_{ab}^{ij} is necessary for finding the approximate solution $|\Psi\rangle$. The exponential operator e^T may be expanded as a Taylor series and if we consider only the T_1 and T_2 cluster operators of T , we can write:

$$e^T = 1 + T + \frac{1}{2!}T^2 + \dots = 1 + T_1 + T_2 + \frac{1}{2}T_1^2 + T_1T_2 + \frac{1}{2}T_2^2 + \dots$$

Though this series is finite in practice because the number of occupied molecular orbitals is finite, as is the number of excitations, it is still very large, to the extent that even modern day massively parallel computers are inadequate, except for problems of a dozen or so electrons and very small basis sets, when considering all contributions to the cluster operator and not just T_1 and T_2 . Often, as was done above, the cluster operator includes only singles and doubles (see CCSD below) as this offers a computationally affordable method that performs better than MP2 and CISD, but is not very accurate usually. For accurate results some form of triples (approximate or full) are needed, even near the equilibrium geometry (in the Franck-Condon region), and especially when breaking single-bonds or describing diradical species (these latter examples are often what is referred to as multi-reference problems, since more than one determinant has a significant contribution to the resulting wave function). For double bond breaking, and more complicated problems in chemistry, quadruple excitations often become important as well, though usually they are small for most problems, and as such, the contribution of T_5 , T_6 etc. to the operator T is typically small.

Furthermore, if the highest excitation level in the T operator is n ,

$$T = T_1 + \dots + T_n$$

then Slater determinants for an N -electron system excited more than n ($< N$) times may still contribute to the coupled cluster wave function $|\Psi\rangle$ because of the non-linear nature of the exponential ansatz, and therefore, coupled cluster terminated at T_n usually recovers more correlation energy than CI with maximum n excitations.

Coupled-cluster equations

The Schrödinger equation can be written, using the coupled-cluster wave function, as

$$H|\Psi_0\rangle = He^T|\Phi_0\rangle = Ee^T|\Phi_0\rangle$$

where there are a total of q coefficients (t -amplitudes) to solve for. To obtain the q equations, first, we multiply the above Schrödinger equation on the left by e^{-T} and then project onto the entire set of up to m -tuply excited determinants, where m is the highest order excitation included in T , that can be constructed from the reference wave function $|\Phi_0\rangle$, denoted by $|\Phi^*\rangle$, and individually, $|\Phi_i^a\rangle$ are singly excited determinants where the electron in orbital i has been excited to orbital a ; $|\Phi_{ij}^{ab}\rangle$ are doubly excited determinants where the electron in orbital i has been excited to orbital a and the electron in orbital j has been excited to orbital b , etc. In this way we generate a set of coupled energy-independent non-linear algebraic equations needed to determine the t -amplitudes.

$$\langle\Phi_0|e^{-T}He^T|\Phi_0\rangle = E\langle\Phi_0|\Phi_0\rangle = E$$

$$\langle\Phi^*|e^{-T}He^T|\Phi_0\rangle = E\langle\Phi^*|\Phi_0\rangle = 0,$$

(note, we have made use of $e^{-T}e^T = 1$, the identity operator, and we are also assuming that we are using orthogonal orbitals, though this does not necessarily have to be true, e.g., valence bond orbitals, and in such cases the last set of equations are not necessarily equal to zero) the latter being the equations to be solved and the former the equation for the evaluation of the energy.

Considering the basic CCSD method:

$$\langle\Phi_0|e^{-(T_1+T_2)}He^{(T_1+T_2)}|\Phi_0\rangle = E,$$

$$\langle\Phi_i^a|e^{-(T_1+T_2)}He^{(T_1+T_2)}|\Phi_0\rangle = 0,$$

$$\langle\Phi_{ij}^{ab}|e^{-(T_1+T_2)}He^{(T_1+T_2)}|\Phi_0\rangle = 0,$$

in which the similarity transformed Hamiltonian, \bar{H} , can be explicitly written down using Hadamard's formula in Lie algebra, also called Hadamard's lemma (see also Baker–Campbell–Hausdorff formula (BCH formula), though note they are different, in that Hadamard's formula is a lemma of the BCH formula):

$$\bar{H} = e^{-T} H e^T = H + [H, T] + (1/2)[[H, T], T] + \dots = (H e^T)_C.$$

The subscript C designates the connected part of the corresponding operator expression.

The resulting similarity transformed Hamiltonian is non-Hermitian, resulting in different left- and right-handed vectors (wave functions) for the same state of interest (this is what is often referred to in coupled cluster theory as the biorthogonality of the solution or wave function, though it also applies to other non-Hermitian theories as well). The resulting equations are a set of non-linear equations which are solved in an iterative manner. Standard quantum chemistry packages (GAMESS (US), NWChem, ACES II, etc.) solve the coupled cluster equations using the Jacobi method and direct inversion of the iterative subspace (DIIS) extrapolation of the t -amplitudes to accelerate convergence.

Types of coupled-cluster methods

The classification of traditional coupled-cluster methods rests on the highest number of excitations allowed in the definition of T . The abbreviations for coupled-cluster methods usually begin with the letters "CC" (for coupled cluster) followed by

1. S - for single excitations (shortened to *singles* in coupled-cluster terminology)
2. D - for double excitations (*doubles*)
3. T - for triple excitations (*triples*)
4. Q - for quadruple excitations (*quadruples*)

Thus, the T operator in CCSDT has the form

$$T = T_1 + T_2 + T_3.$$

Terms in round brackets indicate that these terms are calculated based on perturbation theory. For example, the CCSD(T) method means:

1. Coupled cluster with a full treatment singles and doubles.
2. An estimate to the connected triples contribution is calculated non-iteratively using Many-Body Perturbation Theory arguments.

General description of the theory

The complexity of equations and the corresponding computer codes, as well as the cost of the computation increases sharply with the highest level of excitation. For many applications CCSD, while relatively inexpensive, does not provide sufficient accuracy except for the smallest systems (approximately 2 to 4 electrons), and often times an approximate treatment of triples is needed. The most well known coupled cluster method that provides an estimate of connected triples is CCSD(T), which provides a good description of closed-shell molecules near the equilibrium geometry, but breaks down in more complicated situations such as bond breaking and diradicals. Another popular method that makes up for the failings of the standard CCSD(T) approach is CR-CC(2,3), where the triples contribution to the energy is computed from the difference between the exact solution and the CCSD energy, and is not based on perturbation theory arguments. More complicated coupled-cluster methods such as CCSDT and CCSDTQ are used only for high-accuracy calculations of small molecules. The inclusion of all n levels of excitation for the n -electron system gives the exact solution of the Schrödinger equation within the given basis set, within the Born–Oppenheimer approximation (although schemes have also been drawn up to work without the BO approximation).

One possible improvement to the standard coupled-cluster approach is to add terms linear in the interelectronic distances through methods such as CCSD-R12. This improves the treatment of dynamical electron correlation by satisfying the Kato cusp condition and accelerates convergence with respect to the orbital basis set. Unfortunately, R12 methods invoke the resolution of the identity which requires a relatively large basis set in order to be a good approximation.

The coupled-cluster method described above is also known as the *single-reference* (SR) coupled-cluster method because the exponential ansatz involves only one reference function $|\Phi_0\rangle$. The standard generalizations of the SR-CC method are the *multi-reference* (MR) approaches: state-universal coupled cluster (also known as Hilbert space coupled cluster), valence-universal coupled cluster (or Fock space coupled cluster) and state-selective coupled cluster (or state-specific coupled cluster).

Historical accounts

In the first reference below, Kümmel comments:

Considering the fact that the CC method was well understood around the late fifties it looks strange that nothing happened with it until 1966, as Jiří Čížek published his first paper on a quantum chemistry problem. He had looked into the 1957 and 1960 papers published in Nuclear Physics by Fritz and myself. I always found it quite remarkable that a quantum chemist would open an issue of a nuclear physics journal. I myself at the time had almost gave up the CC method as not tractable and, of course, I never looked into the quantum chemistry journals. The result was that I learnt about Jiří's work as late as in the early seventies, when he sent me a big parcel with reprints of the many papers he and Joe Paldus had written until then.

Josef Paldus also wrote his first hand account of the origins of coupled-cluster theory, its implementation, and exploitation in electronic wave function determination; his account is primarily about the making of coupled-cluster theory rather than about the theory itself.

