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Theoretical Models Incorporating Electron Correlation

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Abstract

Some methods of describing electron correlation are compared from the point of view of requirements for theoretical chemical models. The perturbation approach originally introduced by Møller and Plesset, terminated at finite order, is found to satisfy most of these requirements. It is size consistent, that is, applicable to an ensemble of isolated systems in an additive manner. On the other hand, it does not provide an upper bound for the electronic energy. The independent electron-pair approximation is accurate to second order in a Møller–Plesset expansion, but inaccurate in third order. A series of variational methods is discussed which gives upper bounds for the energy, but which lacks size consistency. Finally, calculations on some small molecules using a moderately large Gaussian basis are presented to illustrate these points. Equilibrium geometries, dissociation energies, and energy separations between electronic states of different spin multiplicities are described substantially better by Moller–Plesset theory to second or third order than by Hartree–Fock theory.

1. Introduction

In practical theoretical chemistry there is much advantage in studying a wide range of problems at a uniform level of approximation. The results of all calculations at one level constitute what may be termed a "theoretical model chemistry" [1]. The effectiveness of any model may be evaluated by comparing some of its details with real chemistry in areas where experimental data are available. If the results of such a comparison are favorable, the model acquires some predictive credibility.

To qualify as a satisfactory theoretical model chemistry, a method ideally should satisfy a number of requirements. In the first place, it should provide well-defined results for the energies of electronic states for any arrangement of fixed nuclei, leading to a set of continuous potential surfaces. Special features such as selection of particular electronic configurations or the imposition of constraints related to the symmetry of the system should be avoided if possible. Second, the method should be such that the amount of computation does not increase too rapidly with the size of the system. Third, the method should have the property of size consistency, that is, application to an ensemble of isolated molecules should give results which are additive for the energy and other properties. Comparison between properties of molecules of different size will not be effective unless this requirement is satisfied. Finally, the calculated electronic energy should be an upper bound to that corresponding to an exact solution of the Schrödinger equation. Such methods are usually termed variational.

Most theoretical model chemistries that have been proposed and examined up to now are of the Hartree–Fock molecular orbital type, using single-determinant wave functions.

Some are semiempirical in character (CNDO [2], INDO [3], MINDO [4]) being partially parameterized to fit experimental data. Others utilize *ab initio* methods, optimizing molecular orbitals which are expanded as linear combinations of a finite set of basis functions. If the basis functions are specified for each atom according to its atomic number, and if they are centered at the nuclear position, the resulting self-consistent molecular orbital calculations constitute a model satisfying most of the requirements outlined above. For the electronic ground states, at least, the resulting energy surface is variational and uniquely defined. If the total number of basis functions is N, the most time-consuming parts of the computation, if carried out in full, require $O(N^4)$ operations. This is the handling of two-electron integrals. Also these Hartree–Fock models are size consistent, at least in the spin-unrestricted form (UHF) in which electrons of different spins occupy independent molecular orbitals [5].

It is well recognized that the principal deficiency of Hartree–Fock models is the neglect of correlation between motions of electrons of opposite spin. The primary purpose of the present paper is to examine and assess various methods of handling corrections for correlation from the point of view of the model requirements listed above. In principle, the correlation energy may be calculated by full configuration interaction in which the wave function is determined as the best linear combination of all possible electron configuration functions. In practice, however, this rapidly becomes impractically time consuming, and simpler schemes must be sought. We begin the survey in the second section with the perturbation approach originally proposed by Møller and Plesset [6]. Various later modifications of this technique [7–13] are often grouped under the name "many-body perturbation theory." The relation between perturbation techniques and configuration interaction has been developed extensively by Löwdin [14]. The general idea is to treat the full Hamiltonian as a perturbed independent electron Hamiltonian and then to expand the energy and wave function in orders of the perturbation. In the Møller–Plesset approach the Hartree–Fock Hamiltonian is used as a starting point. In the third section we consider the independent electron-pair approximation and related methods, introduced by Sinanoğlu [15] and Nesbet [16]. In the fourth section we consider a series of variational techniques which evaluate the expectation value of the Hamiltonian for various trial wave functions and which, therefore, provide rigorous upper bounds to the energy corresponding to full treatment with any given orbital basis. In Section 5, we consider the merits and demerits of these various techniques if used as theoretical models with appropriate basis sets.

As a result of these comparative studies it is argued that the original Møller–Plesset expansion, carried to second or third order, provides correlation techniques which have some advantages over the other methods considered. It therefore seems worthwhile to begin a comprehensive study of theoretical models based on this expansion, appropriately terminated. If the UHF Hamiltonian is used as a starting point, such models may be described as spin-unrestricted Møller–Plesset theory to second or third order (UMP2 or UMP3). In the final section of the paper we commence such a study using a moderately large uncontracted basis set for some small molecules.

2. Møller–Plesset Theory

This theory begins with the Hartree–Fock single-determinant wave function

$$\Psi_0 = (n!)^{-1/2} \det \{\chi_1 \ldots \chi_n\} \tag{1}$$

where the n electrons are assigned to spin orbitals χ_i, $i = 1,\cdots,n$. In practical computations these are written as linear combinations of a finite set of spin-orbital basis functions as

discussed in a later section. If we adopt the spin-unrestricted form of Hartree–Fock theory (UHF), each χ_i satisfies the equation

$$F\chi_i = \epsilon_i \chi_i \tag{2}$$

where F is the one-electron Fock operator and ϵ_i is the eigenvalue corresponding to χ_i. For a finite basis set, Equation (2) is replaced by an appropriate set of matrix equations [5, 17]. The remaining solutions of Equation (2) that are not occupied in Equation (1), χ_a, $a = n + 1, \cdots$, are usually described as virtual spin orbitals.

