

MOLECULAR ENERGETICS: VALENCE BOND AND MOLECULAR ORBITAL METHODS. DENSITY FUNCTIONAL THEORY OF ATOMS AND MOLECULES

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Contents

1. Introduction
 2. Methods for obtaining approximate electronic wavefunctions
 - 2.1 One-determinant approximation and the Hartree-Fock theory
 - 2.2 Many-determinant Wavefunctions
 3. Density functional theory
- Acknowledgements
Glossary
Bibliography
Biographical Sketch

Summary

Molecular orbital and valence bond methods for obtaining approximate electronic wavefunctions are described. Techniques developed for analyzing molecular charge densities are presented together with applications to specific examples. Fundamental concepts of density functional theory and methods derived for the calculation of static properties of molecules are discussed.

1. Introduction

Molecular energetics is a branch of quantum chemistry (See *Schrödinger Equation and Quantum Chemistry*) that studies bound stationary states of molecules looking, in particular, at electronic structure and properties. The methods used for this study are quantum mechanical and have been developed from the early days of quantum chemistry. They constitute the methodological structure underlying that “pattern of understanding” for the interpretation of chemical problems, that is the *theory of valence*, or theory of molecular structure. The advent of electronic computers has given a strong impetus to this field allowing the implementation of quantum mechanical methods already known, but too difficult to use without computers on real problems. Consequently, new methods and, in particular, new sophisticated numerical procedures for the calculation of energies and static properties of molecules have been developed

and methods originally proposed in different fields, e.g. solid-state and nuclear physics, have been successfully applied also to molecules.

In what follows, we will describe these methods making a distinction between those based on wavefunctions, i.e. those proposed for obtaining approximate solutions of the time-independent Schrödinger equation, and the Density Functional Theory (DFT) in which the fundamental quantity is the ground-state electronic density, any other ground-state property being a functional of the density.

Both types of methods refer to the same model of molecule, viewed as a system of nuclei and electrons interacting via coulomb forces and internal electromagnetic forces, the latter associated with the intrinsic magnetic moments of the particles. The coulomb forces give rise to the electrostatic Hamiltonian (\hat{H}_0) which has an electronic (\hat{H}_e), a nuclear (\hat{H}_n) and an electron-nuclei interaction term (\hat{V}_{en}), which in atomic units are

$$\begin{aligned}\hat{H}_0 &= \hat{H}_e + \hat{H}_n + \hat{V}_{en} \\ \hat{H}_e &= -\frac{1}{2} \sum_i^N \Delta_{\vec{r}_i} + \sum_{i<j}^N \frac{1}{|\vec{r}_i - \vec{r}_j|} = \hat{T}_e + \hat{V}_{ee} \\ \hat{H}_n &= -\frac{1}{2} \sum_{\alpha}^{\mathcal{N}} \frac{1}{M_{\alpha}} \Delta_{\vec{R}_{\alpha}} + \sum_{\alpha<\beta}^{\mathcal{N}} \frac{Z_{\alpha} Z_{\beta}}{|\vec{R}_{\alpha} - \vec{R}_{\beta}|} = \hat{T}_n + \hat{V}_{nn} \\ \hat{V}_{en} &= -\sum_{\alpha}^{\mathcal{N}} \sum_i^N \frac{Z_{\alpha}}{|\vec{R}_{\alpha} - \vec{r}_i|}\end{aligned}\tag{1}$$

In this Hamiltonian, M_{α} and Z_{α} are the mass and atomic number of nucleus α , while $\{\vec{r}\}$ and $\{\vec{R}\}$ are vectors, referred to a space-fixed frame, that give the positions respectively of the N electrons and \mathcal{N} nuclei. Energy terms due to internal electromagnetic interactions can be taken into account using an approximate, phenomenological Hamiltonian (\hat{H}') that contains terms arising from interactions between electron spins and orbital motions, terms due to electron spin-spin interactions and “hyperfine” terms due to nuclear spins. This operator is called the “relativistic” Hamiltonian and, for atoms with charge up to about 20, represents a small perturbation of the electrostatic Hamiltonian.

Referring all coordinates to the center of mass of the system, one can separate off the translational kinetic energy of the whole molecule (that of a free particle of mass M equal to the total mass) and is left with the Hamiltonian of the internal motions, given in terms of coordinates referred to the centre of mass of the system. In molecular calculations, it is often more useful to refer the particle coordinates to the nuclear centre of mass. In both cases, anyhow, one introduces some “recoil” term in the kinetic energy part of the Hamiltonian. In the case of a diatomic molecule, for example, referring all the coordinates to the nuclear centre of mass, one gets the following expression for the electrostatic Hamiltonian of the internal motions of the molecule