Relation to other theories

Configuration Interaction

The C_j excitation operators defining the CI expansion of an N-electron system for the wave function $|\Psi_0\rangle$,

$$|\Psi_0\rangle = (1 + C)|\Phi_0\rangle,$$

$$C = \sum_{j=1}^N C_j,$$

are related to the cluster operators T , since in the limit of including up to T_N in the cluster operator the CC theory must be equal to full CI, we obtain the following relationships

$$C_1 = T_1,$$

$$C_2 = T_2 + \frac{1}{2}(T_1)^2,$$

$$C_3 = T_3 + T_1T_2 + \frac{1}{6}(T_1)^3,$$

$$C_4 = T_4 + \frac{1}{2}(T_2)^2 + T_1T_3 + \frac{1}{2}(T_1)^2T_2 + \frac{1}{24}(T_1)^4,$$

etc. For general relationships see J. Paldus, in *Methods in Computational Molecular Physics*, Vol. 293 of *Nato Advanced Study Institute Series B: Physics*, edited by S. Wilson and G.H.F. Diercksen (Plenum, New York, 1992), pp. 99-194.

Symmetry Adapted Cluster

The Symmetry adapted cluster (SAC) approach determines the (spin and) symmetry adapted cluster operator

$$S = \sum_I S_I$$

by solving the following system of energy dependent equations,


$$\begin{aligned} \langle \Phi | (H - E_0) e^S | \Phi \rangle &= 0, \\ \langle \Phi_{i_1 \dots i_n}^{a_1 \dots a_n} | (H - E_0) e^S | \Phi \rangle &= 0, \\ i_1 < \dots < i_n, a_1 < \dots < a_n, n &= 1, \dots, M_s, \end{aligned}$$

where $|\Phi_{i_1 \dots i_n}^{a_1 \dots a_n}\rangle$ are the n -tuply excited determinants relative to $|\Phi_0\rangle$ (usually they are the spin- and symmetry-adapted configuration state functions, in practical implementations), and M_s is the highest-order of excitation included in the SAC operator. If all of the nonlinear terms in e^S are included then the SAC equations become equivalent to the standard coupled-cluster equations of Jiří Čížek. This is due to the cancellation of the energy-dependent terms with the disconnected terms contributing to the product of $H e^S$, resulting in the same set of nonlinear energy-independent equations. Typically, all nonlinear terms, except $\frac{1}{2} S_2^2$ are dropped, as higher-order nonlinear terms are usually small.

References

[1] and references therein

Multi-configurational self-consistent field

| |
|---|
| Electronic structure methods |
| Valence bond theory |
| Generalized valence bond Modern valence bond |
| Molecular orbital theory |
| Hartree–Fock method Møller–Plesset perturbation theory Configuration interaction Coupled cluster Multi-configurational self-consistent field Quantum chemistry composite methods Quantum Monte Carlo Linear combination of atomic orbitals |
| Electronic band structure |
| Nearly free electron model Tight binding Muffin-tin approximation Density functional theory k-p perturbation theory Empty lattice approximation |
|  Book |

Multi-configurational self-consistent field (MCSCF) is a method in quantum chemistry used to generate qualitatively correct reference states of molecules in cases where Hartree–Fock and density functional theory are not adequate (e.g., for molecular ground states which are quasi-degenerate with low lying excited states or in bond breaking situations). It uses a linear combination of configuration state functions (CSF) or configuration determinants to approximate the exact electronic wavefunction of an atom or molecule. In an MCSCF calculation, the set of coefficients of both the CSFs or determinants and the basis functions in the molecular orbitals are varied to obtain the total electronic wavefunction with the lowest possible energy. This method can be considered a combination between configuration interaction (where the molecular orbitals are not varied but the expansion of the wave function) and Hartree–Fock (where there is only one determinant but the molecular orbitals are varied).

MCSCF wave functions are often used as reference states for Multireference configuration interaction (MRCI) or multi-reference perturbation theories like complete active space perturbation theory (CASPT2). These methods can deal with extremely complex chemical situations and, if computing power permits, may be used to reliably calculate molecular ground- and excited states if all other methods fail.

Introduction

For the simplest single bond, found in the H_2 molecule, molecular orbitals can always be written in terms of two functions χ_{iA} and χ_{iB} (which are atomic orbitals with small corrections) located at the two nuclei,

$$\varphi_i = N_i(\chi_{iA} \pm \chi_{iB}),$$

where N_i is a normalization constant. The ground state wavefunction for H_2 at the equilibrium geometry is dominated by the configuration $(\varphi_1)^2$, which means the molecular orbital φ_1 is nearly doubly occupied. The Hartree–Fock model *assumes* it is doubly occupied, which leads to a total wavefunction of

$$\Phi_1 = \varphi_1(\mathbf{r}_1)\varphi_1(\mathbf{r}_2)\Theta_{2,0},$$

where $\Theta_{2,0}$ is the singlet ($S = 0$) spin function for two electrons. The molecular orbitals in this case φ_1 are taken as sums of $1s$ atomic orbitals on both atoms, namely $N_1(1s_A + 1s_B)$. Expanding the above equation into atomic orbitals yields

$$\Phi_1 = N_1^2 [1s_A(\mathbf{r}_1)1s_A(\mathbf{r}_2) + 1s_A(\mathbf{r}_1)1s_B(\mathbf{r}_2) + 1s_B(\mathbf{r}_1)1s_A(\mathbf{r}_2) + 1s_B(\mathbf{r}_1)1s_B(\mathbf{r}_2)] \Theta_{2,0}.$$

This Hartree-Fock model gives a reasonable description of H_2 around the equilibrium geometry - about 0.735\AA for the bond length (compared to a 0.746\AA experimental value) and 84 kcal/mol for the bond energy (exp. 109 kcal/mol). This is typical of the HF model, which usually describes closed shell systems around their equilibrium geometry quite well. At large separations, however, the terms describing both electrons located at one atom remain, which corresponds to dissociation to $H^+ + H^-$, which has a much larger energy than $H + H$. Therefore, the persisting presence of ionic terms leads to an unphysical solution in this case.

Consequently, the HF model cannot be used to describe dissociation processes with open shell products. The most straightforward solution to this problem is introducing coefficients in front of the different terms in Ψ_1 :

$$\Psi_1 = C_{\text{Ion}}\Phi_{\text{Ion}} + C_{\text{Cov}}\Phi_{\text{Cov}},$$

which forms the basis for the valence bond description of chemical bonds. With the coefficients C_{Ion} and C_{Cov} varying, the wave function will have the correct form, with $C_{\text{Ion}}=0$ for the separated limit and C_{Ion} comparable to C_{Cov} at equilibrium. Such a description, however, uses non-orthogonal basis functions, which complicates its mathematical structure. Instead, multiconfiguration is achieved by using orthogonal molecular orbitals. After introducing an anti-bonding orbital

$$\phi_2 = N_2(1s_A - 1s_B),$$

the total wave function of H_2 can be written as a linear combination of configurations built from bonding and anti-bonding orbitals:

$$\Psi_{MC} = C_1\Phi_1 + C_2\Phi_2,$$

where Φ_2 is the electronic configuration $(\varphi_2)^2$. In this multiconfigurational description of the H_2 chemical bond, $C_1 = 1$ and $C_2 = 0$ close to equilibrium, and C_1 will be comparable to C_2 for large separations.

Complete active space SCF

A particularly important MCSCF approach is the **complete active space SCF method (CASSCF)**, where the linear combination of CSFs includes all that arise from a particular number of electrons in a particular number of orbitals (also known as full-optimized reaction space (**FORS-MCSCF**)). For example, one might define CASSCF(11,8) for the molecule, NO, where the 11 valence electrons are distributed between all configurations that can be constructed from 8 molecular orbitals.

Restricted active space SCF


Since the number of CSFs quickly increases with the number of active orbitals, along with the computational cost, it may be desirable to use a smaller set of CSFs. One way to make this selection is to restrict the number of electrons in certain subspaces, done in the **restricted active space SCF method (RASSCF)**. One could, for instance, allow only single and double excitations from some strongly-occupied subset of active orbitals, or restrict the number of electrons to at most 2 in another subset of active orbitals.

References

Further reading

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Density functional theory

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|---|
| Electronic structure methods |
| Valence bond theory |
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| Electronic band structure |
| Nearly free electron model Tight binding Muffin-tin approximation Density functional theory k·p perturbation theory Empty lattice approximation |
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Density functional theory (DFT) is a quantum mechanical modelling method used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functionals, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the name density functional theory comes from the use of functionals of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry.

DFT has been very popular for calculations in solid-state physics since the 1970s. However, DFT was not considered accurate enough for calculations in quantum chemistry until the 1990s, when the approximations used in the theory were greatly refined to better model the exchange and correlation interactions. In many cases the results of DFT calculations for solid-state systems agree quite satisfactorily with experimental data. Computational costs are relatively low when compared to traditional methods, such as Hartree–Fock theory and its descendants based on the complex many-electron wavefunction.

Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially van der Waals forces (dispersion); charge transfer excitations; transition states, global potential energy surfaces and some other strongly correlated systems; and in calculations of the band gap in semiconductors. Its incomplete treatment of dispersion can adversely affect the accuracy of DFT (at least when used alone and uncorrected) in the treatment of systems which are dominated by dispersion (e.g. interacting noble gas atoms) or where dispersion competes significantly with other effects (e.g. in biomolecules). The development of new DFT methods designed to overcome this problem, by alterations to the functional or by the inclusion of additive terms, is a current research topic.

Overview of method

Although density functional theory has its conceptual roots in the Thomas–Fermi model, DFT was put on a firm theoretical footing by the two **Hohenberg–Kohn theorems** (H–K). The original H–K theorems held only for non-degenerate ground states in the absence of a magnetic field, although they have since been generalized to encompass these.

The first H–K theorem demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only 3 spatial coordinates. It lays the groundwork for reducing the many-body problem of N electrons with $3N$ spatial coordinates to 3 spatial coordinates, through the use of functionals of the electron density. This theorem can be extended to the time-dependent domain to develop time-dependent density functional theory (TDDFT), which can be used to describe excited states.

The second H–K theorem defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional.

Within the framework of Kohn–Sham DFT (KS DFT), the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the exchange and correlation interactions. Modeling the latter two interactions becomes the difficulty within KS DFT. The simplest approximation is the local-density approximation (LDA), which is based upon exact exchange energy for a uniform electron gas, which can be obtained from the Thomas–Fermi model, and from fits to the correlation energy for a uniform electron gas. Non-interacting systems are relatively easy to solve as the wavefunction can be represented as a Slater determinant of orbitals. Further, the kinetic energy functional of such a system is known exactly. The exchange–correlation part of the total-energy functional remains unknown and must be approximated.

Another approach, less popular than KS DFT but arguably more closely related to the spirit of the original H–K theorems, is orbital-free density functional theory (OFDFT), in which approximate functionals are also used for the kinetic energy of the non-interacting system.

Note: Recently, another foundation to construct the DFT without the Hohenberg–Kohn theorems is getting popular, that is, as a Legendre transformation from external potential to electron density. See, e.g., Density Functional Theory – an introduction ^[1], Rev. Mod. Phys. 78, 865–951 (2006) ^[2], and references therein. A book, 'The Fundamentals of Density Functional Theory' ^[3] written by H. Eschrig, contains detailed mathematical discussions on the DFT; there is a difficulty for N -particle system with infinite volume; however, we have no mathematical problems in finite periodic system (torus). Note that the correspondence between density and potential should be very non-analytic (for example, we have boundaries in the space of one-particle potential; e.g, those between metal and insulator).

Derivation and formalism

As usual in many-body electronic structure calculations, the nuclei of the treated molecules or clusters are seen as fixed (the Born–Oppenheimer approximation), generating a static external potential V in which the electrons are moving. A stationary electronic state is then described by a wavefunction $\Psi(\vec{r}_1, \dots, \vec{r}_N)$ satisfying the many-electron time-independent Schrödinger equation

$$\hat{H}\Psi = \left[\hat{T} + \hat{V} + \hat{U} \right] \Psi = \left[\sum_i^N \left(-\frac{\hbar^2}{2m_i} \nabla_i^2 \right) + \sum_i^N V(\vec{r}_i) + \sum_{i<j}^N U(\vec{r}_i, \vec{r}_j) \right] \Psi = E\Psi$$

where, for the N -electron system, \hat{H} is the Hamiltonian, E is the total energy, \hat{T} is the kinetic energy, \hat{V} is the potential energy from the external field due to positively charged nuclei, and \hat{U} is the electron–electron interaction energy. The operators \hat{T} and \hat{U} are called universal operators as they are the same for any N -electron system, while \hat{V} is system dependent. This complicated many-particle equation is not separable into simpler single-particle

equations because of the interaction term \hat{U} .

There are many sophisticated methods for solving the many-body Schrödinger equation based on the expansion of the wavefunction in Slater determinants. While the simplest one is the Hartree–Fock method, more sophisticated approaches are usually categorized as post-Hartree–Fock methods. However, the problem with these methods is the huge computational effort, which makes it virtually impossible to apply them efficiently to larger, more complex systems.

Here DFT provides an appealing alternative, being much more versatile as it provides a way to systematically map the many-body problem, with \hat{U} , onto a single-body problem without \hat{U} . In DFT the key variable is the particle density $n(\vec{r})$, which for a normalized Ψ is given by

$$n(\vec{r}) = N \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \Psi^*(\vec{r}, \vec{r}_2, \dots, \vec{r}_N) \Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N).$$

This relation can be reversed, i.e. for a given ground-state density $n_0(\vec{r})$ it is possible, in principle, to calculate the corresponding ground-state wavefunction $\Psi_0(\vec{r}_1, \dots, \vec{r}_N)$. In other words, Ψ is a unique functional of n_0 ,

$$\Psi_0 = \Psi[n_0]$$

and consequently the ground-state expectation value of an observable \hat{O} is also a functional of n_0

$$O[n_0] = \langle \Psi[n_0] | \hat{O} | \Psi[n_0] \rangle.$$

In particular, the ground-state energy is a functional of n_0

$$E_0 = E[n_0] = \langle \Psi[n_0] | \hat{T} + \hat{V} + \hat{U} | \Psi[n_0] \rangle$$

where the contribution of the external potential $\langle \Psi[n_0] | \hat{V} | \Psi[n_0] \rangle$ can be written explicitly in terms of the ground-state density n_0

$$V[n_0] = \int V(\vec{r}) n_0(\vec{r}) d^3r.$$

More generally, the contribution of the external potential $\langle \Psi | \hat{V} | \Psi \rangle$ can be written explicitly in terms of the density n ,

$$V[n] = \int V(\vec{r}) n(\vec{r}) d^3r.$$

The functionals $T[n]$ and $U[n]$ are called universal functionals, while $V[n]$ is called a non-universal functional, as it depends on the system under study. Having specified a system, i.e., having specified \hat{V} , one then has to minimize the functional

$$E[n] = T[n] + U[n] + \int V(\vec{r}) n(\vec{r}) d^3r$$

with respect to $n(\vec{r})$, assuming one has got reliable expressions for $T[n]$ and $U[n]$. A successful minimization of the energy functional will yield the ground-state density n_0 and thus all other ground-state observables.

The variational problems of minimizing the energy functional $E[n]$ can be solved by applying the Lagrangian method of undetermined multipliers. First, one considers an energy functional that doesn't explicitly have an electron–electron interaction energy term,

$$E_s[n] = \langle \Psi_s[n] | \hat{T} + \hat{V}_s | \Psi_s[n] \rangle$$

where \hat{T} denotes the kinetic energy operator and \hat{V}_s is an external effective potential in which the particles are moving, so that $n_s(\vec{r}) \stackrel{\text{def}}{=} n(\vec{r})$.

Thus, one can solve the so-called Kohn–Sham equations of this auxiliary non-interacting system,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_s(\vec{r}) \right] \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r})$$

which yields the orbitals ϕ_i that reproduce the density $n(\vec{r})$ of the original many-body system

$$n(\vec{r}) \stackrel{\text{def}}{=} n_s(\vec{r}) = \sum_i^N |\phi_i(\vec{r})|^2.$$

The effective single-particle potential can be written in more detail as

$$V_s(\vec{r}) = V(\vec{r}) + \int \frac{e^2 n_s(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3 r' + V_{\text{XC}}[n_s(\vec{r})]$$

where the second term denotes the so-called Hartree term describing the electron-electron Coulomb repulsion, while the last term V_{XC} is called the exchange-correlation potential. Here, V_{XC} includes all the many-particle interactions. Since the Hartree term and V_{XC} depend on $n(\vec{r})$, which depends on the ϕ_i , which in turn depend on V_s , the problem of solving the Kohn–Sham equation has to be done in a self-consistent (i.e., iterative) way. Usually one starts with an initial guess for $n(\vec{r})$, then calculates the corresponding V_s and solves the Kohn-Sham equations for the ϕ_i . From these one calculates a new density and starts again. This procedure is then repeated until convergence is reached. A non-iterative approximate formulation called Harris functional DFT is an alternative approach to this.

