MANY-BODY PERTURBATION THEORY AND COUPLED CLUSTER THEORY FOR ELECTRON CORRELATION IN MOLECULES*   ∗2733

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INTRODUCTION

Ten years ago in the *Annual Review of Physical Chemistry,* there was a review article entitled "Many-Body Theories of the Electronic Structure of Atoms and Molecules," by Karl Freed (1). In that article many-body methods were defined to be those techniques which derive their impetus from theories of the N-body problem for which $N \rightarrow \infty$. For the purposes of this review, we further specify these methods as many-body perturbation theory (MBPT) (2–5) and the closely related coupled-cluster methods (CCM) (6–9).

In the ten years since that review appeared, probably no area in theoretical chemistry has undergone more development than has the theory, methodology, and applications of such ab initio many-body methods for

studies of molecules and their interactions. In Freed's article the question is asked, "Do [many-body methods] provide methods or insights which are useful and/or new?" The answer is a resounding "yes!" Furthermore, these methods should have an increasingly important impact on chemistry over the next few decades, both conceptually and in providing highly accurate theoretical predictions for a constantly expanding array of problems.

In the present review, which is very much directed toward the nonspecialist, I hope to present some of the logic underlying the application of many-body theory for chemistry and to illustrate and call attention to several of the contributions that have been made over the last decade. As in any effort of this type, space limitations prohibit any attempt at completeness, but it is hoped that the essence of the developments in the area will be communicated to the reader, along with an assessment of where many important contributions remain to be made.[1]

Besides MBPT/CCM, many-body methods include techniques built upon Dyson's equation and its generalizations, which go under a variety of names such as Green's functions, propagator methods, and equations-of-motion (EOM) techniques. These methods are most often used for obtaining electronic spectra, ionization potentials, electron affinities, and the related transition moments, although they can be used to obtain the total electronic energy of a molecule as well, and thus also potential energy surfaces. In fact, one of the most attractive approaches to excited-state potential surfaces would be to combine EOM methods with ground-state

[1]Abbreviations used: ASGD, antisymmetrized Goldstone diagram; CCD, coupled cluster method limited to double excitation operators (this is also known as CPMET, coupled pair many-electron theory); CCM, coupled cluster method; CCSD, coupled cluster method limited to single and double excitation operators; CCD + ST(4) designates fourth-order single and triple excitation contributions added to the CCD result; CEPA, coupled electron pair approximation; CGTO, contracted Gaussian type orbitals; CHF, coupled Hartree-Fock; CI, configuration interaction (CI specified to include various categories of excitations are designated as D-CI, for double excitations, SD-CI for single and double excitations, and SDTQ-CI for single, double, triple, and quadruple excitations); EN, Epstein-Nesbet partitioning in perturbation theory (Ref. 65); EPV, exclusion principle violating; EOM, equations of motion; GVVT, generalized Van Vleck transformation; ICSCF, internally consistent self-consistent field orbitals; L-CCD, linearized coupled cluster double excitation model; MBPT, many-body perturbation theory [MBPT specified to include ASGD corresponding to single, (S), double, (D), triple, (T), and quadruple (Q), excitations are identified as SDTQ-MBPT(4), with the order dependence identified in the designation]; MP, Møller-Plesset partitioning in perturbation theory (Ref. 64); PCILO, perturbed CI with localized orbitals' semiempirical model; PES, potential energy surface; PPP, Pariser-Parr-Pople semiempirical model; RHF, restricted Hartree-Fock; SCF, self-consistent field model; STO, Slater type orbitals; UHF, unrestricted Hartree-Fock; VB, valence bond model.

solutions obtained by MBPT/CCM (10, 11). These EOM and propagator methods use techniques somewhat different than MBPT/CCM, and embrace a very large literature of their own; consequently, they are not discussed here. These approaches are mentioned in Freed's review article, and have been reviewed more recently by Öhrn (12), Simons (13), Jørgensen (14), and Csanak, Taylor & Yaris (15). An excellent text covering this subject is by Linderberg & Öhrn (16).

Besides the review of Freed (1), a number of other reviews of MBPT and CCM have appeared within the last decade. These include papers by Robb (17), Kutzelnigg (18), Paldus & Čížek (19), part of a review by Musher (20), and Čížek & Paldus (21). The latter paper, as well as a review of much of the effort of our group (22), appears in the proceedings of the 1979 Nobel Symposium on Many-Body Theory of Atomic Systems. These proceedings offer a quite up-to-date account of many-body theory in its most comprehensive sense—embracing atoms, molecules, nuclei, and solids—and are highly recommended.

Each of the previous reviews of MBPT/CCM deals with different aspects of the problem. Robb's review focuses on the relationship between MBPT and the electron-pair theories as originally presented by Sinanoğlu (23) and Nesbet (24). Another article by Freed also addresses this aspect (25). The paper by Paldus & Čížek presents a functional, very readable account of the detailed MBPT theory. Kutzelnigg's article focuses mainly on the coupled-cluster theory and its coupled electron pair approximation (CEPA) versions (26). Also, the older review by Kelly (5) provides an excellent account of the first MBPT calculations for atoms. The well-known book (27) edited by Sinanoğlu & Brueckner brings many of the principal early papers together. The second article by Čížek & Paldus (21) reviews the development of coupled-cluster theory, while the book by Hurley (28) provides a good textbook account of CCM.

Most applications of ab initio MBPT/CCM for *molecular* problems have only been made in the last five years. Hence, no prior review has covered predominantly numerical results for molecules and some of the implications of these results. This appears to be the natural subject for the present effort. To further restrict the scope of the review, with important exceptions, atomic calculations of the type pioneered by Kelly (5) and semi-empirical molecular calculations also are not considered.

Following a discussion of some of the significant concepts underlying MBPT/CCM, together with a synopsis of the theory, we proceed to some informative numerical illustrations of the techniques, demonstrating the deficiencies and the successes of the many-body methods, while emphasizing profitable future areas for research.

CRITERIA FOR A
THEORETICAL MODEL CHEMISTRY

To offer a focus for the subsequent discussion, it is helpful to consider some properties that quantum mechanical methods should attempt to satisfy. In an interesting paper, Pople et al (29) proposed several criteria for approximate numerical applications for molecules, if they are to be suitable as a basis for a "theoretical model chemistry." The definition of the latter is a uniform level of calculation whose effectiveness may be assessed by comparing with experimental data. Considering their suggestions as well as some of our own (31), we think some of the conditions that such a model should satisfy are that it be

1. size-extensive (i.e. scale properly with the size of molecule)
2. generally applicable to a wide class of problems within one framework (i.e. the model should not be dependent on symmetry or specific choices of configurations)
3. invariant to classes of transformations, particularly unitary transformations among degenerate orbitals
4. efficient and cost effective
5. applicable to excited states and open shells
6. able to dissociate a molecule correctly into its fragments.

The best possible solution in a basis set is configuration interaction (CI) with all possible excitations (full CI). Except for efficiency, since full CI is impossible for anything but the smallest molecules, it satisfies all these criteria as well as being variational. However, lacking a coordinate lower bound, a variational upper bound seems to be a less important requirement than it once was in quantum chemistry. There are two primary reasons for this.

First, the quantities that are of interest, such as binding energies—or more generally, the relative energy on a potential energy surface (PES)—and excitation energies, have no variational bounds even if the separate calculations are each variational. In fact, some of the most attractive methods (e.g. EOM and perturbation techniques) for obtaining excitation energies compute the differences directly rather than via two separate calculations, an inherently nonvariational approach. Second, the many-body methods that are routinely used, although nonvariational, usually differ from rigorous variational bounds only in fourth and higher orders of perturbation theory (30). Hence, at least for nonpathological cases for which such higher-order corrections could be important, MBPT/CCM methods as usually employed are quasivariational.

At the current state of development, the first three conditions are easily accomplished by MBPT/CCM. Any approach based upon the linked-diagram theorem is size extensive, as discussed in depth in the next section. A large class of problems can be studied within the general framework of single reference MBPT/CCM calculations, provided that the reference function is an adequate starting point. As long as entire diagrams are evaluated, MBPT is invariant to unitary transformations among degenerate orbitals. CEPA models that include parts of MBPT diagrams usually lack this invariance. CCM models are typically invariant to transformations exclusively among occupied orbitals and among excited orbitals, but not necessarily when the two are mixed.

The efficiency criterion for correlated calculations is very important. To emphasize this aspect, the number of points required to obtain a potential energy surface (PES) rises astronomically with the number of degrees of freedom in the molecule. For a triatomic system, calculations at ten displacements in each degree of freedom require 10^3 points, but for four atoms, already 10^6 calculations would be required. Usually far fewer points actually need to be obtained than suggested by such a brute-force approach, but since each calculation still requires significant amounts of computer time, the importance of efficiency cannot be overestimated.

Many-body methods have traits that enable them to offer distinct computational advantages for many problems compared to some other correlated techniques:

1. A simple second-order perturbation result, which only requires a trivial addition to any SCF code, accounts for typically $\sim 90\%$ of the basis set correlation energy and removes most of the SCF error in other properties.
2. MBPT/CCM offer very efficient techniques for incorporating most of the effect of higher than double excitations in CI.
3. Substantial computational efficiency is gained through the fixed computational formulae (at least for a single reference function) of MBPT/CCM, which are also ideally suited to vector-based computations.

Excited states can be handled with other kinds of many-body approaches such as EOM techniques (32) or with CI; while correct separation is currently most easily achieved using CI methods. The MBPT/CCM theory for treating both these problems exists, but has not yet been implemented into a general-purpose molecular problem. Of course, excited states, as long as they are the lowest state of a given symmetry, are routinely studied with unrestricted Hartree-Fock (UHF) based MBPT/

CCM (29, 30). Also, UHF plus MBPT/CCM usually permit smooth separation on a PES, although for some cases the path toward the separated limit is not always accurate (22).

SIZE-EXTENSIVITY AND THE IMPORTANCE OF HIGHER CI-EXCITATIONS IN THE THEORY OF CORRELATION

MBPT/CCM are relatively new techniques, compared to configuration iteration (CI), for the determination of electron-correlation effects for molecular properties. MBPT/CCM were originally developed for problems in nuclear and solid state physics, where emphasis on correct size-dependence, which we refer to as "size-extensivity" (22, 30),[2] becomes mandatory. Size-extensivity is guaranteed by the evaluation of terms that the many-body development identifies as linked diagrams, hence the Brueckner-Goldstone (2-4) linked-diagram theorem of MBPT/CCM serves as the cornerstone of the theory. In a solid consisting of an infinite number of atoms, the correct size-dependence is obviously crucial, yet even in molecular problems this is a highly desirable trait for an approximate method to possess.

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[2]This term is borrowed from thermodynamics, where an extensive property is one that is proportional to the size of a homogeneous system. Pople et al (29) proposed the term "size-consistency" for a closely related property. A method is considered size-consistent if the energy of a system made up of two subsystems A and B far apart is equal to the sum of the energies A and B computed separately by the same method. For closed-shell systems dissociating to closed-shell fragments, an RHF (restricted Hartree-Fock) reference function is size-consistent, and size-extensivity (or the absence of unlinked diagrams) is then a sufficient condition for size-consistency of a correlated model based upon that reference function. On the other hand, for a single-determinant reference function to be size-consistent when considering open-shell fragments, A and B, a UHF (unrestricted Hartree-Fock) solution will usually be required. Since either a RHF or a UHF function can be used to generate a linked diagram, size-extensive expansion, the condition of size-consistency imposes another requirement on the reference function, in addition to the use of a linked diagram expansion. Hence, some confusion arose over the distinction between proper scaling with size in a homogeneous system ("extensivity") and correct separation of a molecule into its fragments, which is a very different property. Adding to the confusion is the term "separability conditions," which is also sometimes used (18). Hence, we prefer the term size-extensivity to suggest only correct scaling, and discuss correct separation as a second, equally desirable property, to avoid any possible confusion. Although there are fine differences (33), the fundamental element suggested by all three terms is correct scaling with size.

