

efficient cyclization upon irradiation in acetonitrile to produce the spirocyclic enol ethers or esters 56-59. The ease of formation of the salts coupled with the exceptional chemical efficiencies and structural outcomes of these cyclizations indicates that this methodology will have synthetic utility. The results also demonstrate the importance of trialkylsilyl substituents in electron-transfer photochemical studies both as mechanistic probes and as groups to control reaction efficiency and regiochemistry.

### Conclusions

In this Account the features of excited-state reactions proceeding by SET pathways have been outlined in a general way and then specifically by using examples taken from recent studies with iminium and related N-heteroaromatic salts. We have seen how simple methods can be employed in determining when electron transfer is possible in the excited-state manifold and

in predicting the types of reaction pathways that are available by considering the chemical nature of initially generated, charged radicals or diradicals. Moreover, in the cases of iminium salts, electron-transfer-induced photochemical processes appear to represent reasonably versatile carbon-carbon bond-forming methods that can be applied to the synthesis of heterocyclic ring systems. Continuing studies in this general area will no doubt uncover other new excited-state reactions, new mechanisms for old reactions, and new ways of constructing important molecular structures.

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## Is There a Bridge between *ab Initio* and Semiempirical Theories of Valence?

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Molecular electronic structure provides an understanding of physical properties of molecules, their reactivities, and the reaction pathways of complicated chemical reactions. Electronic structure theories have developed along the two strongly contrasting *ab initio* and semiempirical avenues. The former attempt to solve the molecular electronic Schrödinger equation to chemical accuracy. The semiempiricist despairs at the complexity of such calculations and employs experimental data to avoid evaluating the molecular integrals. Practioners of the *ab initio* and semiempirical theories often appear to react to each other as if they were members of warring tribes. This deep division between the *ab initio* and semiempirical approaches is perhaps best understood by a brief review of the history of the development of these methods.

Bonding theories were developed before the advent of large-scale digital computers. Electronic structure theories were first designed to obtain qualitative understanding of general classes of phenomena, and this led to the introduction of simple models.<sup>1-5</sup> A prototype of these early model theories is the Hückel theory for conjugated  $\pi$ -electron hydrocarbons with one  $p_\pi$

orbital per carbon atom. The total electronic energy  $E$  is written as a sum of occupied orbital energies  $\epsilon_i$ . The  $\epsilon_i$  are the eigenvalues of the Hückel-Schrödinger equation,  $H_\pi\phi_i = \epsilon_i\phi_i$ , where  $H_\pi$  is the undefined one-electron Hamiltonian operator. The molecular orbitals  $\phi_i$  are approximated by using a linear combination of the  $p_\pi$  orbitals.  $H_\pi$  is not explicitly represented as an operator. Rather, its nonzero matrix elements between the  $p_\pi$  orbitals are the diagonal one-center Coulomb integral  $\alpha = \langle\phi_i|H_\pi|\phi_i\rangle$  and the nearest-neighbor off-diagonal resonance integral  $\beta = \langle\phi_i|H_\pi|\phi_{i\pm 1}\rangle$ . The unavailability of accurate *ab initio* calculations of  $\alpha$  and  $\beta$  required that these two parameters be fit to experimental data for a typical molecular system. The theory then provides predictions on a wide class of similar chemical compounds.

Hückel theory is widely successful in explaining the extra stability, some spectral data, and dipole moments of a variety of conjugated hydrocarbons.<sup>1-5</sup> The simple model, however, has several problems. First, different values of  $\beta$  are required to calculate different properties such as heats of formation, spectral energies, and ionization potentials. Second, Hückel theory does not explain the spectra of aromatic hydrocarbons such

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as naphthalene for which the model yields the wrong number of absorption bands with the wrong intensity patterns and the wrong energies. This problem can be traced to the neglect of explicit inclusion of electron-electron repulsion operators in  $H_\pi$  despite the fact that repulsion is present in  $H_\pi$  in some average sense.<sup>1-5</sup>

The  $\pi$ -electron theories were subsequently extended to include electron-electron repulsion-type terms explicitly. Pariser-Parr-Pople theory introduced the additional repulsion integrals  $\gamma_{ij} = \langle \phi_i \phi_j | \mathcal{H}_\pi^{\text{PPP}} | \phi_i \phi_j \rangle$  as empirical parameters.<sup>1-5</sup> Some deficiencies of Pariser-Parr-Pople theory were traced to the lack of explicit treatment of the  $\sigma$ -bonded framework.<sup>1-5</sup> This led to the modern development of all-valence-electron semiempirical theories like extended Hückel, MINDO,<sup>6</sup> and MNDO,<sup>7</sup> etc. All of these semiempirical theories are characterized by the use of some model valence shell Hamiltonian  $\mathcal{H}_M^v$  which contains parameters  $\alpha, \beta, \gamma, \dots$  that are determined from data for a small set of compounds. Then the  $\mathcal{H}_M^v$  is used for a wide variety of similar molecular compounds. A striking feature of these theories is their use of only a *minimum basis set of valence orbitals*.

Paralleling the development of semiempirical theories was the emergence of high-speed computers. Early ab initio calculations centered on self-consistent field (SCF) calculations for simple molecular systems. Minimum basis set calculations were found to give poor results for bond energies, although bond lengths and geometries were reasonably reproduced.<sup>8</sup> The calculation of decent energies requires much larger basis sets. This stands in marked contrast with the minimum basis set semiempirical methods. Even large basis set SCF calculations for  $F_2$  predicted it to be unbound, whereas the binding energy is approximately 1.5 eV. Thus, ab initio calculations of bond energies and spectra require the inclusion of correlation effects, i.e., corrections to the SCF model. Such calculations are now possible for small molecules with up to about six first-row atoms; however, semiempirical theories are often necessary to explain and interpret experimental data for larger molecules.

The above historical background presents a stark contrast between the semiempirical and ab initio theories. Ab initio theories require much larger basis sets than the minimum semiempirical bases. Semiempirical computer programs are fast and simple and can be operated directly by the nonspecialist. In contrast, the highly accurate ab initio theories require enormously more computer time, are often only available in very specialized programs, and need great care and understanding to obtain useful predictive results. Configuration interaction (CI) is unnecessary for the majority of semiempirical methods, and sometimes a small amount of CI is introduced to describe transition states for chemical reactions and low-lying excited electronic states. Accurate ab initio calculations are severely complicated due to the requirement for including enormous amounts of CI. Semiempirical calculations are often presented in terms of higher stated accuracies than accurate ab initio ones.