Approximations (exchange-correlation functionals)

The major problem with DFT is that the exact functionals for exchange and correlation are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. In physics the most widely used approximation is the local-density approximation (LDA), where the functional depends only on the density at the coordinate where the functional is evaluated:

$$E_{\text{XC}}^{\text{LDA}}[n] = \int \epsilon_{\text{XC}}(n)n(\vec{r})d^3r.$$

The local spin-density approximation (LSDA) is a straightforward generalization of the LDA to include electron spin:

$$E_{\text{XC}}^{\text{LSDA}}[n_{\uparrow}, n_{\downarrow}] = \int \epsilon_{\text{XC}}(n_{\uparrow}, n_{\downarrow})n(\vec{r})d^3r.$$

Highly accurate formulae for the exchange-correlation energy density $\epsilon_{\text{XC}}(n_{\uparrow}, n_{\downarrow})$ have been constructed from quantum Monte Carlo simulations of jellium.

Generalized gradient approximations (GGA) are still local but also take into account the gradient of the density at the same coordinate:

$$E_{\text{XC}}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int \epsilon_{\text{XC}}(n_{\uparrow}, n_{\downarrow}, \vec{\nabla}n_{\uparrow}, \vec{\nabla}n_{\downarrow})n(\vec{r})d^3r.$$

Using the latter (GGA) very good results for molecular geometries and ground-state energies have been achieved.

Potentially more accurate than the GGA functionals are the meta-GGA functionals, a natural development after the GGA (generalized gradient approximation). Meta-GGA DFT functional in its original form includes the second derivative of the electron density (the Laplacian) whereas GGA includes only the density and its first derivative in the exchange-correlation potential.

Functionals of this type are, for example, TPSS and the Minnesota Functionals. These functionals include a further term in the expansion, depending on the density, the gradient of the density and the Laplacian (second derivative) of the density.

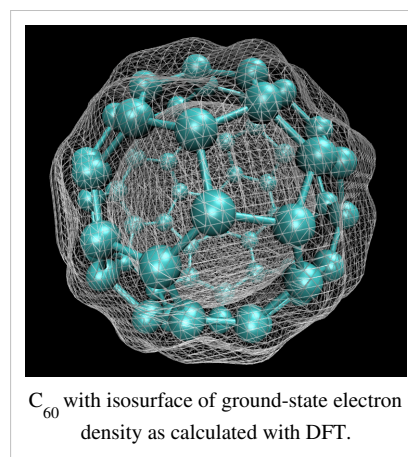
Difficulties in expressing the exchange part of the energy can be relieved by including a component of the exact exchange energy calculated from Hartree–Fock theory. Functionals of this type are known as hybrid functionals.

Generalizations to include magnetic fields

The DFT formalism described above breaks down, to various degrees, in the presence of a vector potential, i.e. a magnetic field. In such a situation, the one-to-one mapping between the ground-state electron density and wavefunction is lost. Generalizations to include the effects of magnetic fields have led to two different theories: current density functional theory (CDFT) and magnetic field density functional theory (BDFT). In both these theories, the functional used for the exchange and correlation must be generalized to include more than just the electron density. In current density functional theory, developed by Vignale and Rasolt, the functionals become dependent on both the electron density and the paramagnetic current density. In magnetic field density functional theory, developed by Salsbury, Grayce and Harris, the functionals depend on the electron density and the magnetic field, and the functional form can depend on the form of the magnetic field. In both of these theories it has been difficult to develop functionals beyond their equivalent to LDA, which are also readily implementable computationally.

Applications

In practice, Kohn-Sham theory can be applied in several distinct ways depending on what is being investigated. In solid state calculations, the local density approximations are still commonly used along with plane wave basis sets, as an electron gas approach is more appropriate for electrons delocalised through an infinite solid. In molecular calculations, however, more sophisticated functionals are needed, and a huge variety of exchange-correlation functionals have been developed for chemical applications. Some of these are inconsistent with the uniform electron gas approximation, however, they must reduce to LDA in the electron gas limit. Among physicists, probably the most widely used functional is the revised Perdew–Burke–Ernzerhof exchange model (a direct generalized-gradient parametrization of the free electron gas with no free parameters); however, this is not sufficiently calorimetrically accurate for gas-phase molecular calculations. In the chemistry community, one popular functional is known as BLYP (from the name Becke for the exchange part and Lee, Yang and Parr for the correlation part). Even more widely used is B3LYP which is a hybrid functional in which the exchange energy, in this case from Becke's exchange functional, is combined with the exact energy from Hartree–Fock theory. Along with the component exchange and correlation functionals, three parameters define the hybrid functional, specifying how much of the exact exchange is mixed in. The adjustable parameters in hybrid functionals are generally fitted to a 'training set' of molecules. Unfortunately, although the results obtained with these functionals are usually sufficiently accurate for most applications, there is no systematic way of improving them (in contrast to some of the traditional wavefunction-based methods like configuration interaction or coupled cluster theory). Hence in the current DFT approach it is not possible to estimate the error of the calculations without comparing them to other methods or experiments.



Thomas–Fermi model

The predecessor to density functional theory was the **Thomas–Fermi model**, developed independently by both Thomas and Fermi in 1927. They used a statistical model to approximate the distribution of electrons in an atom. The mathematical basis postulated that electrons are distributed uniformly in phase space with two electrons in every h^3 of volume. For each element of coordinate space volume d^3r we can fill out a sphere of momentum space up to the Fermi momentum p_f

$$(4/3)\pi p_f^3(\vec{r}).$$

Equating the number of electrons in coordinate space to that in phase space gives:

$$n(\vec{r}) = \frac{8\pi}{3h^3} p_f^3(\vec{r}).$$

Solving for p_f and substituting into the classical kinetic energy formula then leads directly to a kinetic energy represented as a functional of the electron density:

$$t_{TF}[n] = \frac{p^2}{2m_e} \propto \frac{(n^{1/3})^2}{2m_e} \propto n^{2/3}(\vec{r})$$

$$T_{TF}[n] = C_F \int n(\vec{r}) n^{2/3}(\vec{r}) d^3r = C_F \int n^{5/3}(\vec{r}) d^3r$$

where $C_F = \frac{3h^2}{10m_e} \left(\frac{3}{8\pi}\right)^{2/3}$.

As such, they were able to calculate the energy of an atom using this kinetic energy functional combined with the classical expressions for the nuclear-electron and electron-electron interactions (which can both also be represented in terms of the electron density).

Although this was an important first step, the Thomas–Fermi equation's accuracy is limited because the resulting kinetic energy functional is only approximate, and because the method does not attempt to represent the exchange energy of an atom as a conclusion of the Pauli principle. An exchange energy functional was added by Dirac in 1928.

However, the Thomas–Fermi–Dirac theory remained rather inaccurate for most applications. The largest source of error was in the representation of the kinetic energy, followed by the errors in the exchange energy, and due to the complete neglect of electron correlation.

Teller (1962) showed that Thomas–Fermi theory cannot describe molecular bonding. This can be overcome by improving the kinetic energy functional.

The kinetic energy functional can be improved by adding the Weizsäcker (1935) correction:

$$T_W[n] = \frac{1}{8} \frac{\hbar^2}{m} \int \frac{|\nabla n(\vec{r})|^2}{n(\vec{r})} d^3r.$$

Hohenberg–Kohn theorems

1. If two systems of electrons, one trapped in a potential $v_1(\vec{r})$ and the other in $v_2(\vec{r})$, have the same ground-state density $n(\vec{r})$ then necessarily $v_1(\vec{r}) - v_2(\vec{r}) = \text{const}$.

Corollary: the ground state density uniquely determines the potential and thus all properties of the system, including the many-body wave function. In particular, the "HK" functional, defined as $F[n] = T[n] + U[n]$ is a universal functional of the density (not depending explicitly on the external potential).

2. For any positive integer N and potential $v(\vec{r})$ it exists a density functional $F[n]$ such that $E_{(v,N)}[n] = F[n] + \int v(\vec{r})n(\vec{r})d^3r$ obtains its minimal value at the ground-state density of N electrons in the potential $v(\vec{r})$. The minimal value of $E_{(v,N)}[n]$ is then the ground state energy of this system.

Pseudo-potentials

The many electron Schrödinger equation can be very much simplified if electrons are divided in two groups: valence electrons and inner core electrons. The electrons in the inner shells are strongly bound and do not play a significant role in the chemical binding of atoms; they also partially screen the nucleus, thus forming with the nucleus an almost inert core. Binding properties are almost completely due to the valence electrons, especially in metals and semiconductors. This separation suggests that inner electrons can be ignored in a large number of cases, thereby reducing the atom to an ionic core that interacts with the valence electrons. The use of an effective interaction, a

pseudopotential, that approximates the potential felt by the valence electrons, was first proposed by Fermi in 1934 and Hellmann in 1935. In spite of the simplification pseudo-potentials introduce in calculations, they remained forgotten until the late 50's.

