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Some comments on approximate LCAO molecular orbital theory in organometallic chemistry: Getting more by doing less?

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Abstract - The use of approximate LCAO molecular orbital theory as an electronic structural tool in organometallic chemistry is briefly reviewed. The author offers his opinions concerning the advantages and disadvantages of these approximate methods as compared to rigorous Hartree-Fock calculations.

INTRODUCTION

The year 1951 was one of tremendous advances in both theoretical chemistry and organotransition metal chemistry. In that year, Roothaan published his important treatise on quantitative LCAO molecular orbital theory (ref. 1), the starting point for all modern basis set expansion methods for calculating the electronic structure of molecules. During the same year, organotransition metal chemistry entered a new age with the synthesis of ferrocene and the recognition of its unusual sandwich structure (ref. 2). From these concurrent beginnings, electronic structure theory and organometallic chemistry have experienced phenomenal growth and maturation. The interface of these two fields, theoretical organometallic chemistry, also began in the early 1950's with the first reports of molecular orbital treatments of ferrocene (ref. 3). Quantum chemists have continued to be fascinated by the challenges posed by organometallic systems, and theoretical organometallic chemistry has grown to be a thriving, well-recognized chemical discipline (ref. 4).

In its infancy, the application of electronic structure methods to organometallic compounds was largely an exercise in approximation: The generally large size of organometallic molecules, both in terms of numbers of atoms and numbers of electrons, rendered an exact solution of the Roothaan equations untenable (ref. 5). Thus, theoretical organometallic chemistry (not unlike theoretical organic chemistry) developed through the use of approximate molecular orbital methods. As computational capabilities improved, the need for using approximate methods lessened, to the point that it is now possible to do ab initio Hartree-Fock and even correlated treatments of reasonably large organometallic molecules (ref. 6). In spite of these computational advances, however, approximate molecular orbital theory is still the most popular electronic structural probe used to study organometallic complexes. Part of the reason for this popularity is computational expense; while it is indeed possible to do "good" calculations on organometallics, these calculations still tax the capabilities of even the most advanced supercomputer. The primary _raison d'être_ for approximate methods in organometallic chemistry, however, is even more pragmatic: Approximate methods continue to provide theoretical and experimental organometallic chemists with useful, readily interpretable, intuitively reasonable results that often lead to advances in the field.

In this contribution, the field of approximate LCAO molecular orbital theory as applied to transition metal organometallics will be briefly reviewed. The author will offer his opinions concerning the advantages and disadvantages of these methods, and provide some caveats for those investigators who wish to use these methods with no prior training in the field. Many of the points made in this paper are supplementary to those in the excellent recent contribution by Fenske to this journal (ref. 7). I will limit the discussion to approximate and rigorous methods based on the Hartree-Fock method as a starting point or end; the newer breed of $X\alpha$ and local-density-functional (LDF) methods (ref. 8), which are philosophically rather different, will not be discussed here.

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* LCAO = Linear Combination of Atomic Orbitals

WHAT IS APPROXIMATE LCAO MOLECULAR ORBITAL THEORY?

In closed-shell molecular orbital theory (ref. 9), the molecular wavefunction is expressed as a single Slater determinant of doubly-occupied molecular orbitals, ϕ_i. Each ϕ_i satisfies the one-electron Hartree-Fock equation:

$$\hat{f}\phi_i = \epsilon_i\phi_i \tag{1}$$

In eq. 1, $\hat{f}$ is the so-called Fock operator and ϵ_i is the molecular orbital energy. The ϵ_i are given physical meaning through Koopmans' theorem (ref. 10), which allows the ϵ_i to be related to ionization energies of the molecule (ref. 11). Although eq. 1 looks like a standard eigenvalue equation, the construction of $\hat{f}$ requires a knowledge of the ϕ_i. As a result, eq. 1 is actually a pseudoeigenvalue equation, the solution of which requires an iterative procedure: A guess is made for the form of the ϕ_i, which are then used to construct $\hat{f}$, which is then used to solve for new ϕ_i, and so forth. The iterations are continued until the ϕ_i used to construct $\hat{f}$ are sufficiently similar to the ϕ_i obtained by solving equation 1, at which point we have a self-consistent-field (SCF) solution.