The Møller–Plesset procedure treats the full many-electron Hamiltonian $\mathcal{H}$ as the Fock Hamiltonian plus a perturbation. Thus introducing a dimensionless expansion parameter λ, we define

$$\begin{aligned} \mathcal{H}_\lambda &= \mathcal{H}_0 + \lambda V \\ &= \sum_p F_p + \lambda \left\{ \mathcal{H} - \sum_p F_p \right\} \end{aligned} \tag{3}$$

where F_p is the Fock operator for electron p. The eigenfunctions of $\mathcal{H}_0$ are the Hartree–Fock determinant (1) and other determinants in which some of the occupied spin orbitals χ_i are replaced by virtual spin orbitals χ_a. These may be classified into single substitution functions $\Psi_{i\to a}$ (χ_i replaced by χ_a), double substitution functions $\Psi_{ij\to ab}$ (χ_i replaced by χ_a, χ_j replaced by χ_b), and so forth. Note that $\Psi_{ij\to ab}$ is antisymmetric in the suffix pair (ij) and also in the pair (ab). Rayleigh–Schrödinger perturbation theory [18] is then used to obtain expansions for the ground-state wave function and energy,

$$\Psi_\lambda = \Psi^{(0)} + \lambda\Psi^{(1)} + \lambda^2\Psi^{(2)} + \cdots \tag{4}$$

$$\mathcal{E}_\lambda = \mathcal{E}^{(0)} + \lambda\mathcal{E}^{(1)} + \lambda^2\mathcal{E}^{(2)} + \cdots \tag{5}$$

Correlation theories at various levels are obtained by termination of these series and putting $\lambda = 1$. Since unrestricted Hartree–Fock theory is used as a starting point, we shall refer to this method as "unrestricted Møller–Plesset theory" (UMP) to a particular order. For example,

$$\mathcal{E}_{\mathrm{UMP2}} = \mathcal{E}^{(0)} + \mathcal{E}^{(1)} + \mathcal{E}^{(2)} \tag{6}$$

is the UMP2 energy.

The leading terms in Equations (4) and (5) are

$$\begin{aligned} \Psi^{(0)} &= \Psi_0 \\ \mathcal{E}^{(0)} &= \sum_i^{\mathrm{occ}} \epsilon_i \\ \mathcal{E}^{(0)} + \mathcal{E}^{(1)} &= \mathcal{E}_{\mathrm{UHF}} \end{aligned} \tag{7}$$

Higher order terms involve matrix elements of V between eigenfunctions of $\mathcal{H}_0$. If we use suffixes $s,t,\cdots$ for these eigenfunctions, the first-order wave function is

$$\Psi^{(1)} = -\sum_{s>0} (E_s - E_0)^{-1} V_{s0} \Psi_s \tag{8}$$

where E_s is the zero-order energy of $\mathcal{H}_0$ for state s. If s is a single substitution, V_{s0} vanishes by Brillouin's theorem [19]. Also V_{s0} vanishes for triple and higher substitutions because V contains only one- and two-electron terms. By evaluating V_{s0} for double substitutions, Møller and Plesset obtained

$$\Psi^{(1)} = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} a_{ijab} \Psi_{ij \to ab} \tag{9}$$

where the coefficients a_{ijab} are given by

$$\begin{aligned} a_{ijab} &= -D_{abij}^{-1} (ab \| ij) \\ D_{abij} &= \epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j \end{aligned} \tag{10}$$

The general notation adopted for two-electron integrals is [20]

$$(pq \| uv) = \int\int \chi_p^*(1)\, \chi_q^*(2)\, (1/r_{12}) [\chi_u(1)\chi_v(2) - \chi_v(1)\chi_u(2)]\, d\tau_1\, d\tau_2 \tag{11}$$

Here integration is over Cartesian and spin coordinates. Note that

$$a_{ijab} = -a_{jiab} = -a_{ijba} = a_{jiba} \tag{12}$$

A nondimensional measure of the magnitude of the first-order wave function is

$$T^2 = \langle \Psi^{(1)} | \Psi^{(1)} \rangle = \frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} |a_{ijab}|^2 \tag{13}$$

In a similar manner, Møller and Plesset found the second-order energy

$$\begin{aligned} \mathcal{E}^{(2)} &= -\sum_{s>0} (E_s - E_0)^{-1} |V_{0s}|^2 \\ &= -\frac{1}{4} \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} D_{abij}^{-1} |(ij \| ab)|^2 \end{aligned} \tag{14}$$

This is probably the simplest of all general expressions for the correlation energy, requiring little more than a partial transformation of the two-electron integrals to the basis of the UHF spin orbitals to give $(ij \| ab)$.

The theory may be extended to higher orders. The UMP3 energy is given by the Rayleigh–Schrödinger third-order perturbation result [18]

$$\mathcal{E}_{\text{UMP3}} = \mathcal{E}_{\text{UMP2}} + \mathcal{E}^{(3)}$$

$$\mathcal{E}^{(3)} = \sum_{s,t>0} (E_s - E_0)^{-1} (E_t - E_0)^{-1} V_{0s} (V_{st} - V_{00}\delta_{st}) V_{t0} \tag{15}$$

Again only double substitutions s,t contribute and the matrix elements V_{st} can be reduced to two-electron integrals. The resulting expression may be written

$$\begin{aligned} \mathcal{E}^{(3)} = &\frac{1}{8} \sum_{ij}^{\text{occ}} \sum_{abcd}^{\text{virt}} a_{ijab}^* a_{ijcd} (ab \| cd) \\ &+ \frac{1}{8} \sum_{ijkl}^{\text{occ}} \sum_{ab}^{\text{virt}} a_{ijab}^* a_{klab} (kl \| ij) \\ &+ \sum_{ijk}^{\text{occ}} \sum_{abc}^{\text{virt}} a_{ijab}^* a_{kjcb} (ak \| ic) \end{aligned} \tag{16}$$

This formula was given explicitly by Bartlett and Silver [20] who derived it from the Goldstone expansion [8] and associated diagrammatic techniques. It can also be derived directly from Equation (15) by evaluating all appropriate V_{st}.

3. Independent Electron-Pair Approximation

Another correlation method, which has received considerable attention, is the independent electron-pair approximation (IEPA) [15, 16]. This method concentrates on a particular pair of spin orbitals which is occupied in the Hartree–Fock determinant (1). It attempts a full treatment of the correlation of this electron pair under the assumption that the remaining electrons are undisturbed. The total effect is then assumed to be additive for all pairs.