The idea of size-extension is implicit in the work of Brueckner, Goldstone, and co-workers, although Primas was one of the first to emphasize the concept (34). Meyer (26) used this idea as part of the justification of the CEPA models.

Two primary reasons for this are that only approximate methods that scale properly with size are suitable for application to larger molecules, such as those encountered in quantum biochemistry (31); and size-extensivity assists in computing accurate dissociation energies (or, more generally, correct relative energies on the potential surface), which require comparison of a molecule to its smaller fragments (22). The latter aspect is also crucially dependent upon basis set effects and on whether the approximate method being used permits smooth dissociation into the different components, but size-extensivity remains an important aspect. As an added benefit, heats of formation obtained from calculations using size-extensive methods can be added together, just as experimental values are, to obtain the heats of formation of some complex molecules (22), while nonsize-extensive methods, like truncated CI, would normally require "super molecule" calculations to provide these quantities most accurately. This problem is of more than academic interest as pointed out by Ahlrichs (35), since this error is ~ 9 kcal/mole for $2BH_3 \rightarrow B_2H_6$ (35) and is ~ 15 kcal/mole for $CH_3F + F^- \rightarrow CH_3F_2^-$ (36).

Although full CI has the property of correct size-dependence, the failure of truncated CI models, such as CI limited to all single and double excitations (SD-CI), is related to the neglected contributions of higher excitations in the CI method. The example usually employed to illustrate this deficiency in CI is a lattice of noninteracting electron pair bonds, such as a collection of well-separated H_2 molecules or He atoms. The exact wavefunction for a single H_2 molecule may be written in terms of a complete set of natural orbitals as a reference determinant (i.e. the first natural configuration, which is close to the SCF solution) plus all paired double excitations from that determinant. Two noninteracting H_2 molecules would be exactly described by the product of two of these wavefunctions, but the product of the simultaneous double excitations on each H_2 molecule results in contributions to the product wavefunction of terms that correspond to quadruple excitations, if the two H_2 molecules are treated as a "super molecule" in CI. Similarly, a third H_2 molecule requires hextuple excitations, and so forth. However, since the number of configurations is proportional to $(n)^l$, where n is the number of basis functions and l is the level of excitation, a prohibitive $\sim 10^8$ configurations would be necessary for $n = 100$ to include just the quadruple excitations. The fact that much of the effect of such higher excitation terms is tractably included in many-body theory is one of the principal advantages of these techniques.

Since any large molecule can be viewed, in a first approximation, as a superposition of largely noninteracting electron pair bonds, the idealized
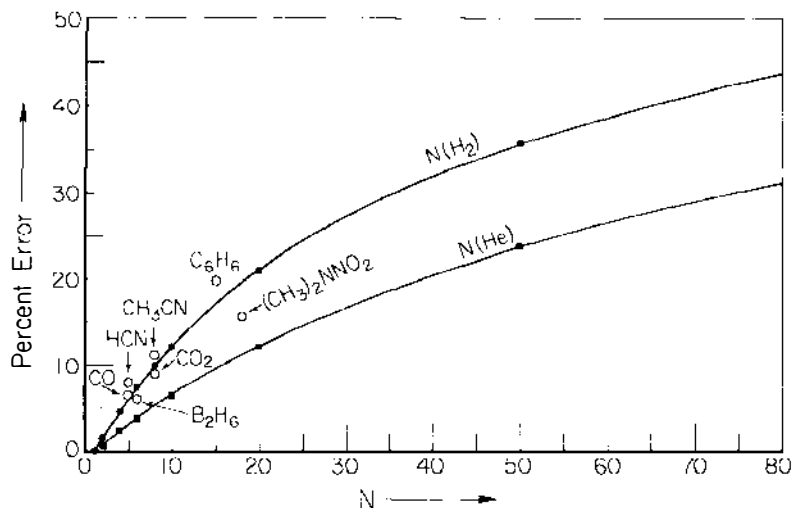
Figure 1   Percentage of error in the correlation energy as measured by D-CI for N separated H_2 molecules and He atoms. Values identified for specific molecules are obtained by actual fourth-order calculations that include quadruple excitations compared to a fourth-order approximation to D-CI. All calculations refer exclusively to the valence electrons, with the K-shell electrons frozen at the SCF level.

$N(H_2)$ model has some significance for the general description of molecular electronic structure. This model problem has been considered by several authors (37–43). Using very good full CI wavefunctions for H_2 to provide the one parameter required (31), it is possible to solve the model problem exactly for the H_2 lattice problem, and thus to determine the error in D-CI (double excitation CI) for N molecules as a function of N (31). These numbers are illustrated in Figure 1 for H_2 and He lattices.

Unlike a size-extensive correlated model, where

$$E_{corr}[N(H_2)] = N[E_{corr}(H_2)],$$

the correlation energy obtained by truncated CI for the lattice is proportional to $\sqrt{N}$ as $N \rightarrow \infty$. Even for $N = 10$ (twenty electrons), the error for $N(H_2)$ amounts to 31 kcal/mole, while for forty-electron systems, which are well within the range of current correlated studies, the error would be about 108 kcal/mole. The differences between the $N(H_2)$ curve and $N(He)$ curve reflect the difference between inner-shell electron pairs and the pairs in covalent bonds. Although there are other errors in molecular calculations that are equally large, or even larger, it is apparent that size-extensivity has a potentially important effect in ab initio correlated calculations. A statement that size-extensivity is important is equiva-

lent to a statement that higher than single- and double-CI excitations are important.

Also shown in Figure 1 are some results for the effect of quadruple excitations on correlation energies obtained in actual calculations. These quantities are determined by comparing fourth-order MBPT results that include quadruple excitation effects with a fourth-order perturbation approximation to D-CI (22, 30). The core electrons are frozen in these examples, so that the number of electron pairs, N, for each molecule corresponds to the valence electrons only. The calculations for benzene and dimethylnitramine use a double-zeta (DZ) basis, while at least double-zeta-plus-polarization (DZP) sets are employed in the other cases. Typically, a larger quadruple-excitation effect is observed with better basis sets, so the 20% error in the correlation energy in benzene, which amounts to 64 kcal/mole, is likely to be an underestimate of the true effect for this system. The actual calculations tend more nearly to follow the $N(H_2)$ curve rather than that for $N(He)$, as would be expected for the valence electron bonds.

Although this example pertains to the total energy, while in chemistry we are mainly concerned with energy differences, failure to maintain proper size-dependence has additional consequences. Using the H_2 lattice problem, Meunier & Levy (40) demonstrate that the density matrix and electron excitation energies will also be drastically affected if these quantities are computed by truncated CI. In each case, as $N \rightarrow \infty$, the CI density matrix and excitation energies will converge to the values corresponding to the SCF reference function, so that a great deal of effort involved in the correlation treatment for an extended system would be of little value. Even for small molecules, however, the effects of quadruple excitations can have observable consequences, as shown for the geometry and force constants of H_2O (33).

OUTLINE OF MBPT/CCM THEORY

The development of MBPT predates CCM, but the latter possesses some conceptual simplifications that recommend that CCM be treated first, with the various orders in MBPT being obtained from the CCM equations. Although, as illustrated by the H_2 lattice, the products of disjoint double-excitation terms that are neglected in CI are fundamentally simple, the standard CI framework cannot exploit this simplicity. Many-body methods accomplish this primarily through the exponential ansatz (6–8), which states that the correct wavefunction may be written in the form

$$\psi = e^T|\Phi_0\rangle, \qquad\qquad 1.$$

where T is an excitation operator which we may define as

$$T = T_1 + T_2 + \ldots + T_n. \qquad 2.$$

The subscripts refer to the number of excited electrons. In the occupation number representation,

$$T_n = 1/n! \sum_{\substack{ijk\ldots \\ abc\ldots}} t_{ijk\ldots}^{abc\ldots} X_a^\dagger X_b^\dagger X_c^\dagger \ldots X_k X_j X_i, \qquad 3.$$

where $a,b,c,\ldots$ are excited orbitals, while $i,j,k\ldots$ are orbitals occupied in Φ_0. In Eq. 1, $|\Phi_0\rangle$ is some suitable, size-extensive reference function, and the amplitudes $t_{ijk\ldots}^{abc\ldots}$,
determined. A double-excitation wavefunction of this type for two separate H_2 molecules, referred to as H_2^A and H_2^B, has the property that (44)

$$\exp(T_2^A + T_2^B)|\Phi_0^A \Phi_0^B\rangle = (\exp T_2^A|\Phi_0^A\rangle)(\exp T_2^B|\Phi_0^B\rangle) \qquad 4.$$

since the cross terms vanish for the noninteracting case.

This approach should be contrasted with the truncated CI technique, for which the D-CI wavefunction for the two H_2 molecules may be written as $(1 + T_2^A + T_2^B)|\Phi_0^A \Phi_0^B\rangle$. This does not correspond to

$$[(1 + T_2^A)|\Phi_0^A\rangle] \times [(1 + T_2^B)|\Phi_0^B\rangle],$$

since the product term, $T_2^A|\Phi_0^A\rangle T_2^B|\Phi_0^B\rangle$ is a quadruple excitation and is thus neglected, so that the result is not size extensive.

The exponential form of the wavefunction, Eq. 1, combined with the condition that the T operator in Eq. 2 contains no disconnected parts (i.e. parts which can be resolved into products of two or more lower T_n operators), is sufficient to guarantee that the energy given by

$$E = \langle \Phi_0|He^T|\Phi_0\rangle \qquad 5.$$

is size-extensive. An alternative expression for the energy is the linked-diagram theorem (1, 2) of MBPT

$$E = \sum_{k=0}^{\infty} \langle \Phi_0|H[(E_0 - H_0)^{-1}H]^k|\Phi_0\rangle_L \qquad 6.$$

which is an expansion of orders in the perturbation $V = (H - H_0)$. When Φ_0 is a self-consistent field (SCF) function, the terms with $k > 0$ represent the correlation energy (45). H_0 is a separable n-particle Hamiltonian whose eigenfunction (at least in a matrix sense) is Φ_0. The subscript L indicates the limitation to linked diagrams, such as those shown in Figure 2. These topological figures provide a convenient mnemonic device for writing down the contribution of any order of perturbation theory solely
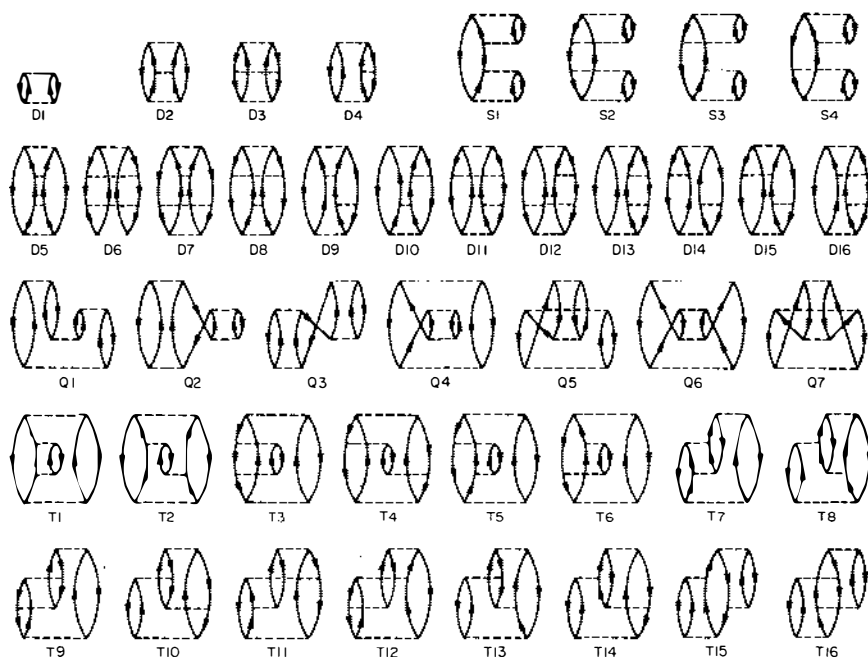
Figure 2 Antisymmetrized Goldstone diagrams (ASGDs) through fourth order MBPT. A Hartree-Fock reference state is assumed. Orders are distinguished by the number of dashed horizontal interaction lines. Particle (p) and hole (h) states are represented by upward and downward directed line segments, respectively. The excitation level of a diagram is distinguished by the number of p-h pairs intersected by an imaginary central horizontal line. In this manner the diagrams have been labeled and counted as contributions to the correlation energy arising from single (S), double (D), triple (T), and quadruple (Q) excitation types.