Roothaan (ref. 1) treated the case in which the MOs ϕ_i are expanded as a linear combination of basis functions, χ_μ:

$$\phi_i = \Sigma\, c_{\mu i}\chi_\mu \tag{2}$$

In eq. 2, the $c_{\mu i}$ are expansion coefficients and the summation is over all χ_μ. When the expansion in eq. 2 is substituted into eq. 1, followed by linear variational minimization of the total energy, the Hartree-Fock-Roothaan matrix equation results:

$$\mathbf{FC} = \mathbf{SC}\epsilon \tag{3}$$

In eq. 3, $\mathbf{F}$ (the Fock matrix) and $\mathbf{S}$ (the overlap matrix) are matrices whose elements consist of integrals calculated over the basis functions χ_μ:

$$F_{\mu\nu} = <\chi_\mu \mid \hat{f} \mid \chi_\nu> \tag{4}$$

$$S_{\mu\nu} = <\chi_\mu \mid \chi_\nu> \tag{5}$$

The matrix $\mathbf{C}$ (the coefficient or eigenvector matrix) is composed of the expansion coefficients $c_{\mu i}$, and ϵ is a diagonal matrix of the orbital energies ϵ_i. The solution of eq. 3 is also an iterative procedure, this time on the expansion coefficients $c_{\mu i}$. An initial guess of $c_{\mu i}$ is used to construct the Fock matrix $\mathbf{F}$. Eq. 3 is then solved using standard techniques of linear algebra, leading to the secular equation

$$|\mathbf{F} - \epsilon\mathbf{S}| = 0 \tag{6}$$

The eigenvectors of eq. 6 are the new expansion coefficients, and the procedure is repeated until self-consistency is achieved.

The most computer-time intensive aspect of rigorous LCAO-MO calculations is the calculation of the Fock matrix elements in eq. 4. Almost all modern approximate LCAO-MO methods involve approximations only to these matrix elements; all other aspects of the solution are handled as they are in an ab initio treatment. Most approximate methods use Slater-type orbitals (STOs) for the basis functions, rather than the Gaussian-type orbitals (GTOs) used in ab initio calculations. STOs are better representations of hydrogenic atomic orbitals, but, although overlap integrals involving STOs can be readily calculated, the rigorous calculation of Fock matrix elements using STOs is much more difficult than with GTOs. In addition, nearly all approximate methods use a minimal basis of STOs, i.e. each atomic orbital is represented by a single STO (or by a fixed linear combination of two or more STOs). A minimal basis provides ease of interpretation at the expense of orbital "flexibility"; because the radial shape of an atomic orbital is constrained at the beginning of the calculation, the molecular orbitals are forced to resemble strongly the atomic orbitals that were presumed.

The first approximate LCAO-MO treatment of transition metal systems was that of Wolfsberg and Helmholz (ref. 12). They used empirical values for the diagonal Fock matrix elements, $F_{\mu\mu}$, and approximated the off-diagonal elements as an overlap-scaled average of the corresponding diagonal elements:

$$F_{\mu\nu} = kS_{\mu\nu}(F_{\mu\mu} + F_{\nu\nu})/2 \tag{7}$$

The constant k in eq. 7 was varied between 1.67 and 2.00. The Wolfsberg-Helmholz method evolved into the extended Hückel (EH) method of Hoffmann (ref. 13). The EH method uses a minimal basis of STOs, empirically chosen values for $F_{\mu\mu}$, and eq. 7 (k = 1.75), or a slight modification thereof (ref. 14), to calculate the values of $F_{\mu\nu}$. The nonempirical Fenske-Hall method (ref. 15) is also loosely derivative of the Wolfsberg-Helmholz method. In the

Fenske-Hall method, the diagonal Fock matrix elements, $F_{\mu\mu}$, are calculated approximately but nonempirically. The off-diagonal elements are calculated by a more complex formalism than eq. 7, but the essential notion that the value of $F_{\mu\nu}$ is related to the values of $F_{\mu\mu}$ and $F_{\nu\nu}$ is retained. Like the EH method, the Fenske-Hall method employs a minimal basis of STOs and only the **F** matrix elements are approximated. The EH and Fenske-Hall methods are the most popular approximate LCAO-MO methods used to study organometallic complexes.

DISADVANTAGES AND ADVANTAGES OF APPROXIMATE LCAO–MO CALCULATIONS

What precautions are necessary in using approximate LCAO-MO methods? What are the intrinsic advantages of these approximate techniques? These are among the most important questions that an uninitiated investigator should ask before using a particular method. All the approximate methods described here suffer from the following disadvantages:

(1) **A method is only as good as its approximations.** All of the approximate methods discussed above were developed for certain types of chemical systems. The transferability of a given method to a chemical system for which it has not previously been used is always a matter that should be carefully and systematically investigated.

(2) **The methods are limited to a single-configuration description.** This disadvantage is, of course, intrinsic to molecular orbital theory. Systems that are inadequately described by a single configuration, such as very weak bonding at long bond lengths, will not be properly described by either approximate or rigorous Hartree-Fock MO theory.

