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Electron Correlation Effects in Molecules

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There has been dramatic progress in the development of electron correlation techniques for the accurate treatment of the structures and energies of molecules. In this review, we give brief and somewhat qualitative descriptions of the different methods that have been developed in recent years. We also discuss the range of applicability as well as the limitations of the methods with a few selected examples. We focus particular attention on electron correlation methods which start from a Hartree−Fock wave function since such single-configuration-based approaches are most easily extended to larger molecules. Multiconfiguration-based correlation techniques are considered briefly. We also present a fairly thorough account of the recent developments and applications using novel quantum Monte Carlo approaches.

I. Introduction

The evaluation of the structures and energies of molecules from first principles has long been a primary goal of quantum chemistry. One of the major stumbling blocks to achieving this goal has been the lack of an accurate theory of electron correlation which is practical enough for reasonable applications to chemically interesting problems. Thus, a dominant research theme in this field for decades has been the development of new theoretical methods for the accurate evaluation of electron correlation energies.[1−10] In the past few years, important theoretical insights from many different research groups coupled with the increasing computational power of modern-day computers have led to the development of sophisticated and accurate theoretical techniques which can now be applied to a variety of problems of chemical interest.

One of the first steps in most theoretical approaches to the electronic structure of molecules is the use of mean-field models or orbital models. Typically, an orbital model such as Hartree−Fock self-consistent-field theory[11] provides an excellent starting point which accounts for the bulk (≈99%) of the total energy of the molecule. However, the component of the energy left out in such a model, which results from the neglect of instantaneous interactions (correlations) between electrons, is crucial for the description of chemical bond formation. The term “electron correlation energy” is usually defined as the difference between the exact nonrelativistic energy of the system and the Hartree−Fock (HF) energy.[12] Electron correlation is critical for the accurate and quantitative evaluation of molecular energies.

Electron correlation effects, as defined above, are clearly not directly observable. Correlation is not a perturbation that can be turned on or off to have any physical consequences. Rather, it is a measure of the errors that are inherent in HF theory or orbital models. This may lead to some ambiguities. While HF theory is well-defined and unique for closed-shell molecules, several versions of HF theory are used for open-shell molecules. Correlation energy for an open-shell molecule is usually defined with respect to unrestricted Hartree−Fock (UHF) theory where the spatial orbitals are different for α and β spins. Some authors prefer to define it with respect to restricted Hartree−Fock theory where the spatial orbitals for α and β spins are identical. Sometimes, it may even be convenient to replace the HF approximation in the above definition with another well-defined approximation such as a multiconfiguration reference function. For this rather general review, we adopt an attitude that a theory of electron correlation refers to any method for accurate treatment of interelectronic interactions starting from a suitable reference wave function.

Another factor needs to be considered in most theories of electron correlation. In actual computations, the orbitals are usually expanded in terms of a finite basis set, i.e., a set of finite atom-centered functions. This introduces an additional error associated with basis set truncation effects. Typically, for any given method, the correlation energy is defined within the finite basis set used, and the convergence with respect to increasing the basis set size is then considered separately. For many of the popular quantum chemical methods, the convergence with respect to the inclusion of higher angular momentum functions in the basis set is rather slow.

The physical ideas behind most theories of electron correlation can be understood from an analysis of the bonding in the simplest molecule, *viz*. H_2. Hartree−Fock calculations with large basis sets show that correlation effects contribute about 25 kcal/mol to the binding energy in H_2. In fact, a frequently used rough rule of thumb is that correlation effects contribute ≈1 eV (23 kcal/mol) for a pair of electrons in a well-localized orbital.[2] For many pairs of electrons in close proximity, correlation effects become very large. For example, they contribute more than 100 kcal/mol to the bond energy in N_2.

The most important type of correlation effect which contributes to chemical bonding is usually termed “left−right” correlation.[2] For H_2, this refers to the tendency that when one electron is near the first hydrogen, the other electron tends to be near the second hydrogen. This is absent in the HF method where the spatial positions of the two electrons occupying the lowest bonding molecular orbital are uncorrelated. The problem gets worse as the two atoms move apart and dissociate. Qualitatively, this can be corrected by including a second configuration where both electrons occupy the antibonding orbital. While this is unfavorable energetically, a mixture of

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the HF configuration with this second configuration provides a better description of the system. This is referred to as "configuration interaction" and is the basis behind many of the electron correlation theories. The second configuration obviously has only a small weight at the equilibrium distance in H_2, but its weight increases as the bond distance increases until the configurations have equal weights at dissociation. Such a left−right correlation is naturally included in valence-bond-type wave functions.

Another type of correlation effect is "in−out" correlation which corresponds to radial correlation in atomic systems. Typically, such effects can be included by having configurations with occupation of higher radial functions, e.g., $(1\sigma_g 2\sigma_g)$ configuration in H_2 composed of 1s and 2s orbitals. A third type of correlation is "angular" correlation which is typically considered by the inclusion of higher angular momentum functions, e.g., $(\pi_u)^2$ configuration in H_2 composed of 2p orbitals. Large basis sets with higher radial and angular momentum functions are necessary to properly include the contributions of all the different correlation effects.

The field of electron correlation has an extensive literature with contributions from many different groups using a variety of approaches. In addition, the general availability of quantum chemical programs[13] has made it possible for an even wider set of authors to treat many different chemical systems with the available computational schemes. It is clearly not possible to give a comprehensive account of all the different theories and applications within the space available. We have elected to give brief and somewhat qualitative descriptions of the different methods that have been developed to describe electron correlation effects. We have also attempted to discuss the range of applicability as well as the limitations of the methods with a few selected examples. We focus particular attention on electron correlation methods which start from a HF wave function since such single-configuration-based approaches are most easily extended to larger molecules. Multiconfiguration-based correlation techniques are considered briefly. We also present a fairly thorough account of the recent developments and applications using novel quantum Monte Carlo approaches.

II. Requirements of Electron Correlation Theories

Before we discuss the details of the different theories of electron correlation, it is useful to understand the criteria which these approximate theories should attempt to satisfy. In other words, a correlation theory constitutes a "theoretical model chemistry"[1] and should have certain desirable characteristics. For example, it should provide a unique total energy for each electronic state at a given geometry and should also provide continuous potential energy surfaces as the geometry changes.

A desirable property of approximate theories is that the resulting energy should be variational; i.e., it should be an upper bound to the exact energy. For many years, this was considered to be an important criterion, and approximate theories such as configuration interaction did satisfy this property. Interestingly, some of the most successful theories of electron correlation in practice today, such as coupled cluster theory, do not provide variational total energies. However, they are so accurate and well tested that the advantage provided by the variational bound to the energy is no longer present in many state-of-the-art correlation theories.

The most important criterion for an accurate electron correlation theory is the property of size consistency or size extensivity.[1,3] This term refers to the linear scaling of the energy with the number of electrons in the system. It is intuitively obvious that an approximate method should have the property of size consistency to allow proper comparisons between small and large molecules. In its simplest realization, a size-consistent method leads to additive energies for infinitely separated systems.[1] While this appears to be a rather trivial requirement, popular methods such as configuration interaction are not size consistent and do not give additive energies for infinitely separated systems. For many years, the importance of size consistency was known but thought to be important only for large molecules. However, in recent years, it has been realized that a size-consistent method is necessary to reach quantitative accuracy even for small molecules.

A useful criterion for an accurate correlation method is correctness for two-electron systems. The electron pair is a central and useful concept in chemistry, and their exact correlation treatment (within a given basis set) is relatively easy to implement. Several of the popular correlation techniques do indeed correlate an electron pair exactly. More importantly, for any molecular system composed of reasonably well-defined electron-pair bonds, such methods provide excellent starting points for inclusion of additional corrections such as those from three-electron correlations. It is now realized that such three-electron correlations, though expensive computationally, are crucial to reach quantitative accuracy. They are best implemented in methods which treat an electron pair exactly.

A final but very important aspect of any correlation scheme is its computational dependence, which determines the range of applicability of the method to interesting chemical problems. In general, correlation techniques are more expensive than the HF method, and the computational requirements of many of the most accurate correlation methods scale as a fairly high power of the size of the system. In addition, many of the correlation techniques involve an iterative solution of a set of coupled equations which adds additional computational steps.