Mathematically, the IEPA method corresponds to finding the optimum wave function of the form

$$\Psi_{ij} = c_0\Psi_0 + \sum_{a}^{\text{virt}} c_{ia}\Psi_{i\to a} + \sum_{b}^{\text{virt}} c_{jb}\Psi_{j\to b} + \sum_{a<b}^{\text{virt}} c_{ijab}\Psi_{ij\to ab} \tag{17}$$

for a particular pair ij. If the resulting energy is $\mathscr{E}_{\text{UHF}} + \epsilon_{ij}$, the total IEPA energy is then

$$\mathscr{E}_{\text{IEPA}} = \mathscr{E}_{\text{UHF}} + \sum_{i<j}^{\text{occ}} \epsilon_{ij} \tag{18}$$

The IEPA method itself can be used with the modified Hamiltonian $\mathscr{H}_\lambda$ [Equation (3)] and the results expanded in powers of λ

$$\Psi_{ij} = \Psi_0 + \lambda\Psi_{ij}^{(1)} + \cdots \tag{19}$$

$$\epsilon_{ij} = \lambda^2\epsilon_{ij}^{(2)} + \lambda^3\epsilon_{ij}^{(3)} + \cdots \tag{20}$$

Only double substitutions involving the pair ij need be considered, leading to

$$\Psi_{ij}^{(1)} = \frac{1}{2}\sum_{ab}^{\text{virt}} a_{ijab}\,\Psi_{ij\to ab} \tag{21}$$

$$\epsilon_{ij}^{(2)} = -\frac{1}{2}\sum_{ab}^{\text{virt}} D_{abij}^{-1}\,|(ij\|ab)|^2 \tag{22}$$

Comparing Equations (14), (18), and (22) it is clear that the IEPA energy is correct to second order in the expansion parameter λ. However, it is not correct to third order. This is evident, since $\epsilon_{ij}^{(3)}$ can only involve integrals containing the occupied orbitals i and j, and it then follows from Equation (17) that $\mathscr{E}_{\text{IEPA}}^{(3)}$ cannot contain terms involving three or more different occupied orbitals $i,j,k,\cdots$. Such terms represent pair–pair interactions and are included in the correct $\mathscr{E}^{(3)}$ [Equation (15)].

4. Variational Methods

As previously noted, neither Møller–Plesset theory to finite order nor the independent electron-pair approximation give energies which are necessarily upper bounds to the exact solution (the result from full configuration interaction if a finite basis is used). In this section we shall consider a number of methods which do have this property. They all proceed by calculating the expectation value of the full Hamiltonian $\mathscr{H}$ using a trial wave function. Again each method can be applied with the Hamiltonian $\mathscr{H}_\lambda$ and the results expanded in powers of λ to find to what order the method is correct.

The first and simplest variational method [21] is one which uses the correct first-order Møller–Plesset wave function as a trial function:

$$\Psi_{\text{VAR1}} = b(\Psi_0 + \Psi^{(1)}) \tag{23}$$

using Equations (1) and (9). The constant b is chosen so that Ψ_{VAR1} is normalized. Thus

$$b^{-2} = 1 + T^2 = 1 + \sum_{i<j}^{\mathrm{occ}} \sum_{a<b}^{\mathrm{virt}} |a_{ijab}|^2 \tag{24}$$

The expectation value of the energy is then

$$\mathscr{E}_{\mathrm{VAR1}} = \mathscr{E}^{(0)} + \mathscr{E}^{(1)} + (1 + T^2)^{-1}[\mathscr{E}^{(2)} + \mathscr{E}^{(3)}] \tag{25}$$

Since T^2 is of second order in λ, the expression (24) is accurate to third order. We may also note that, since T^2 is positive, the correlation correction in Equation (25) will be smaller in magnitude than in $\mathscr{E}_{\mathrm{UMP3}}$ (Equation (16)).

A slightly improved variation method [21] finds the best linear combination of Ψ_0 and $\Psi^{(1)}$,

$$\Psi_{\mathrm{VAR2}} = b_0\Psi_0 + b_1\Psi^{(1)} \tag{26}$$

treating b_0 and b_1 as variational parameters. This leads to a 2×2 secular equation:

$$\begin{vmatrix} \mathscr{E}^{(0)} + \mathscr{E}^{(1)} - \mathscr{E} & \mathscr{E}^{(2)} \\ \mathscr{E}^{(2)} & T^2(\mathscr{E}^{(0)} + \mathscr{E}^{(1)} - \mathscr{E}) - \mathscr{E}^{(2)} + \mathscr{E}^{(3)} \end{vmatrix} = 0 \tag{27}$$

with the solution

$$\mathscr{E}_{\mathrm{VAR2}} = \mathscr{E}^{(0)} + \mathscr{E}^{(1)} + \tfrac{1}{2}T^{-2}(\mathscr{E}^{(2)} - \mathscr{E}^{(3)}) \times \{[1 + 4T^2(\mathscr{E}^{(2)})^2(\mathscr{E}^{(2)} - \mathscr{E}^{(3)})^{-2}]^{1/2} - 1\} \tag{28}$$

Again, it is easily confirmed by expansion that this formula is accurate to third order. Since Equation (23) is a special case of Equation (26), the energy $\mathscr{E}_{\mathrm{VAR2}}$ is less than or equal to $\mathscr{E}_{\mathrm{VAR1}}$.

The next variational method uses a more flexible wave function

$$\Psi_{\mathrm{VAR3}} = b_0\Psi_0 + \sum_{i<j}^{\mathrm{occ}} b_{ij}\Psi_{ij}^{(1)} \tag{29}$$

where $\Psi_{ij}^{(1)}$ is the first-order contribution to the pair function Ψ_{ij} (Equation (21)). The wave function Ψ_{VAR3} may be described as a "linear combination of frozen perturbation pair functions." It leads to a $(N_p + 1) \times (N_p + 1)$ secular equation where N_p is the number of occupied pairs ij. We shall not give detailed formulas for the matrix elements of $\mathscr{H}$, but their derivation is straightforward. Since constraints are removed from Equations (26)–(29), the energy must decrease. Also, since $\mathscr{E}_{\mathrm{VAR2}}$ is correct to third order, $\mathscr{E}_{\mathrm{VAR3}}$ is correct to the same level.

Further relaxation of constraints is possible if the perturbation pair functions in Equation (29) are allowed to change when they interact with each other. One way to allow for this is to transform the virtual spin orbitals in $\Psi_{ij}^{(1)}$ to pair natural spin orbitals $\chi_a\chi_{a'}$ of the types first introduced by Edmiston and Krauss [22], so that

$$\Psi_{ij}^{(1)} = \sum_a b_{ija}\Psi_{ij\to aa'} \tag{30}$$

This reduces the number of terms in $\Psi_{ij}^{(1)}$. Then in a variational calculation with a wave function

$$\Psi_{\mathrm{VAR4}} = b_0\Psi_0 + \sum_{i<j}^{\mathrm{occ}} \sum_{a}^{\mathrm{nat}} b_{ija}\Psi_{ij\to aa'} \tag{31}$$

the coefficients b_{ija} may be varied independently while the natural spin orbitals χ_a, $\chi_{a'}$

are held fixed. This type of method was introduced by Meyer [23] who called it pair natural orbital configuration interaction (PNO-CI). The actual technique used by Meyer is based on spin-adapted pair functions rather than the unrestricted spin-orbital treatment discussed here, but the principles are similar. There are complications due to the fact that PNOs for different pairs are not orthogonal, but these have been overcome and the technique has been applied successfully to a number of molecules [23–25]. From the form of Equation (31) it is clear that $\mathscr{E}_{\mathrm{VAR4}} \leq \mathscr{E}_{\mathrm{VAR3}}$ and that $\mathscr{E}_{\mathrm{VAR4}}$ is correct to third order.