The simplicity and accuracy of semiempirical theories have led many theoreticians to believe that the semiempirical theories are nothing but a fudge or some clever curve-fitting procedure. After all, it is impossible to improve a poor theory, a minimum basis set theory, with even further approximations. On the other hand, practicing experimental chemists often find the accuracy of ab initio SCF calculations to be not worth their expense for large chemical systems. They explain that semiempirical theories are accurate because the empirical parametrization somehow incorporates the effects of correlation. The ab initio theorist notes in reply that the calculations can always be improved by adding more orbitals and configurations. He is still disturbed, however, that when semiempirical theories build in correlation by using experimental data and also introduce some CI, there may be double counting.<sup>1</sup> Most fundamentally, with the wide variety<sup>5</sup> of different semiempirical Hamiltonians  $\mathcal{H}_M^v$  the ab initio theorists finds no systematic way of choosing between the different  $\mathcal{H}_M^v$  models or of improving them.

### Analysis and Interpretation of Semiempirical Theories

These considerations bring us to the title of this paper, "Is There a Bridge between ab Initio and Semiempirical Theories of Bonding?" This question has been stressed in the monograph by Parr.<sup>1</sup> Textbooks generally present semiempirical methods as parameterized SCF calculations.<sup>1-5</sup> However, there is nothing fundamental about the SCF approximation. It even provides an incorrect description of bond dissociation when wave functions are taken as eigenfunctions of total spin.<sup>9</sup> Hence the textbooks' emphasis on the SCF portion of the methods cannot provide the desired bridge.

The fundamental simplification afforded by semiempirical methods involves their use of only a small number of valence orbitals, whereas the ab initio theories require, in practice, rather larger bases. It is this presence of only a small number of valence-shell orbitals that we believe to be the *central* simplifying and most important property of semiempirical theories. Thus, we rephrase our question of whether there exists a bridge between the theories as follows: Can we convert the full molecular electronic Schrödinger equation to one with a small number of valence orbitals in some effective valence shell Hamiltonian  $\mathcal{H}^v$  and still maintain chemical accuracy? This question shifts the emphasis to the calculation of an effective Hamiltonian that acts *only* in the space of a set of prechosen valence-shell orbitals.<sup>10-12</sup> Semiempirical theories are then characterized by their varying choice of model forms  $\mathcal{H}_M^v$  for  $\mathcal{H}^v$ . Early theoretical analyses appear to present explicit forms for  $\mathcal{H}_\pi$ . However, these analyses were made before the ability to actually perform the corresponding ab initio calculations. Subsequent ab initio work shows that these approximate model  $\mathcal{H}_\pi$  are insufficient to describe the electronic structure of simple molecules such as butadiene and benzene.<sup>13</sup> Furthermore, on a more fundamental level

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these simple  $\pi$  Hamiltonians as mathematical objects require for their complete solution an *infinite* basis set of  $\sigma, \delta, \dots$  as well as  $\pi$  orbitals; they cannot therefore be the simple minimum basis set  $\mathcal{H}_\pi$  mimicked by semiempirical theories.<sup>12</sup>

It is useful to pause to analyze this interpretation of semiempirical theories. Given a particular  $\mathcal{H}_M^v$  and its valence shell orbitals (v), we may construct a complete set of basis functions for the valence states as follows: Let  $\{\Delta_p\}$  be a set of  $N$ -electron Slater determinants with filled core and the remaining electrons distributed among the valence shell orbitals in all distinct ways. Hence, the  $\{\Delta_p\}$  are designated solely by the configuration of occupied valence shell orbitals. The most general eigenfunction  $\mathcal{H}_M^v$  is given by a linear superposition of all of the  $\{\Delta_p\}$  as<sup>14</sup>

$$\phi_j = \sum_p C_{pj} \Delta_p \quad (1)$$

The expansion coefficients  $C_{pj}$  in (1) are determined from the solution of the semiempirical Schrödinger equation, which in matrix form is

$$\mathcal{H}_M^v C_j = E_j C_j \quad (2)$$

Experimental energies  $E_j$  are used in (2) to determine the parameters in  $\mathcal{H}_M^v$ . Then the model  $\mathcal{H}_M^v$  is utilized to calculate energy for new molecular systems that have not been employed in the parameterization. Approximate treatments of (1) and (2) are often sufficient to obtain an accurate representation of the eigenvalues of  $\mathcal{H}_M^v$ , thereby greatly reducing the computational labor. Note that the definition (eq 1 and 2) of semiempirical theories automatically eliminates the parameterization-CI paradox because the correlation built into  $\mathcal{H}_M^v$  is distinct from that incorporated into the valence shell CI (eq 2).<sup>10-12</sup>

$\mathcal{H}_M^v$  matrix elements and the coefficients  $C_j$  are labeled by the configuration of the valence shell orbitals. Hence, there is a bridge between ab initio and semiempirical theories<sup>10-12</sup> if we can convert the full molecular Schrödinger equation in an infinite orbital basis to only the valence shell problem

$$\mathcal{H}^v C_j = E_j C_j \quad (3)$$

Here  $\mathcal{H}^v$  is some valence shell Hamiltonian. The matrix elements of  $\mathcal{H}^v$  and  $C_j$  are again labeled only by configurations of valence electrons in  $\Delta_p$ . Thus, we wish to determine whether some  $\mathcal{H}^v$  can be systematically calculated while still retaining chemical accuracy. We first ask whether a  $\mathcal{H}^v$  exists such that (3) is *exact for all valence states*? Since the answer to this question is yes, we can proceed with the determination of the exact  $\mathcal{H}^v$ .<sup>10-12,15,16</sup>

### Determination of the Exact Hamiltonian $\mathcal{H}^v$

Consider the full nonempirical Schrödinger equation with the exact many-electron Hamiltonian  $H$ . Partition the  $\mathbf{H}$  matrix into four large blocks. First, there is the