III. Single-Configuration-Based Theories

As mentioned earlier, the most widely used techniques start from a single configuration, typically that from a Hartree−Fock (HF) self-consistent-field wave function.[11] In this section, we present a brief discussion of such electron correlation techniques and present their current status. In the HF method, the wave function Ψ_0 is a product of one-electron wave functions (referred to as molecular spin orbitals), antisymmetrized with respect to interchange of electronic coordinates. This is frequently referred to as a Slater determinantal form of wave function. The molecular spin orbitals themselves are expanded as a linear combination of atom-centered basis functions. In a HF calculation, each electron moves in an average field due to all the other electrons, and the expansion coefficients of the molecular orbitals are determined in a self-consistent fashion. The resulting molecular orbitals are eigenfunctions of the "Fock operator". If there are n electrons and N atomic spin orbitals, solution of the HF equations results in n occupied molecular spin orbitals and $(N - n)$ unoccupied (or virtual) molecular spin orbitals.

The representation of the wave function in terms of a single configuration as in Hartree−Fock theory is inadequate to treat the correlations between the motions of different electrons. While the antisymmetry which is implicit in a determinantal wave function keeps electrons of the same spin partially correlated, the correlation between the motions of electrons with opposite spins is neglected in Hartree−Fock theory. The correlation energy as defined above is thus a measure of this inadequacy of HF theory.

In most techniques, electron correlation effects are introduced by allowing the wave function to be a linear combination of many electron configurations. The other configurations are generated by replacing occupied spin orbitals in Ψ_0 by virtual spin orbitals and may be classified as single, double, triple, quadruple (S, D, T, Q) ⋯ excitations. T_1, T_2, T_3, T_4, ⋯ are operators which generate linear combinations of all single, double, triple, quadruple, ⋯ excitations involving expansion coefficients to be determined.

A. Perturbation Theory. One of the most common treatments of electron correlation is based on perturbation theory. Though extensive applications using perturbation theory have been performed relatively recently compared to older methods such as configuration interaction, low-order perturbation theory has become very pervasive because of its wide applicability to a variety of problems. We discuss it first in this review because it provides a convenient framework to describe the dominant electron correlation effects.

Møller−Plesset (MP) or many-body perturbation theory[14] treats the electron correlation as a perturbation on the Hartree−Fock problem. Here the zeroth-order Hamiltonian is the Fock operator derived from the HF wave function. This provides a convenient and unique description for closed-shell systems and for open-shell systems based on an unrestricted HF wave function.[15,16] For restricted open-shell wave functions (where the α and β spatial orbitals are identical), however, the perturbation treatment is not unique, and there are several variants being explored.[17]

In the MP scheme, the wave function and the energy are expanded in a power series of the perturbation. It is easily shown that the HF energy is correct to first order;[14] thus, perturbation energies start contributing from second order. We use the common notation that the total energies correct to given order are denoted as MP*n*.[15] Thus, MP2, MP3, MP4, ⋯ denote the total energies correct to second, third, fourth, ⋯ order, respectively. In perturbation theory, the different correlation contributions emerge through their interaction with the starting HF wave function Ψ_0. Since the Hamiltonian contains only one- and two-electron terms, only single and double excitations can contribute via direct coupling to Ψ_0 in the lowest orders. However, the self-consistent optimization of the HF wave function prevents direct mixing between single excitations and Ψ_0. Thus, the second- and third-order energies have contributions only from double excitations. In higher orders, there is indirect coupling via double excitations, and thus the fourth- and fifth-order energies have contributions from single, double, triple, and quadruple excitations.

The importance of the different terms that contribute to electron correlation energies can be judged from the order in which they first contribute in a perturbation expansion. Thus, the importance of double excitations is immediately obvious from perturbation theory since they are the only correlation contributions up to third order. Single, triple, and quadruple excitations first contribute in fourth order. When the MP4 method was first implemented in the late 1970s,[15,16,18] the importance of some of these contributions was not fully recognized. The use of the HF starting point diminishes the effects of single excitations, and their moderate correlation contributions were fairly well understood from previous configuration interaction studies. The connection between quadruple excitations in MP4 theory and size-consistency corrections in configuration interaction calculations or the relationship between MP4 and coupled cluster theory (*vide infra*) are important factors that contributed to the development of more accurate correlation methods. Perhaps the most important outcome of the development of the MP4 method was in understanding the importance of triple excitations. Systematic studies including triple excitations were performed for the first time,[15,16,18] and they showed that such three-electron correlation contributions are surprisingly large and cannot be neglected in any quantitative treatment of electron correlation. Understanding the fifth-order terms (MP5) also contributed further to the refinement of electron correlation techniques.[19,20] A complete analysis of the sixth-order terms (MP6) has also been performed recently.[21]

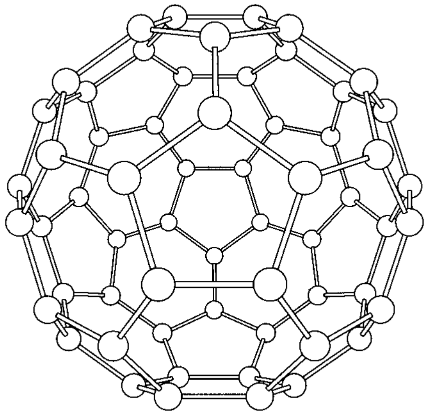

Figure 1. Icosahedral C_{60} molecule, viewed down a 5-fold axis.

Perturbation theory truncated at any order is size-consistent. The computational dependence increases steeply with the order of perturbation theory. Thus, MP2, MP3, MP4, and MP5 scale as the fifth, sixth, seventh, and eighth power of the size of the system. A major advantage of these methods is that they are not iterative unlike configuration interaction or coupled cluster schemes. In MP4 theory, the term which scales as the seventh power of the size of the system is the contribution of triple excitations. However, these terms can be evaluated using matrix operations and can be vectorized effectively on supercomputers. Thus, MP4 theory has been fairly widely used in spite of its seventh-order dependence. If triples are excluded from the MP4 method, the resulting MP4(SDQ) technique[15a] (including singles, doubles, and quadruples) can be evaluated with a sixth-order computational dependence. Fifth-order theory (MP5) has been implemented[19,20] though it is feasible only for small systems.

MP2 or second-order perturbation theory is by far the most applicable method for the treatment of electron correlation effects. There are two reasons for the wide applicability of the MP2 method. First, it is the only scheme discussed in this section which scales as the fifth power of the size of the system. All other correlation schemes scale as sixth (or higher) power. In addition, the MP2 method can be formulated and implemented completely without requiring the storage of two-electron integrals or many other intermediate quantities.[22] Such "direct"[23] formulations or "semidirect" schemes (where only a specified storage space is used) have made it possible to perform very large MP2 calculations even on workstations. For example, MP2 geometry optimizations have been performed on C_{60} (Figure 1) with fairly large polarized basis sets.[24] Table 1 lists the optimized bond lengths for the two distinct bonds in C_{60} at the HF and MP2 levels with three different basis sets. The experimentally observed difference between the two bond lengths (0.05 Å) is well reproduced at the MP2 level whereas HF theory overestimates this difference. These MP2 calculations with the TZP basis set involved 1140 basis functions and were performed using the full icosahedral symmetry of the C_{60} molecule.[24]

Apart from the energy itself, evaluation of molecular properties is also efficient for the MP2 method. Efficient implementations of the analytical first and second derivatives of the MP2

TABLE 1: Optimized Bond Lengths[a] (Å) for C_{60}

method[c]	parameter[b] r_{6-5}	r_{6-6}
HF/DZ	1.451	1.368
HF/DZP	1.453	1.372
HF/TZP	1.448	1.370
MP2/DZ	1.470	1.407
MP2/DZP	1.451	1.412
MP2/TZP	1.446	1.406
expt	1.45	1.40

[a] From the work of Häser et al.[24] [b] r_{6-5} refers to the bond length between a hexagon and a pentagon; r_{6-6} refers to the bond length between two hexagons. [c] DZ, DZP, and TZP refer to double-zeta, polarized double-zeta, and polarized triple-zeta basis sets, respectively.