Further relaxation of constraints on the trial wave function can be achieved by treating each part of $\Psi_{ij}^{(1)}$ independently. This corresponds to finding the best wave function of the form

$$\Psi_{\mathrm{VAR5}} = b_0\Psi_0 + \sum_{i<j}^{\mathrm{occ}} \sum_{a<b}^{\mathrm{virt}} b_{ijab}\Psi_{ij\to ab} \tag{32}$$

This is equivalent to complete configuration interaction involving all double substitutions, CI (HF + D). An even more flexible function is obtained by also including single substitutions, CI (HF + S + D),

$$\Psi_{\mathrm{VAR6}} = b_0\Psi_0 + \sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{virt}} b_{ia}\Psi_{i\to a} + \sum_{i<j}^{\mathrm{occ}} \sum_{a<b}^{\mathrm{virt}} b_{ijab}\Psi_{ij\to ab} \tag{33}$$

Each of these improvements lowers the calculated energy further.

5. Basis Set Expansions and Computational Features

As indicated previously, practical computations normally utilize basis-set expansions for the spin orbitals. Suppose that there are N basis functions φ_μ in one-electron Cartesian space. Then the spin-orbital basis consists of the $2N$ functions $\varphi_\mu\alpha$ and $\varphi_\mu\beta$. In the UHF approximation, if there are n_α α-electrons and n_β β-electrons ($n = n_\alpha + n_\beta$), the occupied spin orbitals may be written

$$\begin{aligned} \chi_i^\alpha &= \sum_{\mu}^{N} c_{\mu i}^{\alpha}\, \varphi_\mu\alpha, \qquad i = 1, \cdots, n_\alpha \\ \chi_i^\beta &= \sum_{\mu}^{N} c_{\mu i}^{\beta}\, \varphi_\mu\beta, \qquad i = 1, \cdots, n_\beta \end{aligned} \tag{34}$$

Similar expressions apply for the virtual spin orbitals χ_a^α and χ_a^β.

To carry out a calculation of the UMP second-order energy (14), the main task after determining the UHF spin orbitals (34) is the transformation of the two-electron integrals from the original basis functions to the set $(ij\|ab)$. This transformation may be carried out treating each suffix in turn. The computation time will be dominated by the first suffix i which runs over n_α and n_β values. The total number of multiplications required for this step is asymptotically $\frac{1}{2}(n_\alpha + n_\beta)N^4 = \frac{1}{2}nN^4$. Subsequent transformation for the other suffixes requires only $O(n^2N^3)$ multiplications. Once the elements $(ij\|ab)$ are available, $\mathscr{E}^{(2)}$ may be evaluated directly from Equation (14). If $n_\alpha = n_\beta$ and the α- and β-molecular orbitals coincide in pairs, the computation time may be approximately halved.

The third-order energy calculation may be carried out with Equation (16) using the first-order coefficients a_{ijab} already obtained [from Equation (10)]. The first term in Equation (16) appears to require the large set of transformed integrals $(ab\|cd)$. If $N \gg n$, this transformation requires $O(N^5)$ multiplications and may be prohibitively expensive. However, this difficulty may be avoided by transforming back to the spin-orbital basis functions

$$\tilde{a}_{ij\mu\nu} = \sum_{ab}^{\text{virt}} a_{ijab} c_{\mu a} c_{\nu b} \tag{35}$$

and rewriting the first term in $\mathcal{E}^{(3)}$ [Equation (16)] as

$$\frac{1}{8} \sum_{ij}^{\text{occ}} \sum_{\mu\nu\lambda\sigma} \tilde{a}_{ij\mu\nu} \tilde{a}_{ij\lambda\sigma} (\mu\nu \| \lambda\sigma) \tag{36}$$

Here all variables are real and the elements $(\mu\nu\|\lambda\sigma)$ are defined by Equation (11) with spin-orbital basis functions instead of the χ functions. Evaluation of Equation (36) then requires asymptotically $n^2N^4/8$ multiplications. The two remaining parts of $\mathcal{E}^{(3)}$ [Equation (16)] require the further transformed integrals $(kl\|ij)$ and $(ak\|ic)$ followed by summations involving $o(n^3N^3)$ terms.

6. Comparison of Methods

In this section we shall compare methods of handling electron correlation from the point of view of the model criteria discussed in the Introduction. In Table I we list the main features of the methods, including the order of the asymptotic time taken for a calculation (large n,N), correctness to second or third order in λ if the Møller–Plesset Hamiltonian Equation (3) is used, size consistency when applied to an ensemble of isolated systems, and the upper bound feature associated with the variational methods. In addition we shall consider the behavior of the methods when the Hartree–Fock Equations (2) have degenerate solutions. Under these circumstances the spin orbitals χ_i are not uniquely defined, and any degenerate set may be subjected to an arbitrary unitary transformation. For a theoretical method to lead to a uniquely defined energy, it is necessary that the result is invariant to such transformations.

The Møller–Plesset expansions for the energy, terminated at second order (UMP2) or third order (UMP3), do have the property of size consistency. If the theory is applied to a set of isolated molecules, every nonvanishing term in Equation (14) or (16) must refer exclusively to one molecule, since one or more of the two-electron integrals would otherwise vanish. More generally, the Møller–Plesset energy expansion is size consistent if terminated at any order since the full calculation [for any value of λ in Equation (3)] in a group of isolated molecules can be broken down into additive calculations on single molecules. The Møller–Plesset expansion terminated at any finite order is also invariant under unitary transformations within a degenerate orbital set. This follows since the complete Hamiltonian and the Fock Hamiltonian are both invariant under such transformations.