Ab initio Pseudo-potentials

A crucial step toward more realistic pseudo-potentials was given by Topp and Hopfield and more recently Cronin, who suggested that the pseudo-potential should be adjusted such that they describe the valence charge density accurately. Based on that idea, modern pseudo-potentials are obtained inverting the free atom Schrödinger equation for a given reference electronic configuration and forcing the pseudo wave-functions to coincide with the true valence wave functions beyond a certain distance r_l . The pseudo wave-functions are also forced to have the same norm as the true valence wave-functions and can be written as

$$R_l^{PP}(r) = R_{nl}^{AE}(r).$$

$$\int_0^{r_l} dr |R_l^{PP}(r)|^2 r^2 = \int_0^{r_l} dr |R_{nl}^{AE}(r)|^2 r^2.$$

where $R_l(r)$ is the radial part of the wavefunction with angular momentum l , and PP and AE denote, respectively, the pseudo wave-function and the true (all-electron) wave-function. The index n in the true wave-functions denotes the valence level. The distance beyond which the true and the pseudo wave-functions are equal, r_l , is also l -dependent.

Software supporting DFT

DFT is supported by many Quantum chemistry and solid state physics software, often along with other methods. Versatile software packages for DFT include: the Vienna Ab initio Simulation Package (VASP),^[4] QUANTUM-ESPRESSO,^[5] ABINIT, GPAW,^[6] Gaussian,^[7] BigDFT, WIEN2k and so on.^[8]

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External links

- Walter Kohn, Nobel Laureate (<http://www.vega.org.uk/video/programme/23>) Freeview video interview with Walter on his work developing density functional theory by the Vega Science Trust.
- Klaus Capelle, A bird's-eye view of density-functional theory (<http://arxiv.org/abs/cond-mat/0211443>)
- Walter Kohn, Nobel Lecture (<http://nobelprize.org/chemistry/laureates/1998/kohn-lecture.pdf>)
- Density functional theory on arxiv.org (<http://xstructure.inr.ac.ru/x-bin/theme3.py?level=1&index1=447765>)
- FreeScience Library -> Density Functional Theory (<http://freescience.info/books.php?id=30>)
- Density Functional Theory – an introduction (<http://arxiv.org/abs/physics/9806013>)
- Electron Density Functional Theory – Lecture Notes (http://www.fh.huji.ac.il/~roib/LectureNotes/DFT/DFT_Course_Roi_Baer.pdf)
- Density Functional Theory through Legendre Transformation (<http://ptp.ipap.jp/link?PTP/92/833/>) pdf (<http://ann.phys.sci.osaka-u.ac.jp/~kotani/pap/924-09.pdf>)
- Kieron Burke : Book On DFT : " THE ABC OF DFT " <http://dft.uci.edu/materials/bookABCDFT/gamma/g1.pdf>
- Modeling Materials Continuum, Atomistic and Multiscale Techniques, Book (<http://www.modelingmaterials.org/the-books>)

Quantum chemistry composite methods

| |
|---|
| Electronic structure methods |
| Valence bond theory |
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| Hartree–Fock method Møller–Plesset perturbation theory Configuration interaction Coupled cluster Multi-configurational self-consistent field Quantum chemistry composite methods Quantum Monte Carlo Linear combination of atomic orbitals |
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Quantum chemistry composite methods (also referred to as thermochemical recipes) are computational chemistry methods that aim for high accuracy by combining the results of several calculations. They combine methods with a high level of theory and a small basis set with methods that employ lower levels of theory with larger basis sets. They are commonly used to calculate thermodynamic quantities such as enthalpies of formation, atomization energies, ionization energies and electron affinities. They aim for chemical accuracy which is usually defined as within 1 kcal/mol of the experimental value. The first systematic model chemistry of this type with broad applicability was called Gaussian-1 (G1) introduced by John Pople. This was quickly replaced by the Gaussian-2 (G2) which has been used extensively. The Gaussian-3 (G3) was introduced later.

Gaussian-n Theories

Gaussian-2 (G2)

The G2 uses seven calculations:

1. the molecular geometry is obtained by a MP2 optimization using the 6-31G(d) basis set and all electrons included in the perturbation. This geometry is used for all subsequent calculations.
2. The highest level of theory is a quadratic configuration interaction calculation with single and double excitations and a triples excitation contribution (QCISD(T)) with the 6-311G(d) basis set. Such a calculation in the Gaussian and Spartan programs also give the MP2 and MP4 energies which are also used.
3. The effect of polarization functions is assessed using an MP4 calculation with the 6-311G(2df,p) basis set.
4. The effect of diffuse functions is assessed using an MP4 calculation with the 6-311+G(d, p) basis set.
5. The largest basis set is 6-311+G(3df,2p) used at the MP2 level of theory.

6. A Hartree-Fock geometry optimization with the 6-31G(d) basis set used to give a geometry for:
7. A frequency calculation with the 6-31G(d) basis set to obtain the zero-point vibrational energy (ZPVE)

The various energy changes are assumed to be additive so the combined energy is given by:

$$\text{EQCISD(T) from 2} + [\text{EMP4 from 3} - \text{EMP4 from 2}] + [\text{EMP4 from 4} - \text{EMP4 from 2}] + [\text{EMP2 from 5} + \text{EMP2 from 2} - \text{EMP2 from 3} - \text{EMP2 from 4}]$$

The second term corrects for the effect of adding the polarization functions. The third term corrects for the diffuse functions. The final term corrects for the larger basis set with the terms from steps 2, 3 and 4 preventing contributions from being counted twice. Two final corrections are made to this energy. The ZPVE is scaled by 0.8929. An empirical correction is then added to account for factors not considered above. This is called the higher level correction (HC) and is given by $-0.00481 \times (\text{number of valence electrons} - 0.00019 \times (\text{number of unpaired valence electrons}))$. The two numbers are obtained calibrating the results against the experimental results for a set of molecules. The scaled ZPVE and the HLC are added to give the final energy. For some molecules containing one of the third row elements Ga - Xe, a further term is added to account for spin orbit coupling.

Several variants of this procedure have been used. Removing steps 3 and 4 and relying only on the MP2 result from step 5 is significantly cheaper and only slightly less accurate. This is the G2MP2 method. Sometimes the geometry is obtained using a density functional theory method such as B3LYP and sometimes the QCISD(T) method in step 1 is replaced by the coupled cluster method CCSD(T).

Gaussian-3 (G3)

The G3 is very similar to G2 but learns from the experience with G2 theory. The 6-311G basis set is replaced by the smaller 6-31G basis. The final MP2 calculations use a larger basis set, generally just called G3large, and correlating all the electrons not just the valence electrons as in G2 theory, additionally a spin-orbit correction term and an empirical correction for valence electrons are introduced. This gives some core correlation contributions to the final energy. The HLC takes the same form but with different empirical parameters. A Gaussian-4 method has been introduced. An alternative to the Gaussian-n methods is the correlation consistent composite method.

Gaussian-4 (G4)

Gaussian 4 (G4) theory is an approach for the calculation of energies of molecular species containing first-row (Li-F), second-row (Na-Cl), and third row main group elements. G4 theory is an improved modification of the earlier approach G3 theory. The modifications to G3- theory are the change in an estimate of the Hartree-Fock energy limit, an expanded polarization set for the large basis set calculation, use of CCSD(T) energies, use of geometries from density functional theory and zero-point energies, and two added higher level correction parameters. According to the developers, this theory gives significant improvement over G3-theory.

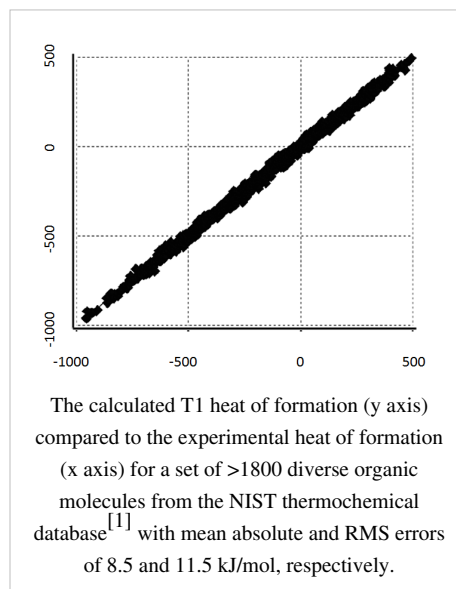
T1

The T1 method. is an efficient computational approach developed for calculating accurate heats of formation of uncharged, closed-shell molecules comprising H, C, N, O, F, Si, P, S, Cl and Br, within experimental error. It is practical for molecules up to molecular weight ~ 500 a.m.u.