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subblock  $H_{PP}$  of the Hamiltonian matrix, which involves the matrix elements of  $\mathbf{H}$  between the valence shell determinantal functions  $\{\Delta_p\}$  in the primary space P. In addition, there is a set of complementary determinantal functions  $\{\Delta_q\}$  in the secondary space Q involving at least one electron excited out of a core orbital c and/or at least one electron occupying an excited orbital e. The  $\{\Delta_p, \Delta_q\}$  represents a complete basis set for the full  $N$ -electron Hamiltonian  $H$ .  $H_{QQ}$  involves the matrix elements of  $H$  within the secondary space  $\{\Delta_q\}$  functions, whereas  $H_{PQ}$  and  $H_{QP}$  contain the off-diagonal matrix elements of  $H$  between  $\{\Delta_p\}$  and  $\{\Delta_q\}$ .  $C_P$  and  $C_Q$  contain the coefficients of  $\{\Delta_p\}$  and  $\{\Delta_q\}$ , respectively, in the exact wave function. The exact Schrödinger equation is written in block matrix form as

$$\begin{pmatrix} H_{PP} & H_{PQ} \\ H_{QP} & H_{QQ} \end{pmatrix} \begin{pmatrix} C_P \\ C_Q \end{pmatrix} = E \begin{pmatrix} C_P \\ C_Q \end{pmatrix} \quad (4)$$

Equations 4 are equivalent to the block matrix equations

$$H_{PP}C_P + H_{PQ}C_Q = EC_P \quad (5a)$$

$$H_{QP}C_P + H_{QQ}C_Q = EC_Q \quad (5b)$$

Matrix inversion yields the "solution" to (5b) as

$$C_Q = (E1_Q - H_{QQ})^{-1}H_{QP}C_P \quad (6)$$

where  $1_Q$  is the unit matrix in Q space, and the inverse matrix is defined solely within Q space. When eq 6 is substituted for  $C_Q$  into (5a), we obtain the valence shell Schrödinger equation

$$\mathcal{H}^v C_P = EC_P \quad (7)$$

where the exact effective valence-shell Hamiltonian  $\mathcal{H}^v$  is defined by<sup>10-12,15,16</sup>

$$\mathcal{H}^v \equiv H_{PP} + H_{PQ}(E1_Q - H_{QQ})^{-1}H_{QP} \quad (8)$$

### Properties of $\mathcal{H}^v$

Note that in (7) the individual components of  $C_P$  are labeled by valence shell configurations only, while the matrix  $\mathcal{H}^v$  in (8) is likewise defined by sets of valence-electron configurations. Thus, (8) is exactly of the required matrix form (eq 3) necessary for understanding the theoretical basis of the semiempirical Schrödinger equations.<sup>2</sup> The energy  $E$  in (7) is the exact valence-state energy, and  $\mathcal{H}^v$  in (8) depends on  $E$ . This equation provides an explicit formula for the evaluation of the exact  $\mathcal{H}^v$  given some choice of the valence shell orbitals  $\{v\}$ . In principle,  $\mathcal{H}^v$  depends on the choice of the valence shell orbitals  $\{v\}$ , but all choices must produce the same *exact valence-state energies for all valence states*.

The structure of (7) and (8) provides considerable information. The  $H_{PP}$  term is the "theoretical part" of  $\mathcal{H}^v$ , i.e., that part which emerges from the literal interpretation of  $\mathcal{H}^v$  as merely a minimum basis set valence shell calculation. This  $H_{PP}$  is supplemented by the additional term involving excitations to the complete set of excited functions  $\{\Delta_q\}$ . We have termed<sup>11</sup> this contribution the "correlation part" of  $\mathcal{H}^v$  despite the slight difference in the meaning of correlation here from its usage in ab initio calculations. It does show how semiempirical  $\mathcal{H}_M^v$ , which are approximations to (8), must have their parameters different from the purely theoretical values generated by  $H_{PP}$ ; i.e., they must include "corrections for correlation".

### Perturbation Treatment of $\mathcal{H}^v$

The inverse matrix in (8) is infinite dimensional, so approximations are required. The first involves the use of a large but limited basis set, and is well studied for ab initio calculations. In addition, Rayleigh-Schrödinger perturbation expansions of the inverse matrix expanded  $E$  about zero-order energies  $E_p^0$ .<sup>15,16</sup> These expansions also separate  $H$  and its four subblocks into their zeroth order parts and the perturbation  $V$ ,  $H = H_0 + V$ . Then the perturbation expansion for  $\mathcal{H}^v$  through third order in  $V$  can be written in the sum over states form<sup>16,18,19</sup>

$$\begin{aligned} \mathcal{H}^v_{pp'} &\equiv \langle \Delta_p | \mathcal{H}^v | \Delta_{p'} \rangle = \\ &H_{pp'} + \frac{1}{2} \sum_q V_{pq} V_{qp'} [(E_p^0 - E_q^0)^{-1} + (E_{p'}^0 - E_q^0)^{-1}] + \\ &\frac{1}{2} \sum_{q,q'} V_{pq} V_{q'q'} V_{q'p'} [(E_p^0 - E_q^0)^{-1} (E_{p'}^0 - E_{q'}^0)^{-1} + (E_p^0 - \\ &E_{q'}^0)^{-1} (E_p^0 - E_q^0)^{-1}] - \\ &\frac{1}{2} \sum_{q,p''} [V_{pq} V_{qp''} V_{p''p'} (E_{p'}^0 - E_q^0)^{-1} + \\ &V_{p''p'} V_{p''q} V_{qp'} (E_p^0 - E_q^0)^{-1}] (E_{p'}^0 - E_q^0)^{-1} + O(V^4) \quad (9) \end{aligned}$$

where  $E_p^0$  and  $E_q^0$  are the eigenvalues of  $H_0$ ,  $H_0 \Delta_{p(q)} = E_{p(q)} \Delta_{p(q)}$ . The derivation of (9) employs quasidegenerate perturbation theory that requires that the set of valence shell states emerging from (7) must be quasidegenerate, i.e. must have closely lying energies  $\{E_p\}$ . The valence spaces utilized in semiempirical methods do *not* satisfy these quasidegenerate restrictions, and this would appear to be a serious impediment to the use of this formulation to calculate  $\mathcal{H}^v$  for comparison with the semiempirical  $\mathcal{H}_M^v$ . This consideration led to the initial use of an  $E$ -dependent formulation<sup>10-12</sup> for which the quasidegenerate restriction is not required. However, recent extensive theoretical work<sup>16,20-23</sup> has extended eq 9 for calculations on interesting valence shell systems that would otherwise not appear to conform to the stringent quasidegeneracy requirements of (9).