$$\begin{aligned}
 \hat{H}_0 &= \left[-\frac{1}{2\mu} \Delta_{\vec{R}} + \frac{Z_a Z_b}{R} \right] \\
 &+ \left[-\frac{1}{2} \sum_i^N \Delta_{\vec{r}_i} + V_{ee}(\vec{r}_1, \dots, \vec{r}_N) + V_{en}(\vec{R}, \vec{r}_1, \dots, \vec{r}_N) \right] \\
 &+ \left[-\frac{1}{2M_{ab}} \sum_{ij}^N \vec{\nabla}_{\vec{r}_i} \cdot \vec{\nabla}_{\vec{r}_j} \right] \\
 &= \hat{H}_n + \hat{H}_{el} + \hat{T}_{ee}
 \end{aligned} \tag{2}$$

where

$$\mu = \frac{M_a M_b}{M_a + M_b}; \quad M_{ab} = M_a + M_b; \quad \vec{R} = \vec{R}_a - \vec{R}_b \tag{2}$$

and $M_{a,b}$ are the masses of the two atoms a and b , whose positions are $\vec{R}_{a,b}$.

From now on, since we are interested only in the internal energies of molecules that do not contain heavy atoms, we will consider only the electrostatic Hamiltonian \hat{H}_0 , disregarding the translational energy and looking for solutions of the time-independent Schrödinger equation

$$\hat{H}_0 \Psi(\{\vec{r}\}, \{\vec{R}\}) = E \Psi(\{\vec{r}\}, \{\vec{R}\}) \tag{3}$$

Unfortunately, exact analytical solutions of this equation cannot be obtained even for simple molecules. There is, however, a simplifying feature, valid for the most part of molecules that is the possibility of separating electronic and nuclear motions as suggested by the *Born-Oppenheimer (BO) approximation*. This possibility rests on the fact that mass ratio between electrons and nuclei is roughly $m/M \simeq 10^{-3} - 10^{-5}$, while forces acting on both are of comparable magnitude. It follows that the motion of the nuclei is much slower than that of the electrons and the two motions can be treated separately. More in detail, Born and Oppenheimer (1927) proved the following relationship among the energy separations of electronic levels (ϵ_{el}), vibrational levels (ϵ_{vib}) and rotational levels (ϵ_{rot}) of a molecule

$$\epsilon_{rot} \simeq x^2 \epsilon_{vib} \simeq x^4 \epsilon_{el}; \quad x = (m/M)^{1/4} \tag{4}$$

Since an energy separation ϵ is associated with an angular frequency $\omega = \epsilon / \hbar$, one can estimate that during a rotation of the whole molecule, the nuclei make about 100 vibrations around their equilibrium positions and the electrons about 10000 revolutions. The mathematical consequence of this fact is that solutions of Eq. (4) can be expressed, in good approximation, as the product of an electronic and a nuclear function.

$$\Psi(\{\vec{r}\}, \{\vec{R}\}) \simeq \Phi^{el}(\{\vec{r}\}, \{\vec{R}\}) \Phi^{nu}(\{\vec{R}\}) \tag{5}$$

both (approximate) solutions of separate time-independent Schrödinger equations

$$\hat{H}_{el} \Phi^{el}(\{\vec{r}\}, \{\vec{R}\}) = \varepsilon(\{\vec{R}\}) \Phi^{el}(\{\vec{r}\}, \{\vec{R}\})$$

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} \quad (6)$$

$$\hat{H}_{nu} \Phi^{nu}(\{\vec{R}\}) = E \Phi^{nu}(\{\vec{R}\})$$

$$\hat{H}_{nu} = \hat{H}_n + \varepsilon(\{\vec{R}\}) \quad (7)$$

where recoil terms, as \hat{T}_{ee} in (2), are neglected. The electronic wavefunction $\Phi^{el}(\{\vec{r}\}, \{\vec{R}\})$ which describes the motion of the electrons around a fixed nuclei configuration $\{\vec{R}\}$ depends explicitly on electronic coordinates and parametrically on nuclear coordinates, where parametric dependence means that different sets of nuclear coordinates correspond to different electronic functions. The electronic energy $\varepsilon(\{\vec{R}\})$, regarded as a function of the nuclear coordinates and added to the nuclear repulsion energy V_{nn} , is called *potential energy surface*, since it is the effective potential that governs the nuclear motion. One should, however, remember that a wavefunction (6) cannot be, in any case, an exact wavefunction because of the nuclear kinetic energy operator that couples electronic states: $\langle \Phi_l^{el}(\{\vec{r}\}, \{\vec{R}\}) | \hat{T}_n | \Phi_m^{el}(\{\vec{r}\}, \{\vec{R}\}) \rangle \neq 0$. BO approximation disregards, indeed, these terms and allows one to disentangle electronic and nuclear motion and to study separately the electronic motion for any fixed nuclei configuration. In the next section, we will analyze several methods proposed for obtaining approximate solutions of the time-independent Schrödinger equation (7) for electrons in a molecule.