(3) **Minimal basis sets can be woefully inadequate.** Because the approximate methods described here use a minimal basis set, <u>the choice of basis set is the most important decision an investigator has to make</u>. It is this author's opinion that poor basis set choice is the most common error made in the application of approximate MO theory. Unfortunately, there are few well-founded means to determine the quality of a minimal basis set for molecular calculations, particularly for unoccupied atomic orbitals (such as the 4s and 4p AOs of a first-row transition metal). Within the confines of a minimal basis, the best procedure is to choose STO basis functions for a series of atoms in a consistent, systematic fashion (ref. 16).

(4) **The use of approximations invalidates the variation principle.** The variation principle, as applied to rigorous electronic structure methods, guarantees that any change to the wavefunction that leads to a lower energy is an improvement to the wavefunction. This guarantee is lost as soon as approximations are employed. As a result, the use of approximate methods to determine the total energy of a molecule (and, perforce, properties of the total energy such as molecular geometry or potential energy curves) is on far less secure footing than when ab initio methods ar used.

(5) **Open shell molecules are generally treated incorrectly.** Open-shell LCAO-MO theory, also first treated rigorously by Roothaan (ref. 17), is far more complex than closed-shell theory. The approximate methods discussed here treat open-shell molecules in a closed-shell fashion, a formally incorrect albeit ofttimes useful approach (ref. 18).

Given this broad spectrum of disadvantages for approximate methods, why do so many investigators choose to continue to use them? The answer, of course, is that the disadvantages of these methods are often outweighed by the advantages of using them. The major advantages of approximate LCAO-MO methods are the following:

(1) **Approximate methods are computationally inexpensive.** In the early days of computational chemistry, a major impetus for the development of approximate methods was the need for electronic structural tools that could be applied to relatively large molecules (more than 10 atoms); the limited computational capacity of the time ruled out the possibility of performing higher level calculations. While the modern-day advances in computing have made this advantage less critical, approximate methods are, of course, still less computationally demanding than rigorous methods, to the point that many of the codes can be run on advanced personal computers.

(2) **Minimal basis sets lead to easily interpreted MOs and wavefunctions.** As mentioned above, a minimal basis set can be a poor one for molecular calculations. However, a <u>well-chosen</u> minimal basis set can lead to an adequate qualitative (and sometimes quantitative) description of the bonding in a molecule. The use of a proper minimal basis leads to a more straightforward analysis of MOs than is possible with an extended basis; the minimal basis better fosters the description of a molecule in terms of constituent atomic orbitals. Hence, it is generally easier to extract chemically-useful information from a minimal basis set calculation than from a calculation using a more correct basis set.

(3) **Population analysis is easy and straightforward to interpret.** Most approximate LCAO-MO methods use Mulliken population analysis (ref. 19) as a means of "translating" MO results into chemically intuitive concepts—atomic charges, composition of the orbitals, bonding or antibonding character, and the like. Although Mulliken population analysis is an additional approximation, it is an extremely useful one, especially when coupled with a minimal basis set. As with all approximations, Mulliken population analysis must be used with care; the populations can be very unreliable, especially if very diffuse basis functions are used.

(4) **Fragment analysis is widely used.** Most approximate MO methods readily facilitate viewing the MOs of a molecule as resulting from the interaction of MOs of smaller fragments of the molecule (ref. 20). This fragment approach is extremely useful in organometallic chemistry, wherein, for example, the important bonding interactions in a complex can be traced to the interactions of the metal atom with a series of ligands (ref. 21). While fragment analysis is, in principle, equally straightforward in rigorous Hartree-Fock theory, most Hartree-Fock practicioners do not perform this type of analysis.

(5) **The orbital energies and compositions yielded by approximate methods are often more chemically reasonable than those of ab initio Hartree-Fock methods.** The major advantage of approximate LCAO-MO methods concerns their correctness with respect to explaining observable properties of molecules. This author need not expound on the usefulness of approximate methods; the tremendous body of literature by Hoffmann and coworkers (ref. 4), by Fenske and coworkers (ref. 7, 11), and by others attests to the utility of approximate methods in explaining chemical trends in organometallic chemistry. In fact, the approximations used, while developed for computational expediency, often yield orbitals that are superior to those of ab initio SCF calculations (ref. 22). We can, rather facetiously, consider the approximate methods to be "ab intuitiono" techniques: The methods are advantageous in that they often provide a connection between an orbital description and chemical intuition.