### Nonclassical Terms in $\mathcal{H}^v$

Equation 9 displays the explicit contributions from determinants  $\{\Delta_q\}$  with core excitations and/or excitations to a complete set of excited orbitals. Whereas the term  $H_{pp'}$  in (9) has matrix elements between  $\Delta_p$  and  $\Delta_{p'}$  that differ by *no more* than two spin orbitals, the second term on the right side has elements that differ by *three spin orbitals*, etc., for subsequent terms. Hence, the traditional decomposition of  $\mathcal{H}^v$  into a core energy  $E_c$ , a sum of one-body effective operators  $\mathcal{H}_i^v$ , and of two-body effective operators  $\mathcal{H}_{ij}^v$ , is not in accord with (9). The exact  $\mathcal{H}^v$  must contain three-body effective operators  $\mathcal{H}_{ijk}^v$  as well as higher many-electron nonclassical terms.<sup>10-12,16</sup>

$$\mathcal{H}^v = E_c + \sum_i \mathcal{H}_i^v + \frac{1}{2!} \sum_{i \neq j} \mathcal{H}_{ij}^v + \frac{1}{3!} \sum_{i \neq j \neq k} \mathcal{H}_{ijk}^v + \dots \quad (10)$$

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Note that the leading contributions to the  $\mathcal{H}_{ijk}^v$  do *not* arise from triple excitations out of the valence space; in  $O(V^2)$  they come from  $\Delta_q$  involving only single excitations of either a core ( $c \rightarrow v, e$ ) or a valence electron ( $v \rightarrow e$ ).<sup>15,16</sup> These  $\mathcal{H}_{ijk}^v$  are associated with the effects called semiinternal correlations by Sinanoğlu.<sup>24</sup>

Ab initio calculations customarily reoptimize orbitals for each state. In contrast, (9) utilizes the same set of valence shell orbitals for all the valence states of the system. The perturbation expansion in (9) adjusts for this orbital change. Difficulties with such a perturbation expansion are anticipated if the different valence states involve qualitatively different types of orbitals.  $\mathcal{H}^v$  of (9) may be represented in a form<sup>15,16</sup> where the individual operators in (10) are independent of the number of occupied valence electrons. Hence, the  $\mathcal{H}^v$  of (10), in principle, can be utilized for all valence states of the system with all possible charges. This is similar to the use in semiempirical theories of a common set of valence orbitals (albeit somewhat undefined) and parameters for all valence states of the positive and negative ions as well as the neutral. Whether approximate  $\mathcal{H}^v$  calculations can display this remarkable property must be tested by numerical calculations.

It is desirable to evaluate the individual matrix elements of  $\mathcal{H}_i^v$ ,  $\mathcal{H}_{ij}^v$ ,  $\mathcal{H}_{ijk}^v$ , ..., for comparison with semiempirical  $\mathcal{H}_{Mi}^v$ ,  $\mathcal{H}_{Mij}^v$ . The derivation of such formulas<sup>15,16</sup> is quite involved and relies on the use of quasidegenerate many-body perturbation methods<sup>16,25</sup> or equivalent algebraic approaches<sup>15</sup> that are rather specialized. Nevertheless, the program is to perform ab initio calculations of the individual matrix elements of  $\mathcal{H}_i^v$ ,  $\mathcal{H}_{ij}^v$ ,  $\mathcal{H}_{ijk}^v$ , ..., within the valence shell basis  $\{v\}$  and to use them in (7) to evaluate the valence-state energies.

### Ab Initio Calculations of the Valence Shell Hamiltonian

$\mathcal{H}^v$  calculations using (9) have been carried out for atomic systems<sup>20,22</sup> and some small diatomic molecules.<sup>21,26</sup> These provide systematic ab initio determinations of the one-center and two-center matrix elements of the  $\mathcal{H}_i^v$ ,  $\mathcal{H}_{ij}^v$ ,  $\mathcal{H}_{ijk}^v$ , ..., operators for comparison with semiempirical  $\mathcal{H}_M^v$  as well as the magnitude of the matrix elements of  $\mathcal{H}_i^v$ ,  $\mathcal{H}_{ij}^v$ , ..., that have no apparent direct counterpart in  $\mathcal{H}_M^v$ . We analyze whether the one-center matrix elements of our  $\mathcal{H}^v$  are transferrable between the atom and simple diatomic molecules.<sup>27</sup>

Second-order calculation with (9) are a perturbative analogue of Gershgorin and Shavitt's  $B_k$  method for performing approximate CI calculations,<sup>28</sup> while the third-order treatment is a perturbative analogue of the method of Segal and Wetmore<sup>29</sup> for improvements upon this  $B_k$  method. (Neither of these methods, however, generate the matrix elements of  $\mathcal{H}_i^v$ ,  $\mathcal{H}_{ij}^v$ , ..., we desire.) In these CI methods the computer determines the configuration-state functions of the primary P space, whereas in our method the valence shell orbitals fix the

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P space. This implies that if our P space includes the most important configurations for the valence-state wave functions, a third-order calculation is sufficient for good ab initio type accuracy. Problems with the calculation of  $\mathcal{H}^v$  are twofold. First, as the size of the valence space increases, the valence orbitals become less and less "quasidegenerate", and the above formulation encounters difficulties.<sup>16</sup> Furthermore, as the number of valence orbitals increases, the number of  $\mathcal{H}_{ijk}^v, \dots$ , matrix elements increases enormously, making the calculations prohibitive. This motivates the initial consideration of rather simple cases having important bearing on our understanding of the fundamental basis for semiempirical theories.

### Calculations For First-Row Atoms with 2s, 2p Valence Space

The first calculation, performed with formalism 9, was for the carbon atom.<sup>20</sup> The basis set contained 5s, 4p, and 2d Slater-type orbitals. Core and 2s, 2p valence orbitals were determined from an SCF calculation for the ground  $^3P$  state of C. The third-order calculation of  $\mathcal{H}^v$  using (9) produced 80% of the ground-state correlation energy.<sup>30</sup> Excitation energies from the ground state of C were obtained to a mean absolute error of 0.25 eV. Both results are as anticipated from this type of ab initio calculation with the given basis set. However, the calculation enables us to test whether the same  $\mathcal{H}^v$ , calculated for C, can be used without any additional effort to compute the valence-state energy levels of the ions  $C^+, C^{2+}, C^{3+}$ . Expectations, based on ab initio calculations by conventional means are that this same calculation for C should not be accurate for the ions because of the large orbital changes necessary to describe the ions. However, using (7) with the Hamiltonian (9), determined for C, provides the same accuracy as for the neutral!