T1 method as incorporated in Spartan consists of:

1. HF/6-31G* optimization.
2. RI-MP2/6-311+G(2d,p)[6-311G*] single point energy with dual basis set.
3. An empirical correction using atom counts, Mulliken bond orders, HF/6-31G* and RI-MP2 energies as variables.

T1 follows the G3(MP2) recipe, however, by substituting an HF/6-31G* for the MP2/6-31G* geometry, eliminating both the HF/6-31G* frequency and QCISD(T)/6-31G* energy and approximating the MP2/G3MP2large energy using dual basis set RI-MP2 techniques, the T1 method reduces computation time by up to 3 orders of magnitude. Atom counts, Mulliken bond orders and HF/6-31G* and RI-MP2 energies are introduced as variables in a linear regression fit to a set of 1126 G3(MP2) heats of formation. The T1 procedure reproduces these values with mean absolute and RMS errors of 1.8 and 2.5 kJ/mol, respectively. T1 reproduces experimental heats of formation for a set of 1805 diverse organic molecules from the NIST thermochemical database with mean absolute and RMS errors of 8.5 and 11.5 kJ/mol, respectively.



Correlation consistent Composite Approach (ccCA)

This approach, developed at the University of North Texas by Angela K. Wilson's research group, utilizes the correlation consistent basis sets developed by Dunning and co-workers. Unlike the Gaussian-n methods, ccCA does not contain any empirically fitted term. The B3LYP density functional method with the cc-pVTZ basis set, and cc-pV(T+d)Z for third row elements (Na - Ar), are used to determine the equilibrium geometry. Single point calculations are then used to find the reference energy and additional contributions to the energy. The total ccCA energy for main group is calculated by:

$$E_{\text{ccCA}} = E_{\text{MP2/CBS}} + \Delta E_{\text{CC}} + \Delta E_{\text{CV}} + \Delta E_{\text{SR}} + \Delta E_{\text{ZPE}} + \Delta E_{\text{SO}}$$

The reference energy $E_{\text{MP2/CBS}}$ is the MP2/aug-cc-pVnZ (where n=D,T,Q) energies extrapolated at the complete basis set limit by the Peterson mixed gaussian exponential extrapolation scheme. CCSD(T)/cc-pVTZ is used to account for correlation beyond the MP2 theory:

$$\Delta E_{\text{CC}} = E_{\text{CCSD(T)/cc-pVTZ}} - E_{\text{MP2/cc-pVTZ}}$$

Core-core and core-valence interactions are accounted for using MP2(FC1)/aug-cc-pCVTZ:

$$\Delta E_{\text{CV}} = E_{\text{MP2(FC1)/aug-cc-pCVTZ}} - E_{\text{MP2/aug-cc-pVTZ}}$$

Scalar relativistic effects are also taken into account with a one-particle Douglas Kroll Hess Hamiltonian and recontracted basis sets:

$$\Delta E_{\text{SR}} = E_{\text{MP2-DK/cc-pVTZ-DK}} - E_{\text{MP2/cc-pVTZ}}$$

The last two terms are Zero Point Energy corrections scaled with a factor of 0.989 to account for deficiencies in the harmonic approximation and spin-orbit corrections considered only for atoms.

Complete basis set methods (CBS)

These methods by Petersson and coworkers^[2] have some similarity to G2 and G3 but contain an MP2 extrapolation to the complete basis set limit as one step.

Weizmann- n Theories

The Weizmann- n ab initio methods (W_n , $n = 1-4$) are highly-accurate composite theories devoid of empirical parameters. These theories are capable of sub-kJ/mol accuracies in prediction of fundamental thermochemical quantities such as heats of formation and atomization energies, and unprecedented accuracies in prediction of spectroscopic constants. The ability of these theories to successfully reproduce the CCSD(T)/CBS (W_1 and W_2), CCSDT(Q)/CBS (W_3), and CCSDTQ5/CBS (W_4) energies relies on judicious combination of very large Gaussian basis sets with basis-set extrapolation techniques. Thus, the high accuracy of W_n theories comes with the price of a significant computational cost. In practice, for systems consisting of more than ~ 9 non-hydrogen atoms (with C1 symmetry), even the computationally more economical W_1 theory becomes prohibitively expensive with current mainstream server hardware.

In an attempt to extend the applicability of the W_1 and W_2 ab initio thermochemistry methods, explicitly correlated versions of these theories have been developed (W_1-F_{12} and W_2-F_{12}). W_1-F_{12} was successfully applied to large aromatic systems (e.g., tetracene) as well as to systems of biological relevance (e.g., DNA bases).


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Quantum Monte Carlo

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| Electronic structure methods |
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Quantum Monte Carlo is a large class of computer algorithms that simulate quantum systems with the idea of solving the quantum many-body problem. They use, in one way or another, the Monte Carlo method to handle the many-dimensional integrals that arise. Quantum Monte Carlo allows a direct representation of many-body effects in the wave function, at the cost of statistical uncertainty that can be reduced with more simulation time. For bosons without frustration, there exist numerically exact and polynomial-scaling algorithms. For fermions, there exist very good approximations and numerically exact exponentially scaling quantum Monte Carlo algorithms, but none that are both.

Background

In principle, any physical system can be described by the many-body Schrödinger equation as long as the constituent particles are not moving "too" fast; that is, they are not moving near the speed of light. This covers a wide range of electronic problems in condensed matter physics, so if we could solve the Schrödinger equation for a given system, we could predict its behavior, which has important applications in fields from computers to biology. This also includes the nuclei in Bose–Einstein condensate and superfluids such as liquid helium. The difficulty is that the Schrödinger equation involves a function of a number of coordinates that is exponentially large in the number of particles, and is therefore difficult, if not impossible, to solve even using parallel computing technology in a reasonable amount of time. Traditionally, theorists have approximated the many-body wave function as an antisymmetric function of one-body orbitals.^[1] This kind of formulation either limits the possible wave functions, as in the case of the Hartree–Fock (HF) approximation, or converges very slowly, as in configuration interaction. One of the reasons for the difficulty with an HF initial estimate (ground state seed, also known as Slater determinant) is that it is very difficult to model the electronic and nuclear cusps in the wavefunction. However, one does not

generally model at this point of the approximation. As two particles approach each other, the wavefunction has exactly known derivatives.

Quantum Monte Carlo is a way around these problems because it allows us to model a many-body wavefunction of our choice directly. Specifically, we can use a Hartree-Fock approximation as our starting point but then multiplying it by any symmetric function, of which Jastrow functions are typical, designed to enforce the cusp conditions. Most methods aim at computing the ground state wavefunction of the system, with the exception of path integral Monte Carlo and finite-temperature auxiliary field Monte Carlo, which calculate the density matrix.

There are several quantum Monte Carlo methods, each of which uses Monte Carlo in different ways to solve the many-body problem:

Quantum Monte Carlo methods

- Stochastic Green function (SGF) algorithm : An algorithm designed for bosons that can simulate any complicated lattice Hamiltonian that does not have a sign problem. Used in combination with a directed update scheme, this is a powerful tool.
- Variational Monte Carlo : A good place to start; it is commonly used in many sorts of quantum problems.
- Diffusion Monte Carlo : The most common high-accuracy method for electrons (that is, chemical problems), since it comes quite close to the exact ground-state energy fairly efficiently. Also used for simulating the quantum behavior of atoms, etc.
- Path integral Monte Carlo : Finite-temperature technique mostly applied to bosons where temperature is very important, especially superfluid helium.
- Auxiliary field Monte Carlo : Usually applied to lattice problems, although there has been recent work on applying it to electrons in chemical systems.
- Reptation Monte Carlo : Recent zero-temperature method related to path integral Monte Carlo, with applications similar to diffusion Monte Carlo but with some different tradeoffs.
- Gaussian quantum Monte Carlo