in terms of molecular integrals. The rules for interpreting such diagrams have been presented (46). The close relationship between Eqs. 5 and 6 will become more evident below, where the solutions of the CCM equations are considered.

The usual choice for Φ_0 is an SCF function of the restricted or unrestricted form. Although this choice is not mandatory, it is computationally simpler, since many terms vanish for this case. For closed-shell systems near equilibrium, a restricted Hartree-Fock (RHF) function is usually a good choice for Φ_0. However, it is well-known that such a function will not separate correctly upon dissociation for any molecule that fails to separate into closed-shell fragments. An unrestricted Hartree-Fock (UHF) function will usually, but not always (47), separate correctly. However, such a function may suffer from extensive spin contamination, particularly when a UHF function is used for a multiply bonded

singlet molecule like N_2 (22). For most open-shell doublets, triplets, etc, UHF functions have only a small amount of spin-contamination, in general, and can usually be employed without excessive error (22). In the UHF or closed-shell RHF case, Brillouin's theorem eliminates any need to consider non-Hartree-Fock single-particle terms.

It is also possible to treat open-shell problems with Roothaan RHF methods (48, 48a), but these do not treat all multiplicities in an equivalent way; they require additional non-Hartree-Fock terms in the summations, and they are not useful for treating entire potential energy surfaces. Multi-reference function methods, which are more appropriate in such cases, are discussed below. For some properties, such as excitation spectra and ionization potentials, open-shell RHF MBPT should be useful.

The CCM theory, built upon Eqs. 1 and 2, originated in nuclear physics primarily through the work of Coester & Kümmel (6, 7), with Čížek (8) presenting the theory in a suitable form for quantum chemistry. Čížek, Paldus, and co-workers have made many applications to π-electron systems within the Pariser-Parr-Pople (PPP) semi-empirical framework (9). Paldus, Čížek & Shavitt made the first, and still one of the most informative, ab initio applications in a minimum basis study of BH_3 (49). This paper considers effects of T_1, T_2, T_3, and T_4 in the CCM equations.

Restricting the T operator just to bi-excitations defines the coupled-cluster doubles (CCD) model, also known as coupled-pair many electron theory (CPMET). The first results from generally applicable computer programs using the CCD model were reported by Bartlett & Purvis (30), Pople et al (50), and Taylor et al (51).

Using the CCD model, equations for the amplitudes can be obtained by back-projecting $He^{T_2}|\Phi_0\rangle$ onto the space of double excitations. These lead to a set of nonlinear coupled equations for the amplitudes of the form (8, 30)

$$0 = \langle ab| |ij\rangle - D_{ijab}t_{ij}^{ab} + \sum_{c>d}\langle ab| |cd\rangle t_{ij}^{cd} + \sum_{k>\ell}\langle k\ell| |ij\rangle t_{k\ell}^{ab}$$

$$+ \sum_{k,c}\{-\langle kb| |jc\rangle t_{ik}^{ac} + \langle ka| |jc\rangle t_{ij}^{bc} + \langle kb| |ic\rangle t_{jk}^{ac}$$

$$- \langle ka| |ic\rangle t_{jk}^{bc}\} + \sum_{\substack{k>\ell \\ c>d}}\langle k\ell| |cd\rangle \{t_{ij}^{cd}t_{k\ell}^{ab} - 2(t_{ij}^{ac}t_{k\ell}^{bd} + t_{ij}^{bd}t_{k\ell}^{ac})$$

$$- 2(t_{ik}^{ab}t_{j\ell}^{cd} + t_{ik}^{cd}t_{j\ell}^{ab}) + 4(t_{ik}^{ac}t_{j\ell}^{bd} + t_{ik}^{bd}t_{j\ell}^{ac})\} . \qquad 7.$$

The antisymmetrized two electron integrals

$$\langle pq| |rs\rangle = (pr|qs) - (ps|qr),$$

are defined relative to the molecular orbital basis set, while $D_{ijab} = (\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b)$ is composed of the SCF orbital energies. From the number of operators involved, the highest terms in the exponential expansion that contribute to these amplitudes are quadratic.

Notice that there are no more amplitudes to determine in the wavefunction $e^{T_2}|\Phi_0\rangle$ than in the standard D-CI, yet at the modest cost of solving a nonlinear equation, we now have a size-extensive method and the inclusion of most of the effects of CI quadruple excitations. The latter follows by comparison, since the CI quadruple excitation operator C_4 is equivalent to

$$C_4 = T_4 + (1/2)\,T_2^2 + (1/2)T_1^2T_2 + T_1T_3 + (1/4!)T_1^4. \qquad 8.$$

However, as Sinanoğlu observed (23), T_4 corresponds to a true four-particle interaction and is very small, while two simultaneous two-particle interactions, which correspond to T_2^2, are far more important. This is also supported by the fact that all quadruple excitation terms in fourth-order perturbation theory come from T_2^2, with T_4 only starting to contribute in fifth-order. Since $T_1 = 0$ for Brueckner orbitals and is usually small for SCF orbitals, the last three terms are normally less important. Hence, with only little more effort than D-CI we obtain a substantial extension of the D-CI theory.

The iterative solution of Eq. 7, which defines several MBPT models, proceeds in the following fashion. Initially all amplitudes are assumed to be zero, giving

$$t_{ij}^{ab}(1) = \langle ab|\,|ij\rangle/D_{ijab} \qquad 9.$$

with energy

$$E_2 = \sum_{\substack{a>b \\ i>j}} \langle ab|\,|ij\rangle\, t_{ij}^{ab}(1)\,. \qquad 10.$$

This is the second-order perturbation energy, which corresponds to the antisymmetrized diagram D1 in Figure 2. The next iteration, also only of the linear terms, defines

$$t_{ij}^{ab}(2) = \sum_{c>d}\langle ab|\,|cd\rangle t_{ij}^{cd}(1) + \sum_{k>1}\langle k\ell|\,|ij\rangle\, t_{k\ell}^{ab}(1) + \sum_{k,c}\{-\langle kb|\,|jc\rangle t_{ik}^{ac}(1)$$
$$+ \langle ka|\,|jc\rangle t_{ik}^{bc}(1) + \langle kb|\,|ic\rangle t_{jk}^{ac}(1) - \langle ka|\,|ic\rangle t_{jk}^{bc}(1)\}\,, \qquad 11.$$

$$E_3 = \sum_{\substack{a>b \\ i>j}} \langle ab|\,|ij\rangle\, t_{ij}^{ab}(2)\,. \qquad 12.$$

E_3 is given by the third-order diagrams D2, D3, and D4 (Figure 2). The next iteration of the linear term would be the same as in Eq. 11, except that $t_{ij}^{ab}(2)$ would be used in place of $t_{ij}^{ab}(1)$ to give $t_{ij}^{ab}(3;L)$. However, we show elsewhere (52) that this computation is not necessary, since

$$E_4^D = \sum_{\substack{a>b \\ i>j}} \langle ab||ij\rangle t_{ij}^{ab}(3;L) \doteq \sum_{\substack{a>b \\ i>j}} |t_{ij}^{ab}(2)|^2/D_{ijab}.\qquad 13.$$

E_4^D corresponds to diagrams D5-D16 in Figure 2.

The first nonlinear iteration contributes

$$t_{ij}^{ab}(3;N) = \sum_{\substack{k>\ell \\ c>c}} [\langle k\ell||cd\rangle \{t_{ij}^{cd}(1)t_{k\ell}^{ab}(1)] - 2[t_{ij}^{ac}(1)t_{k\ell}^{bd}(1) + t_{ij}^{bc}(1)t_{k\ell}^{ac}(1)]$$

$$-2[t_{ik}^{ab}(1)t_{j\ell}^{cd}(1) + t_{ik}^{cd}(1)t_{j\ell}^{ab}(1)] + 4[t_{ik}^{ac}(1)t_{j\ell}^{bc}(1) + t_{ik}^{bd}(1)t_{j\ell}^{ac}(1)]\},\qquad 14.$$

which provides the amplitudes for

$$E_4^Q = \sum_{\substack{a>b \\ i>j}} \langle ab||ij\rangle t_{ij}^{ab}(3;N)\qquad 15.$$

or diagrams Q1-Q7. The superscripts D and Q refer to the two components of fourth-order perturbation theory corresponding to double- and quadruple-excitation diagrams. This defines the perturbation theory model DQ-MBPT(4). A similar consideration of the coupled-cluster single and double excitation (CCSD) wavefunction, $e^{T_1+T_2}|\Phi_0\rangle$, leads in addition to the fourth-order contribution of single excitations, which we define as SDQ-MBPT (4). This adds the S1-S4 diagram (Figure 2). The triple excitation diagrams T1-T16 (Figure 2) arise from T_3 in Eq. 2.

In this manner, each of the terms in the linked-diagram expansion of MBPT, Eq. 6, can be obtained from the general CCM equations. This development emphasizes two alternative viewpoints, the infinite-order summation of selected terms, and the evaluation of all terms at some finite order. When higher-order terms are important, a model like CCSD, which neglects the triple-excitation terms in fourth-order, may well be preferable to SDTQ-MBPT(4) which includes these terms. On the other hand, when good convergence is obtained, SDQ-MBPT(4) ≈ CCSD and the largest remaining error will be the fourth-order triple excitation terms. The latter applies to most cases where the reference function Φ_0, as a nondegenerate RHF or UHF function, is adequate for the problem at hand. In such examples DQ-MBPT(4) usually differs from CCD by

<1 kcal/mole (22). For more difficult cases, where a single Φ_0 suffers from some near degeneracy, CCD or CCSD might be preferred (30, 52–54).