This remarkable feature<sup>31</sup> of the  $\mathcal{H}^v$  method as a purely ab initio computational scheme is further illustrated by the F atom, the first-row atom and its ions with the largest number of known energy levels. The error (difference between calculated and experimental values) of the excitation energies and ionization potentials for F and its ions<sup>22</sup> is presented in Figure 1 vs. the sequential order of the individual 2s, 2p valence-shell energy levels. Listed at the top of the figure are the ions. In curve N the 2s and 2p orbitals are chosen from ground-state SCF calculations for F. The third-order calculations (solid lines) exhibit larger errors for the more highly positive ions. This is not disturbing since the original calculation is for F. However, the calculation labeled S employs 2s and 2p orbitals from a  $F^+$  ground-state SCF calculation and provides a good representation of the energy levels of all of the valence states of  $F^+$  and all the other ions. Likewise using valence orbitals coming from  $F^{2+}$  (curves D),  $F^{3+}$  (curves T), or  $F^{6+}$  (curves B) also yields very good descriptions of all these states. (The larger errors observed for the F energy levels are associated with the overcrowding of the 2p subshell<sup>16</sup> and are common problems in ab initio

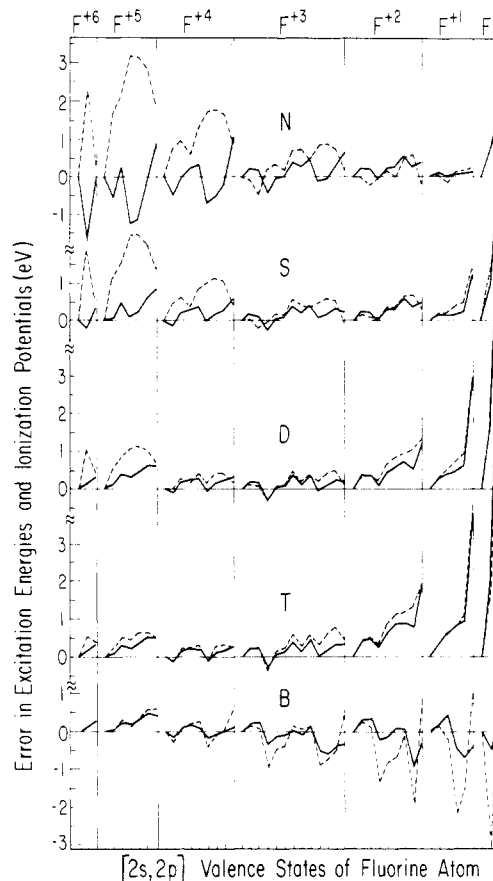


Figure 1. Errors in calculated excitation energies and ionization potentials for F and its ions as calculated with  $\mathcal{H}^v$  method for 2s-2p valence states.<sup>22</sup> Solid lines give third-order results while dashed lines are for second order. Valence states are in sequential order, and vertical lines separate charge states.

treatments.) If calculations completely converged within the given basis set, all curves in Figure 1 would be identical. The similarity between the third-order results indicate reasonable convergence.

F and a number of other atomic systems<sup>20,22</sup> demonstrate that the  $\mathcal{H}^v$  method, as a purely ab initio technique, has the amazing property of simultaneously providing the energy levels of not only the neutral but the ionic states of the system. The results indicate that the idea of utilizing an effective valence shell Hamiltonian is a physically sound concept.

### $\mathcal{H}^v$ for First-Row Atoms

The viability of the  $\mathcal{H}^v$  method as an ab initio tool enables its calculated  $\mathcal{H}_{ij}^v, \mathcal{H}_{ij}^v, \mathcal{H}_{ijk}^v$ , to be compared with values used in semiempirical theories. Table I displays some of the  $\mathcal{H}^v$  matrix elements for the L shell of C. The one-electron, one-center integrals deviate from those of MINDO<sup>7</sup> and most other semiempirical methods by an average of 15 eV. Experimental values of the  $\mathcal{H}^v$  matrix elements are given in the last column.  $\langle 2s | \mathcal{H}_1^v | 2s \rangle$  is just the negative of the ionization potential of the  $^2S$  state of  $C^{3+}$  while  $\langle 2p | \mathcal{H}_1^v | 2p \rangle$  is that for the  $C^{3+} \ ^2P$  state.<sup>32</sup> Four matrix elements of  $\mathcal{H}_{ij}^v$  and five of  $\mathcal{H}_{ijk}^v$  can be determined from known energy levels of states of  $C^{3+}, C^{2+}$ , and  $C^+$ ,<sup>33</sup> and they are also

(30) Third-order calculations: Sheppard, M. G.; Freed, K. F., unpublished results.

(31) Another formulation of  $\mathcal{H}^v$  due to Westhaus does not share this property; it is valid only for a fixed number of electrons. Westhaus, P.; Bradford, E. G. *J. Chem. Phys.* 1976, 64, 4276. Westhaus, P.; Moghtaderi, M. *Ibid.* 1980, 72, 4174.

(32) "Atomic Energy Levels". *Natl. Bur. Stand. (U.S.) Circ.* 1971, No. 35.

(33) Yeager, D. L.; Sheppard, M. G.; Freed, K. F. *J. Am. Chem. Soc.* 1980, 102, 1270.