At this point some other variants of many-body perturbation theory should be mentioned. One is the use of a potential which modifies the virtual spin orbitals so that they are eigenfunctions of a Hamiltonian representing the field of $(n-1)$ rather than the full set of n electrons [26]. Such spin orbitals are better representations of orbitals associated with electronic excited states. Normally the $(n-1)$ potential is obtained by removing an electron from the highest occupied orbital. This procedure, however, destroys the size consistency of the full UMP expansion since the electron removed would have to be taken from a particular one of a set of isolated molecules (at least if the molecules are different). Also, if the highest occupied orbital is one of a degenerate set, the method will lose invariance to unitary transformations within such a set.

A second modification of perturbation theory which has been proposed is the denominator shift [26–28]. In this procedure the inverse energy denominators in Equations

(14) and (16) are replaced by the differences between the correct diagonal matrix elements in the full configuration interaction matrix. In other words, the off-diagonal parts of this matrix are treated as perturbations on the diagonal parts. This procedure is size consistent, but by treating off-diagonal elements within a degenerate set on a different basis to corresponding diagonal elements, it loses invariance to unitary transformations within degenerate sets. This has been noted by Ostlund and Bowen [29].

The IEPA method, as already noted, is accurate only to second order in the Møller–Plesset expansion. It is size consistent since individual electron pairs will be localized in single molecules if the method is applied to a set of isolated molecules and the energy formula (18) then ensures additivity. However, the neglect of third-order terms in Equation (16) involving three distinct suffixes i,j,k implies that the method is not invariant to unitary transformation within degenerate sets of orbitals.

The series of variational methods discussed in Section 4 have most properties in common. As already noted, they are all correct to third order in the Møller–Plesset expansion and all provide definite upper bounds to the energy corresponding to full solution of the configuration interaction problem. However, they all have the disadvantage of not being size consistent. This has been pointed out several times, particularly by Meyer [23]. Since all the variational methods are accurate to third order in a Møller–Plesset expansion and since all orders are size consistent in the exact expansion, the failure of size consistency for VAR1-VAR6 must occur at fourth or higher order. It is instructive to consider the fourth-order energy in more detail. In Rayleigh–Schrödinger perturbation theory $\mathscr{E}^{(4)}$ is given by

$$\mathscr{E}^{(4)} = -\mathscr{E}^{(2)} \sum_{s>0} (E_s - E_0)^{-2} |V_{0s}|^2 - \sum_{s,t,u>0} (E_s - E_0)^{-1}(E_t - E_0)^{-1}(E_u - E_0)^{-1} V_{0s}(V_{st} - V_{00}\delta_{st}) \times (V_{tu} - V_{00}\delta_{tu})V_{u0} \quad (37)$$

When applied to the Møller–Plesset expansion, summation over s and u may be limited to double substitutions, but the suffix t should run over all substitutions up to quadruple [13]. Although the complete expression (37) must be size consistent, the two parts into which it is divided are not so individually. If the formula is applied to a set of L identical isolated molecules, the first part gives a contribution proportional to L^2. This L^2 dependence is only canceled by the second part if quadruple substitutions are included in t. This cancellation eliminates contributions of unlinked clusters to Equation (37) [15]. Consequently all the variational methods described in the previous section, which are limited to substitutions no higher than double, fail the size-consistency test. These difficulties are evident in the fourth-order terms in the expansions of the first two variational methods from Equations (24) and (28):

$$\mathscr{E}^{(4)}_{\mathrm{VAR1}} = -T^2\mathscr{E}^{(2)} \quad (38)$$

$$\mathscr{E}^{(4)}_{\mathrm{VAR2}} = -T^2\mathscr{E}^{(2)} + [\mathscr{E}^{(3)}]^2/\mathscr{E}^{(2)} \quad (39)$$

$-T^2\mathscr{E}^{(2)}$ will be proportional to L^2, whereas the other term in Equation (39) is proportional to L. The effect of the term $-T^2\mathscr{E}^{(2)}$ on the size consistency of configuration interaction theories has been recognized by Langhoff and Davidson [15b].

Some of the variational methods are invariant to unitary transformations within a degenerate set of orbitals. This is clearly true for VAR1 and VAR2 since T^2, $\mathscr{E}^{(2)}$, and $\mathscr{E}^{(3)}$ are invariant. It is also true for configuration interaction involving all double or all double

TABLE I. Features of electron correlation theories.

Method	Order of Asymptotic Time	Correct to Second Order	Correct to Third Order	Size Consistent	Upper Bound	Transformation Invariant
UMP2	nN^4	yes		yes		yes
UMP3	n^2N^4	yes	yes	yes		yes
IEPA	n^2N^4	yes		yes		
VAR1-VAR6	n^2N^4	yes	yes		yes	
CEPA	n^2N^4	yes	yes	yes		

and single substitutions (VAR5, VAR6). This is because the full space spanned by such functions is invariant. However, invariance may not apply to the remaining methods (VAR3, VAR4) if they involve arbitrary specification of pairs within a degenerate set.

One other method listed in Table I is the coupled electron-pair approximation (CEPA) due to Meyer [23]. This is a modification of the above variational methods which avoids the size-consistency problem but no longer gives an upper bound for the energy. All CEPA methods are still accurate to third order in a Møller-Plesset expansion, but modification of the diagonal elements in the configuration interaction matrix alters the first term of the fourth-order contribution. For the first CEPA method of Meyer [18] the first part of Equation (37) is reduced to

$$-\sum_{i<j}^{occ} T_{ij}^2 \epsilon_{ij}^{(2)} \tag{40}$$

where

$$T_{ij}^2 = \langle \Psi_{ij}^{(1)} | \Psi_{ij}^{(1)} \rangle = \frac{1}{2} \sum_{ab} |a_{ijab}|^2 \tag{41}$$

This revision eliminates the L^2 dependence of $\mathcal{E}^{(4)}$ so that CEPA is size consistent in fourth order. However, it should be noted that triple and quadruple substitutions are not included explicitly, so the resulting fourth-order term is not exact. Also, like other methods treating pairs separately, invariance to unitary transformations within a degenerate set of spin orbitals may be lost.

From this comparative discussion it is clear that the UMP2 procedure is very suitable as the simplest type of theoretical model incorporating electron correlation. The nN^4 step is straightforward and the total computation involved is not much greater than a Hartree-Fock calculation. Of the various n^2N^4 methods, UMP3 is probably simplest to execute and is also satisfactory for model purposes. The various variational methods have severe fourth-order errors for larger systems, lacking size consistency. CEPA and UMP3 should give similar results for a given basis set. Both are size consistent, both are correct in third order, and both are incorrect in fourth order. In view of the fact that $\mathcal{E}^{(2)}$ and $\mathcal{E}^{(3)}$ probably account for a large fraction of the total correlation energy (97.6% for helium [30]), these higher order differences may not be very significant.

