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Perspective

Perspective on “An extended Hückel theory. I. Hydrocarbons”

Hoffmann R (1963) J Chem Phys 39:1397–1412

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Abstract. An overview is given on how the title paper by Hoffmann has influenced theoretical studies of molecules and solids over the years. The strengths and weaknesses of the extended Hückel theory are also discussed.

Key words: Extended Hückel theory, advantages and disadvantages – Structure–property correlation – Extended Hückel theory, history and impact – Roald Hoffmann

1 Introduction

Physical properties of molecules and solids are intimately related to their atom arrangements. To understand this structure–property relationship, it is necessary to examine how the electronic structure of a system depends on its atom arrangement by performing electronic structure calculations at a certain level of approximation. The level of calculation one needs to employ depends on the nature of the answer one hopes to find from the calculations. An important role of an electronic structure theory is to provide a conceptual framework in which to think, to organize experimental knowledge [1]. In this role, theoretical predictions need not be quantitative but should provide a bias for correct thinking [1]. For the past three and a half decades, the extended Hückel (EH) theory [2] devised by Hoffmann has provided such a role. In this paper, we briefly review how this semiempirical theory has influenced our understanding of physical and electronic properties of discrete molecules and extended solids. Then we discuss the strengths and weaknesses of the EH theory to help avoid misusing EH calculations.

2 EH theory

The genesis of the EH method [2] was the linear combination of atomic orbitals/molecular orbital (MO) study of polyhedral molecules by Hoffmann and Lipscomb [3]. The title paper published by Hoffmann in 1963 [2] was featured as a citation classic in *Current Contents* in 1989 [4], where Hoffmann described the background of the EH method in detail. The firm foundation of the EH method was given in the title paper [2] and in the subsequent three papers published under the general title of “*Extended Hückel theory*” in 1964 [5–7]. In the EH method the MOs ψ_i ($i = 1, 2, \ldots, m$) of a system are constructed using a set of valence atomic orbitals $\{\chi_1, \chi_2, \chi_3, \ldots, \chi_m\}$. The effective one-electron Hamiltonian, H^{eff}, determining the energies e_{i} of the MOs is not specified, but its matrix representation, $H_{\mu\nu} = \langle \chi_\mu | H^{\mathrm{eff}} | \chi_\nu \rangle$, in an atomic orbital basis is defined semiempirically; namely, the diagonal element $H_{\mu\mu}$ is approximated by the valence state ionization potential (VSIP) of the atomic orbital χ_μ [8, 9]

$$H_{\mu\mu} = -\mathrm{VSIP} \tag{1}$$

and the off-diagonal element $H_{\mu\nu}$ is approximated by the Wolfsberg–Helmholz formula [8],

$$H_{\mu\nu} = KS_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu})/2\ , \tag{2}$$

where $S_{\mu\nu}$ is the overlap integral $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ and $K = 1.75$. In the weighted Wolfsberg–Helmholz approximation [10], the coefficient K of Eq. (2) is replaced with another coefficient K', which is given by

$$K' = K + \Delta^2 + \Delta^4(1 - K)\ , \tag{3}$$

where $\Delta = (H_{\mu\mu} - H_{\nu\nu})/(H_{\mu\mu} + H_{\nu\nu})$. Equation (3) is used to reduce the extent of counterintuitive orbital mixing [10, 11]. The variational theorem leads to a set of simultaneous equations:

$$\sum_{\mu=1}^{m} (H_{\mu i} - e_i S_{\mu i}) C_{\mu i} = 0 \quad (i = 1, 2, \ldots, m)\ . \tag{4}$$

The solution of these equations provides the energies e_i of the MOs ψ_i.

The approximations of the EH theory in leading up to Eq. (4) are very crude, and so it has serious drawbacks that first-principles electronic structure theories do not. In this age of powerful computers and commercial program packages of first-principles electronic structure theories, one may ask if there is any room for the use of the semi empirical EH theory in chemistry and physics. The answer is an emphatic yes, because the EH theory possesses a few advantages that no first-principles theory can ever match (see Sect. 4). For these reasons, EH calculations have been extensively used to study structure–property relationships in all kinds of materials, from molecules to solids, from organic to inorganic compounds.