TABLE 2: Calculated Excitation Energies (eV) Obtained with MP and QCI Methods[a]

atom	excitation	HF	MP2	MP3	MP4	QCISD(T)	expt
Sc	$d^1s^2 \rightarrow d^2s^1$	1.01	1.29	1.41	1.46	1.49	1.33
Ti	$d^2s^2 \rightarrow d^3s^1$	0.59	0.49	0.75	0.77	0.81	0.69
V	$d^3s^2 \rightarrow d^4s^1$	0.23	−0.24	0.20	0.12	0.21	0.11
Cr	$d^4s^2 \rightarrow d^5s^1$	−1.07	−1.65	−1.04	−1.24	−1.10	−1.17
Mn	$d^5s^2 \rightarrow d^6s^1$	3.19	1.76	2.60	1.98	2.24	1.97
Fe	$d^6s^2 \rightarrow d^7s^1$	1.83	0.21	1.40	0.37	0.86	0.65
Co	$d^7s^2 \rightarrow d^8s^1$	1.61	−0.58	1.12	−0.49	0.33	0.17
Ni	$d^8s^2 \rightarrow d^9s^1$	1.37	−1.37	0.92	−1.46	−0.18	−10.33
Ni	$d^9s^1 \rightarrow d^{10}$	4.32	−0.51	4.46	−3.42	1.70	1.57
Cu	$d^9s^2 \rightarrow d^{10}s^1$	−0.29	−3.28	−0.47	−3.63	−1.85	−1.85

[a] From the work of Raghavachari and Trucks.[32]

energy[25,26] are now available in popular quantum chemistry programs. Molecular geometries are significantly improved at the MP2 level relative to the HF results.[27,28] Vibrational frequencies and other properties have also been studied extensively with the MP2 method.[27,29] Recent results on NMR chemical shifts with the MP2 method also show promise.[30]

There have been only a few applications with the MP3 method. In most cases, the improvement obtained at third order does not justify the significantly higher computational expense. The fourth-order MP4 method, however, is used fairly widely. As mentioned earlier, the inclusion of the contributions of triple excitations for the first time has made MP4 studies fairly valuable. An analysis of the trends in the MP2, MP3, and MP4 energies shows, however, that for many systems the convergence of perturbation theory is slow or oscillatory, indicating that higher-order terms are important.[31,32] Slow convergence is seen in many molecules where spin contamination effects in the starting UHF wave function are significant.[31] Oscillatory behavior is seen in multiply bonded systems such as N_2 where correlation effects are typically overestimated at fourth order.[15c] An extreme case of oscillation occurs in transition metal systems, particularly if 3d to 4s excitations are involved.[32] Table 2 lists the atomic excitation energies for the first-row transition metal elements Sc−Cu using perturbation theory up to MP4. For the ^2S to ^2D electronic transition in the Cu atom, for example, the excitation energies using an spdf basis set at the MP2, MP3, and MP4 levels are 3.28, 0.47, and 3.63 eV, respectively, compared to the experimental value of 1.85 eV.[32] Infinite-order techniques such as the quadratic configuration interaction method or the coupled cluster method (*vide infra*) are replacing the perturbation treatments in such cases.

B. Configuration Interaction. Among the many schemes introduced to overcome the deficiencies of the Hartree−Fock method, perhaps the most simple and general technique to address the correlation problem is the method of configuration interaction (CI).[33] The CI method has been in practice from the early 1950s[34] and was the dominant and preferred electron correlation technique until the early 1980s when it was superseded by size-consistent techniques such as perturbation theory or coupled cluster methods. Many of the concepts related to the different electron correlation techniques are still conveniently introduced from the framework of configuration interaction.

Conceptually simple, configuration interaction is a straightforward application of the linear variational technique to the calculation of electronic wave functions. A linear combination of configurations (or Slater determinants) is used to provide a better variational solution to the exact many-electron wave function. In principle, by increasing the number of configurations included, the CI method is capable of providing arbitrarily accurate solutions to the exact wave function. Using common notation, the CI wave function mixes the Hartree−Fock wave function with single, double, triple, quadruple, ⋯ excited configurations, and the coefficients which determine the amount of mixing are determined variationally. If all possible excited configurations are included, the method gives the exact solution within the space spanned by a given basis set and is referred to as full configuration interaction (FCI).

The number of configurations in a FCI expansion grows exponentially with the size of the system. Clearly, FCI results are not practical for many-electron systems with large basis sets. However, they do provide "exact" solutions for small molecules with limited basis sets.[35] Such FCI calculations, though they cannot be compared to experimental results due to basis set limitations, nevertheless have been invaluable benchmarks for the calibration of approximate correlation techniques. When used with modest basis sets, they aid in evaluating the inherent errors due to the deficiency of the correlation methodology.

The number of configurations which can be included in a practical FCI calculation has grown dramatically over the years. Novel algorithmic developments including sparse matrix techniques utilizing the power of vector supercomputers have contributed toward this progress.[36,37] Recently, there has been significant progress in "controlled error" FCI methods[38] where the energy is accurate to some specified tolerance. Extrapolation techniques can then be employed to make accurate estimates of the FCI energy in the limit of zero tolerance. Calculations with up to several billion configurations have now been performed with the FCI method.[38]

The current status of such FCI calculations for a variety of molecular systems has been reviewed recently by Bauschlicher *et al.*[35] Among the earlier FCI calculations,[39] studies on water at R_e, $1.5R_e$, and $2.0R_e$ with double-zeta and polarized double-zeta basis sets have been compared to the results of almost all approximate electron correlation treatments. Other examples are CH_2 (singlet and triplet), NH_2 at several bond lengths, simple reactions such as $F + H_2 \rightarrow FH + H$, loosely bound systems such as He_2, etc.[39] Future extensions of FCI methods to systems containing more valence electrons or with larger basis sets will be very useful.

It is clear from the above examples that FCI calculations are only feasible for small molecules containing very few valence electrons. In order to turn the FCI equations into practical equations which can be applied to a much wider variety of problems, truncation of the configuration space is necessary, leading to limited CI techniques. The most common treatment is CI with all single and double excitations (CISD)[33] where triple, quadruple, ⋯ excitations are completely neglected. As mentioned earlier, double excitations contribute dominantly to the electron correlation energies. Single excitations contribute relatively little to the correlation energies, though they appear to be important for accurate evaluation of molecular properties. The CISD method is an iterative technique where the computational dependence of each iteration scales as the sixth power of the size of the system. Nevertheless, the CISD method has been applied to a wide range of chemically interesting problems. With the computational power available in today's workstations, CISD calculations can be easily performed on systems containing about 10 non-hydrogen atoms (e.g., naphthalene) using polarized double-zeta or triple-zeta basis sets.

The variational nature of the CI method also makes the analytical evaluation of the energy derivatives considerably simpler.[40−42] The CISD method has thus been used to evaluate a wide range of molecular properties such as geometries, vibrational frequencies, dipole moments, etc.[43] However, all the advantages of the CISD method are offset by its major deficiency; *viz.* the CISD energy is not size-consistent. The energy does not scale linearly with the size of the system, and CISD energy is not additive for infinitely separated systems. For example, the CISD energy for two infinitely separated He atoms is different from twice the energy of a single He atom. The reason for this deficiency is simple. For a single He atom which contains only two electrons, the CISD method is identical to FCI. However, for two infinitely separated He atoms, the CISD method does not include all excitations since it does not include the simultaneous excitation of electrons in both He atoms which is a quadruple excitation. In fact, for noninteracting He gas, the CISD energy for N atoms is proportional to $\sqrt{N}$.

Many correction schemes have been proposed to correct the CISD energies for this lack of size consistency. Langhoff and Davidson[44] were the first to propose a correction ("Davidson correction") for the effects of quadruple excitations, $\Delta E_{\mathrm{DC}} = \Delta E_{\mathrm{CISD}}(1 - C_0^2)$, where ΔE_{CISD} is the CISD correlation energy and C_0 is the coefficient of the Hartree−Fock configuration in the normalized CISD wave function. Many variants of this correction formula[45] have been proposed though the original Davidson correction is used most widely. Such corrections are easily justified by considering the contributions of quadruple excitations in a simple fourth-order perturbation expansion of the electron correlation energy. Alternative corrections for the lack of size consistency have also been proposed. A careful analysis of N noninteracting He atoms yields a correction formula which is exact for that case.[46] The performance of these and other size-consistency correction formulas has been carefully analyzed recently.[47] Overall, due to the approximate nature of such corrections and due to the efficient formulation of exactly size-consistent schemes, traditional methods such as CISD are no longer the methods of choice in ground state quantum chemical applications. For electronic excited states, however, the ease of definition of the CI method for any state of interest makes it an attractive method, and such calculations are performed fairly widely.

