

stretching vibration and the $\sim 310\text{-cm}^{-1}$ band to the M-OH₂ (equatorial) stretching vibration.

As it is suggested that all three configurations have a similar stability,¹⁴ it is impossible to draw a definite conclusion about the

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configuration of [Sc(OH₂)₇]³⁺ ion from the present experimental data.

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FEATURE ARTICLE

Coupled-Cluster Approach to Molecular Structure and Spectra: A Step toward Predictive Quantum Chemistry

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One goal of ab initio quantum chemistry is to be predictive. Predictive quantum chemistry requires a very accurate inclusion of the essential effects of electron correlation. Coupled-cluster theory offers a novel, elegant approach for correlation that has had a dramatic impact on the field in the past decade and is destined to have increasing importance in the future. This survey assesses that development, provides a variety of illustrative applications, and emphasizes some of the new concepts that emerge from many-electron cluster theory.

Preface

In the application of ab initio quantum chemistry we have reached a certain level of capability. As stated in the Pimentel report¹

“With today’s computers, the structure and stability of any molecular compound with up to three first-row atoms can be calculated almost to the best accuracy available through experiment. This capability gives to the chemist many situations not readily accessible to experimental measurement. Short-lived reaction intermediates, excited states, and even saddle points of reaction can now be understood, at least for small polyatomic molecules.”

The considerable success of predictive, ab initio quantum chemistry is apparent. Yet, for quantum chemistry to advance, the qualifications in the above quote (“three first-row atoms”, “almost to the best accuracy”, “small polyatomic molecules”) have to be addressed. The questions chemists are asking theorists for small molecules frequently require much greater detail than currently available, and accurate studies of large molecules will become essential. What is prohibiting us from obtaining the accuracy we want?

In the solution of the bound-state Schrödinger equation for molecules, there are really only a few limitations: basis sets, electron correlation, the number of atomic degrees of freedom, relativistic effects, and other corrections like that due to the Born-Oppenheimer approximation.

The limitation on the size of molecule for which the Schrödinger equation can be approximated accurately largely comes from the above limitations. The computer resources required for the simplest ab initio method, Hartree-Fock self-consistent-field (SCF) calculations scale as the fourth power of the number of basis

functions (n^4); n is typically 2-5 times the number of electrons. Yet without electron correlation we can seldom expect to be predictive. Correlated calculations scale at least as n^5 but usually $\sim n^6$ - n^7 . Considering that there are roughly $3N$ degrees of freedom for N atoms and that even with analytical gradients several correlated calculations will typically need to be performed for each degree of freedom, the determination of potential energy surfaces which entails locating minima and saddle points for different electronic states is difficult, even without the added complication of relativistic effects and other corrections.

The purpose of this article is to primarily focus on one of these limitations, *the correlation problem*, and one prominent new approach to its solution, coupled-cluster (CC) theory. Besides providing highly accurate results, CC theory offers some new concepts in quantum chemistry. For ab initio CC methods to reach their ultimate accuracy, however, the question of basis sets and gradient methods are equally essential and will be briefly addressed in the context of CC theory.

Introduction

The coupled-cluster theory of electron correlation owes some of its conceptual basis to the correlated electron pair theories of Nesbet² and Sinanoglu.³ However, the rigorous structure has its origins in the so-called linked diagram theorem⁴ which states that the exact electronic wave function and energy can be written as a sum of only *linked diagrams* in field theory language or, equivalently, as an *exponential* of cluster operators. This guarantees correct scaling with the number of electrons, or size ex-

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tensivity. Though similar in concept to that of Ursell and Mayer in statistical mechanics, the exponential ansatz that defines the coupled-cluster approach to electronic and nuclear structure was introduced by Coester and Kümmel.⁵ Explicit equations for the simplest method, coupled-cluster doubles (CCD), were first derived by Cizek,⁶ who also presented a diagrammatic approach to derive working equations for general CC models. CC theory can be viewed as a way to systematically sum classes of terms (i.e., diagrams) in many-body perturbation theory (MBPT)^{4,7-9} to all orders, as shown by Hubbard.¹⁰ Today, the distinction between MBPT and CC theory is that MBPT (later also becoming known in chemistry as Møller–Plesset (MP) perturbation theory¹¹ is usually used to include *all* terms through some finite order in electron correlation with full fourth order (MBPT(4)) being common,¹² while CC theory sums selected categories of MBPT diagrams to *all* orders.⁹