The implications of these advantages, particularly the last one, are quite profound. An investigator can be faced with the dilemma of performing either a "quick and dirty" minimal basis set approximate calculation, or an extended basis set ab initio calculation with the inclusion of some electron correlation. In many instances, the advantages of the former approach, in terms of computational expense and chemical interpretability far outweigh the advantages of the latter with respect to computational rigor.

WHAT SHOULD A NONTHEORETICIAN BELIEVE?

Given the manifold advantages and disadvantages of approximate methods vis-à-vis ab initio methods, the nontheoretician is often placed in the position of not knowing which calculations to believe or which results to trust. To paraphrase from a recent talk by Hoffmann: "Theoreticians are purveyors of methods; all of us are trying to sell you a bill of goods (ref. 23)." In this last section, I will offer some of my thoughts on how a nontheoretician should approach the question of what to believe.

In any electronic structural investigation, there are two important questions that must be asked: (i) What approximations are inherent to the theoretical approach used? (ii) What approximations are being made to the underlined chemical model under investigation? To clarify these questions, consider electronic structural studies of the reactions of biscyclopentadienyl complexes of the early transition metals. Is it best to do a correlated ab initio calculation on a model complex in which the Cp rings are modeled by Cl atoms (ref. 24), to do an ab initio single-configuration calculation in which Cp rings are actually used (ref. 25), or to do a more extensive study using approximate MO theory (ref. 26)? Unfortunately, there is not a simple answer to this question, for it must be recognized that _all methods are useful within their own limitations!_ Thus, an approximate method is very useful for obtaining a qualitative view of the bonding and the frontier orbitals of a molecule, whereas a more rigorous method is usually essential for the detailed and precise calculation of a reaction pathway. Investigators must consider what information they wish to extract from a calculation before choosing a method.

There is a general inverse correlation between the rigor of the electronic structural method used and the correctness of the chemical model studied. This relationship can be represented as a hyperbola, as shown in Fig. 1. Computational advances move the hyperbola farther from the origin. Thus, for a given chemical model, increases in computing power allow more rigorous theory to be used. Likewise, for a given level of theory, computational advances have allowed truer chemical models to be applied. It is important to note that, in general, the ease with which an electronic structure calculation can be interpreted increases as the chemical model becomes more correct and as the theoretical model becomes less rigorous. The hyperbola of Fig. 1 is closely related to the "hyperbola of quantum chemistry" advanced by Pople (ref. 27) and recently expanded upon by Karplus (ref. 28). Because proponents of methodologies at all points along this hyperbola attempt to sell their methods as the most appropriate, Fig. 1 can be considered the "hyperbola of hyperbole" for electronic structure calculations. Caveat emptor!
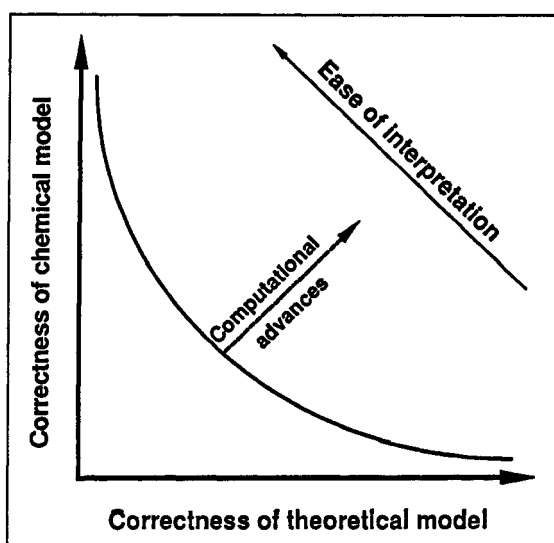
Fig. 1. The "hyperbola of hyperbole," which diagrams
the inverse relation between the correctness of the
theoretical model and the correctness of the
chemical model used.

FINAL COMMENTS

Approximate LCAO-MO calculations have been and will continue to be a valuable tool in
organometallic chemistry. They originated as the only means by which the bonding in
organometallic compounds could be studied in the 1950's; in the spirit of Coulson's
delightful 1960 summation of the state of molecular structure calculations (ref. 29),
organometallic electronic structure originated among the less-than-rigorous but highly
pragmatic "group II" quantum chemists. Although a relative newcomer to the field, I have
had the good fortune to be involved in many studies of organometallic electronic structure,
at several levels of theory. Of these various investigations, the ones using approximate
LCAO-MO methods generally yield the information that is most easily transferred from the
computer to the laboratory. I hope this contribution encourages further applications of
approximate theory in organometallic chemistry, and that such investigations are undertaken
thoughtfully and with the requisite care.

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