7. Illustrative Calculations

In this section we shall describe some UMP2, UMP3, and related results obtained on small molecules with an uncontracted Gaussian basis of moderate size. The aim is to explore the extent to which such simple models with correlation correct known deficiencies of Hartree-Fock theory.

TABLE II. d exponents in (841/41) basis.

Atom	α_d
Li	0.200
Be	0.255
B	0.401
C	0.626
N	0.923
O	1.292
F	1.750
Ne	2.304

The basis set used is of the type (841/41), that is, 8s, 4p, and 1d sets of uncontracted Gaussians on each non-hydrogen atom (Li to Ne) and 4s, 1p sets on each hydrogen. Most s and p exponents are taken from the tabulation of Hartree–Fock optimized functions due to van Duijneveldt [31]. For B to Ne, his (8s,4p) bases are used directly. For Li and Be, the outermost four s functions in his 8s sets are supplemented with p functions having the same exponents. For hydrogen, his 4s set is used. Although these functions were chosen to minimize atomic Hartree–Fock energies, they should provide a useful span of the (sp) space for Møller–Plesset calculations. The remaining functions are of polarization types, and these are selected to minimize UMP2 energies. The d-exponent α_d for the functions $(3z^2 - r^2, x^2 - y^2, xy, xz, yz)\exp(-\alpha_d r^2)$ is chosen to minimize $\mathcal{E}_{\mathrm{UMP2}}$ for the electronic ground states of each heavy atom. The values are listed in Table II. (Actually these optimizations were carried out with a (951) basis, but tests indicated that (841) optimizations led to almost identical results.) The value for Li was selected by extrapolation from the others since optimization led to 4.66, which is clearly associated with the inner shell region and not compatible with the values for other atoms. The p exponent for hydrogen is taken to be $\alpha_p = 0.75$ as an approximate average of values which give lowest $\mathcal{E}_{\mathrm{UMP2}}$ for the diatomic hydrides LiH to FH.

The second-order theoretical model UMP2/(841/41) was used to determine equilibrium geometries for the ground and some low-lying excited states of diatomic and triatomic molecules AH and AH_2. The bond lengths r_e and angles θ_e are listed in Tables III and IV together with some corresponding UHF/(841/41) data and experimental values. Ideally, the theoretical equilibrium bond lengths and bond angles should be compared with the corresponding experimental equilibrium data. For BH_2, CH_2 (both multiplicities) and NH_2 the experimental equilibrium geometries are not available, and the values quoted correspond instead to the lowest vibrational quantum level. These results show that the second-order correlation correction greatly improves the agreement between theoretical and experimental bond lengths. For the independent lengths listed, the mean absolute differences between theory and experiment are 0.010 Å (UHF) and 0.003 Å (UMP2). Comparable results have been obtained with the CEPA method by Meyer and Rosmus [44]. The bond angles for $CH_2(^1A_1)$, NH_2, and OH_2 are 1–2° too small in the UMP2/(841/41) model. This is probably due to the limitation of the basis set rather than the absence of higher order correlation energies. A Hartree–Fock study of OH_2 with a larger basis than that used here [45] gives a bond angle of 106.6°, indicating that at the limit

TABLE III. Bond lengths, in angstroms, for AH and AH_2 molecules.

Molecule	UHF/(841/41)	UMP2/(841/41)	Expt.
H_2 ($^1\Sigma_g^+$)	0.737	0.740	.742[a]
LiH ($^1\Sigma^+$)	1.611	1.593	1.595[a]
BeH ($^2\Sigma^+$)	1.346	1.340	1.343[b]
BH ($^1\Sigma^+$)	1.231	1.235	1.232[c]
CH ($^2\Pi$)	1.113	1.123	1.120[d]
CH ($^4\Sigma^-$)	1.075	1.087	
NH ($^3\Sigma^-$)	1.026	1.037	1.036[e]
OH ($^2\Pi$)	0.952	0.967	0.971[a]
FH ($^1\Sigma^+$)	0.896	0.912	0.917[f]
BeH_2 ($^1\Sigma_g^+$)	1.330	1.323	
BH_2 ($^2A_1$)	1.188	1.189	1.18[g,l]
CH_2 ($^3B_1$)	1.074	1.080	1.078[h,l]
CH_2 ($^1A_1$)	1.102	1.112	1.11[i,l]
NH_2 ($^2B_1$)	1.013	1.026	1.024[j,l]
OH_2 ($^1A_1$)	0.941	0.957	0.957[k]

[a] From [32].
[b] From [33].
[c] From [34].
[d] From [35].
[e] From [36].
[f] From [37].
[g] From [38].
[h] From [39].
[i] From [40].
[j] From [41].
[k] From [42].
[l] Experimental value uncorrected for the effects of zero-point vibration.

UHF overestimates the angle by about 2°. Combination with the angle reduction of 2.9° obtained here, going from UHF/(841/41) to UMP2/(841/41), indicates that the UMP2 limiting bond angle is probably accurate to a few tenths of a degree.

Following these equilibrium structure determinations, a series of third-order calculations was carried out using the UMP2/(841/41) geometries. The resulting total energies, together with the UHF/(841/41) energies at the appropriate geometries, are listed in Table V. These results show that, in all cases, $\mathcal{E}_{UMP3}$ is lower than $\mathcal{E}_{UMP2}$. The variational

TABLE IV. Bond angles for AH_2 molecules.

Molecule	UHF/(841/41)	UMP2/(841/41)	Expt.
BeH_2	180.0	180.0	
BH_2	127.5	128.5	131[a,f]
CH_2 ($^3B_1$)	131.4	132.1	136[b,f]
CH_2 ($^1A_1$)	102.7	101.3	102.4[c,f]
NH_2	103.2	101.7	183.4[d,f]
OH_2	105.3	102.4	104.5[e]

[a] From [38].
[b] From [43].
[c] From [40].
[d] From [41].
[e] From [39].
[f] Experimental value uncorrected for the effects of zero-point vibration.

energy $\mathcal{E}_{VAR1}$ is above $\mathcal{E}_{UMP3}$ as required by Equation (25). $\mathcal{E}_{VAR2}$ is sometimes lower than $\mathcal{E}_{UMP3}$, but other times it is higher. For Ne, FH, and OH_2, $\mathcal{E}_{VAR2}$ also lies above $\mathcal{E}_{UMP2}$. These trends reflect the increasing effect of the lack of size consistency of variational methods as the number of electrons increases.