3 Brief history of the use of EH calculations

During the years 1963–1973, EH calculations were largely applied to organic molecules. The concept of orbital symmetry conservation, introduced by Woodward and Hoffmann [12], provided a strong influence on what qualitative features to find from electronic structure calculations. To arrive at the concept of orbital symmetry conservation, it was necessary to know the frontier MOs of organic molecules and how their nodal properties vary as the molecular geometry changes. It must be noted that Hoffmann carried out EH calculations for a large number of organic molecules [2, 5–7] before his celebrated collaboration with Woodward, which led to the series of five communications [13–17] establishing the concept of orbital symmetry conservation. During the period 1963–1972, the concept of orbital interaction was firmly established. The most significant review resulting from EH calculations in this period is "Interaction of orbitals through space and through bonds" by Hoffmann [18].

Since 1974 the focus of EH calculations has shifted from organic molecules to compounds of transition-metal elements. This shift began with the work of Rösch and Hoffmann [19] and that of Hoffmann et al. [20]. It is interesting to note that around the time of this shift an efficient program package of first-principles electronic structure theory (i.e., Gaussian 70) became available and enabled one to study the structural details of organic molecules on a quantitative basis. Representative studies on polyene conformational preferences in organometallic compounds were carried out by Albright and coworkers [21, 22]. These studies established that rotational barriers are quite well reproduced by EH calculations. Chemical reactivities of transition-metal compounds were examined in a number of papers. Representative studies on this topic include the work of Tatsumi et al. [23] on reductive elimination of d^8 organotransition-metal complexes, that of Eisenstein and Hoffmann [24] on reactivity of transition-metal complexed olefins towards a nucleophile, and that of Saillard and Hoffmann [25] on C—H and H—H activation in transition-metal complexes. Studies by Hoffmann's group during the years 1974–1982 made it possible to describe the structure and bonding of transition-metal compounds in terms of fragment MOs (FMOs). These studies eventually led to the development of the isolobal analogy between organic and inorganic compounds [26, 27].

Studies of the structures and bonding in extended solids based on the EH theory started with the work of Whangbo and Hoffmann [28] in 1978 and that of Whangbo et al. [29] in 1979. These papers showed that electronic structures of solid-state materials can also be described using the concepts of perturbation and orbital interaction, thus laying down the foundation for the electronic structure studies of solids and surfaces by S. Alvarez, J.K. Burdett, E. Canadell, J.-F. Hallet, R. Hoffmann, T.R. Hughbanks, S. Lee, G.J. Miller, M.-H. Whangbo and their coworkers in the 1980s and 1990s. These research efforts led to a number of review articles and monographs on the structures and bonding in solids [30–39]. Representative studies of chemical reactivity and bonding on surfaces include the work of Saillard and Hoffmann [25] on C—H and H—H activation on surfaces and that of Sung and Hoffmann [40] on bonding of carbon monoxide to metal surfaces.

Beginning with the work of Parkinson et al. [41] in 1991, the EH theory has been extensively used to interpret atomic- and molecular-scale images of scanning tunneling microscopy (STM) and atomic force microscopy (AFM). These studies showed that an STM image of a surface is well described by the electron density map resulting from the frontier orbitals of the surface, and an AFM image by that from all the occupied orbitals of the surface. These STM and AFM studies for a variety of layered compounds and overlayers were reviewed in the book by Magonov and Whangbo (42) in 1996.

4 Strengths and weaknesses of the EH theory

In predicting the optimum structure of a system (in particular, bond-length optimization), EH calculations are not reliable if trusted blindly as one might with the program packages of first-principles electronic structure theories. For systems of known geometry, however, EH calculations have been invaluable as evidenced by numerous studies over the years.

The energy levels and orbitals generated by EH calculations for a system do not depend on the number of electrons the system has, because the EH theory does not consider electron–electron repulsion explicitly. Consequently, the EH method does not provide a correct way of describing the relative energies of different electronic states available for a given system. For example, consider a molecular system that has two electrons to fill its two energy levels, for example the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). The ground state of this system can be a singlet state in which the HOMO is doubly occupied or a triplet state in which the HOMO and LUMO are each singly occupied with the same spin. In EH calculations the total energy of a system is given by the sum of the energies of its occupied orbitals, thus predicting that the singlet state is always more stable than the triplet state, in disagreement with experiment. However, it is important to recognize that EH calculations do provide information concerning when such a failure is likely to occur. The essential effect of electron–electron repulsion is to make the double occupancy of an orbital energetically unfavorable; therefore, the triplet state becomes more stable than the singlet state if the HOMO–LUMO energy difference is small enough [43]. Thus, when EH calculations for a molecule lead to a small HOMO–LUMO gap, Δe, one must note that the system may adopt a triplet state as the ground state.