Table I  
Valence-Shell Hamiltonian Matrix Elements for  
L Shell of Carbon (eV)

matrix element	SCF <sup>c</sup>	MINDO/		
		3 <sup>7</sup>	calcd <sup>20,30</sup>	expt <sup>32,33</sup>
$\langle 2s   \mathcal{H}_1^v   2s \rangle$		-51.79	-64.59	-64.50
$\langle 2p   \mathcal{H}_1^v   2p \rangle$		-39.18	-56.37	-56.49
$\langle sx   \mathcal{H}_{12}^v   sx \rangle^a$	15.08	11.47	18.41	18.20
$\langle sx   \mathcal{H}_{12}^v   xs \rangle$	3.12	2.43	3.19	3.10
$\langle xy   \mathcal{H}_{12}^v   xy \rangle$	14.13	9.84	18.17	18.17
$\langle xy   \mathcal{H}_{12}^v   yx \rangle$	0.79	0.62	0.50	0.52
$\langle sxy   \mathcal{H}_{123}^v   \widetilde{sxy} \rangle^b$	0	0	-2.15	-1.86
$\langle sxy   \mathcal{H}_{123}^v   \widetilde{syx} \rangle$	0	0	0.15	-0.12
$\langle sxy   \mathcal{H}_{123}^v   \widetilde{xsy} \rangle$	0	0	-0.35	0.06
$\langle xyz   \mathcal{H}_{123}^v   \widetilde{xyz} \rangle$	0	0	-2.99	-2.98
$\langle xyz   \mathcal{H}_{123}^v   \widetilde{xzy} \rangle$	0	0	-0.11	-0.17

<sup>a</sup>  $\langle sx | \mathcal{H}_{12}^v | sx \rangle \equiv \langle 2s(1)2p_x(2) | \mathcal{H}_{12}^v | 2s(1)2p_x(2) \rangle$ .

<sup>b</sup>  $\langle sxy | \mathcal{H}_{123}^v | \widetilde{sxy} \rangle \equiv \langle sxy | \mathcal{H}_{123}^v | sxy \rangle - \langle sxy | \mathcal{H}_{123}^v | yxs \rangle$ .

<sup>c</sup>  $\langle ij | \mathcal{H}_{12}^v | i'j' \rangle$  with  $i, j, i', j'$  2s and 2p SCF orbitals.

listed in Table I. The agreement between calculated and experimental values is very good. Integrals not listed in the table are dependent on the particular choice of the 2s and 2p valence orbitals.<sup>33</sup> The column labeled SCF provides the "theoretical" values of the two-electron integrals. Note that the 2s-2p and the 2p<sub>x</sub>-2p<sub>y</sub>  $\mathcal{H}_{ij}^v$  Coulomb integrals are larger than SCF values, which in turn are larger than one-center Coulomb integrals of MINDO<sup>7</sup> or any semiempirical theory. Our  $\mathcal{H}^v$  includes all the exchange and hybrid integrals; no ZDO approximation is invoked. The two exchange integrals in Table I are significant and are close to their SCF values and experiment. Three-body interactions vanish for both the theoretical (SCF) integrals and semiempirical theories. Nevertheless,  $\mathcal{H}_{ijk}^v$  integrals in Table I are as large as 3 eV in good agreement with experiment!

Our purely ab initio  $\mathcal{H}^v$  appears to differ considerably from the one-center part of the  $\mathcal{H}_M^v$ . The  $\mathcal{H}^v$  one-electron, one-center integrals for first-row atoms<sup>20,22</sup> are 10-60 eV lower than those of semiempirical theories.<sup>7</sup> Our two-electron repulsion integrals are larger than the SCF values, which in turn are larger than those used by MINDO and other semiempirical theories. Three-electron integrals are as large as 4 eV, and they are absent in semiempirical theories. This striking discrepancy, however, has a rather simple rationale. Just as a one-electron Fock operator in SCF theory contains an average of the two-electron interactions, the  $\mathcal{H}_M^v$  of semiempirical theories must somehow average our  $\mathcal{H}_{ijk}^v$  into their  $\mathcal{H}_{Mi}^v$  and  $\mathcal{H}_{Mij}^v$ . Given this idea it is possible to construct such averages<sup>34</sup> to obtain "ab initio-semiempirical integrals" from our  $\mathcal{H}^v$  formulation that are similar to those of MINDO. The importance of this exercise lies, however, not in an attempt to calculate the "best" one-center integrals but to understand the physical meaning of this averaging process as follows: The averaging of  $\mathcal{H}_{ijk}^v$  interactions into semiempirical  $\mathcal{H}_{Mi}^v$  and  $\mathcal{H}_{Mij}^v$  is expected to be valid for similar molecules to those for which the parameters are determined. Carbon atoms in organic compounds locally have a rather narrow range of electronic environments. The hybridization varies, but the formal charge remains relatively close to 0. From the one-center integrals alone it would not appear to be unreasonable to believe that

(34) Freed, K. F.; Sun, H. *Isr. J. Chem.* 1980, 19, 99.

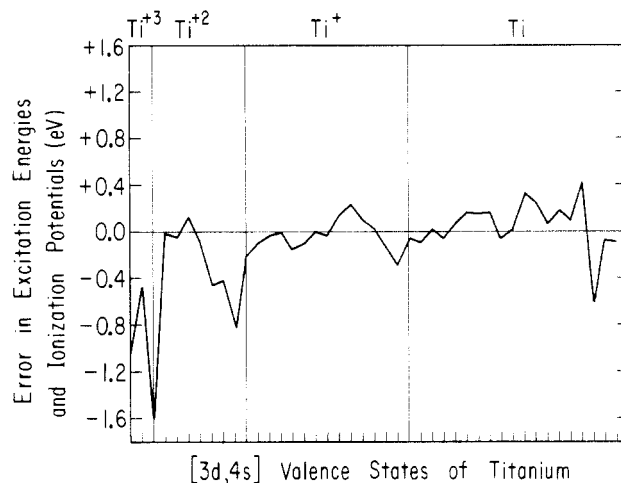


Figure 2. Errors in calculated excitation energies and ionization potentials for Ti and its ions from second-order  $\mathcal{H}^v$  calculations<sup>23</sup> with 3d-4s valence space.

an optimal set of  $\mathcal{H}_{Mi}^v$  and  $\mathcal{H}_{Mij}^v$ , containing the averages of our  $\mathcal{H}_{ijk}^v$  matrix elements, could somehow be obtained for this range of local electronic structures. However, if these same  $\mathcal{H}_{Mi}^v$  and  $\mathcal{H}_{Mij}^v$  were required to adequately describe not only this narrow range of C valence states but also the energy levels of C<sup>+</sup> and C<sup>2+</sup>, then a single average set of  $\mathcal{H}_{Mi}^v$  and  $\mathcal{H}_{Mij}^v$  would not suffice. It would be necessary to explicitly incorporate the  $\mathcal{H}_{ijk}^v$ . Perhaps it is fortunate for organic chemistry that the range of local electronic structure is so narrow that construction of a semiempirical theory seems reasonable.