A number of formal developments in the CCM theory have been made by Paldus, Čížek, and co-workers that deal with open-shell systems (55), excitation energies (11), and the spin-symmetry adapted form of the theory (56). Nakatsuji and co-workers have developed and applied an open-shell symmetry adapted cluster theory (57–59). Harris has also considered excitation energies, grafting EOM techniques onto the CCM equations (10). Other papers by Živković (60) and Živković & Monkhorst (61) discuss excited-state solutions to the CCM equations. Monkhorst also considers CCM predictions of properties other than the energy (62). Freeman succeeded in solving the electron gas problem with CCM (63).

The correlation contributions in Eqs. 9–15 are calculated iteratively solely from a list of transformed molecular integrals and associated denominators composed of orbital energies. Very efficient computer programs for carrying out these computations can be constructed, and such programs are well-suited to vector-oriented computers.

The computational effort of second-order perturbation theory has an approximately n^4 dependence on the number of basis functions, while third-order and the fourth-order contributions of single, double, and quadruple excitations, as well as the CCD and CCSD models, are asymptotically proportional in effort to n^6. The quadruple excitation contributions in fourth order and in CCD can be factored, since these correspond to T_2^2 rather than T_4. The latter type of term, which would occur in the most general case, would require an n^8 procedure. This factorization offers a dramatic gain in efficiency over attempting to include quadruple excitations in a CI procedure. The fourth-order triple excitation terms, on the other hand, correspond to T_3 rather than $T_1 T_2$ and hence do not factor, requiring an n^7 procedure. Perhaps of even greater significance for computational purposes is that, if higher than fourth-order contributions of T_3 are to be computed, as would be done in a CCM model that includes T_3, it would be necessary to save the t_{ijk}^{abc} amplitudes, and this would require storage space proportional to n^6.

Some other CI models use a multireference space instead of a single reference function, and include all single and double excitations relative to the several reference functions. In this case, presumably, the most important triple and quadruple excitations are introduced into the calculation. Although, just like any truncated CI model, this is not rigorously size-extensive, it should be much better than single-reference SD-CI, and may be comparable or even superior to single-reference MBPT/CCM models,

which are rigorously size extensive and incorporate higher excitations. In this review the term CI, when unspecified, means a single-reference, truncated CI model.

Before focusing on MBPT/CCM applications and the individual orders of perturbation theory, it is useful first to recognize some of the flexibility inherent in the MBPT/CCM methodology.

The Jacobi type iterative solution of the CCD equations described above is implicitly of Møller-Plesset (MP) type, since the simple denominators D_{ijab} are those used by Møller & Plesset in their classic 1934 paper on perturbation theory relative to an SCF reference function (64).[3] Numerous other choices are possible. For example, the "diagonal" terms in the linear summation of Eq. 7, $\langle ab| |ab\rangle$, $\langle ij| |ij\rangle$, $\langle jb| |jb\rangle$, $\langle ja| |ja\rangle$, $\langle ib| |ib\rangle$, and $\langle ia| |ia\rangle$ could be combined with D_{ijab}, with the other summation indices suitably restricted, to provide a different partitioning known as the Epstein-Nesbet (EN) approach (65). In many-body language, such denominator "shifts" are used to sum certain kinds of terms in perturbation theory to all orders. Obviously, this technique will give very different results for equivalent orders in perturbation theory, although at convergence the final results must be the same. Some study of the nonlinear terms will also lead to certain "quasidiagonal" parts that might be incorporated into the denominator of an iterative scheme. In fact, the latter is necessary to make the connection between the rigorous CCD model and the CEPA approximations to it (18, 66).

In addition to the flexibility in the partitioning used in solving the CCD equations, it is also possible to get very different order-by-order results by different choices for the molecular orbitals involved in the calculations [the equations would then include extra terms in the non-SCF case (49)]. Alternative choices could be natural orbitals, Brueckner orbitals, modified SCF orbitals proposed by Davidson (termed ICSCF for "internally consistent") (67, 68), or those obtained by incorporating modified one-electron potentials (e.g. V^{N-1}) into the calculation. In the last case, the

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[3]To avoid confusion, a point should be made pertaining to the terminology in the field. In the calculations of Pople and co-workers (29, 38, 50) emphasis is placed on the SCF perturbation theory of Møller & Plesset, coupled with the specification of the reference function, rather than on the later MBPT developments employing the diagrammatic theory. This leads to the specification of their models as, for example, UMP3, for third-order Møller-Plesset perturbation theory with unrestricted Hartree-Fock reference function, and UMP4DQ, for fourth-order MB perturbation theory limited to effects of double and quadruple excitations. In our system, $UMP3 = D\text{-}MBPT(3)$ and $UMP4DQ = DQ\text{-}MBPT(4)$, where the reference function is understood to be UHF for an open-shell case and RHF for a closed-shell case. In most cases MP denominators are used, although Epstein-Nesbet denominators, which are often referred to as "shifted," have also been employed in some studies (52).

Arnau-Huzinaga (69) and Silverstone-Yin (70) approach provides V^{N-1} modified orbitals, which may be written as a transformation exclusively among the usual virtual SCF orbitals. For this category of transformations, when only excited orbitals are mixed among themselves (and/or occupied orbitals among themselves), the CCD equations are invariant, so again the converged results will be the same, but not the various orders in perturbation theory. The CCD equations are not invariant to more general transformations that mix occupied and excited orbitals together, like natural orbits or Brueckner orbitals, but the full CI or a full coupled-cluster result would be invariant. Insofar as a given model begins to approach the full result, invariance to even very general transformations will begin to be observed.

A third degree of flexibility is the reference function itself. An SCF function is often convenient, but for some applications just a product of bond-functions, as is used in the PCILO (perturbed CI with localized orbitals) semi-empirical perturbation method (72), or even a product of symmetrically orthogonalized atomic orbitals, may be preferable. For example, the latter two reference functions have certain localization characteristics that may be exploited in an extended system like a metal surface or a large biochemical molecule.

The enormous number of possibilities raises the question of what is the best MBPT model. It would be useful to know, for example, what choice of denominators, orbitals, or reference functions would give second-order results that are consistently closest to the basis set limit for the correlation energy or, perhaps, even to experiment.

Little work in this area has been done. Papers by Bartlett and co-workers (52, 71, 73) have considered the order-by-order perturbation convergence of the MP and EN partitionings relative to SCF orbitals, with the former found to offer much better convergence than the latter for most systems, since the pair-like terms included in the EN partitioning to all orders tend to be biased toward negative contributions. Similar results have also been found in the direct CI procedures for the solution of the CI eigenvalue problem (74). For the case of Be or LiH, and similar systems in which relatively separated electron pairs are involved, the pair-like terms included in EN do heighten the convergence, making E_2^{EN} a superior approximation compared to E_2^{MP}, but for more than four electrons this is seldom the case. [A potential exception would be for localized orbitals (41).] This is due to the pair-pair interactions, as emphasized by Micha (75) and Barr & Davidson (76), that tend to be positive and large for more complicated molecules. In related work Paldus studied the convergence of the CCD equations for Be as a continuous function of a parameter weighting the denominator from MP to EN, finding the best

convergence for a point closer to the EN denominator (77). In all studies of convergence Padé approximants are routinely used to enhance the speed of the convergence (52). The lowest $[N, N - 1]$ approximant is the well-known geometric approximation.

Denominator shifts employing similar "conjoint" (33) (or less appropriately, EPV, for exclusion principle violating) terms that come from the quadratic part of the CCD equations were originally used by Kelly (5). This technique has been found to be important by Freeman & Karplus (78) in obtaining potential curves for diatomic molecules. Prime & Robb discuss a related, but more general type of denominator shift (79), building upon a development by W. J. Taylor (80). An important objection to denominator shifts is that the inclusion of "diagonal" elements of higher order diagrams can result in expressions at a given order that would not be invariant to transformations among degenerate orbitals (81) and may, in fact, give the wrong size-dependence (41).

Different types of basis functions may also be considered. Adamowicz & Sadlej (82) and Pan & King (83) have investigated the use of explicitly correlated Gaussian geminal basis functions in perturbation theory and electron pair theory.

Some work by Silver, Bartlett & Wilson (84) studied the convergence of lower-order perturbation theory with V^{N-p} orbitals, for various choices of p. Although second-order results could be quite varied for different potentials, by third-order there is already little difference in the net results in these studies. This problem has also been studied by Hiroike (85). To the contrary, Lindgren et al found important improvements when using Brueckner orbitals instead of Hartree-Fock orbitals in studies of hyperfine structures in alkali atoms (86). This might be expected due to the importance of single excitation effects for such properties.

The most drastic modification of the theory described above is the generalization to multiple reference functions. Several frameworks for the multireference MBPT/CCM problem have been proposed (87–92), although few applications have yet been made. For many molecular problems it is apparent that multireference techniques will be preferred. This area is discussed in the final section.

However, unlike traditional perturbation methods, in which the perturbation is expected to be small, it should be recognized that single reference MBPT/CCM has been developed from an inherently "infinite-order" perturbation theory viewpoint. [This terminology derives from Löwdin (93).] This means that via the infinite-order CCM models, or by using techniques like denominator shifts to employ geometric series arguments to sum classes (or components) of diagrams to all orders, conver-

gence can often be accomplished even for highly difficult cases. A prime example is found in H_2 at large separation, where the $1\sigma_g^2$ and $1\sigma_u^2$ configurations are equally important, and logic would recommend that both functions be included in the reference space. Despite this, a single reference CCD calculation based on the $1\sigma_g^2$ configuration will give a good potential curve all the way to the dissociation limit (94). Similar studies on Li_2 and N_2 using denominator modifications also illustrate this point (78).

An intermediate level between single-reference and multireference functions in MBPT has been considered by Kirtman & Cole (95). In this study they have proposed that a valence bond (VB) function should be the reference function for a perturbation approach. If this could be accomplished conveniently, one would have the advantage that, unlike an RHF function, the valence-bond solutions would frequently separate correctly, thus leading to a more accurate zeroth-order approximation to a potential energy curve. A UHF function will normally separate correctly, but as illustrated with the N_2 example (22) (described below), the spin contamination becomes too great to give a realistic potential curve in the intermediate range between equilibrium and the separated atom limit. Obviously, when the zeroth-order solution is superior, then equivalent corrections should be obtained in lower orders of perturbation theory.

There are several difficulties with the VB approach, however. The nonorthogonalities that are involved in the original VB theory make the computation time rise as $N!$ for N electrons. Hence, it is usually necessary to invoke strong orthogonality conditions in order to obtain the solution (96, 97). However even with such approximations, the different VB orbitals are eigenfunctions of different one-electron Hamiltonians, eliminating the convenient N-electron Hamiltonian of SCF theory. This feature is also true for Hartree theory and most open-shell RHF-SCF theories, although recent work suggests that a convenient, formal solution to this problem may be found (98). This is an important question, since the elimination of unlinked diagrams is the basis for the size-extensivity of the MBPT/CCM methods, and this elimination is facilitated by the separability of the N-particle Hamiltonian. Kirtman & Cole resort to a type of exchange perturbation theory to account for the different one-electron Hamiltonians. Second-order results are reported for H_2 and LiH.

Although it is important to develop and apply the multireference techniques for open-shell problems, for problems involving near degeneracies, and for the accurate description of bond breaking, the point at which efficiency versus accuracy considerations favor the multireference approach over the single-reference method, or over more general VB-based methods, has not yet been determined.