It is important to note the solid-state counterpart [44] of this observation. When the unit cell of a solid contains an odd number of electrons, the highest-occupied band of this system becomes half filled. If electron–electron repulsion is neglected, the levels of the bottom half of the band are each doubly filled, and those of the top half are empty, thereby leading to a metallic state. Thus EH calculations predict that a system with a partially filled band is always metallic, in conflict with experiment. This is again a serious failure, if results of EH calculations are accepted blindly. However, EH calculations do provide information concerning when such a failure is likely to occur. For a system with a partially filled band, a magnetic insulating state may become more stable than the metallic state when the width of the partially filled band is narrow. The metallic and magnetic insulating states are similar in that they possess a partially filled band, but they differ in the way the band levels are occupied. In a magnetic-insulating state, a partially filled band has all its band levels singly filled [44]; therefore, when EH calculations for a system lead to narrow partially filled bands, one must consider the possibility that its ground state is magnetic-insulating rather than metallic.

The fact that EH calculations do not depend on the number of electrons in a system gives rise to advantages that no first-principles theory can ever provide. EH calculations are simple and fast. Consequently, they can be used to study those molecular and extended solids that contain so many atoms per unit cell that first-principles calculations are impossible or difficult to apply. It is intellectually challenging and satisfying to find correct explanations and correct predictions for such problems by employing an imperfect method such as the EH theory. In addition, our research life may be too short to leave the problems untackled until the arrival of a computer powerful enough to treat the problems at the level of first-principles theories. The simplicity of the EH method does not necessarily mean that the electronic structures it generates are unreliable. The usefulness of any calculation, be it first-principles or semiempirical, rests ultimately on the test of whether the calculated results are consistent with experimental observations and provide insight into experimental problems under question. EH calculations carried out for a variety of materials manifest that the EH theory is useful if one asks the kinds of questions that it can answer.

EH calculations for a complex system can be approximated by those for the relevant part of the system. For example, in the organic conducting salts (BEDT-TTF)$_2X$ with a mononegative anion X^-, where BEDT-TTF refers to bis(ethylenedithio)tetrathiafulvalene, the layers of the (BEDT-TTF)$_2^+$ cations alternate with layers of the X^-, anions [34, 45]. It is the cation layers that are largely responsible for the transport properties of the salt, and the cation layers are separated by the anion layers. Therefore, for the purpose of studying the transport properties of a (BEDT-TTF)$_2X$ salt, the electronic band structure of the salt can be well approximated by that of an isolated cation layer. Such an approximation greatly simplifies the computational task and has been widely applied to a variety of organic conducting salts [34, 45]. In a similar manner, for the purpose of studying the transport properties of the hexagonal alkali tungsten bronze A_xWO$_3$ (A = K, Rb, Cs; $x < 1/3$), the electronic band structure of this bronze can be approximated by that of the WO$_3^{x-}$ lattice [46]. In EH calculations, these kinds of approximations are valid, and as a consequence simplify the task of calculations enormously.

In EH calculations it is easy to express the orbitals of a composite system A-B in terms of the orbitals of its fragments A and B even if the fragments are functional groups. This FMO analysis is useful and meaningful in EH calculations because the orbitals of a fragment are transferable from one molecule to another as long as its geometry remains the same. For instance, consider a composite molecule A-B in which the fragments A and B are joined by a single bond. In principle, this molecule can be divided into A$^+$ and B$^-$, A$^-$ and B$^+$, A$^-$ and B$^-$, etc. In EH calculations, the energies and the nodal properties of fragment orbitals do not depend on the number of electrons a fragment has. However, in any theory taking electron–electron repulsion into consideration, the number of electrons in a fragment should be assigned to calculate its orbitals, and the energies and the nodal properties of fragment orbitals depend on the number of electrons a fragment has, and so it is complicated to perform an FMO analysis [47, 48]. Nevertheless, a meaningful FMO analysis can be carried out within the framework of self-consistent-field MO (SCF-MO) theory if fragment orbitals are defined by the Fock matrix partitioning method [47, 48] rather than by SCF-MO calculations on molecular fragments. In this case, the orbitals of a fragment become "environment-adjusted" fragment orbitals [47, 48], and so the transferability of fragment orbitals from one molecule to another is not so good as in EH calculations.