### $\mathcal{H}^v$ for Transition-Metal Atoms

Transition-metal systems display a wide range in formal charge and high- and low-spin character as the bonding situation is varied. To date semiempirical theories of the all-valence-electron MINDO type sophistication have not been developed to describe both bond energies and spectral energies for transition-metal compounds. It is traditional to utilize different sets of semiempirical parameters for each formal charge and for high- and low-spin compounds. If the transition-metal atoms'  $\mathcal{H}_{ijk}^v$  are as large as for first-row atoms, then it would not appear to be possible to design a set of  $\mathcal{H}_{Mi}^v$  and  $\mathcal{H}_{Mij}^v$  for the transition-metal atoms to cover such a wide range of atomic electronic states. Thus, having large  $\mathcal{H}_{ijk}^v$  in transition-metal atoms would help to explain previous difficulties with the development of all-valence-electron-type semiempirical theories of transition-metal bonding and spectra.

Calculations of correlation energies in the first-row transition-metal atoms are only beginning to appear.<sup>35</sup> Most of these center on the difficult tasks of evaluating the lowest 4s → 3d excitation energies. Our  $\mathcal{H}^v$ , on the other hand, describes the energy levels of all of the valence states of the transition-metal atoms and their ions. Thus, it is necessary to establish whether the formulation can, in fact, describe the correlation energies of all the valence states of these transition-metal atoms. Figure 2 displays calculated second-order results for the titanium atom where we present the error

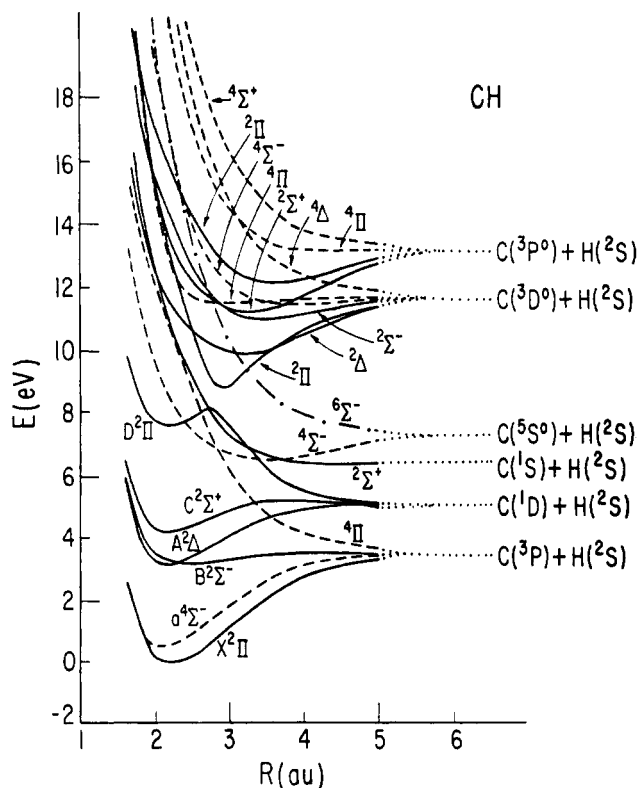
(35) Botch, B. H.; Dunning, T. H., Jr.; Harrison, J. F. *J. Chem. Phys.* 1981, 75, 3466. Bauschlicher, C. W., Jr.; Walch, S. P.; Partridge, H. *J. Chem. Phys.* 1982, 76, 1033.

(calculated minus experimental) in the excitation energy versus the *sequential* ordering of the energy level. The 4s and 3d valence orbitals are chosen from ground-state Ti SCF calculations, but results with ground-state  $Ti^+$  orbitals are rather similar.<sup>23</sup> Again, a single calculation for the neutral atom suffices to describe the energy levels of that atom and all of its ions with the amazing mean absolute error of about 0.2 eV. The errors increase in going across the transition series because the number of energy levels and different charge states increases too greatly for even the  $\mathcal{H}^v$  method.<sup>23,26</sup> Accurate  $\mathcal{H}^v$  calculations can be performed for a few charge states at a time, and they provide<sup>37</sup>  $\mathcal{H}_{ijk}^v$  matrix elements as large as 4eV. This agrees with expectations that the  $\mathcal{H}_{ijk}^v$  in transition-metal systems are too large to permit simple semiempirical theories with only  $\mathcal{H}_{M_i}^v$  and  $\mathcal{H}_{M_{ij}}^v$  to describe the full range of states that are pertinent to the bonding in these systems. It is anticipated that a full theory of these systems will somehow require the introduction of  $\mathcal{H}_{ijk}^v$  or their equivalent. Note that the use of population-dependent semiempirical parameters<sup>38,39</sup> is qualitatively equivalent to the use of  $\mathcal{H}_{ijk}^v$ . Our calculated  $\mathcal{H}_{ijk}^v$  matrix elements should enable a test of the more convenient population-dependent methods.

### $\mathcal{H}^v$ for Molecules

$\mathcal{H}^v$  calculations are being pursued for small diatomic molecules to study the bond length dependence of two-center  $\mathcal{H}^v$  matrix elements and the transferability of one-center matrix elements between the atoms and the molecule. Cases most extensively studied to date are the  $CH_2$  and  $Li_2$ <sup>26</sup> molecules. The CH calculations involve Slater-type functions with 4s3p1d basis functions on C and 2s1p on H. The valence shell is taken to be all of the orbitals whose origins are 2s and 2p on C and 1s on H, the 2 $\sigma$ , 3 $\sigma$ , 1 $\pi$ , and 4 $\sigma$  molecular orbitals. The valence shell determinants  $\{\Delta_p\}$  are by no stretch of the imagination a quasidegenerate set. Nevertheless, careful analysis has shown how the  $\mathcal{H}^v$  formulation can be utilized to perform the quasidegenerate many-body perturbation calculations for such a system with this large valence space.<sup>16,21,22</sup>

A small four-configuration MCSCF calculation, which properly describes dissociation, is performed at each internuclear separation  $R$  for the ground state of CH. Occupied valence orbitals along with the lower lying 4 $\sigma$  virtual orbital provide the definition of the valence orbitals at that internuclear separation  $R$ .  $\mathcal{H}^v$  is calculated and used to evaluate the energy levels of *all* the valence states of both CH and  $CH^+$  at that  $R$ . Figure 3 displays the calculated potential curves for CH. Rydberg (intruder) states do not emerge from the calculations despite their presence in the higher energy regime. Calculated excitation energies, bond lengths, and force constants are in good agreement with other accurate ab initio calculations and with experiment. The  $\mathcal{H}^v$  method provides a global overview of *all* of the valence states simultaneously and indicates the origins of maxima in some of the excited-states' potential curve.