C. Quadratic Configuration Interaction. Quadratic configuration interaction (QCI) is a technique suggested by Pople *et al.*[48] which introduces size consistency exactly in CISD theory. It can be viewed as somewhat intermediate between configuration interaction and coupled cluster theory considered in the next section.[49,50] The CISD method consists of a set of linear equations in the configuration expansion coefficients (for single and double excitations) which are solved iteratively. In the QCISD method, these equations are modified by the introduction of additional terms, quadratic in the expansion coefficients, which make the method size consistent. Specifically, a term T_1T_2 ("disconnected triples") is included in the equation for single excitations and a term ${}^1/_2T_2{}^2$ ("disconnected quadruples") is included in the equation for double excitations. These terms are equivalent to including the higher excitations needed for size consistency in the CISD method. In addition to the resulting QCISD method, a *noniterative* treatment of triple excitations was introduced, leading to the QCISD(T) technique.[48]

We mention the QCI techniques only briefly in this review since the coupled cluster method discussed in the next section is formally a more complete theory. However, three points of the QCI method are very important. First, as in the case of the CISD method, the QCISD technique is exact for two electrons within the basis set space. However, unlike CISD, the QCISD method is size consistent and thus also exact for the noninteracting He gas. Second, the accuracy of the QCISD(T) method has been well tested by extensive applications to a wide variety of molecules. For example, the atomic excitation energies involving the transition metal atoms Sc−Cu are well reproduced by the QCISD(T) method as seen from Table 2.[32] The popularly used Gaussian-2 method (*vide infra*) for the evaluation of bond energies of molecules relies on the accuracy of the underlying QCISD(T) method. Third, the correction formula for triple excitations in the QCISD(T) method included a novel feature which made it more accurate than previously proposed formulas.

When the QCISD method was proposed in 1987,[48] it was well recognized that triple excitations are crucial in deriving accurate correlation energies. It was also realized that iterative evaluation of their contributions was not computationally feasible. As mentioned earlier, the contributions of triple excitations first occur in MP4 through their interaction with double excitations. Computational schemes had been proposed which included an MP4-like term for the contribution of triple excitations.[51] However, in the correction formula for triple excitations proposed for the QCISD(T) method, there were *two different noniterative* terms. While one was analogous to the MP4 term, the other resulted from the interaction of triple and single excitations which is analogous to an interaction occurring first in fifth-order perturbation theory. In retrospect, the presence of two different contributions in the triples correction has proved to be an important insight which is necessary for quantitative accuracy. In fact, the success of the QCISD(T) method for difficult problems such as ozone[52] eventually led to the proposal of the analogous coupled cluster method. Very recently, the more computationally demanding QCISDT method which includes the iterative contributions of triple excitations has also been proposed.[53]

D. Coupled Cluster Theory. Based on a well-founded theoretical structural framework, coupled cluster theory (CC) is steadily increasing in prominence as an effective and accurate technique for the treatment of electron correlation effects.[54−57] The CC method starts with the exponential form of wave function $\Psi = \exp(T)\Psi_0$ where $T = T_1 + T_2 + \cdots$. The exponential form of the operator introduces an efficient way of including the effects of higher excitations and also elegantly ensures size consistency in the calculated energy.

While many of the theoretical ideas on coupled cluster theory for molecular systems were formulated in the late 1960s,[53] it was not until the late 1970s that practical implementations started to take place.[58] The earliest implementation of CC theory used the wave function $\exp(T_2)\Psi_0$ and was referred to as CCD (coupled cluster doubles) or CPMET (coupled pair many-electron theory).[58,59] Today, the CC method is typically carried out including all single and double excitations (CCSD) with the wave function $\Psi = \exp(T_1 + T_2)\Psi_0$. First implemented in 1982,[60] the CCSD method has steadily increased in popularity. Today there are a wide variety of implementations[61] and computer program packages[13] available to perform CCSD calculations which are being used by many groups. The CCSD method is size consistent and exact for two electrons within the basis set space. Typically, a set of projection equations—one

TABLE 3: CCSD(T) Performance for Structures and Vibrational Frequencies[a]

parameter[b]	basis set	mean abs error	parameter[b]	basis set	mean abs error
r_{X-H}	spdf	0.0020	ν_{X-H}	spdf	11.0
r_{X-H}	spdfg	0.0014	ν_{X-H}	spdfg	8.3
r_{X-Y}	spdf	0.0057	ν_{X-Y}	spdf	14.8
r_{X-Y}	spdfg	0.0024	ν_{X-Y}	spdfg	6.4
θ	spdf	0.44	ν_{bends}	spdf	11.5
θ	spdfg	0.34	ν_{bends}	spdfg	8.6

[a] From the work of Lee and Scuseria.[57] [b] r, θ, and ν refer to bond length (Å), bond angle (deg), and vibrational frequency (cm^{-1}). X and Y represent first-row non-hydrogen atoms.

for the correlation energy and one for each of the unknown coefficients in the T operators—are used to solve iteratively for the wave function and the energy. The equations to be solved are nonlinear in the configuration expansion coefficients, but fast convergence is achieved relatively easily in most cases.[57]

As mentioned earlier, the contributions of triple excitations have to be included in any quantitative treatment of electron correlation. The CCSD method is exact for two electrons but still neglects these important three-electron correlations. Many schemes have been developed to evaluate their contributions effectively. One possible solution within coupled cluster theory is to formulate the CCSDT method[62] with the exponential form of the wave function [$\Psi = \exp(T_1 + T_2 + T_3)\Psi_0$]. Though accurate, the CCSDT method has an eighth-order dependence on the size of the system and is not practical. Several approximate schemes, referred to as CCSDT-*n*, were devised by Bartlett *et al.*[63] to make the calculations tractable. However, all these approximate CCSDT-*n* methods involve the treatment of triples (a seventh-order step) in an *iterative* manner. Such calculations are still too expensive to be generally applicable. Based on analogy with MP4 theory, a noniterative scheme, referred to as CCSD+T(CCSD),[51b] was proposed but was found to be insufficiently accurate for difficult examples. Finally, in analogy with the QCISD(T) method, a scheme referred to as CCSD(T) was proposed by Raghavachari *et al.*[64] Again, the triples correction formula has two terms, one each resulting from their interaction with single and double excitations. Proposed in 1989, the CCSD(T) method has remained one of the most accurate schemes available to evaluate electron correlation effects.[57,65]

The CCSD(T) method has been efficiently implemented in a variety of quantum chemistry program packages. Analytical energy derivatives can be evaluated for the CCSD method as well as the CCSD(T) method.[66] In conjunction with relatively large basis sets (spdf or spdfg), the CCSD(T) method has been used to investigate the equilibrium geometries, harmonic and fundamental vibrational frequencies, heats of formation, binding energies, dipole moments, polarizabilities, and other properties of a variety of small molecules.[57] Impressive accuracy has been attained for all the above properties, in most cases exceeding that achieved by other theoretical techniques. Table 3 lists the mean absolute errors for bond lengths and vibrational frequencies obtained with the CCSD(T) method for a set of small molecules from a recent review by Lee and Scuseria.[57] Impressive accuracy of ≈0.002 Å for bond lengths and ≈10 cm^{-1} for vibrational frequencies can be seen from Table 3. Electronic excited state formalisms based on CCSD theory have also been developed by several groups.[67] Accuracy of 0.1−0.2 eV has been obtained for low-lying electronic states which are dominantly one-electron excitations from the reference configuration.

Apart from the large basis set studies on small molecules, the CCSD and CCSD(T) methods have also been used with polarized double- and triple-zeta spd basis sets for larger molecules. Though a direct and accurate evaluation of bond energies is not possible with such basis sets, they are frequently adequate to provide reliable geometries, vibrational frequencies, and energy differences. The largest CCSD(T) calculation reported to date has been the study of three structural isomers of C_{20} with a polarized double-zeta basis set.[68]

TABLE 4: Comparison of Correlation Techniques in Fourth Order[a]

cost	method	S	D	T	Q
iterative o^2v^4	CISD	√	√		×
	QCISD	√	√		√
	CCSD	√	√		√
	BD	√	√		√
iterative o^2v^4 + one o^3v^4	CCSD + T(CCSD)	√	√	√	√
	QCISD(T)	√	√	√	√
	CCSD(T)	√	√	√	√
	BD(T)	√	√	√	√
iterative o^3v^4	CCSDT-*n*	√	√	√	√
iterative o^3v^5	CISDT	√	√	√	×
	QCISDT	√	√	√	√
	CCSDT	√	√	√	√

[a] √ indicates that this term is included correctly. × indicates that this term is only included partially.