Semiempirical applications of CC theory were presented in the 1960s (for a review see ref 13), with a minimum basis ab initio example presented by Paldus et al. in 1972.¹⁴ General purpose ab initio programs for chemically interesting applications of the CCD method were developed in 1978 by ourselves¹⁵ and Pople et al.¹⁶ (See also ref 17 for a different computational approach.) Purvis and I formulated and implemented the full CCSD (single and double excitations) method.¹⁸ Later, Lee, Kucharski, and I devised and implemented CCSDT-1,¹⁹ which includes only the principal triple-excitation effects. Finally, results obtained by using the full CCSDT method were presented by Noga and myself.²⁰

Besides the investigators mentioned above, several other quantum chemistry groups have adopted and developed CC methods for different chemical applications, including Dykstra, Kaldor, Kutzelnigg, Monkhorst, Mukherjee, Nakatsuji, Simons, Schaefer, and co-workers.²¹ CC methods have now been de-

veloped for ionization potentials,²² some different approaches for excitation energies,^{23,24} properties,²⁵ electron affinities,²⁶ for energy gradients²⁷⁻²⁹ to help in efficiently searching potential energy surfaces and to predict vibrational spectra; and a variety of multireference extensions.³⁰ The CC approach is taking its place among the most accurate and applicable quantum chemical methods available today.

The following article summarizes *my group's* work in this rapidly evolving field. Following a discussion of the rationale for the CC approach and a synopsis of the theory, the article presents a series of numerical examples to illustrate the accuracy attainable and some limitations. Since CC theory and some of its multireference generalizations use rather different ideas than more conventional quantum chemical methods, I will also attempt to describe these different concepts without undue technical detail.

Rationale for Coupled-Cluster Theory

The primary element that distinguishes “many-body” quantum mechanical methods like CC and its finite-order MBPT approximations from most correlated methods is correct scaling with size. This is an essential property in accurate applications of theory to chemistry and a consequence of the underlying dependence on the linked diagram theorem of many-body methods.

To illustrate, consider the solution to the Schrödinger equation for a lattice of M noninteracting molecules $p = 1$ to M . If $\Psi(p)$ is the wave function for the p th molecule, we have $H(p)\Psi(p) = E(p)\Psi(p)$. Hence, the “lattice” wave function Ψ^L is the simple product

$$\Psi^L = \prod_{p=1}^M \Psi(p) \quad (1a)$$

$$H^L \Psi^L = E^L \Psi^L, \quad E^L = \sum_{p=1}^M E(p) \quad (1b)$$

(Antisymmetrization is irrelevant since there is no overlap of the component wave functions.) H^L and E^L are the Hamiltonian and a *nondegenerate* energy for the noninteracting lattice. This is simply a statement that the energy scales properly with molecular size, or is (size) “extensive”.³¹

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In the Hartree–Fock or self-consistent-field (SCF) single-determinant approximation, each $\Psi(p)$ is replaced by $\Phi_0(p)$, which is in turn usually represented as a determinant of n_p molecular (spin) orbitals, ϕ_j^p , one for each of the n_p electrons

$$\Phi_0(p) = \mathcal{A}(\phi_1^p \dots \phi_{n_p}^p) \quad (2)$$

(\mathcal{A} is the antisymmetrizer $(n_p!)^{-1/2} \sum_{\mathcal{P}} (-1)^{\rho} \mathcal{P}$ where \mathcal{P} indicates the permutation operator and ρ is its parity which simply forms a determinant of the spin orbital product). The orbitals ϕ_j^p are assumed localized on the p th molecule. $\Phi_0(p)$ can represent a closed-shell (RHF) or open-shell (UHF, ROHF) single-determinant solution. The latter “independent-particle model” constitutes the foundation for much of our qualitative understanding of molecules and a large part of our quantitative calculations, but it should be remembered that “orbitals” are just an approximation to reality for more than one-electron systems. Clearly, the lattice wave function Φ_0^L and energy E_{SCF}^L

$$\Phi_0^L = \prod_{p=1}^M \Phi_0(p), \quad E_{\text{SCF}}^L = \sum_{p=1}^M E_{\text{SCF}}(p) \quad (3)$$

satisfy the extensive property.