Implementations

- ALPS ^[2]
 - CASINO ^[3]
 - CHAMP ^[4]
 - Monte Python ^[5]
 - PIMC++ ^[6]
 - pi-qmc ^[7]
 - QMcBeaver ^[8]
 - QmcMol ^[9]
 - QMCPACK ^[10]
 - Qumax ^[11]
 - Qwalk ^[12]
 - TurboRVB ^[13]
 - Zori ^[14]
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 - [4] <http://pages.physics.cornell.edu/~cyrus/champ.html>
 - [5] <http://code.google.com/p/montepython/>
 - [6] <http://cms.mcc.uiuc.edu/pimcpp/>
 - [7] <http://code.google.com/p/pi-qmc/>
 - [8] <http://qmcbeaver.sourceforge.net/>
 - [9] <http://www.lct.jussieu.fr/pagesequipe/qmcmol/qmcmol/>
 - [10] <http://qmcpack.cmscc.org/>
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External links

- QMCWIKI (<http://www.qmcwiki.org/>)
- Joint DEMOCRITOS-ICTP School on Continuum Quantum Monte Carlo Methods (http://cdsagenda5.ictp.trieste.it/full_display.php?ida=a0332&fid=)
- FreeScience Library - Quantum Monte Carlo (<http://freescience.info/books.php?id=35>)
- UIUC 2007 Summer School on Computational Materials Science: Quantum Monte Carlo from Minerals and Materials to Molecules (<http://www.mcc.uiuc.edu/summerschool/2007/qmc/>)
- Quantum Monte Carlo in the Apuan Alps VIII (<http://www.vallico.net/tti/tti.html>) - international QMC workshop, Vallico Sotto, Tuscany, Italy, 27 July - 3 August 2013 - Announcement (http://www.vallico.net/tti/qmcitaa_13/), Poster (<http://www.tcm.phy.cam.ac.uk/~mdt26/posterc13.png>)
- Quantum Monte Carlo and the CASINO program VIII (<http://www.vallico.net/tti/tti.html>) - international QMC summer school, Vallico Sotto, Tuscany, Italy, 4 August - 11 August 2013 - Announcement (http://www.vallico.net/tti/qmcatcp_13), Poster (<http://www.tcm.phy.cam.ac.uk/~mdt26/poster.png>)
- Quantum Monte Carlo simulator (Qwalk) (<http://nanohub.org/tools/qwalk>)

K·p perturbation theory

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In solid-state physics, **k·p perturbation theory** is an approximation scheme for calculating the band structure (particularly effective mass) and optical properties of crystalline solids. It is pronounced "k dot p", and is also called the "k·p method". This theory has been applied specifically in the framework of the **Luttinger–Kohn** model (after Joaquin Mazdak Luttinger and Walter Kohn), and of the **Kane model** (after Evan O. Kane).

Background and derivation

Bloch's theorem and wavevectors

According to quantum mechanics (in the single-electron approximation), the electrons in any material have wavefunctions which can be described by the following Schrödinger equation:

$$\left(\frac{\mathbf{p}^2}{2m} + V \right) \psi = E\psi$$

where \mathbf{p} is the quantum-mechanical momentum operator, V is the potential, and m is the mass of an electron. (This equation neglects the spin-orbit effect; see below.)

In a crystalline solid, V is a periodic function, with the same periodicity as the crystal lattice. Bloch's theorem proves that the solutions to this differential equation can be written as follows:

$$\psi_{n,\mathbf{k}}(\mathbf{x}) = e^{i\mathbf{k}\cdot\mathbf{x}} u_{n,\mathbf{k}}(\mathbf{x})$$

where \mathbf{k} is a vector (called the *wavevector*), n is a discrete index (called the *band index*), and $u_{n,\mathbf{k}}$ is a function with the same periodicity as the crystal lattice.

For any given n , the associated states are called a band. In each band, there will be a relation between the wavevector \mathbf{k} and the energy of the state $E_{n,\mathbf{k}}$, called the band dispersion. Calculating this dispersion is one of the primary applications of $k\cdot p$ perturbation theory.

Perturbation theory

The periodic function $u_{n,\mathbf{k}}$ satisfies the following Schrödinger-type equation:

$$H_{\mathbf{k}}u_{n,\mathbf{k}} = E_{n,\mathbf{k}}u_{n,\mathbf{k}}$$

where the Hamiltonian is

$$H_{\mathbf{k}} = \frac{p^2}{2m} + \frac{\hbar\mathbf{k} \cdot \mathbf{p}}{m} + \frac{\hbar^2 k^2}{2m} + V$$

Note that \mathbf{k} is a vector consisting of three real numbers with units of inverse length, while \mathbf{p} is a vector of operators; to be explicit,

$$\mathbf{k} \cdot \mathbf{p} = k_x(-i\hbar\frac{\partial}{\partial x}) + k_y(-i\hbar\frac{\partial}{\partial y}) + k_z(-i\hbar\frac{\partial}{\partial z})$$

In any case, we write this Hamiltonian as the sum of two terms:

$$H = H_0 + H'_{\mathbf{k}}, \quad H_0 = \frac{p^2}{2m} + V, \quad H'_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} + \frac{\hbar\mathbf{k} \cdot \mathbf{p}}{m}$$

This expression is the basis for perturbation theory. The "unperturbed Hamiltonian" is H_0 , which in fact equals the exact Hamiltonian at $\mathbf{k}=0$ (i.e., at the Gamma point). The "perturbation" is the term $H'_{\mathbf{k}}$. The analysis that results is called "k-p perturbation theory", due to the term proportional to $k\cdot p$. The result of this analysis is an expression for $E_{n,\mathbf{k}}$ and $u_{n,\mathbf{k}}$ in terms of the energies and wavefunctions at $\mathbf{k}=0$.

Note that the "perturbation" term $H'_{\mathbf{k}}$ gets progressively smaller as \mathbf{k} approaches zero. Therefore, k-p perturbation theory is most accurate for small values of \mathbf{k} . However, if enough terms are included in the perturbative expansion, then the theory can in fact be reasonably accurate for any value of \mathbf{k} in the entire Brillouin zone.

Expression for a nondegenerate band

For a nondegenerate band (i.e., a band which has a different energy at $\mathbf{k}=0$ from any other band), with an extremum at $\mathbf{k}=0$, and with no spin-orbit coupling, the result of $k\cdot p$ perturbation theory is (to lowest nontrivial order):

$$u_{n,\mathbf{k}} = u_{n,0} + \frac{\hbar}{m} \sum_{n' \neq n} \frac{\langle u_{n,0} | \mathbf{k} \cdot \mathbf{p} | u_{n',0} \rangle}{E_{n,0} - E_{n',0}} u_{n',0}$$

$$E_{n,\mathbf{k}} = E_{n,0} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \sum_{n' \neq n} \frac{|\langle u_{n,0} | \mathbf{k} \cdot \mathbf{p} | u_{n',0} \rangle|^2}{E_{n,0} - E_{n',0}}$$

The parameters that are required to do these calculations, namely $E_{n,0}$ and $\langle u_{n,0} | \mathbf{p} | u_{n',0} \rangle$, are typically inferred from experimental data. (The latter are called "optical matrix elements".)

In practice, the sum over n *often includes only the nearest one or two bands, since these tend to be the most important (due to the denominator). However, for improved accuracy, especially at larger \mathbf{k} , more bands must be included, as well as more terms in the perturbative expansion than the ones written above.*

Effective mass

Using the expression above for the energy dispersion relation, a simplified expression for the effective mass in the conduction band of a semiconductor can be found. To approximate the dispersion relation in the case of the conduction band, take the energy E_{n0} as the minimum conduction band energy E_{c0} and include in the summation only terms with energies near the valence band maximum, where the energy difference in the denominator is smallest. (These terms are the largest contributions to the summation.) This denominator is then approximated as the

band gap E_g , leading to an energy expression:

$$E_c(\mathbf{k}) \approx E_{c0} + \frac{(\hbar k)^2}{2m} + \frac{\hbar^2}{E_g m^2} \sum_n |\langle u_{c,0} | \mathbf{k} \cdot \mathbf{p} | u_{n,0} \rangle|^2$$

The effective mass in direction ℓ is then:

$$\frac{1}{m_\ell} = \frac{1}{\hbar^2} \sum_m \frac{\partial^2 E_c(\mathbf{k})}{\partial k_\ell \partial k_m} \approx \frac{1}{m} + \frac{2}{E_g m^2} \sum_{m, n} \langle u_{c,0} | p_\ell | u_{n,0} \rangle \langle u_{n,0} | p_m | u_{c,0} \rangle$$

Ignoring the details of the matrix elements, the key consequences are that the effective mass varies with the smallest bandgap and goes to zero as the gap goes to zero. A useful approximation for the matrix elements in direct gap semiconductors is:^[1]

$$\frac{2}{E_g m^2} \sum_{m, n} |\langle u_{c,0} | p_\ell | u_{n,0} \rangle| |\langle u_{c,0} | p_m | u_{n,0} \rangle| \approx 20 \text{eV} \frac{1}{m E_g},$$

which applies within about 15% or better to most group-IV, III-V and II-VI semiconductors.^[2]

In contrast to this simple approximation, in the case of valence band energy the *spin-orbit* interaction must be introduced (see below) and many more bands must be individually considered. The calculation is provided in Yu and Cardona.^[3] In the valence band the mobile carriers are *holes*. One finds there are two types of hole, named *heavy* and *light*, with anisotropic masses.