STUDIES OF MOLECULAR
CORRELATION ENERGIES

The first molecular calculations using many-body methods were made by Kelly for H_2 (99) and by Miller & Kelly for H_2O (100), using one-center expansion techniques and numerical methods similar to those used for atoms. Lee, Dutta & Das made similar calculations (101), with recent work by McDowell (102). Although it is highly desirable to develop purely numerical methods for molecules to avoid the limitations inherent in basis set methods, the multicenter nature of molecular charge distributions presently requires the use of conventional finite basis sets of Slater type orbitals (STO) or of contracted Gaussian type orbitals (CGTO). In an interesting series of papers (103), McDowell has discussed the systematic elimination of the basis set error by using MBPT techniques.

Schulman & Kaufman (104) used the formal structure of MBPT and finite basis sets in calculating the second-order correlation energy and polarizability for H_2. These authors also investigated sum rules to assess the accuracy of their basis sets, an idea that should be used more frequently. This was followed by similar studies of molecular correlation energies, but with some consideration of higher-order effects, by Robb (105), Bartlett & Silver (71), and Freeman & Karplus (78). In addition, Kaldor demonstrated the accuracy of finite-basis MBPT calculations by comparing them with Kelly's numerical results for Be (106).

Additional studies without approximation at the full third-order level have been made by Urban, Kellö & Hubač (107), Bartlett et al (73), Pople et al (29), Kvasnicka & Laurinc (108), and Wilson & Silver (109). It should also be noted that when an SCF reference function is used, and until terms beyond the third order in perturbation theory are included, the first two interations of SCF-based direct CI calculations (110) are equivalent to D-MBPT(3). However, in the process of converging to the D-CI solution, the size-extensivity of the D-MBPT(3) model is lost because the truncated CI approach incorporates unlinked diagram terms in fourth and higher orders of perturbation theory (30). This results in the paradoxical situation that a second- or third-order perturbation result for the correlation effects is likely to be superior to the converged D-CI or SD-CI model, particularly for extended systems, and often even better for some properties of smaller molecules (33). Approximating these unlinked diagram terms is the basis for the widely used Davidson's (111) approximation for quadruple CI excitations (112–114).[4]

[4] Actually, two alternative viewpoints on how to approximate the quadruple and higher excitations in CI have been taken. Bartlett & Shavitt (112) proposed the viewpoint that the unlinked diagrams in fourth-order should be approximated and thereby eliminated from the

In subsequent work, Bartlett & Shavitt computed fourth- and higher-order MBPT contributions due to double excitations (52), and Krishnan & Pople (115), Bartlett & Purvis (30), and Pople et al (50) developed general purpose programs for the computation of fourth-order quadruple- and single-excitation terms. The latter two papers also report CCD results for a series of molecules. The triple-excitation diagrams have now been computed by Krishnan et al (116), Kvasnicka et al (117), and Wilson and co-workers (118, 119). At the level of quadruple and triple excitations, MBPT/CCM offers a great deal of previously unattainable information about the correlation problem for nontrivial molecules.

In a substantial achievement, Saxe, Schaefer & Handy have recently carried out an all-electron full CI calculation for H_2O in a DZ (double zeta) basis set (120). This calculation involved 256,473 configurations and required about six hours on a CDC 7600 computer (H. F. Schaefer, private communication). Since full CI is the best possible solution in the basis set, it is highly informative to compare MBPT/CCM predictions of the correlation energy with the CI results. Table 1 provides this information. Second-order perturbation theory, which is the simplest MBPT approximation, provides 94% of the full CI correlation energy, with the full fourth-order perturbation theory accounting for all but 1 mh, or 99.3% of the correlation energy. The remainder of the full CI result is associated with contributions from higher-order perturbation theory, but most of these are included in the infinite order CCD result.

Since CCD reduces to DQ-MBPT(4) in fourth-order, the difference between the results of these two models provides a measure of the higher order contributions generated by the T_2 operator, which correspond to higher order effects due to even excitations. This difference is 0.668 mh. Adding the fourth-order contribution of single and triple excitations [the latter computed by Wilson & Guest (119)] to the CCD result gives agreement with the full CI to 0.3 mh, or 99.8% of the full CI, and agreement with SDTQ-CI (single, double, triple, and quadruple excitation CI) to 99.96% or 0.06 mh.

When the very good agreement between CCD plus the fourth-order single and triple excitation terms [CCD + ST(4)] is combined with the

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CI, and thereby derived Davidson's formula. This was generalized to all orders by Siegbahn (113). This approach is general for any system, although no effort was made to separate the "conjoint" components that remain in the linked diagrams from the "disjoint" terms (33). Other authors, Pople et al (38), Davidson & Silver (39), and Brändas et al (43) have obtained approximations based upon detailed considerations of a model problem like the H_2 lattice discussed in the third section. This approach would seem to be somewhat dependent on an idealized system. Luken (114) has also studied this problem from the viewpoint of Sinanoğlu's electron pair theory.

Table 1 Comparison of many-body results with full CI[a]
(H_2O 14 CGTO-DZ basis set, $E_{SCF} = -76.00984$)

Model	Configurations	Correlation energy (Hartree a.u.)	ΔE (full CI) (kcal/mole)	ΔE (SDTQ-CI) (kcal/mole)
SD-CI[b]	361	−0.14018	4.9	4.8
SDTQ-CI[b]	17,678	−0.14777	0.2	0.0
FULL CI[b]	256,743	−0.14803	0.0	−0.2
D-MBPT(2)		−0.13948	5.4	5.2
D-MBPT(3)		−0.14087	4.5	4.3
D-MBPT(4)		−0.14392	2.6	2.4
DQ-MBPT(4)		−0.14476	2.1	1.9
SDQ-MBPT(4)		−0.14565	1.5	1.3
SDTQ-MBPT(4)[c]		−0.14704	0.6	0.5
CCD		−0.14544	1.6	1.5
CCD + ST(4)		−0.14771	0.2	0.0

[a]MBPT/CCM calculations, R. J. Bartlett.
[b]The CI calculations are by Saxe, Schaefer & Handy (120).
[c]The triple excitation component of SDTQ-MBPT(4) is computed by Wilson & Guest (119).

fact that these MBPT/CCM calculations require only a few seconds on the CDC 7600, compared to six hours for the full CI or a few minutes for the SDTQ-CI, the potential efficiency and accuracy of the many-body methods is emphasized. Of course, H_2O at equilibrium is well-described by a closed-shell SCF reference function, which is clearly the dominant configuration, so MBPT/CCM methods based upon a single reference function are easily applicable. With open shells or near degeneracies, even a single-reference UHF-based MBPT/CCM approach may not be as reliable (30, 120a), and multireference function techniques are sometimes preferred, with a consequent loss in efficiency.

In another calculation on H_2O (33), a very good 39 STO basis set is used (121). For this basis the full CI or even SDTQ-CI is out of the question. However, one can still readily carry out SDQ-MBPT (4) and CCD calculations. The inclusion of fourth-order triple excitations, an n^7 problem, adds a great deal to the time for the calculation (118), but their magnitude in the examples studied is typically of the same order as the other fourth-order components. A suggested rule-of-thumb is that the triple excitation terms are about three times as large as the singles contribution (122). These results are displayed in Table 2. The CCD model with the addition of the fourth-order single and triple excitations is essen-

Table 2 Comparison of many-body results with SD-CI[a]
(H_2O 39 STO basis set, $E_{SCF} = -76.06423$)

Model	Correlation energy (Hartree a.u.)	ΔE(SD-CI) (kcal/mole)
SD-CI[b] (4,120 configurations)	−0.27558	0
D-MBPT(2)	−0.28178	−3.9
D-MBPT(3)	−0.28502	−5.9
D-MBPT(4)	−0.28934	−8.6
DQ-MBPT(4)	−0.28614	−6.6
CCD	−0.28621	−6.7
SDQ-MBPT(4)	−0.28817	−7.9
SDTQ-MBPT(4)[c]	−0.29604	−12.8
CCD + ST(4)	−0.29611	−12.9
Exp.	−0.370	−59.2

[a]The MBPT/CCD calculations are reported by Bartlett, Shavitt & Purvis (33).
[b]The CI calculation is by Rosenberg & Shavitt (121).
[c]The triple excitation component is computed by Wilson (118).

tially equivalent to SDTQ-MBPT (4) for this system, and accounts for 80% of the estimated total correlation energy of H_2O. A second-order calculation recovers 95% of this, third-order recovers an additional 1.1%, and fourth-order 3.7%. The fourth-order contributions are −4.3 mh for double excitation diagrams, −2 mh for singles, −7.9 mh for triples, and +3.2 mh for quadruple excitation diagrams.

As measured by fourth-order results, the net effect of quadruple excitations in CI would be about −13.9 mh,[5] or about 4.7% of the computed correlation energy (33). Adding in the triples as well, the higher CI excitations account for 21.8 mh or about 7.4% of the correlation energy, compared to 5.1% in the DZ basis calculation.

In this study of H_2O a quartic force field was also predicted at several levels of MBPT/CCM approximation, and compared with SCF and SD-CI (33, 125). The SCF predictions of the bond length and angle are within 2% of experiment, while SD-CI is accurate to about 0.5%. The low-order many-body models D-MBPT(2) and D-MBPT(3) give some-

[5]It is important to distinguish between quadruple excitation diagrams and CI quadruple excitations, since the former contains components which derive from double excitations in the CI model (30, 33). These double-excitation terms are responsible for the quadruple excitation diagrams being positive. This also introduces the separation of the renormalization terms in fourth-order perturbation theory into the "conjoint" (or EPV) and "disjoint" parts mentioned in this review. Hubač and co-workers (123, 124) present a detailed study of these interrelationships.

what better agreement with experiment than SD-CI. The error in CCD is $<0.2\%$, and SDQ-MBPT(4) improves this to $<0.1\%$.

In the prediction of the force constants, the SCF results show errors of more than 30% for even some quadratic constants, while SD-CI is usually fairly close to the various MBPT/CCM results, normally $<10\%$ in error. For $f_{R\theta}$, though, there is about a 16% difference between SD-CI and SDQ-MBPT(4), with the CI result much further from experiment. There are differences between various reported experimentally derived values of the force constants, and to a lesser degree even for the bond length and bond angle, so convergence to a particular set of experimental values cannot be taken as evidence for any general superiority of MBPT/CCM to SD-CI, although one would certainly expect that the higher excitation terms like the quadruples included in SDQ-MBPT(4) and CCD should help in improving the accuracy of the SD-CI calculations. In fact, adding Davidson's approximation for quadruple excitations to SD-CI significantly improves the results of the model in this example (125), and this is a generally observed phenomenon for highly accurate CI studies (126). What is most important here, however, is that size-inextensive models show some significant differences from SD-CI even for a small molecule like H_2O. We would certainly expect this to be the case for larger systems, but even for H_2O, at the sophistication of current ab initio quantum chemistry, there are observable consequences of size-inextensive models that should be realized and corrected.

The fractions of the correlation energy attained within a given basis set with the MP denominator and ordinary SCF occupied and excited orbitals are presented in several places (22, 29, 30, 33, 50). The typical behavior is illustrated in Table 3 for some molecules we have studied. The higher than fourth-order terms are measured by means of the CCD model, which only includes the T_2 operator in Eq. 2, hence single- and triple-excitation contributions are not included.