**Figure 3.** Potential curves for CH from third-order  $\mathcal{H}^v$  calculations with valence space given by 2 $\sigma$ , 3 $\sigma$ , 1 $\pi$  and 4 $\sigma$  orbitals. Separated atom limits given, and dotted lines show extrapolations to these limits.

The same  $\mathcal{H}^v$  describes the energy levels of  $CH^-$  even though all but the lowest two electronic states lie in the continuum with respect to electron detachment.<sup>40</sup> However, the H-atom orbital exponents used in the CH calculations are rather poor for describing the  $H^-$  dissociation limit. Calculations with hydrogenic type exponents on H have been made for the negative ion resonance states of  $CH^-$ . The  $\mathcal{H}^v$  method in this case can be shown<sup>40</sup> to be a sensible realization of the Fehbach method for describing resonance states. There is almost no available theory or experiment performed for molecular negative ion resonance states associated with the introduction of the extra electron into vacant valence orbitals. The calculations are, therefore, of interest in probing the electronic structure of the negative ion resonances.<sup>40</sup>

An additional calculation for CH has been carried out in which the valence orbitals are the 2s and 2p *atomic valence orbitals* of C and the 1s H orbital in order to study the  $R$ -dependence of the one- and two-center integrals. The form of a few of the two-center integrals has been analyzed<sup>41</sup> as follows: The one-center, one-electron integrals of  $\mathcal{H}_i^v$  vary as  $A - BR^{-1}$ , with  $A$  the limiting atomic value. The coefficient  $B$  provides the effective nuclear charge  $z_{eff}$  on one center that is perceived by an electron on the other atomic center. Hence, 1s on H sees a  $z_{eff}$  of 4.1 on C, and 2s on C sees a  $z_{eff}$  of 1.0 on H. 2p on C sees different  $z_{eff}$ 's on H for  $\sigma$  and  $\pi$  orbitals, 1.5 and .9, respectively. This is reasonable in view of the fact that the  $p\sigma$  orbital points towards the proton. A spherical average yields the effective charge of 1.1. These results are in accord with

(36) Martin, R. L.; Hay, P. J. *J. Chem. Phys.* 1981, 75, 4539.

(37) Lee, Y. S.; Freed, K. F., unpublished results.

(38) Hashmall, J. A.; Raynor, S. *J. Am. Chem. Soc.* 1977, 99, 4894.

(39) Åsbrink, L.; Fridh, C.; Lindholm, E.; de Bruijn, S.; Chong, D. P. *Phys. Scri.* 1980, 22, 475.

(40) Sun, H.; Freed, K. F. *J. Chem. Phys.* 1982, 76, 5051.

(41) Sun, H.; Freed, K. F., unpublished results.

general assumptions concerning the one-center integrals in semiempirical theories.

The H 1s-C 2s  $\mathcal{H}_{ij}^v$  Coulomb integral varies like  $A(R^2 + B^2)^{-1}$  and is consistent with that of semiempirical methods.<sup>42</sup> On the other hand, the one-center  $\mathcal{H}_{ij}^v$  2s-2s Coulomb integral is *not* independent of  $R$ ; rather it behaves at shorter distances as  $A + BR^{-2}$ . The  $R^{-2}$  term can be interpreted physically as follows: The atomic  $\mathcal{H}^v$  integral contains 2s-2s correlation involving excitation of 2s to a complete set of excited orbitals. However, in the CH molecule the 1s on H is now in the valence space, so that correlation of (2s)<sup>2</sup> into the space occupied by the 1s on H is now forbidden. This leads to a decrease in the 2s-2s correlation energy which becomes greater as  $R$  is decreased. It is clear from this preliminary account that there are certain aspects of the one- and two-center molecular  $\mathcal{H}^v$  matrix elements that differ from the customarily assumed forms in semiempirical theories. In addition, there are a large number of three-body interactions whose role in  $\mathcal{H}^v$  remains to be analyzed.

Recent  $\mathcal{H}^v$  calculations have been made for the  $\pi$  Hamiltonian,  $\mathcal{H}_\pi$ , of butadiene.<sup>43</sup> These contain hybrid, exchange multicenter and  $\mathcal{H}_{ijk}^v$  integrals that are absent in semiempirical methods. A preliminary analysis of the results indicate why semiempirical  $\pi$  methods require different parameters to calculate different properties.

### Concluding Remarks

We have shown that it is possible to introduce an effective valence shell Hamiltonian  $\mathcal{H}^v$  that *exactly*

(42) Klopman, G. *J. Am. Chem. Soc.* **1964**, *86*, 4550. Ohno, K. *Theor. Chim. Acta* **1964**, *3*, 219.

(43) Lee, Y. S.; Freed, K. F., *Chem. Phys. Lett.* **1983**, *94*, 202.

describes the energy levels of *all* of the valence states of a system along with its ions. This  $\mathcal{H}^v$  generates a valence shell problem only, but the contributions from core excitations and a complete set of excited orbitals are incorporated into  $\mathcal{H}^v$ . Accurate ab initio calculations of  $\mathcal{H}^v$  can be provided within a perturbation formulation for small systems involving small valence spaces.

The ab initio  $\mathcal{H}^v$  approach has the remarkable property of simultaneously describing a wide range of valence states of a system and its ions. This  $\mathcal{H}^v$  provides a bridge between ab initio and semiempirical theories because  $\mathcal{H}^v$  can be calculated from first principles and it is the quantity being mimicked and approximated by semiempirical theories of valence. The calculated  $\mathcal{H}^v$  differs in a number of respects from the  $\mathcal{H}_M^v$  assumed in semiempirical theories, but the differences can be understood on the basis of simple physical concepts which may be helpful in further developing and refining semiempirical theories of valence. It should be noted in passing that another wide range of semiempirical theories of electronic structure is based on the use of a density functional formalism. Recent progress has been made with the derivation of explicit expressions for the density functional that can be evaluated by ab initio methods.<sup>44</sup> However, to date calculations have not yet been performed.

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