***k-p* model with spin-orbit interaction**

Including the spin-orbit interaction, the Schrödinger equation for u is:

$$H_{\mathbf{k}} u_{n,\mathbf{k}} = E_{n,\mathbf{k}} u_{n,\mathbf{k}}$$

where

$$H_{\mathbf{k}} = \frac{p^2}{2m} + \frac{\hbar \mathbf{k} \cdot \mathbf{p}}{m} + \frac{\hbar^2 k^2}{2m} + V + \frac{1}{4m^2 c^2} (\vec{\sigma} \times \nabla V) \cdot (\hbar \mathbf{k} + \mathbf{p})$$

where $\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is a vector consisting of the three Pauli matrices. This Hamiltonian can be subjected to the same sort of perturbation-theory analysis as above.

Calculation in degenerate case

For degenerate or nearly degenerate bands, in particular the valence bands in certain materials such as gallium arsenide, the equations can be analyzed by the methods of degenerate perturbation theory. Models of this type include the "Luttinger-Kohn model" (a.k.a. "Kohn-Luttinger model"), and the "Kane model".


Notes and references

[1] A *direct gap* semiconductor is one where the valence band maximum and conduction band minimum occur at the same position in \mathbf{k} -space, usually the so-called Γ -point where $\mathbf{k} = 0$.

[2] See Table 2.22 (<http://books.google.com/books?id=W9pdJZoAeyEC&pg=PA244&dq=isbn:3540254706#PPA71,M1>) in Yu & Cardona, *op. cit.*

[3] See Yu & Cardona, *op. cit.* pp. 75-82

Muffin-tin approximation

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The **muffin-tin approximation** is a shape approximation of the potential field in an atomistic environment. It is most commonly employed in quantum mechanical simulations of electronic band structure in solids. The approximation was proposed by John C. Slater. Augmented plane wave method is a method which uses muffin tin approximation. It is a method to approximate the energy states of an electron in a crystal lattice. The basis approximation lies in the potential in which the potential is assumed to be spherically symmetric in the muffin tin region and constant in the interstitial region. Wave functions (the augmented plane waves) are constructed by matching solutions of the Schrödinger equation within each sphere with plane-wave solutions in the interstitial region, and linear combinations of these wave functions are then determined by the variational method. Many modern electronic structure methods employ the approximation. Among them are the augmented plane wave (APW) method, the linear muffin-tin orbital method (LMTO) and various Green's function methods. One application is found in the variational theory developed by Korringa (1947) and by Kohn and Rostocker (1954) referred to as the *KKR method*. This method has been adapted to treat random materials as well, where it is called the *KKR coherent potential approximation*.


In its simplest form, non-overlapping spheres are centered on the atomic positions. Within these regions, the screened potential experienced by an electron is approximated to be spherically symmetric about the given nucleus. In the remaining interstitial region, the potential is approximated as a constant. Continuity of the potential between the atom-centered spheres and interstitial region is enforced.

In the interstitial region of constant potential, the single electron wave functions can be expanded in terms of plane waves. In the atom-centered regions, the wave functions can be expanded in terms of spherical harmonics and the eigenfunctions of a radial Schrödinger equation. Such use of functions other than plane waves as basis functions is termed the augmented plane-wave approach (of which there are many variations). It allows for an efficient

representation of single-particle wave functions in the vicinity of the atomic cores where they can vary rapidly (and where plane waves would be a poor choice on convergence grounds in the absence of a pseudopotential).

References

LCAO method

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A **linear combination of atomic orbitals** or **LCAO** is a quantum superposition of atomic orbitals and a technique for calculating molecular orbitals in quantum chemistry.^[1] In quantum mechanics, electron configurations of atoms are described as wavefunctions. In mathematical sense, these wave functions are the basis set of functions, the basis functions, which describe the electrons of a given atom. In chemical reactions, orbital wavefunctions are modified, i.e. the electron cloud shape is changed, according to the type of atoms participating in the chemical bond.

It was introduced in 1929 by Sir John Lennard-Jones with the description of bonding in the diatomic molecules of the first main row of the periodic table, but had been used earlier by Linus Pauling for H_2^+ .^{[2][3]}

A mathematical description follows.

An initial assumption is that the number of molecular orbitals is equal to the number of atomic orbitals included in the linear expansion. In a sense, n atomic orbitals combine to form n molecular orbitals, which can be numbered $i = 1$ to n and which may not all be the same. The expression (linear expansion) for the i th molecular orbital would be:

$$\phi_i = c_{1i}\chi_1 + c_{2i}\chi_2 + c_{3i}\chi_3 + \cdots + c_{ni}\chi_n$$

or

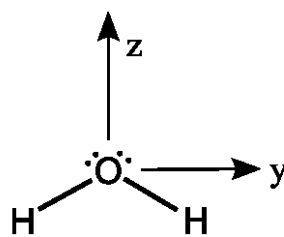
$$\phi_i = \sum_r c_{ri}\chi_r$$

where ϕ_i (ϕ) is a molecular orbital represented as the sum of n atomic orbitals χ_r (χ), each multiplied by a corresponding coefficient C_{ri} , and r (numbered 1 to n) represents which atomic orbital is combined in the term. The coefficients are the weights of the contributions of the n atomic orbitals to the molecular orbital. The Hartree-Fock procedure is used to obtain the coefficients of the expansion.

The orbitals are thus expressed as linear combinations of basis functions, and the basis functions are one-electron functions centered on nuclei of the component atoms of the molecule. The atomic orbitals used are typically those of hydrogen-like atoms since these are known analytically i.e. Slater-type orbitals but other choices are possible like Gaussian functions from standard basis sets.

By minimizing the total energy of the system, an appropriate set of coefficients of the linear combinations is determined. This quantitative approach is now known as the Hartree-Fock method. However, since the development of computational chemistry, the LCAO method often refers not to an actual optimization of the wave function but to a qualitative discussion which is very useful for predicting and rationalizing results obtained via more modern methods. In this case, the shape of the molecular orbitals and their respective energies are deduced approximately from comparing the energies of the atomic orbitals of the individual atoms (or molecular fragments) and applying some recipes known as level repulsion and the like. The graphs that are plotted to make this discussion clearer are called **correlation diagrams**. The required atomic orbital energies can come from calculations or directly from experiment via Koopmans' theorem.

This is done by using the symmetry of the molecules and orbitals involved in bonding. The first step in this process is assigning a point group to the molecule. A common example is water, which is of C_{2v} symmetry. Then a reducible representation of the bonding is determined demonstrated below for water:

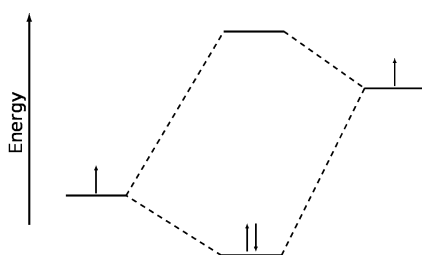


| C_{2v} | E | C_2 | $\sigma_v(xz)$ | $\sigma'_v(yz)$ | | |
|-----------------|---|-------|----------------|-----------------|----------|-----------------|
| A_1 | 1 | 1 | 1 | 1 | z | x^2, y^2, z^2 |
| A_2 | 1 | 1 | -1 | -1 | R_z | xy |
| B_1 | 1 | -1 | 1 | -1 | x, R_y | xz |
| B_2 | 1 | -1 | -1 | 1 | y, R_x | yz |
| Γ_σ | 2 | 0 | 0 | 2 | | |

$$\Gamma_\sigma = A_1 + B_2$$

Each operation in the point group is performed upon the molecule. The number of bonds that are unmoved is the character of that operation. This reducible representation is decomposed into the sum of irreducible representations. These irreducible representations correspond to the symmetry of the orbitals involved.

MO diagrams provide simple qualitative LCAO treatment.



Quantitative theories are the Hückel method, the extended Hückel method and the Pariser–Parr–Pople method.

External links

- [LCAO @ chemistry.umeche.maine.edu](http://chemistry.umeche.maine.edu) Link ^[4]

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