The SCF theory makes the assumption that one electron moves in an *average field* of $n_p - 1$ other electrons. Electrons are charged, however, and have instantaneous interactions among themselves, which causes their motions to be “correlated”. Since the effect of electron correlation is to keep electrons apart, diminishing their mutual repulsions, the exact “correlated” wave function for a molecule has a lower energy. The energy difference is called the “correlation” energy, or correlation error when referring to molecular properties in general. We will define the correlation error as the difference between the HF (RHF, UHF, or ROHF) result and the “exact” result once correction has been made for relativistic effects, $\Delta E = E_{\text{HF}} - E_{\text{exact}}$. The *correlation problem* has been the focal point of ab initio quantum chemistry for about 30 years.³² Without allowance for electron correlation we cannot expect to be “predictive” for most properties.

For simplicity, let us think of each of our $\Psi(p)$ above as ground-state H_2 molecules, which are conceptually like a series of noninteracting electron pair bonds in a saturated molecule. Then $\Phi_0(p) = \mathcal{A}(1\sigma_g\alpha(1)1\sigma_g\beta(2))$, where the molecular spin orbitals are given their usual $1\sigma_g$ designation with α or β spin attached. To introduce electron correlation into H_2 , we conceive of a set of unoccupied molecular orbitals (MO), $1\sigma_u, 2\sigma_g, 1\pi_u, \dots$, that along with $1\sigma_g$ form a complete (usually infinite) set of orbitals. In practice, a finite linear combination of AO's (usually contracted Gaussian functions) is used to represent the MO's, thereby restricting the number of MO's to the same dimension as that for the AO basis and thereby introducing the inevitable basis set error. We introduce electron correlation by formally allowing the two electrons to spend “time” in each of these previously unoccupied spin orbitals so that the electrons are better able to spatially avoid each other. Labeling the occupied orbitals i, j, k, l, \dots and the unoccupied orbitals a, b, c, d, \dots , this is accomplished via configuration interaction by constructing the wave function

(31) This term, introduced in ref 15 above, is related to the term “size consistent” introduced in Pople et al.¹¹ but does not mean exactly the same thing. Strictly speaking, (size) extensive means a method has no unlinked diagrams. Pople et al.'s term means that a quantum chemical method should give the same results in the noninteracting limit where only atoms (or fragments) are present when they are treated separately, or if they were treated as a supermolecule. The extensive condition guarantees the additivity in the noninteracting limit in the latter, but the converse is not true. Once interactions are introduced, extensivity or the absence of unlinked diagrams is well-defined, but size consistency is defined only in the noninteracting limit. Also, extensivity is rigorously defined for an atom, unlike size consistency which requires a molecular definition. In the following text we use the noninteracting limit initially as a pedagogical device to introduce the exponential ansatz, but at the end, we guarantee there are no unlinked diagrams in the CC method by virtue of the exponential ansatz, regardless of the degree of interaction. See footnote 2, p 364, ref 9a, for other distinctions between extensivity and size consistency, particularly with regard to correct separation of a molecule into its fragments, which is a different property.

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$$\Psi(p) = \Phi_0(p) + \sum_{i,a} C_i^a D_i^a + \sum_{\substack{i<j \\ a<b}} C_{ij}^{ab} D_{ij}^{ab} = \Phi_0(p) + \chi(p) \quad (4)$$

The singly and doubly excited determinants are

$$D_i^a = \mathcal{A}(\phi_a(1) \phi_j(2)) \quad \text{and} \quad D_{ij}^{ab} = \mathcal{A}(\phi_a(1) \phi_b(2))$$

The coefficients C_i^a and C_{ij}^{ab} weight the “time” the electrons are allowed to spend in the “unoccupied” orbitals. The two-electron antisymmetrized products define a Hilbert space, and $\Psi(p)$ is the exact, “correlated” solution for H_2 in the MO basis, with $\chi(p)$ the correlation correction to the reference wave function, $\Phi_0(p)$.

Just as the single-determinant approximation satisfies the extensive property, the product of CI wave functions like those in eq 4 must be the exact solution for the full lattice (within the MO basis).

Before we analyze that solution further, however, we can simplify the analysis by choosing our orbitals $\{\phi_j^p\}$ not to be HF–SCF orbitals, but, instead, the “natural orbitals”, which are a transformation of the SCF orbitals. These orbitals have the advantage that $C_i^a = 0$, and $\chi(p)$ only consists of double excitations. Our product wave function for the lattice is then

$$\Psi^L = \prod_p (\Phi_0(p) + \chi(p)) = \prod_p \Phi_0(p) + \sum_k \prod_p \Phi_0(p) \chi(k) / \Phi_0(k) \\ \Psi^L = \Phi_0^L + \sum_k \Phi_0^L \chi(k) / \Phi_0(k) + \sum_{k,l} \Phi_0^L \chi(k) \chi(l) / \Phi_0(k) \Phi_0(l) + \dots \quad (5)$$

and the energy for the lattice is

$$E^L = ME(\text{H}_2) = M[E_{\text{REF}}(\text{H}_2) + \Delta E(\text{H}_2)] \quad (6)$$

The exact wave function in eq 5 consists of double, quadruple, hextuple, etc., up to $2M$ -tuple excitations for M H_2 molecules. Equation 5 is equivalent to a “complete” CI in a *complete* basis of orbitals (the exact solution) and is the “full” CI in a finite basis (basis set limit solution).