Table VI lists the contributions to the correlation energy (at the same UMP2 geometries). The third-order contribution to the independent electron-pair approximation $\mathcal{E}^{(3)}_{IEPA}$ is included for some of the systems. This is obtained from Equation (16) by omitting all terms involving three or four distinct occupied spin orbitals, *i, j, k, l.* Finally the nondimensional quantity T from Equation (13) is listed.

The $\mathcal{E}^{(2)}$ values for the atomic ground states parallel estimates made previously [46] for infinitely large basis sets. The (841/41) basis accounts for about 70% of these limiting values. For the AH and AH_2 molecules, the $\mathcal{E}^{(2)}$ energies are close to those of the isoelectronic atomic states. For H_2 our value of $\mathcal{E}^{(2)}$ (−0.02789) is somewhat smaller in magnitude than that of Schulman and Kaufman [47] (−0.032) who used a larger basis. The $\mathcal{E}^{(3)}$ values computed are all negative, thereby increasing the absolute magnitude of the calculated correlation energy. The value of −0.00592 for H_2 compares well with −0.00550 obtained by Kaldor [48] with the Schulman-Kaufman basis. As the number of electrons is increased, the absolute value of $\mathcal{E}^{(3)}$ first increases but then decreases, becoming almost zero for the ten-electron systems. It is interesting to compare this with the independent-pair approximation $\mathcal{E}^{(3)}_{IEPA}$ which increases in magnitude with the number of electrons. $\mathcal{E}^{(3)}$ and $\mathcal{E}^{(3)}_{IEPA}$ are approximately equal for atoms up to carbon, but become sharply different for larger atoms. This means that the pair–pair interactions in third order become more important so that for neon the corresponding energy contributions almost cancel $\mathcal{E}^{(3)}_{IEPA}$. This feature of the pair approximation in neon was first found by Barr and Davidson [49a] and Micha [49b]. A direct comparison can also be made with the work of Bartlett and Silver on hydrogen fluoride [50]. Most of their work involved denominator shifts, but they have reported values of $\mathcal{E}^{(2)} = -0.30557$ and $\mathcal{E}^{(3)}_{IEPA} = -0.05083$ using an STO basis containing more basis functions than used here. These numbers are consistent with the corresponding entries in Table VI. Bartlett and Silver

TABLE V. Total energies, in hartrees, using the (841/41) basis.

Molecule[a]	UHF[b]	UMP2[c]	UMP3[c]	VAR1[c]	VAR2[c]
H	-.49928	-.49928	-.49928	-.49928	-.49928
Li	-7.43178	-7.46022	-7.46399	-7.46391	-7.46445
Be(^{1}S)	-14.57124	-14.62945	-14.64187	-14.63990	-14.64209
Be(^{3}P)	-14.50407	-14.53741	-14.54145	-14.54133	-14.54185
B(^{2}P)	-24.52813	-24.60118	-24.61675	-24.61459	-24.61749
B(^{4}P)	-24.44694	-24.48876	-24.49418	-24.49393	-24.49466
C(^{3}P)	-37.68404	-37.77678	-37.79329	-37.79091	-37.79338
C(^{5}S)	-37.58882	-37.64599	-37.65292	-37.65243	-37.65325
N	-54.38785	-54.50415	-54.51887	-54.51629	-54.51767
O	-74.78785	-74.94214	-74.95579	-74.95210	-74.95277
F	-99.36960	-99.57034	-99.57942	-99.57432	-99.57440
Ne	-128.48170	-128.73622	-128.73669	-128.73000	-128.73014
H_2	-1.13111	-1.15901	-1.16492	-1.16462	-1.16602
LiH	-7.98296	-8.03437	-8.04348	-8.04260	-8.04413
BeH	-15.14379	-15.20378	-15.21388	-15.21285	-15.21443
BH	-25.12458	-25.22264	-25.24196	-25.23810	-25.24085
CH($^2\Pi$)	-38.27102	-38.39285	-38.41265	-38.40826	-38.41041
CH($^4\Sigma^-$)	-38.28034	-38.38172	-38.39570	-38.39315	-38.39456
NH	-54.96460	-55.11562	-55.13248	-55.12747	-55.12844
OH	-75.39131	-75.59415	-75.60622	-75.59876	-75.59886
FH	-100.01629	-100.27909	-100.28036	-100.27018	-100.27046
BeH_2	-15.76149	-15.84565	-15.86071	-15.85836	-15.86054
BH_2	-25.75349	-25.85799	-25.87527	-25.87189	-25.87394
CH_2($^3B_1$)	-38.92715	-39.06281	-39.08049	-39.07562	-39.07690
CH_2($^1A_1$)	-38.88076	-39.03448	-39.05617	-39.04903	-39.05048
NH_2	-55.56672	-55.75918	-55.77570	-55.76698	-55.76729
OH_2	-76.02632	-76.28366	-76.28949	-76.27663	-76.27681

[a] Electronic ground state unless otherwise specified.
[b] At UHF optimized geometry.
[c] At UMP2 optimized geometry.

did not evaluate the full $\mathcal{E}^{(3)}$, but our analysis suggests that here, as elsewhere, the IEPA method will overestimate the correlation energy by a substantial amount.

Results for dissociation energies of ground state systems are collected in Table VII

TABLE VI. Correlation energy components, in hartrees, using the (841/41) basis.

Molecule[a]	$\varepsilon^{(2)}$	$\varepsilon^{(3)}$	$\varepsilon^{(3)}_{\text{IEPA}}$	T
Li	-.02845	-.00376	-.00381	.04969
Be(^{1}S)	-.05821	-.01242	-.01293	.16962
Be(^{3}P)	-.03334	-.00404	-.00415	.05592
B(^{2}P)	-.07305	-.01557	-.01611	.15810
B(^{4}P)	-.04182	-.00543	-.00572	.07284
C(^{3}P)	-.09274	-.01651	-.01866	.14907
C(^{5}S)	-.05717	-.00693	-.00816	.08752
N	-.11630	-.01472	-.02056	.14190
O	-.15429	-.01365	-.02526	.14993
F	-.20075	-.00907	-.03050	.15778
Ne	-.25452	-.00048	-.03511	.16422
H_2	-.02789	-.00592	-.00592	.09527
LiH	-.05145	-.00910		.12143
BeH	-.06000	-.01010		.12248
BH	-.09807	-.01932		.18459
CH($^2\Pi$)	-.12189	-.01980		.17875
CH($^4\Sigma^-$)	-.10148	-.01397		.15017
NH	-.15112	-.01686		.17537
OH	-.20304	-.01207		.18954
FH	-.26310	-.00127	-.04244	.20012
BeH_2	-.08420	-.01506		.15575
BH_2	-.10451	-.01728		.16887
CH_2($^3B_1$)	-.13570	-.01768	-.02238	.18117
CH_2($^1A_1$)	-.15391	-.02169	-.02756	.20578
NH_2	-.19276	-.01653		.20851
OH_2	-.25799	-.00583		.22631