5 Use of EH calculations

In EH calculations, one should pay attention to the parameters of the atomic orbitals used to construct the matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$. In the EH method valence atomic orbitals are approximated by Slater-type orbitals (STOs). A single-zeta STO, χ_μ, is defined by

$$\chi_\mu(r, \theta, \phi) \propto r^{n-1} \exp(-\zeta r) Y(\theta, \phi) \ , \tag{5}$$

where n is the principal quantum number, ζ is the exponent, and $Y(\theta, \phi)$ is the spherical harmonic. In a double-zeta STO, a linear combination of two exponential functions is used as

$$\chi_\mu(r, \theta, \phi) \propto r^{n-1}[c_1 \exp(-\zeta_1 r) + c_2 \exp(-\zeta_2 r)] Y(\theta, \phi) \ . \tag{6}$$

The ζ values for single-zeta STOs, the ζ_1, ζ_2, c_1 and c_2 values for double-zeta STOs, and the VSIP values can be taken from results of atomic electronic structure calculations using the Hartree–Fock method [49, 50]. There are two program packages for EH theory that allow one to perform EH calculations for molecules and solids. One is YAeHMOP [51], which is freely available; the other is CAESAR [52], which is a commercial program designed to run on personal computers. Detailed descriptions on how to carry out EH calculations using the program package CAESAR have been given by Ren et al. [52]. The freely available program package CACAO, originally written by Mealli and Proserpio [53], is designed to do EH calculations for molecules. This package allows one to generate Walsh diagrams and orbital interaction diagrams as well as to plot perspective views of MOs.

When results of EH calculations for a molecule or a solid of known structure are not consistent with the physical properties of the molecule or the solid, it is necessary consider two possible sources leading to this disagreement:

1. The failure is caused by the assumptions inherent in any electronic structure theory. For example, because of electron–electron repulsion, the lowest possible spin state of a molecule may not be the ground state, and the metallic state of a solid may be less stable than the corresponding magnetic insulating state. In this case, one should consider an alternative way of filling the calculated energy levels with electrons to generate a high-spin state for a molecule and a magnetic insulating state for a solid. Then one should attempt to extract, from results of EH calculations, useful information needed to go beyond a one-electron electronic structure theory.
2. The failure is not caused by the assumptions of electronic structure theory but originates from the use of EH approximations. In this case, it is important to analyze the source of the failure from the viewpoint of the atomic parameters employed, modify the parameters appropriately, and repeat the calculations. This task is not difficult, if one becomes familiar with the concepts of perturbation and orbital interaction. In spirit, this process is not different from what one does with first-principles calculations. For example, when a chosen basis set or correlation level does not give correct results, one tries another basis set or correlation level. First-principles methods are based on rigorous theoretical and mathematical formulations, but their actual calculations do include approximations.

6 Concluding remarks

Approximate electronic structures calculated by the EH method may not provide quantitative predictions, but they are mostly adequate for qualitative structure–property correlation analysis. The relevance of the EH method lies in this role of facilitating the search for structure–property correlations. When used in conjunction with the concepts of perturbation and orbital interaction, EH calculations have been instrumental in discovering a number of qualitative concepts useful for thinking about the structures and properties of various organic and inorganic materials. To name a few, examples include FMOs [26, 27], orbital correlation diagrams [12, 27], through-space and through-bond interactions [18, 27], and the isolobal analogy [26, 27] for molecular systems; a band orbital picture of magnetic-insulating states [30, 31, 44], an orbital-mixing view of electronic phase transitions in metals [30, 37, 54], and hidden Fermi surface nesting [37, 55, 56] for solid-state materials; and tip-force induced local stiffness variation [42, 57] in STM and AFM.

In closing, it is refreshing to read what Hoffmann had to say about theory 25 years ago [1]:

> In my mind, the most important role of theory in chemistry is to provide a framework in which to think, to organize experimental knowledge. I picture chemistry as a living organism – an ever-expanding amorphous sphere with extensions along frontier areas, capable of movement, progress, that may be lightning fast and excruciatingly slow. I see theory as a kind of primitive nervous system of this organism, needed to organize the frontier information, to connect it to the accumulated store of knowledge, to communicate among the myriad advancing areas. The cues for further action that this nerve system gives need not be 100% correct – how could it be? Only a slight bias for the correct option, when a million decisions are to be made, endows the organism with the statistical equivalent of an intuition.

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