Now consider the configuration interaction model limited to double excitations (CID). For a single H_2 molecule we have eq 4, and for the lattice

$$\Psi_{\text{CID}}^L = \Phi_0^L + \sum_k C_k \Phi_0^L \chi(k) / \Phi_0(k) = \Phi_0^L + \sum_{\substack{i<j \\ a<b}} C_{ij}^{ab} D_{ij}^{ab} \quad (7)$$

Since the CID wave function is exact for each H_2 molecule, and since their product is given by eq 5, eq 7 cannot be the exact wave function for the lattice. Instead, the new CI coefficients $\{C_{ij}^{ab}\}$ are to be determined by the variational principle to obtain the lowest possible energy, so the higher excitation effects neglected are partly replaced by adding additional flexibility through the coefficients, but we still have an error. How large is the error?

We can readily solve the model problem for M H_2 molecules,³³ and we find that the correlation energy error in CID for $M = 2$ is 1.5%, 4.8% for $M = 4$, and 10% for $M = 8$. For a molecule with a separated pair structure of the size of benzene ($M = 21$) the error would be more than 20%, or ~ 200 kcal/mol. As the molecule gets larger, there are much greater errors. Clearly, if we also include quadruple excitations in CI, we would now have an exact result for $M = 2$ but would have errors starting with $M = 3$. Similarly, we can continue to reduce this “extension” error the more high excitations we include, until we reach the full CI, which has all up to $2M$ -fold excitations and is the exact, size-extensive result.

Rather than absolute energies, energy differences are of importance in chemistry; and these, too, are affected by the extensivity property. One particularly important property for chemistry is that the heat of reaction for $A + B \rightarrow C + D$ should be obtained by differences of heats of formation for the components. However, since $\Delta H_f(C+D) = \Delta H_f(C) + \Delta H_f(D)$ only when $\Psi(C+D) = \Psi(C)\Psi(D)$, the extensivity property is essential to even construct a table of *computed* ΔH_f to use in such analyses. Furthermore,

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if the two states whose difference is of interest do not scale correctly, then the difference will not necessarily do so. Hence, excitation energies between different electronic states are another property that will not automatically scale properly with size.³⁴ Also, the electronic density, which is ultimately responsible for all observable properties, will not have the correct M dependence if its corresponding approximate wave function does not.³⁴ Clearly, it is desirable that the theories employed in quantum chemistry be extensive and essential for anticipated application to biochemically important molecules, polymers, surface phenomena, and the solid state.

Coupled-Cluster Equations

To ensure the extensive property, many-body quantum chemical methods like coupled-cluster (CC) theory differ from CI as they are based upon an *exponential* wave function

$$\Psi_{\text{CC}} = \exp(T)\Phi_0 \quad (8)$$

T is defined to be an operator that creates excitations from an independent particle reference, where

$$T = \sum_q T_q = T_1 + T_2 + T_3 + \dots \quad (9)$$

The operation of T_2 gives, e.g.

$$T_2\Phi_0 = \sum_{\substack{i>j \\ a>b}} t_{ij}^{ab} D_{ij}^{ab} \quad (10)$$

The coefficients (operator amplitudes), $\{t_{ij}^{ab}\}$, are different from the CI coefficients $\{C_{ij}^{ab}\}$ since for the CCD wave function the exponential expansion

$$\psi_{\text{CCD}} = \exp(T_2)\Phi_0 = (1 + T_2 + T_2^2/2 + T_2^3/3! + \dots)\Phi_0 \quad (11a)$$

gives

$$\psi_{\text{CCD}} = \Phi_0 + \sum_{a>b} t_{ij}^{ab} D_{ij}^{ab} + 1/2 \sum_{\substack{i>j \\ a>b}} \sum_{\substack{k>l \\ c>d}} t_{ij}^{ab} t_{kl}^{cd} D_{ij}^{ab} D_{kl}^{cd} + \dots \quad (11b)$$