2. Methods for obtaining approximate electronic wavefunctions

Since the electronic Hamiltonian (7) does not contain any spin operator, its eigenfunctions may depend only on the spatial coordinates of the electrons. However, we know that each electron has an intrinsic angular momentum (spin) and, furthermore, the Pauli principle requires the electronic wavefunctions be antisymmetric under coordinate permutations (see *Schrödinger Equation and Quantum Chemistry*). Therefore, we want to construct approximate eigenfunctions $\{\Phi\}$ of \hat{H}_{el} that fulfill both these requirements. A general way for obtaining this result is through the following expansion.

$$\Phi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) = \sum_j C_j \Theta_j(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \quad (8)$$

where \vec{x} indicates all the variables needed in referring to a given electron, i.e. the spatial variables \vec{r} and the spin variable s

$$\vec{x} \equiv (\vec{r}, s); \int d\vec{x} \equiv \sum_s \int d\vec{r} \quad (9)$$

The wavefunctions $\{\Theta_j\}$ are *antisymmetrized spin-orbital products* or *Slater determinants*

$$\begin{aligned} & \Theta_j(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N) \\ &= M_j \sum_P \epsilon_P \hat{P} [\psi_a(\vec{x}_1) \psi_b(\vec{x}_2) \dots \psi_w(\vec{x}_N)] \\ &= M_j \begin{vmatrix} \psi_a(\vec{x}_1) & \psi_b(\vec{x}_1) & \dots & \psi_w(\vec{x}_1) \\ \psi_a(\vec{x}_2) & \psi_b(\vec{x}_2) & \dots & \psi_w(\vec{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_a(\vec{x}_N) & \psi_b(\vec{x}_N) & \dots & \psi_w(\vec{x}_N) \end{vmatrix} \\ &= M_j \det |\psi_a(\vec{x}_1) \psi_b(\vec{x}_2) \dots \psi_w(\vec{x}_N)| \end{aligned} \quad (10)$$

where \hat{P} is an index permutation and $\epsilon_p = \pm 1$ its parity, M_j a normalization constant and $\{\psi(\vec{x})\}$ are *spin-orbitals*, i.e. products of a spatial function (*orbital*) $\phi(\vec{r})$ and a spin eigenfunction $\eta_{\pm}(s)$

$$\begin{aligned} \psi(\vec{x}) &= \phi(\vec{r}) \eta_{\pm}(s); \\ \hat{s}_z \eta_{\pm}(s) &= \pm \frac{\hbar}{2} \eta_{\pm}(s) \rightarrow \begin{pmatrix} \eta_+(s) \equiv \alpha(s) \\ \eta_-(s) \equiv \beta(s) \end{pmatrix} \end{aligned} \quad (11)$$

If the set of all products of N spin-orbitals is complete, any wavefunction can be exactly represented as in Eq.(9), provided all the determinants that can be obtained from the complete set of spin-orbitals, are included in the expansion. However, since working with complete sets is usually impossible, the quality of any approximate wavefunction depends, in a crucial way, on the choice of the spin-orbitals used in the determinants. The best spin-orbitals are those that yield an accurate wavefunction with the smallest number of determinants.

Two main types of orbitals have been proposed: *atomic orbitals (AOs)*, centered on the nuclei of the molecule, and *molecular orbitals (MOs)* that extend over the whole molecule, being usually constructed as *linear combinations of atomic orbitals (LCAO)*. The use of AOs has led to the *valence bond (VB) method*, in which the wavefunctions are many-determinant and the AOs centered on different nuclei of the molecule are *non-orthogonal*. The use of MOs has led, instead to the *molecular orbital (MO) method* that has evolved from the *one-determinant approximation* toward procedures based on many-determinant wavefunctions. A typical feature of the MO method is the use of *orthogonal* orbitals that greatly simplify the expression of the matrix elements required

for energy calculations and make this method much easier to work with than the VB method. The latter, however, has played an important role in the development of quantum chemistry, allowing a clear definition of important chemical concepts and the development of sophisticated techniques based on group-theoretic methods.

In the next sections, we first analyze the MO method, both in the one-determinant approximation and in its generalizations for many-determinant wavefunctions; then we describe the VB method.

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Biographical Sketch

Renato Colle was born in Belluno, Italy, on 9 October 1949, studied at Scuola Normale Superiore (SNS) of Pisa during 1973-75 for Ph.D., and worked there as Assistant Professor of Chemistry during 1975-81. In 1978 and 1980 respectively he visited Technisch-Chemisches Labor der ETH of Zurich and the Department of Physics, University of Chicago, as a Research Associate. During 1981-90 he was Associate Professor of Chemical Physics at the SNS. In 1985 he was a Visiting Professor at the Department of Physics, University of Chicago. Since 1991 he is a Full Professor of "Chimica Fisica dei Materiali Solidi" at the University of Bologna and was Scientific Director of a Joint Research Project of the European Community during 1994-98.