The worst case for second-order perturbation theory is BH_3, which reflects the residual degeneracy in this system. However, even though the third-order contribution is comparatively large, the higher-order effects are modest, showing good convergence. The fourth-order single-excitation contribution to BH_3 amounts to only -0.18 mh (30). Diborane shows a somewhat similar behavior, and the single excitations give only -0.14 mh (127). The multiply-bonded molecules CO, CO_2, N_2, HCN, and CH_3CN have a large E_2, with a positive E_3, except for HCN. In a larger basis including double-polarization functions, E_3 for HCN is positive (128). The negative single-excitation contribution for each of these molecules is somewhat larger, being -7, -12, -5, -4, and -5 mh, respectively (30, 22).

Table 3 Percentage of the correlation energy obtained by different orders of perturbation theory[a]

Molecule	Second-order	Third-order	Fourth-order (DQ)	Higher order (DQ)
BH_3	80.0	16.5	3.0	0.50
H_2O	97.7	1.5	0.7	0.06
NH_3	94.3	5.0	0.6	0.12
CH_4	89.6	9.3	0.9	0.16
CO	100	−1.6	1.6	−0.09
CO_2	103.2	−4.1	0.9	0.0
HCN	98.0	0.7	1.0	0.18
N_2	101.0	−2.2	1.3	−0.11
HNO	98.9	−0.5	1.9	−0.26
HCO	99.5	−0.2	0.7	−0.05
CH_2O	97.7	0.1	2.9	−0.01
C_6H_6	95.6	0.6	3.8	—
$(CH_3)_2NNO_2$	94.1	4.4	1.5	—
CH_3CN	96.5	−2.2	3.7	—
B_2H_6	85.2	13.2	1.6	—

[a] The basis set is at least of double zeta plus polarization quality, except for C_6H_6 and $(CH_3)_2NNO_2$, where a double zeta basis is used.

The fourth-order DQ contribution is comparable in size to E_3, although it can be larger. The usual justification for this is that effects of quadruple excitations are included here for the first time, although it is too much to expect that the perturbation series will be monotonically decreasing. When the DQ terms derived from T_2 are included to all orders, as is done in the CCD model, one still generally finds little differences between CCD and DQ-MBPT(4) as shown in Table 3 (22), implying that even though the fourth-order contribution can be larger than E_3, there is really no problem with convergence through DQ-MBPT(4) for most cases. When the single-reference function MBPT/CCM method is used for problems where near degeneracies are encountered, convergence can be far worse (30, 129).

Even though the fourth-order DQ contribution can be larger than E_3, once fourth-order single and triple excitations are included, the magnitude of the total fourth-order term is even greater, since both these new contributions are negative, thus augmenting the negative DQ component. In the SCF case, due to Brillouin's theorem, this is the lowest order in which these terms can appear, accounting for their significant effect. Since there are only a few examples where higher-order T_1 contributions

are considered (49, 129), and only one example that includes T_3 to higher order (49), less justification for adequate convergence of the SDTQ-MBPT(4) model is available, although it is anticipated that this level should also be well converged.

In addition to the applications made by Battelle's group, very thorough studies of molecular correlation energies are presented by Pople and co-workers in a series of papers (29, 38, 50, 115, 116, 122). In the first major effort (29), Pople et al reported on calculations at the level of second- and third-order perturbation theory for a variety of atoms and hydride molecules, including some considerations of multiplet splittings, dissociation energies, and second-order predictions of bond lengths and angles. For geometries, these authors find that D-MBPT(2) shows a mean difference between theory and experiment of only 0.003 Å, compared to 0.01 Å at the UHF level, while bond angles are accurate to a few degrees. As seen in Table 3, E_2 is generally sufficient to account for ~90% of the basis set correlation energy and Pople et al show that it also removes at least 50% of the error remaining in the UHF predictions of geometries.

In a subsequent paper (38), Pople and co-workers compared D-MBPT (3) with variational D-CI and SD-CI predictions of correlation energies, dissociation energies, and multiplet separations for the same series of atoms and molecules. At the third-order level there is not much difference between MBPT and the CI results for small molecules, as one would expect from the fact that D-MBPT(3) corresponds to the initial iterations leading to the D-CI result. It is difficult to separate the effects of size-extensivity in D-MBPT(3) versus D-CI from the higher-order contributions included in D-CI, but this paper also considers a size-extensivity correction to D-CI that suggests that there is about a 2 kcal/mole effect in multiplet splittings and dissociation energies for the simple systems studied.

The potentially more significant differences between MBPT/CCM and SD-CI models start to appear at the fourth order of perturbation theory. As described above, the inclusion of most of the effects of CI quadruple excitations in MBPT/CCM via the factorizable T_2^2 term enables MBPT/CCM to include such higher-excitation effects comparatively easily, while only for small model problems is it possible to do CI calculations that include the full set of quadruple excitations, as in the work of Saxe et al (120). In fact, a very large number of MBPT/CCM calculations that include quadruple excitation effects have been made for rather complicated systems, and some of the results are shown in Table 3. The general size of the error due to neglect of CI quadruple excitations is illustrated in Figure 1 for a few examples, and ranges up to 20% for benzene.

A paper by Krishnan & Pople (115) reports SDQ-MBPT(4) results for

the same series of molecules studied in their previous papers on SD-CI and second- and third-order perturbation theory. These authors point out that this model, neglecting triple excitation terms, is correct through fourth-order for an assembly of isolated two-electron systems.

Bartlett & Purvis (30) discussed the fourth-order theory and its relationship to CCD, with emphasis on the cancellations in the fourth-order theory that distinguish many-body models from truncated CI. A number of results in DZP or better basis sets for BH_3, NH_3, CO, HCN, CO_2, and N_2 are presented at the SDQ-MBPT(4) and CCD levels, showing that DQ-MBPT(4) results are quite close to the CCD values. This paper also points out the convergence problems encountered when one attempts to use an RHF reference function in an MBPT calculation of the N_2 potential curve, just beyond the N_2 bifurcation into an RHF and a UHF solution. The problem is further considered in another paper (22).

Pople et al (50) reported CCD results and compared these with the linearized (L-CCD) model and DQ-MBPT(4) for their usual set of first-row atoms and hydride molecules. The L-CCD model, which neglects the nonlinear terms in Eq. 7, corresponds to the sum of just the double-excitation MBPT diagrams to all orders, or D-MBPT(∞) (30), and is also known as CEPA(0) (18). Since the nonlinear terms are generally positive, L-CCD results overestimate the CCD correlation energies by as much as 6 mh for some of the molecules studied. However, since the neglected fourth-order single- and triple-excitation diagrams are negative, the errors in L-CCD compensate to some extent for the omission of these terms. These authors also observe the close coincidence of CCD with DQ-MBPT(4) in their applications.

Nakatsuji has applied his symmetry-adapted cluster theories to Be, BH_3, and H_2O (59), including some study of the excited states.

Krishnan (130) et al defined a new 6-311G** basis set and predicted geometries and atomization energies for a series of small molecules at the D-MBPT(3), DQ-MBPT(4), and SDQ-MBPT(4) levels. Agreement with experimental bond lengths and angles is not substantially improved over the simple D-MBPT(2) predictions for most examples. In particular, SDQ-MBPT(4) tends to increase the bond lengths between first-row atoms due to the effects of the single excitations. The atomization energies at the SDQ-MBPT(4) level are within 5 to 13% of the experimental values. The effect of single substitutions are as large as 3–4 kcal/mole in multiple-bonded systems, but much smaller for hydride molecules.

A large group of molecules with single, double, and triple bonds have been studied with SDTQ-MBPT(4) to assess the effect of the triple-excitation terms (122). These calculations use a 6-31G* basis which, unlike the DZP results in Table 3, do not have polarization functions on the

H atoms. However, the general behavior is quite similar. Using the correlation energy through fourth-order as the reference point, the second-order energy accounts for a low of 79.2% for BH_3 and 82.5% for B_2H_6, to a high of 96.6% for HF and 95.9% for F_2. Of the twenty-six molecules studied, all but five exceed 90% recovery in second-order. The third-order results have a maximum of 15.9% for BH_3 and 12.8% for B_2H_6, as well as a surprisingly high 10.0% for CH_4, but are less than 10% for all the other molecules. The fourth-order contribution varies from about 2 to 7%. The maximum is given by HCN, CO, N_2, all triple-bonded molecules. As pointed out by Frisch et al (122), the heat of formation of NH_3 from N_2 and H_2 has a contribution of 5.5 kcal/mole solely from triple excitation terms.

Wilson & Saunders (118), have also studied the contribution of triple-excitation diagrams to molecular correlation energies. In applications to Ne, it is found that these terms account for -1.1 mh in the largest basis studied. In H_2O, using the same basis set that had previously been used by Bartlett et al in their MBPT/CCD study for the H_2O quartic force field, the contribution of triple excitations is -7.9 mh. (It should be noted that the original papers had errors that suggested much larger contributions of -9 and -21 mh for the triple excitations in Ne and H_2O, respectively.) Other calculations by Guest & Wilson (131) emphasized that the triple-excitation terms are largest for multiple-bonded systems, including N_2, CO, SiO, and SiS. In addition, it is found that E_4^T changes from -9 mh to -34 mh in a range of internuclear separations for N_2 compared to 4.5 mh to 8.4 mh for E_4^Q. This dramatic change is probably partially due to the instability in MBPT treatments of N_2 based upon an RHF reference function at internuclear distances past equilibrium, as discussed previously (22, 30) and in the last section.

CEPA models (18, 26) are basically a modification of SD-CI, which accounts in an approximate way for higher excitations. Ahlrichs (66) has discussed in detail the relationships between CEPA with MBPT and CCD. CEPA models may be derived by making different approximations for the nonlinear term in the CCD equation, which corresponds to the fourth-order quadruple excitation diagrams of MBPT. These models have been extensively applied (18). With the recent SDQ-MBPT(4) and CCD results becoming available, it is now possible to begin to assess the accuracy of the different CEPA models for inclusion of such higher excitation terms. Ahlrichs & Zirz (132) offer a series of pertinent comparisons for the correlation energy. CEPA(1) agrees with the rigorous fourth-order effect of quadruple excitations to within 0.6% for a series of molecules. CEPA(2) usually overshoots by 1–2% and CEPA(0) by 1–3%. However,

since the fourth-order triple-excitation diagrams are negative, the latter two models may actually be closer to reality in many cases.

DISSOCIATION ENERGIES, POTENTIAL ENERGY SURFACES, AND PROPERTIES OTHER THAN THE ENERGY

In addition to papers devoted to the theory or to studies of the various components of the correlation energy, MBPT/CCM models are now being used routinely to investigate a variety of chemically interesting questions. Most of the more recent applications involve at least some fourth-order MBPT contributions, and often even CCD as in the quartic force field for H_2O (33).

Considering polyatomic systems first, in a series of studies (128, 133), the isomerization energies for the reactions $CH_3NC \rightarrow CH_3CN$, $HNC \rightarrow HCN$, $LiNC \rightarrow LiCN$, and $BNC \rightarrow BCN$ were investigated at the SDQ-MBPT(4) level as well as the activation barriers for the first two isomers. The isomerization energy and activation barrier in the methylisocyanide system are in good agreement with experiment. For the $HNC \rightarrow HCN$ isomerization an unpublished experimental value (134) is 10 ± 1 kcal/mole, but these calculations, as well as other MBPT calculations of Pople et al (50) and CI calculations of Pearson et al (135), tend to support a value of 15 ± 2 kcal/mole for this isomerization. The theoretical results seem to be vindicated by a recent, as yet unpublished ion cyclotron resonance experiment of Pau & Hehre, who report 14.8 ± 2 kcal/mole (W. J. Hehre, private communication). Thorough studies of the HCN and HNC potential surfaces near equilibrium have also been made by Taylor et al (51) using CCD and various CEPA models.