E. Other Correlation Techniques. Apart from the correlation methods discussed above, there have been many other techniques which have been suggested and widely used over the years. In particular, several versions of CEPA (coupled electron pair approximation)[69,70] and CPF (coupled pair functional)[71] techniques have been successfully applied for a variety of problems. With the advent of new methods such as CCSD(T) which are size-consistent, exact within the basis set for two electrons, and correct to fourth order in perturbation theory, the need for these older methods appears limited. In particular, CEPA and CPF neglect the effects of triple excitations and include the contributions of quadruples only approximately in fourth order. These and other related methods are not considered in this review.

A noteworthy method which appears promising is based on Brueckner orbitals[72] instead of the Hartree−Fock orbitals as in the other methods. Brueckner orbitals are defined to be that set of orbitals for which the single excitation coefficients are zero, and these are often close to the natural orbitals for the system. The interesting aspect of Brueckner orbital methods which is not present in CC or QCI methods is that the equations defining the method are sufficient to determine the Brueckner orbitals themselves as well as the correlated total energy. However, since the Brueckner orbitals are not known, they have to be evaluated in an iterative manner which makes these calculations computationally more demanding.[58d] Handy *et al.*[73] have proposed the BD and BD(T) methods based on Brueckner orbitals which are analogous to the CCSD and CCSD(T) schemes. Preliminary applications[73] suggest that the BD method should extend the range of applicability of UHF-based methods in cases where spin contamination effects are significant. However, sufficient numerical results to permit a critical evaluation of the BD or BD(T) methods are not yet available. The BDT method, analogous to the CCSDT method, has also been proposed.[74]

F. Scaling and Limitations of Correlation Theories. The different correlation methods discussed so far can be compared to each other based on different criteria. From a theoretical point of view, a variety of techniques have been previously compared to each other based on their correctness in a low-order perturbation expansion.[20] For example, Table 4 lists the comparison of different correlation techniques in fourth order, and similar comparisons have been performed in fifth and sixth orders.[20,53] Accurate schemes such as QCISD(T) or CCSD(T) are correct to fourth order in a perturbation expansion and differ only slightly in fifth order. Another way of measuring the accuracy of different methods is by comparing their energies to the FCI energies for model problems or by calibrating their actual performance for difficult problems such as in calculating the geometry and vibrational frequencies of ozone.[8] Methods including the perturbative triples correction such as QCISD(T) or CCSD(T) perform very well in such comparisons.

In this section, we summarize the computational dependence of the different correlation techniques which is also listed in Table 4. In this context, it is important to distinguish between the iterative and noniterative computational requirements in methods where there is a one-time evaluation at the convergence of an iterative scheme. In this discussion we use the symbols o and v to denote the number of occupied and virtual spin orbitals. We assume that v is much larger than o as is typical in most realistic calculations with reasonably large basis sets.

Perturbation theoretical energies do not require any iterative steps. The rate-limiting steps in MP2, MP3, MP4, and MP5 calculations scale as ov^4, o^2v^4, o^3v^4, and o^3v^5. As mentioned earlier, the seventh-order scaling of the MP4 energy is in evaluating the contributions of triple excitations. The eighth-order step in the MP5 calculation is to evaluate a term resulting from triples−triples interactions.

The other techniques involve iterative steps. The leading term in the different iterative schemes CISD, QCISD, CCSD, or BD is o^2v^4 and is in fact identical for all the methods. However, the CISD method involves fewer o^3v^3 steps and is thus somewhat less expensive. In addition, these steps have to be applied at each iteration, which requires a further multiplicative factor n_{iter}, the number of iterations required for a converged solution.

The triples contributions introduce another order of complexity but are necessary for a quantitative solution. The schemes CCSD+T(CCSD), CCSD(T), QCISD(T), and BD(T) introduce the triples in a noniterative manner, so that the o^3v^4 step has to be evaluated only once. This, however, is still practical and can be applied to reasonably large problems. The approximate CCSDT-*n* models all include triples contributions in an iterative manner including at least the linear terms. Thus, all these methods require an o^3v^4 computation to be performed in each of n_{iter} iterations. This may limit the applicability of such methods in the case of larger molecules. The complete CISDT, QCISDT, or CCSDT calculations involve the evaluation of o^3v^5 interactions in *each iteration*. Thus, such schemes are applicable to only the smallest problems of practical interest. Overall, the CCSD(T) and QCISD(T) methods appear to be the most accurate, yet computationally tractable, schemes though recent experience on some challenging systems indicates that CCSD(T) is applicable for a wider range of problems.[75]

While the correlation effects within a given basis set are accurately treated by methods such as CCSD(T), the convergence of the calculated results with respect to basis set expansion is rather slow.[76−78] If we consider the classic problem of chemical bond formation, very high angular momentum functions appear to be necessary to derive the bond energies to chemical accuracy. For example, extensive calibration studies[78] of the contributions of higher angular momentum functions to the bond energy of N_2 have shown that f, g, and h functions contribute about 8, 3, and 1 kcal/mol, respectively, to the binding energy of N_2. Even for problems simpler than explicit bond breaking, basis sets involving spdf functions are typically necessary to get accurate results.[57]

The slow convergence of the electron correlation energy with the size of the basis set is now understood to result from the singularity in the interelectronic Coulomb repulsion energy at small separations, i.e., the existence of a cusp in the electronic wave function which approaches $(1 + {}^1/_2 r_{ij})$ at small r_{ij}. An accurate solution of the electronic cusp can be achieved by employing wave functions with explicit dependence on the interelectronic distance r_{ij}.[79] The difficulty of integral evaluation of such Hylleraas wave functions makes it difficult to implement such methods in a general manner. Recently, however, there have been two different approaches to deal with the electronic cusp problem. Kutzelnigg *et. al*[80] have used clever approximations in integral evaluations using closure approximations which make it possible to incorporate explicitly the interelectronic cusp behavior into the wave functions of polyatomic molecules. The method has been formulated for several electron correlation schemes including the coupled cluster method[81] though interesting applications have only been possible thus far at the MP2 level. The complete basis set (CBS) method of Petersson *et al*.[82] provides an alternative approach in which extrapolation techniques are used to overcome the slow convergence caused by the electronic cusp. Using the asymptotic convergence properties of the pair energies, infinite basis set limits have been obtained for a variety of small molecules.

G. Gaussian-2 Theory. The accuracy and range of applicability of single-configuration-based correlation techniques can be illustrated by the successes of a widely used composite model referred to as Gaussian-2 (G2) theory.[83] G2 theory and other related methods[84] were developed with the explicit goal of evaluating bond energies, heats of formation, ionization energies, and electron affinities of atoms and molecules to chemical accuracy (within 1 − 2 kcal/mol).

In G2 theory, a sequence of well-defined calculations are performed to arrive at the total energy of a given molecular species. A series of additivity approximations are made to make these techniques fairly widely applicable. G2 theory depends on the accuracy of the QCISD(T) correlation treatment and the transferability of basis set effects from perturbation theory. Initially, a QCISD(T) calculation with a polarized triple-zeta basis set,[11] 6-311G(d,p), is performed. The effects of diffuse sp functions and multiple sets of polarization functions (2df) are evaluated with the MP4 level of theory. The effects of larger basis sets containing (3df) polarization functions on nonhydrogen atoms and (2p) functions on hydrogens are evaluated with the MP2 method. The different corrections are all assumed to be additive. Since the basis set convergence is still very slow, a "higher level correction" which depends on the number of electrons in the system is applied to take into account the remaining deficiencies. Using such a composite but completely defined scheme, the atomization energies of a large number of molecules containing first- and second-row elements have been calculated with a mean deviation of 1.2 kcal/mol from experiment (Table 5).[83] Similar accuracy is also achieved for ionization energies, electron affinities, proton affinities, etc. Applications to small clusters of carbon (C_2−C_7) and silicon (Si_2−Si_7) indicate that such bond energies can be evaluated to an accuracy of 0.1−0.2 eV.[85] The exposed accuracy of G2 theory is high enough that in many instances these values have been used to correct experimentally derived energies. Comprehensive reviews of applications involving the G2 method have been recently reported.[86,87]

IV. Multiconfiguration-Based Theories

In the previous section, we discussed the different correlation techniques which have been developed starting from a HF wave