[a] Electronic ground state unless otherwise specified.

and compared with the available experimental data. The correlation corrections clearly improve the agreement. The Hartree–Fock dissociation energies are too low by an average of about 35 kcal/mole whereas the UMP results are low by an average of only 9 kcal/mole. The third-order (UMP3) results are better than second-order (UMP2) for the molecules with fewer electrons, but for OH and FH bonds there is a slight deterioration, due to the already noted smallness of $\mathcal{E}^{(3)}$ for these systems. In a previous study on molecular cor-

TABLE VII. Dissociation energies for gound states D_e in kcal/mole.

	UHF	UMP2	UMP3	Expt.
$H_2 \rightarrow H + H$	83.2	100.7	104.4	109.4[a]
$LiH \rightarrow Li + H$	32.6	47.0	50.3	58.0[b]
$BeH \rightarrow Be + H$	46.0	47.1	45.6	48.7[c]
$BH \rightarrow B + H$	61.0	76.7	79.0	82.2[d]
$CH \rightarrow CH + H$	55.0	73.3	75.4	83.7[e]
$NH \rightarrow N + H$	48.6	70.4	71.7	87.7[a,f]
$OH \rightarrow O + H$	65.4	95.8	94.9	106.8[a]
$FH \rightarrow F + H$	92.5	131.4	126.5	140.7[a]
$BeH_2 \rightarrow Be H + H$	74.3	89.5	92.6	
$BH_2 \rightarrow BH + H$	81.3	85.4	84.1	
$CH_2 \rightarrow CH + H$	98.4	107.1	105.8	106.1[a]
$NH_2 \rightarrow NH + H$	64.5	90.5	90.3	98.5[a]
$OH_2 \rightarrow OH + H$	85.2	119.4	115.5	125.5[a]

[a] Based on experimental total energies as given in [50, Table 4]. These energies are derived principally from heats of formation as given in [51], and vibrationally corrected using available spectroscopic data. For further details, see [50].

[b] D_0 taken from [52]. ω_e, $\omega_e x_e$, and $\omega_e y_e$ taken from [32].

[c] From [53].

[d] D_0 taken from [34]. Note that this is a combined theoretical—experimental estimate. Values for ω_e, $\omega_e x_e$, and $\omega_e y_e$ taken from [34].

[e] Values of D_0, ω_e, and $\omega_e x_e$ taken from [35].

[f] A more recent determination [54] of the dissociation energy for NH obtains a value (vibrationally corrected, using ω_e and $\omega_e x_e$ from [36] of 78.5 kcal/mole. This value is not taken into account in the JANAF compilation [51].

relation energies [55] it was noted that electron correlation should play an important part in reactions involving the formation or destruction of electron-pair bonds. Comparison of the UHF/(841/41) data in Table VII for the dissociations involving, for example, H_2, LiH, CH, and FH with the corresponding experimental information clearly demonstrates the deficiency of the UHF method in describing this type of reaction. Here the effect of correlation is very prominent. The UMP3 energies are within 10 kcal/mole of the experimental energies for all systems except OH and FH, whereas the corresponding UHF results are typically too low by 20–50 kcal/mole. In those reaction systems not directly involving rupture of electron-pair bonds (for example, BeH, HB-H, and HC-H), the effect of electron correlation is expected to be smaller, and indeed the overall agreement between theory and experiment is much better. Even the UHF/(841/41) model does relatively well in describing these reactions.

Table VIII gives energy differences between states of different spin multiplicity. It is well recognized that Hartree–Fock theory cannot describe such differences well since correlation energies are generally greater in states with low resultant spin. The results in Table VIII show that such energy differences are significantly changed and brought into better agreement with experiment as we proceed to UMP2 and UMP3. For the atoms excellent agreement is obtained with beryllium, but there is still a residual error with

TABLE VIII. Energy separations, in kcal/mole.

	UHF	UMP2	UMP3	Expt
$Be(^3P) - Be(^1S)$	42.2	57.8	63.0	62.8[a]
$B(^4P) - B(^2P)$	50.9	70.5	76.9	82.4[a]
$C(^5S) - C(^3P)$	59.8	82.1	88.1	96.4[a]
$CH(^4\Sigma^-) - CH(^2\Pi)$	-5.8	7.0	10.6	17.1[b]
$CH_2(^3B_1) - CH_2(^1A_1)$	-29.1	-17.8	-15.3	-19.0[c]

[a] From [56].
[b] From [57].
[c] From [58].

boron and carbon. For the diatomic molecule CH the UHF/(841/41) model incorrectly predicts the $^4\Sigma^-$ species to be more stable than the $^2\Pi$. At the UMP2 level the correct energy ordering is obtained, but a sizable gap remains between the theoretical and experimental values. Further improvement is obtained at the UMP3 level. Considerable theoretical work has been done on the low-lying electronic states of CH_2 [59]. The recent work by Staemmler [60] using the previously described IEPA method obtained an energy separation of 10 kcal/mole. An earlier work by McLaughlin and coworkers [61] using an extended basis with a fairly large configuration interaction obtained an energy difference of 13.8 kcal/mole. The UMP2/(841/41) procedure obtains a −17.8-kcal splitting, a marked improvement over the UHF result. The addition of the third-order term further reduces the magnitude of the energy separation by 2.5 kcal/mole.

It is not yet clear whether the remaining deficiencies in the UMP description of dissociation energies and energy differences between states of different multiplicity are due to the limitations imposed by the (841/41) basis or the omission of higher order terms in the Møller–Plesset energy expansion. With regard to basis set effects, deficiencies are possibly due to the *spd* part of the basis being incomplete, and to the omission of basis functions of higher angular momentum (such as *f* functions). The effect of basis set size on multiplet splittings is currently under investigation and will be discussed more fully in a future publication [62].

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