CCD and SDQ-MBPT(4) applications have been made by Adams et al (136) in a study of the stepwise decomposition of methyl alcohol, $CH_3OH \rightarrow CH_3O \rightarrow CH_2O \rightarrow CHO \rightarrow H + CO$. This paper reports a series of dissociation energies and predicted geometries for these molecules. The geometries for the known species are typically accurate to $<.01$ Å for bond lengths and to within a couple of degrees for angles. This work provides a prediction for the experimentally unknown structure of methoxy.

The binding energies for the borane-containing molecules, B_2H_6, H_3BCO, and H_3BNH_3 have been of substantial interest to chemists for some time. For a long period, different experiments obtained different binding energies for the first two, while the third has yet to be experimentally obtained. Redmon et al (127) studied these molecules with MBPT methods, obtaining exceptional agreement with the now accepted experi-

mental values and making a prediction of the binding energy of borazane. Good agreement with previous CEPA calculations is also observed (35).

In more complete studies of potential surfaces, a reaction path for the unimolecular decomposition of $HCO \rightarrow H + CO$ has been determined (137, 138) and used to provide a rate constant. Adams et al (138) have also provided reaction paths for the three lowest states of the HNO radical. The SDQ-MBPT(4) model was used to provide a global potential energy surface for the $O(^3P) + H_2O$ collision in order to predict vibrational excitation cross sections (139). The He + LiH surface has been studied at the D-MBPT(3) level (140).

The reaction path for formaldehyde offers a particularly interesting study. Goddard & Schaefer (141), using SD-CI techniques and Davidson's correction to estimate the effects of quadruple excitations, determined the barriers and dissociation energies for the molecular products $H_2 + CO$, the radical products $H + HCO$, and for the rearrangement to hydroxycarbene. The results of the CI calculations suggest an alternative interpretation (142) of the photodissociation experiments of Houston & Moore (143) for the $H_2CO \rightarrow H_2 + CO$ route. This system has since been studied with SDQ-MBPT(4) by Harding et al (144) as part of their H_4CO surface, and by Adams et al (145) at the SDQ-MBPT(4) and CCD level. Although the MBPT/CCM calculations show somewhat better predictions of dissociation energies, in essentials (and with the correct zero-point energy for the hydroxycarbene transition state) the predicted barriers support the CI results of Goddard & Schaefer. However, more recent SDTQ-MBPT(4) results of Frisch et al (145a) obtain a substantial ~ 5 kcal/mole reduction in the activation barrier for molecular product dissociation due to a change in basis set and another $\sim 3-4$ kcal/mole once triple excitation contributions are included, bringing the calculations into agreement with experiment.

Table 4 presents a summary of some of the results obtained in these efforts, compared with SCF, second-order perturbation theory, and experiment. Second-order perturbation theory removes most of the error in the SCF results for these dissociation and isomerization energies, which is an encouraging result for such a simple addition to an SCF calculation.

In addition to their thorough study of the H_4CO surface, Harding et al have investigated the unimolecular decomposition of methanol (146). Pople et al (50) have also studied the 1,2 hydrogen shifts in C_2H_2, HCN, CH_2O, and N_2H_2 at the SDQ-MBPT(4) level, finding *cis* and *trans* forms of HCOH and HNNH that differ by about 6 kcal/mole. A thorough D-MBPT(3) study of the isomers formed by 1,2 and 1,3 intramolecular hydrogen shifts in CH_3-NO and their associated transition states was reported by Adeney et al (147).

Table 4 Comparison of thermochemistry results obtained by SCF and MBPT/CCD with experiment (All basis sets are at least DZP quality.)

Reaction	Ref.	SCF	E_2	MBPT/CCD Results	MBPT/CCD Model	Experiment
$2 BH_3 \rightarrow B_2H_6$	(127)	18.5	37.5	35.6	SDQ-MBPT(4)	36.6 ± 2[d]
$BH_3 + CO \rightarrow H_3BCO$	(127)	8.0	25.1	20.5	D-MBPT(4)	20.4 ± 2[d]
$BH_3 + NH_3 \rightarrow H_3BNH_3$	(127)	20.5	32.0	30.1	D-MBPT(4)	—
$HNC \rightarrow HCN$	(128)	10.7	18.0	15.0	SDQ-MBPT(4)	(10.3 ± 1)[e]
$HNC \rightarrow [H_N{}^C]$[a]	(128)	−33.4	−30.1	−29.5	SDQ-MBPT(4)	—
$BNC \rightarrow BCN$	(128)	−18.9	−9.8	−12.4	SDQ-MBPT(4)	—
$LiNC \rightarrow LiCN$	(128)	−6.4	−2.3	−3.9	SDQ-MBPT(4)	—
$CH_3NC \rightarrow CH_3CN$	(133)	19.2	26.2	22.8	SDQ-MBPT(4)	$23.7 \pm .14$[f]
$CH_3NC \rightarrow [CH_{3C}{}^N]$[b]	(133)	−44	−40	−40	SDQ-MBPT(4)	−38.4[g]
$H + CO \rightarrow HCO$	(137)	4.8	11.8	13.6	CCD	15.7 ± 1.5[h]
$HCO \rightarrow [HCO]$[c]	(137)	−12.8	−17.4	−18.1	CCD	—
$H_2CO \rightarrow H_2 + CO$	(145)	−7.2	−3.9	−3.9	CCD	−1.9[i]
$H_2CO \rightarrow H + HCO$	(145)	−68.6	−82.8	−86.0	CCD	$−86.0 \pm 1.0$[j]

[a] Square bracket indicates a transition state. This result includes a 4 kcal/mole zero point correction for the transition state.

[b] Square bracket indicates a transition state. This result includes a 4.8 kcal/mole zero point correction for the transition state.

[c] This result includes a 5 kcal/mole zero point correction for the transition state.

[d] Ref. (145b).

[e] Ref. (134). Ref. (128) concludes that this experimental value is in error. The result should be 15 ± 2 kcal/mole.

[f] Ref. (145c).

[g] Ref. (145d).

[h] Ref. (145e).

[i] Ref. (145f).

[j] Ref. (145g).

Kenney et al (148) used high-order D-MBPT to study the singlet-triplet separation in the series of compounds $H_2C:$, $H_2CC:$, $H_2CCC:$, predicting a singlet ground state for vinylidene and vinylidene carbene.

Because of its correct size-dependence, one of the natural places to apply MBPT/CCM is in the emerging area of ab initio quantum biochemistry (31). An example of this is the work of Weinstein et al (149) and Osman et al (150), who investigated the stacking of complexes of 5- and 6-hydroxytryptamine with imidazolium (represented by model compounds) to probe receptor sites for hallucinogenes. No doubt many more applications of this type will appear in the next decade.

Earlier studies from the Carnegie-Mellon group used low-order perturbation corrections to study the relative stability of the difluoroethylene isomers (151), the internal rotation of allene (152), the nature of the carbon beryllium bond in CH_2Be (153), and a series of highly unusual electron deficient carbon compounds that violate van't Hoff stereochemistry (154). De Frees et al (155) studied geometries of several complicated species like FOOF at the D-MBPT(2) level.

A number of diatomic potential energy curves have been studied with fourth-order MBPT methods and with CCD. These include Mg_2 (156, 157), Be_2 (30, 120a), and N_2 (22). These calculations offer information concerning the applicability of single-reference MBPT-CCD for entire potential curves. Later work by Chiles & Dykstra (158) studied He_2, Be_2, and Mg_2 at the CCD and CEPA levels.

In lower-order studies, Urban & Kellö used D-MBPT(3) for potential energy curves for BH, F_2, and N_2 in the vicinity of equilibrium, in order to determine spectroscopic constants and to compare with CI (159). The authors observe a substantial difference between SD-CI and D-MBPT(3) for F_2 and attribute this to the failure of SD-CI to be size-extensive. CEPA comparisons with D-MBPT(2) were also reported and found to be in very good agreement. Kellö et al have also studied the proton affinity of H_2O at the third-order level (160). Hubač & Urban have used D-MBPT(3) to obtain ionization potentials for Ne and H_2O (161). Additional third-order near-equilibrium potential curve applications to BH (162), BF, N_2, CO (163), and CH^+ (164) and full curves for He_2 (165) and Be_2 (166) have also appeared. D-MBPT(3) computations on He_2 with the EN denominator are found to have an erroneous behavior as previously observed and explained by Malrieu (41).

Except for the cases of He_2 and Be_2 and similar molecules, an RHF reference function cannot provide a potential curve of correct form all the way to separation, and the utility of single-determinant RHF as a basis for D-MBPT(3) for such problems is questionable. Either very high-order theories like CCM need to be used to attempt to overcome the erroneous behavior of RHF at large separations, or a UHF reference function should be employed, when suitable. Ultimately, multireference MBPT approaches should be developed for these categories of problems.

In studying properties other than potential curves, correlation corrections to the coupled Hartree-Fock (CHF) perturbation theory are of substantial interest. A paper by Caves & Karplus has analyzed the problem diagrammatically (167). Numerical MBPT results are now starting to become available.

Adamowicz & Sadlej (168) computed second-order correlation correc-

tions to the CHF polarizability of Be. These authors found a substantial correction of 20% due to this term, which is consistent with other work (169–171). This calculation employed electric field variant Gaussian bases, as proposed by Sadlej (172), which offer an interesting concept for such studies.

Bartlett & Purvis used finite-field methods with SDQ-MBPT(4) to obtain dipole moments, polarizabilities, and hyperpolarizabilities for the HF molecule (170). In that work particular attention was paid to the choice of basis set required to describe such properties, using numerical Hartree-Fock calculations (173) as a guide. In another effort, these authors applied this technique to H_2O (171), including an investigation of the hyperpolarizability as a function of bond stretching and bending. Correlation is found to have a very large effect on hyperpolarizabilities, implying that CHF perturbation methods cannot adequately treat this problem. Also, the hyperpolarizability tensor elements are quite sensitive to bond stretching.

Nuclear spin coupling constants in H_2 have been studied by Itagaki & Saika (174). Using a large Gaussian basis set and second-order correlation contributions, augmented by some additional terms up to fourth-order, these authors obtained a result within $\sim 10\%$ of the experimental value for the Fermi contact term.

In another study these authors determined the correlation energy and dipole polarizability for H_2 (175). This paper also discussed the decoupling of the energy denominators in MBPT, and employed these techniques to relate the polarizability diagrams of double-perturbation theory to the field dependent energy, as it would be employed in finite-field applications. They have also studied the electric field gradient in the HD molecule with MBPT, obtaining quite good agreement with other very extensive calculations (176).

D-MBPT(2) was used by Yoshioka & Jordan to obtain dipole moments, polarizabilities, and electron affinities for the highly polar LiF and BeO molecules (177). Using a large and flexible basis set, they found that D-MBPT(2) gave almost perfect agreement with experiment for the dipole moments of LiF. There are no experimental values for the other quantities.

The interesting work of Kelly & Carter concerning photoionization cross sections for atoms should also be mentioned (178), because of its implications for molecular studies.

Bent et al have investigated Jahn-Teller distortions in the methoxy radical, coupling MBPT methods with a clever treatment of the dynamic Jahn-Teller effect (179).