TABLE 5: Atomization Energies (kcal/mol) Calculated with G2 Theory[a]

molecule	atomization energy	molecule	atomization energy	molecule	atomization energy
LiH	56.6(0.6)	SH_2	173.0(−0.2)	CO_2	384.6(2.7)
BeH	45.5(−1.4)	ClH	102.6(0.4)	Na_2	19.2(2.6)
CH	80.5(0.6)	Li_2	25.9(1.9)	Si_2	73.6(−0.4)
$CH_2(^3B_1)$	178.6(−1.0)	LiF	137.5(−0.1)	P_2	114.7(−1.4)
$CH_2(^1A_1)$	172.0(1.4)	HCCH	387.2(−1.7)	S_2	97.4(−3.3)
CH_3	289.1(−0.1)	C_2H_4	531.7(−0.2)	Cl_2	55.8(−1.4)
CH_4	393.2(0.7)	C_2H_6	666.6(0.3)	NaCl	98.8(1.3)
NH	77.9(−1.1)	CN	176.0(−0.6)	SiO	188.8(−1.7)
NH_2	170.1(0.1)	HCN	302.8(1.0)	SC	170.5(1.0)
NH_3	276.5(−0.2)	CO	258.0(1.8)	SO	120.8(−2.7)
OH	101.6(0.3)	HCO	271.4(1.1)	ClO	61.2(−2.1)
OH_2	219.6(0.3)	H_2CO	359.3(2.1)	ClF	61.0(0.7)
FH	136.3(1.1)	H_3COH	482.3(1.5)	Si_2H_6	503.0(2.9)
$SiH_2(^1A_1)$	147.1(2.7)	N_2	223.8(−1.3)	CH_3Cl	372.1(1.1)
$SiH_2(^3B_1)$	123.8(0.4)	H_4N_2	404.4(−1.0)	CH_3SH	445.0(−0.1)
SiH_3	213.5(−0.5)	NO	150.6(0.5)	HOCl	156.8(0.5)
SiH_4	304.8(2.0)	O_2	115.6(−2.4)	SO_2	248.9(−5.1)
PH_2	144.9(0.2)	HOOH	252.1(−0.2)		
PH_3	226.4(−1.0)	F_2	36.6(−0.3)		

[a] From the work of Curtiss *et al.*[83] Values in parentheses are differences between G2 theory and experiment (i.e., G2 − experiment).

function. Methods such as CCSD(T) and QCISD(T) perform very accurately in many cases. However, for such methods to be successful, the starting HF configuration should still be the dominant component of the correlated wave function. In such cases, the correlation energies, though large, arise from relatively small contributions from a vary large number of configurations. This is usually referred to as "dynamical" electron correlation.

However, there are also many cases where such methods are not very useful because the starting HF wave function is not even qualitatively correct. For example, for a dissociating molecule with stretched bond lengths, the gap between the bonding and antibonding orbitals becomes very small, and excitations involving such antibonding orbitals become very important. A correlation treatment starting from a single HF configuration with occupied bonding orbitals may have large errors in such cases. It may be preferable to treat the system starting from a small number of configurations which arise from treating the bonding and antibonding orbitals on an equal footing. Such correlation involving large contributions arising from a few orbitals is referred to as "nondynamical" electron correlation.

Multiconfigurational self-consistent-field (MCSCF) wave functions are used to treat nondynamical correlation effects.[88,89] In this case, instead of a single configuration as in the HF method, a relatively small number of selected configurations are used. The weights of the configurations in such an expansion are optimized simultaneously with the orbitals by a variational procedure. By a proper choice of MCSCF configurations, qualitatively correct behavior in processes such as bond breaking can be achieved. Traditionally, the configurations included in an MCSCF calculation are selected using chemical insight and a knowledge of the important orbitals in the problem under investigation. Unfortunately, such a configuration selection may introduce a bias in the calculations, particularly if convergence with respect to the selection of configurations is not tested.

The bias involved in the selection of individual configurations in an MCSCF calculation can be removed by the complete active space (CAS) approach.[90] Here a set of active orbitals are identified, and all possible configurations of the active electrons in the space of the active orbitals are included in the MCSCF expansion. All the other orbitals are kept doubly occupied or empty as in a HF calculation. The selection of the active orbitals may still be a problem, particularly for larger molecules. Obviously, if all electrons and orbitals are included in the CAS space, the method is identical to full CI.

The inclusion of nondynamical correlation effects by an MCSCF method still is not adequate in many cases. Though qualitatively correct behavior is obtained, dynamical correlation effects have to be included for quantitatively accurate results. The CI approach has been successfully used, particularly for the treatment of excited states of molecules or reactive potential energy surfaces. In the MRD-CI method,[91] all double excitations with respect to a modest number of MCSCF configurations are considered, and those exceeding a certain threshold are included in the final variational treatment. Extrapolation procedures are sometimes used to estimate the approach to the full CI energy. Such MRD-CI methods have been successfully used over the years for a wide variety of problems in electronic spectroscopy.[92] In other applications, multireference CI procedures based on a CASSCF wave function have been used to calculate accurate binding energies of small molecules.[93] However, such CI methods are still not size consistent, and a generalized Davidson-type correction is frequently used to correct the energies.[94] Size-consistent formalisms such as multireference coupled cluster theory[95] have also been developed and applied to a modest number of systems.

A particularly successful method developed in recent years is based on second-order perturbation theory.[96] When applied to a CAS wave function, the method is referred to as CASPT2.[97] Unlike the Møller−Plesset perturbation theory based on the HF method, the choice of the zeroth-order Hamiltonian for the multireference case is not unique. In a popular implementation,[97] the diagonal and nondiagonal elements of the Fock matrix are used in the zeroth-order Hamiltonian. While variations are possible, well-defined models have been constructed and used to obtain electronic excited states for a fairly wide variety of organic molecules. Calculations up to about 12−15 active orbitals have been performed with this method.[98] Relatively large systems up to the size of porphine have been used to yield electronic excited states accurate to within 0.2 eV in many cases.[98]

The generalized valence bond (GVB) method[99] represents another popularly used electron correlation technique. GVB represents a class of MCSCF methods where valence bond type coupling between electron pairs is used to simplify the wave function. Chemical insight is frequently used to choose the active orbitals and to simplify the problem. Wave functions involving complicated spin couplings of a large number of electrons and orbitals can be used in the most general unrestricted GVB method. However, the form of GVB wave function which is most often used in practice is referred to as GVB-PP, where PP denotes perfect pairing (simplest type of spin pairing) between pairs of nonorthogonal orbitals coupled into a singlet. The advantage of such GVB-PP wave functions is that physical interpretation through association of each electron with an individual orbital is still possible, though some account of electron correlation is already included. A properly selected GVB-PP wave function can qualitatively describe all the important aspects of the potential energy surface for the molecule of interest including bond breaking. However, as in most MCSCF calculations, some configuration interaction type treatment is also necessary to attain quantitative accuracy.[100]

V. Quantum Monte Carlo Methods

Many different Monte Carlo techniques have been proposed for solving the Schrödinger equation, and they are collectively referred to as quantum Monte Carlo (QMC) methods. They provide an entirely different way of treating the effects of electron correlation. In most forms the QMC method treats electron correlation explicitly, and in some forms it treats electron correlation exactly. Unlike the conventional techniques discussed in the previous sections, QMC methods provide "error bars" in quantum calculations.[101]

Quantum Monte Carlo methods have given extremely accurate predictions of energies and structures for molecular systems containing a few electrons. For example, a QMC calculation[102] for the H_3^+ molecular ion was the first quantum calculation to achieve an absolute accuracy of 1.0 μhartree for a polyatomic system. In many such cases,[103−111] QMC methods can provide solutions of the time-independent Schrödinger equation without systematic error.

For systems with more than a few interacting electrons, neither QMC nor any other method can at present provide such "exact" results. However, for many larger systems QMC calculations provide some of the lowest-energy, most accurate results available. Many successful Monte Carlo calculations have been carried out using approximately correct fixed nodal hypersurfaces for systems ranging from atoms such as Be or Fe to solids such as carbon and silicon.[112−124]

The several QMC techniques currently used in calculations of electronic structure include the variational quantum Monte Carlo method (VQMC), the diffusion quantum Monte Carlo method (DQMC), and the Green's function Monte Carlo method (GFQMC).[125−127] Another method, the path integral quantum Monte Carlo (PIQMC), has interesting possibilities but has not yet found many applications. Several recent reviews of QMC methods are available.[128−133]

The VQMC method is similar to the conventional analytic variational method, but the integrals required are evaluated by Monte Carlo procedures. The first applications with the VQMC method for small molecules were made by Conroy in the late 1960s.[126] In a typical VQMC application, the expectation value of the energy for a trial function Ψ_t is determined using Metropolis sampling based on Ψ_t^2. The expectation value $\langle E\rangle$ is given by the average of local energies $E_{loc} = H\Psi_t/\Psi_t$.