Many MBPT finite-field and related studies of electric and magnetic properties, NMR chemical shifts, and spin-spin coupling constants will doubtlessly appear soon in the literature.

MULTIREFERENCE SPACE MBPT METHODS

In order to be able to describe many processes at the level of accuracy required in current quantum chemistry applications, it frequently appears to be necessary to employ multireference determinants in MBPT/CCM. To illustrate the nature of the problem, Figure 3 shows potential energy curves for the ground state of N_2 (22). It is evident that RHF-based MBPT calculations follow the experimental curve accurately until about 2.6 a.u., where the erroneous separation of the RHF reference function can no longer be corrected by the D-MBPT(6) procedure. Using the same reference function, but treating correlation at the CCD level, which includes the effects of quadruple excitations, the applicability of the RHF + CCD model is extended to slightly longer bond lengths, where instabilities with solutions of the CCD equations begin to occur (129).

On the other hand, after the bifurcation of the SCF solution for N_2 into separate UHF and RHF results, it is also possible to use UHF + MBPT/CCM to obtain potential curves. Unlike the RHF-based models, the UHF solution separates correctly to two ^4S N atoms and, in fact, gives a dissociation energy which is only about 0.6 eV too small, but it is apparent that the path toward dissociation is in error. This is primarily due to a large amount of spin contamination for this singlet state. The N_2 UHF multiplicity along the curve is about 3.5, and correlation of the D-MBPT(6) model is unable to introduce a high enough level of correction to improve it. It should be possible to correct this problem partially by annihilating the principal (triplet) component of the spin contamination, although there are problems with this approach as discussed by Rossky & Karplus (180).

Another intriguing potential solution has its impetus in the observation that if the lowest of the various single-reference MBPT/CCD curves for N_2 could be connected together smoothly, then it would be possible to obtain a good potential curve solely from a single-reference function. The orbitals in the single reference function MBPT/CCD solution change from RHF to UHF, however. Consequently, this smooth connection could be accomplished systematically by using some variational or stationary principle to obtain the lowest correlated solution as a function of the orbitals. In other words, this would be an MBPT/CCM analogue of multiconfigurational SCF theory (181).
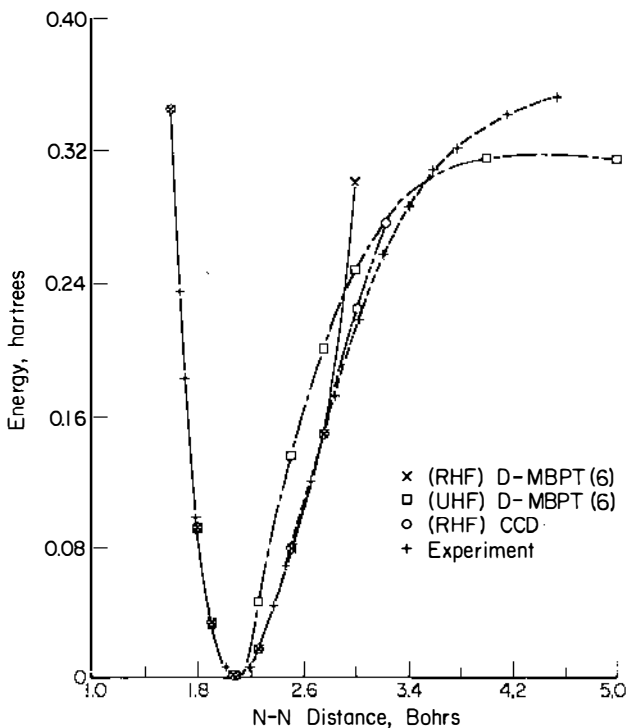
N-N POTENTIAL CURVE

Figure 3 (UHF) and (RHF)D-MBPT(6) and (RHF)-CCD potential energy curves for N_2.
The minima of the curves are superimposed. The D-MBPT(6) correlated UHF curves are
higher in energy than the D-MBPT(6) RHF curves between $R = 2.0$ Bohr and $R = 2.7$
Bohr. The (RHF)-CCD result extends the reliability of the curve over the (RHF)-D-
MBPT(6) approximation to somewhat larger R values, but ultimately the approximation
becomes unstable.

However, the most universal solution to this type of problem is to em-
ploy multireference functions that, presumably, include within the refer-
ence space all important configurations for correct dissociation. Besides
this bond breaking problem, similar difficulties, susceptible to the same
approach, may be encountered with open-shell problems and with various
treatments of some excited states.

The multireference analogue of the linked diagram theorem has been
developed by Brandow (87), with other work by Mukherjee et al (89),
Lindgren (88), Levy (91), Hose & Kaldor (90), and Kirtman (92). See
also the related CCM work of Banerjee & Simons (182).

Although these developments can have important differences, the basic

structure is similar. The use of more than one reference function requires the consideration of an effective Hamiltonian matrix whose order is the number of reference functions $|\Phi\rangle = |\Phi_1^0 \Phi_2^0 \ldots \Phi_m^0\rangle$. The effective Hamiltonian matrix is represented as a sum of matrices

$$\overline{H} = H_0 + H_1 + H_2 + \ldots \qquad\qquad 16.$$

that correspond to orders in the perturbation, whose diagonalization yields the energies and the "model" functions defined solely within the space of reference functions. This idea is well-known from textbook accounts of degenerate perturbation theory, but now generalized to the nondegenerate case.

One way the effective Hamiltonian is defined in many-body theory is to introduce a wave-operator, Ω, such that $\Omega\Phi_i^0 = \psi_i$, the correct eigenfunction of the Schrödinger equation. Ω is the same for each state so this is not the typical Brillouin-Wigner energy dependent wave operator (93). If one also defines a projector onto the reference space

$$P = \sum_{k=1}^{m} |\Phi_k^0\rangle \langle \Phi_k^0 |,$$

it then follows that $P\psi_i = \psi_i^0$, where the $\{\psi_i^0\}$ are the "model" functions expressed solely within the reference space. Then with a slight manipulation of the Schrödinger equation, $H\psi_i = \psi_i E_i$, we obtain (88)

$$\overline{H}\psi_i^0 = \psi_i^0 E_i \qquad\qquad 17.$$

for $\overline{H} = PH\Omega P$.

From $PH\Omega P = |\Phi\rangle \overline{H} \langle\Phi|$ and $\psi_i^0 = |\Phi\rangle C$, Eq. 16 is regained by expanding the operator Ω in powers of the perturbation. The solutions to Eq. 17 provide the exact energies and the model functions. The operator $\overline{H}$ is nonhermitian so the $\{\psi_i^0\}$ are not necessarily orthogonal, although Hermitian combinations can be constructed (183). From this point a series of equations for the Ω operator may be defined recursively from zeroth-order. The existence of a size-extensive connected diagram expansion emerges through the prescription for the different developments for the Ω operator, as presented elsewhere (87–91).

Through first order, the effective Hamiltonian matrix of Eq. 16 is Hermitian. Its eigenvalues and eigenvectors correspond to the CI solution in terms of the reference determinants $\{\Phi_\alpha^0\}$, $\alpha = 1$ to m. If this space were chosen to consist of the SCF determinant and all single excitations, the eigenvectors would correspond to the Tamm-Dancoff approximation (32) and the ground-state energy would simply be the SCF result. This usually provides a reasonable first approximation to the electronic excitation spectra. The remaining configurations start to contribute in second order. For the SCF plus all singles choice, double and triple excitations will

begin to mix in at second order, and up to pentuple excitations in third order (184).

On the other hand, if we were interested in the ground-state potential curve of H_2 we would want the two configurations $\Phi_1^0 = A(1\sigma_g^2)$ and $\Phi_2^0 = A(1\sigma_u^2)$ to be in the reference space. These configurations differ by a double excitation. Here the solution through first-order corresponds to the two-configuration CI result, while the additional configurations begin to contribute in second order. In the general (not two-electron) case, any configurations that differ from Φ_1^0 or Φ_2^0 by two or fewer excitations will contribute in second order, including double excitations from Φ_2^0 which are quadruple excitations relative to Φ_1^0. A full third-order treatment would involve hextuple excitations relative to Φ_1^0. The hope, of course, is that by using both important configurations in the reference space, the remaining effects can be treated adequately by low orders in perturbation theory.

The relatively high levels of excitation encountered in the multi-reference theory, even at low order, recommend the use of many-body, diagrammatic techniques that, in addition to facilitating size-extensivity, are more suited to handling higher categories of excitation than configuration based schemes. One also hopes that some of the partial summation techniques common to many-body and coupled-cluster theory (88) will be able to sum selectively many of the dominant, physically significant contributions to all orders.

One other comment that is pertinent to the Brandow-stimulated approaches to the multidimensional many-body theory is that the choice of reference space is not as arbitrary as one would like. In their diagrammatic development of the above equations, it turns out that only with specific choices of reference functions does a connected diagram theorem easily emerge. In particular, they require that if the configurations $A(\sigma_1^2)$, $A(\sigma_2^2)$, and $A(\sigma_3^2)$ are important in a problem, then the proper spin-coupled combinations of the configurations $A(\sigma_1\sigma_2)$, $A(\sigma_1\sigma_3)$, and $A(\sigma_2\sigma_3)$ must also be included in the reference space. Then, instead of nine matrix elements, one must compute four times as many.

The theory of Hose & Kaldor (185) permits the use of an arbitrary reference space at the cost of introducing a certain type of unlinked diagram which, however, does not destroy the size-extensivity of the model.

Another approach pursued by Kirtman (92) and discussed by Brandow (183), is the generalized Van Vleck transformation (GVVT) (186). Although it is ultimately similar to the wave operator approach above (183, 187, 188), the GVVT development generates a Hermitian effective Hamiltonian whose eigenvectors are consequently orthogonal. Full, rather than intermediate normalization is convenient. Furthermore, and potentially

most important, the GVVT method can be developed entirely within a Lie algebraic structure (34), which can ensure a properly size-extensive connected diagram description for general reference spaces.

A very limited number of applications of the multireference MBPT theory have so far been made. Kaldor applied Brandow's method to some excited states of H_2 (189), obtaining good results through third-order. Another paper by Stern & Kaldor studied states of BH (190), including their transition moments.

Lindgren's development using atomic numerical methods has been applied to open shell atoms by Morrison & Rajnak (191) and Morrison & Salomonson (192), while Salomonson, Lindgren & Mårtensson (193) have studied Be and C^{2+} as an example for cases of two important reference configurations, $1s^2 2s^2$ and $1s^2 2p^2$, for a closed-shell system. For Be, the second-order two-reference calculation recovers 93.6% of the correlation energy compared to 80.9% for second-order with only the $1s^2 2s^2$ configuration as reference.

The work of Hegarty & Robb based upon the Brandow approach should be mentioned (194). Also, the related CI perturbation method of Davidson & Bender for a multireference problem is pertinent (195). In the latter case, these authors used their method to study several states of Mg_2.

Hose & Kaldor applied their new general reference space approach to excited states of He_2 (185). These authors make the important point that the use of a complete model space of the type required in Brandow's theory spans a very broad energy range, while still leaving out other states within that energy range, which can cause severe convergence problems for perturbation theory [the problem of intruder states (183, 185)].

In a somewhat different vein, certain forms of the multireference function theory have also been frequently used in developing effective valence shell or pi-electron theories for molecules. Work of this type is reported by Brandow (183), Freed and co-workers (196), Westhaus and co-workers (197), Baker, Hegarty & Robb (198), and others (199, 200).

ACKNOWLEDGMENTS

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