In determining $\langle E\rangle$, it is not necessary to carry out analytic integrations, and the trial wave function may take any desired functional form. It may even include interelectronic distances r_{ij} explicitly. Thus, relatively simple trial functions may incorporate electron correlation effects rather accurately and produce expectation values of the energy well below those of the Hartree−Fock limit.

The DQMC or random walk simulation of the Schrödinger equation was suggested by Fermi in the 1940s and was applied in calculations of a few simple problems. The DQMC method may be considered as based on the similarity of the Schrödinger equation to the diffusion equation. If the wave function is defined as a function of imaginary time as well as position, one may obtain the Schrödinger equation in imaginary time:

$$\frac{\partial\Psi(\vec{X},\tau)}{\partial\tau} = \frac{\hbar^2}{2m}\nabla^2\Psi(\vec{X},\tau) - V\psi(\vec{X},\tau) \quad (1)$$

This is identical in form to Fick's diffusion equation to which a first-order reaction rate term is added,

$$\partial C(\vec{X},t)/\partial t = D\nabla^2 C(\vec{X},t) - kC(\vec{X},t) \quad (2)$$

A random walk procedure is used to simulate the differential equation. An initial distribution of particles or "walkers" is allowed to diffuse and multiply in a series of finite time steps. With increasing time and number of iterations, the normalized distribution of walkers approaches a "steady-state" distribution fluctuating about an average steady-state distribution which corresponds to the lowest-energy wave function satisfying the time-independent Schrödinger equation.

The Green's function quantum Monte Carlo method is similar to the DQMC method but takes advantage of the properties of Green's functions to eliminate errors associated with finite time steps. It was first applied by Kalos[134] in studies of the quantum mechanics of liquid helium clusters. The GFQMC method also has advantages in the treatment of nodal surfaces (see below) for few-electron problems, but it is seldom used for larger problems.

The DQMC and GFQMC methods yield samples of the wave function from which, in principle, all the properties of a system may be determined. The energy E may be determined directly from the growth rate of a walker population, but an importance sampling scheme proposed by Grimm and Storer[135] usually gives a higher accuracy in the energy.

Importance sampling can be used in a way which takes advantage of any prior knowledge of the wave function in the form of a trial wave function. The variances in the local energy and in the estimate of the true energy are greatly reduced by a good trial wave function. An ideal trial wave function is not only accurate but simple and compact to facilitate computations of the local energy which must be made repeatedly. The most successful thus far have been based on single-determinant self-consistent-field functions multiplied by electron−electron correlation functions of the Bijl[138] or Jastrow type which satisfy the cusp condition at $r_{ij} = 0$. It is possible to obtain very high accuracies by extending DQMC to calculate corrections to trial wave functions rather than the complete wave function.[136,137] Other more complex trial functions have also been proposed and used successfully for a number of different molecular systems.[115,139−141]

Unless the distribution of walkers in a DQMC or GFQMC calculation is restricted in some way, it will proceed to the nodeless ground-state wave function of a boson system. For a system of two or more electrons of the same spin the wave function must be antisymmetric to the exchange of electrons of the same spin and must contain one or more nodal hypersurfaces. The problem of restricting the distribution in order to obtain the desired solutions for fermion systems—the node problem[142,143]—has been the subject of a number of investigations.

Until the development of QMC methods, the structure and properties of nodal hypersurfaces received very little attention. In general, the symmetry properties alone are insufficient to specify the node structure of a system. DQMC calculations for small atoms and molecules using approximately correct nodal structures obtained from optimized single-determinant SCF calculations typically recover more than 90% of the correlation energies of these species and yield total electronic energies lower than the lowest-energy analytic variational calculations. These results suggest that optimized single-determinant wave functions have node structures which are reasonably correct. A careful investigation of the node structure of the wave function for the water molecule—in the 30-dimensional configuration space of this 10-electron system—has now been carried out.[143]

A. Exact Cancellation Methods. The "exact cancellation method" of QMC[144] may be used to solve the Schrödinger equation for systems of a few electrons without systematic error. It is not variational, and it does not give an upper bound to the energy. It gives the energy directly along with an error bar corresponding to a statistical or sampling error. To judge the

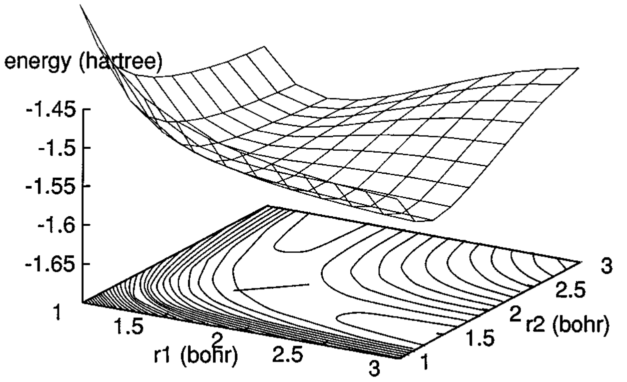

Figure 2. H−H−H potential energy surface obtained with quantum Monte Carlo techniques.[103]

accuracy of the calculations, it is not necessary to compare the results with experimental measurements. Neither "calibration" nor "benchmarking" is required.

In the exact cancellation method, a collection of positive and negative walkers (with appropriate enforcement of symmetry restraints) can be made to reproduce the distribution of walkers for the lowest-energy fermion ground state of a specified symmetry. Cancellation of positive and negative walkers in close proximity can be carried out efficiently on the basis of probabilities.[145] However, the requirements of cancellation limit the applications to systems having a small number of electrons (i.e., 2−4) or nonbonded systems in which the nodal surfaces are favorably located. Several related cancellation methods have also been investigated.[146,147]

One early application was that for the molecular ion H_3^+, which gave an energy of −1.343 835 ± 0.000 001 hartrees.[102] This was the first quantum calculation of any type to achieve an accuracy of 1.0 μhartree in the total energy of a polyatomic system. Other applications to nodeless systems include calculations for nuclei and electrons of the molecule H_2. This avoids the Born−Oppenheimer approximation in determining the energy of the molecule and results in an uncertainty of only 0.2 cm^{-1} in that energy.

Exact quantum Monte Carlo calculations[103] have produced a potential energy surface for the reaction $H + H_2 \rightarrow H_2 + H$ accurate to within ±0.01 kcal/mol at the saddle point and within ±0.10 kcal/mol or better elsewhere on the surface. This surface is illustrated in Figure 2. For the dimer He−He exact quantum Monte Carlo calculations[104] yield energies accurate within ±0.000 0003 hartree or ±0.10 K at the equilibrium separation of 5.6 bohrs. For the total energy, the quantum Monte Carlo calculations are more accurate than the lowest-energy variational calculations by approximately 1200 K. Nevertheless, the calculated potential energy curves—the energies relative to separated atoms—for the Monte Carlo and the lowest-energy variational calculations are in excellent agreement with each other and with an experimental−theoretical compromise curve based mostly on experimental data. Other systems for which exact cancellation has been used to overcome the node problem include the weakly attractive H−He pair[148] and the trimer He_3.[107]

In its current form the exact cancellation method is limited to applications similar to those listed here. The higher dimensionality and lower symmetry of larger systems require prohibitively large numbers of walkers for cancellation to be effective. Nevertheless, when it can be used, the exact cancellation method is clearly the method of choice for small systems.

B. Released-Node Method. Another "exact" method giving results without systematic error is known as the released-node method.[108,149] This method has been applied with success to molecules containing a few electrons and to extended systems such as the electron gas. It has been applied to molecular systems of 10 electrons with only limited success.

In this method, the nodes are released to obtain a "transient estimate" of the wave function. The wave function is obtained as the difference between positive and negative populations which, in effect, are released from an approximate distribution obtained from a fixed-node calculation. The higher states decay away to produce a transient approximation to the fermion ground state before both positive and negative distributions approach the boson ground state, and the difference between them disappears. The computational effort for high accuracy is large, and use of the transient-estimate method is restricted to systems with characteristics especially favorable to it.

Released-node calculations of several varieties have been carried out for the molecule LiH.[108−111] The calculated energies are lower than those of prior variational calculations, and they are in excellent agreement with the nonrelativistic energies derived from experimental measurements. For the most recent calculations,[111] the uncertainty in the calculated total energy for LiH at an internuclear separation of 3.015 bohrs is ±0.000 05 hartree.

Released-node calculations for the electron gas[149] with 54 electrons were carried out more than a dozen years ago. Results of those calculations have provided data on electron correlation essential for the LDA approximation of density functional theory. It is likely that similar calculations will also provide the information essential for higher-level approximations in density functional theory.

C. Fixed-Node Methods. The fixed-node method[112,113] was the first method to be proposed for treating the node problem in QMC. It has the advantage of simplicity, and the energies determined in such calculations, though not exact, are upper bounds to the true energy. The energies are "variational" with respect to the assumed node structure. Generally, it has been found that wave functions having nodes which are approximately correct yield excellent energies. Nearly correct nodal surfaces are most readily available from approximate wave functions provided by analytic variational calculations at the SCF level.

Fixed-node calculations may be carried out using a simple diffusion quantum Monte Carlo procedure[150] with importance sampling[114] or with a Green's function approach.[151] The boundary condition of $\Psi = 0$ at the nodal surface is treated as a sink for walkers. Importance sampling is easily incorporated using a trial wave function which specifies the nodal surface.

Accurate calculations for systems with nodes include those for the first-row atoms, along with their negative and positive ions, and the molecular systems H_4,[152] H−H−H,[153,154] LiH,[155,156] H_2O,[118] CH_4,[117,118] HF,[119] and many others. The trial wave functions for most of these calculations were taken from relatively simple analytic variational calculations at the SCF level. For example, a typical trial function for the 10-electron system methane[118] is given by the product of the SCF function, which is a ten-by-ten determinant made up of two five-by-five determinants, and a Bijl or Jastrow function for each combination of electrons.

For systems of 10 or more electrons the fixed-node DQMC total energies are generally lower than those of analytic variational calculations.[150,153,157,158] In the case of methane, fixed-node DQMC calculations[117,118] have given a total electronic energy 35 kcal/mol below that of the lowest analytic variational calculation and only about 1−2 kcal/mol above the energy estimated from measurements. This corresponds to the recovery of 99.3% of the correlation energy. For H_2O and HF the recovery of correlation energy in similar calculations is 93−95%.

The case of the F−H−H system—the potential energy surface for the reaction $F + H_2 \rightarrow HF + H$—illustrates the problems which may result from the residual node location error in fixed-node calculations. The calculated barrier height (relative) for collinear reaction from QMC calculations with nodes from SCF calculations is about 4.6 kcal/mol.[119] The node location error for reactants $F + H_2$ is about 8 kcal/mol, but that for the barrier region is unknown, although it may be expected to be similar. One is left with the same problem as in analytic variational calculations: one must compare results with experiment to determine the accuracy of the calculation. In this case the collinear barrier height from the best available analytic calculations[159] is about 2 kcal/mol, and this appears to be consistent with experimental observations.

For systems containing atoms heavier than Ne, the problem of treating both core and valence electrons in QMC calculations increases rapidly with nuclear charge. The energy associated with the core electrons becomes large, and the statistical error in that energy tends to produce an unacceptable statistical error in the total energy. Further, the time step for core electrons must be shorter than that for valence electrons, and this leads to inefficient calculations. One method of improving the efficiency is the "damped core" method in which the core electrons are treated by VQMC and the valence electrons by DQMC.[160] This method has been applied in a few cases and several variants have been proposed, but the most successful approach thus far has been to eliminate core electrons entirely with the use of pseudopotentials.

D. Use of Pseudopotentials. As in conventional quantum chemical studies, quantum Monte Carlo calculations can be applied to systems which have been greatly simplified by the use of pseudopotentials or pseudo-Hamiltonians (effective potentials or effective Hamiltonians). Since this has the effect of eliminating the "variational upper bound" properties of fixed-node QMC calculations and the "exact" properties of cancellation QMC, one loses important characteristics and introduces uncertainties with the use of pseudopotentials, but often there is little choice. The available alternatives are less attractive. The optimistic expectation is that the errors in total energies will be nearly the same for different nuclear configurations and will cancel each other when relative energies are determined by subtraction.

The pseudopotentials normally used in analytic variational calculations are nonlocal potentials which involve angular projection operators which cannot be simply transferred into QMC calculations. In the first QMC calculations[161] to use pseudopotentials, this difficulty was avoided with the use of simplified effective potentials. Though their use has been debated, the errors introduced have thus far been found to be small. In later work nonlocal effective potentials[162−164] have been used with success as have their more complex counterparts, effective Hamiltonians. These too introduce errors which are not easily analyzed or understood, but they appear to be small. These matters have been discussed in recent reviews.[164,165]

Quantum Monte Carlo calculations using pseudopotentials and pseudo-Hamiltonians have been made for atoms ranging from Li[166] to Y.[165] The number of noncore electrons treated has been limited to about eight per atom as in the determination of the electron affinity of Br.[167] In some cases as for PsCl, positrons have been included in the same way as electrons.[168]

Calculations of energies for the ^2D and ^2F states of atomic Sc and Y illustrate the accuracies obtained in fixed-node diffusion quantum Monte Carlo calculations using simple effective potentials. In these fixed-node calculations[165] the computed excitation energies for the transitions between the two states were 1.5(3) and 1.4(2) eV respectively for Sc and Y. These may be compared to the experimental values of 1.43 and 1.36 eV, respectively.

The valence correlation energy for Ne calculated by fixed-node DQMC with a two-electron effective potential is in excellent agreement with previous full-CI benchmark calculations.[169] The calculation recovered 98−100% of the valence correlation energy, and no significant error due to the effective potential approximation could be detected.

Fixed-node QMC calculations[122] with nonlocal pseudopotentials have also carried out for a number of configurations of carbon clusters C_{10} to C_{20} and indicate the utility of these methods. Companion calculations using Hartree−Fock, density functional, and coupled-cluster methods allow a comparison of results. In calculations for ring, bowl, and cage structures of C_{20}, different methods make different predictions for the lowest-energy structure as follows: HF, ring; LDA, cage; DQMC, bowl. Though the experimental energies for such species are not yet known, these results indicate the extreme importance of electron correlation in determining the structures of such systems.

Applications to systems with larger numbers of electrons have been made primarily in the area of crystalline solids. This is an area in which QMC methods appear to have very definite advantages over other methods. One of the first applications of QMC with pseudopotentials was in VQMC calculations for carbon (diamond), carbon (graphite), and silicon (diamond structure).[170] Cell sizes of up to 216 electrons (corresponding to 54 carbon atoms) were used. Results for several basic properties of these materials were found in very good agreement with experiment. Fixed-node DQMC calculations have also been performed for silicon and have given an extremely accurate prediction for the cohesive energy of the lattice.[124]

VI. Density Functional Theory

Traditionally developed and applied to the study of solids, density functional theory[171] is being increasingly applied to the study of molecules. In this method, the correlation energy (along with the exchange energy) is treated as a functional of the three-dimensional electron density. While the exact functional is not known, many approximate functionals have been developed and used successfully for a variety of problems. The original scheme used widely for solids[172] was derived from the available numerical results of the uniform electron gas[149] and is referred to as "local density functional" method. While quite successful for geometries and vibrational frequencies, the local density functional method is known to overestimate the binding energies of molecules substantially.[173] A variety of "gradient corrected density functional" methods[174,175] have been developed which have been remarkably successful for a range of problems including binding energies of molecules.[174,176] The attractive aspect of such methods is that computationally they are comparable to or cheaper than Hartree−Fock calculations. They converge relatively rapidly with basis set expansion so that moderate polarized basis sets yield converged results. Their major deficiency is that they cannot be systematically improved, and derivation of newer more accurate functionals appears to be difficult. While not as accurate as CCSD(T), the combination of speed and sufficient accuracy makes them particularly effective for larger molecules. With the advent of newer algorithms with near-linear scaling,[177,178] they are computationally feasible for the study of large molecules. The reader is referred to some recent reviews of this rapidly growing field.[178−180]

VII. Conclusions

It is clear that dramatic progress in the treatment of electron correlation effects has been achieved. Accurate techniques are now available for evaluating the structures and properties of many small molecules. However, successful methods such as CCSD(T) are not yet currently applicable to large molecules due to the stringent basis set requirements and high-order scaling with system size. Future work focusing on the development of efficient and accurate techniques for larger molecules is needed. Among the promising avenues of exploration are local orbital methods,[181,182] approximate integral schemes,[183−185] and pseudospectral techniques.[186,187] For Monte Carlo methods, additional techniques to evaluate energy derivatives and molecular properties are needed. As new techniques develop and mature, exciting applications in novel areas of chemistry will be possible.

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