and we have quadruple, hextuple, etc., excitations introduced into the wave function via a number of "disconnected" terms like $T_2^2/2$ until $T_2^n/n!$ vanishes for $n/2$ electrons. However, these higher excitation terms are not introduced in the most general way possible, since their coefficients are *products* of just double-excitation coefficients. If n_{occ} and n_{virt} are respectively the numbers of occupied and "virtual" (i.e., unoccupied) orbitals, then there would be asymptotically $\sim n_{\text{occ}}^4 n_{\text{virt}}^4 \sim n^8$ quadruple excitations with an equivalent number of coefficients to determine in the CI (requiring about an $\sim n^{10}$ computational procedure). But there are only $\sim n_{\text{occ}}^2 n_{\text{virt}}^2 \sim n^4$ double-excitation coefficients to determine in CCD (an $\sim n^6$ procedure), which is obviously far simpler computationally. In practice, the product approximation to quadruple and higher excitations is very accurate (as is further discussed in the numerical examples in the next section).

The formal advantages are as significant as the computational advantages of the exponential wave function. For the H_2 lattice example, an individual H_2 molecule has the CCD wave function

$$\Psi_{\text{CCD}}(p) = \exp[T_2(p)]\Phi_0(p) \quad (12)$$

and for the lattice

$$\Psi_{\text{CCD}}^L = \exp(T_2^L)\Phi_0^L = \prod_p \exp[T_2(p)]\Phi_0(p) = \prod_p \psi_{\text{CCD}}(p) \quad (13)$$

$$E_{\text{CCD}} = ME_{\text{CCD}}(\text{H}_2) \quad (14)$$

Equation 12 follows since $T_2(q)\Phi_0(p) = 0$ ($q \neq p$) for orbitals localized on the different units. As is the case for both the HF case and the exact solutions, *CC theory satisfies the extensive property by providing a product wave function for the noninteracting case.* Note that none of the above discussion is limited

to two-electron or identical units.

Since the different cluster operators commute, CCSD is defined by the wave function $\exp(T_1 + T_2)\Phi_0 = \exp(T_1)\exp(T_2)\Phi_0$; this adds terms like $T_1T_2\Phi_0$ which are "disconnected" triple-excitation contributions plus *all* other products involving T_1 and T_2 .

Similarly, we can add additional electron clusters as in the CCSDT approximation, which means $\exp(T_1 + T_2 + T_3)\Phi_0$, where we have now included "connected" triple-excitation contributions like $T_3\Phi_0$ along with additional disconnected terms involving T_3 like T_1T_3 and T_2T_3 , etc. The next contribution T_4 , i.e., connected quadruple excitations, would define CCSDTQ.

Since in the limit of all excitations CC theory must be equal to full CI, we can equate the *CI excitation operators*, C_n , and the cluster operators, T_n , to be

$$C_1 = T_1$$

$$C_2 = T_2 + T_1^2/2$$

$$C_3 = T_3 + T_1T_2 + T_1^3/3!$$

$$C_4 = T_4 + T_2^2/2 + T_1^2T_2/2 + T_1T_3 + T_1^4/4!$$

$$C_5 = T_5 + T_1T_4 + T_2T_3 + T_1^2T_3/2 + T_1^3T_2/2 + T_1T_2^2/6 + T_1^5/5! \quad (15)$$

⋮

More specifically, for the antisymmetrized coefficients, $C_{ij}^{ab} = t_{ij}^{ab} + t_{ij}^{ba} - t_{ij}^{ab} - t_{ij}^{ba}$, etc. Below we will use these definitions of C_n to avoid writing all the T products.

Now we need equations for determining the coefficients in the correlation energy and the CC wave function. This is accomplished by inserting the CC wave function into the Schrödinger equation (subtracting the reference energy $\langle \Phi_0 | H | \Phi_0 \rangle$ from both sides for simplicity, $H_N = H - \langle \Phi_0 | H | \Phi_0 \rangle$) and projecting. We have

$$H_N \exp(T)\Phi_0 = \Delta E \exp(T)\Phi_0 \quad (16)$$

Projecting from the left by Φ_0 , and using eq 15, we obtain

$$\Delta E = \langle \Phi_0 | H_N (C_2 + C_1) | \Phi_0 \rangle \quad (17)$$

Similarly, projection by different categories of excitations provides equations for the coefficients. Through CCSDT these are

$$C_i^a \Delta E = \langle D_i^a | H_N (1 + C_1 + C_2 + C_3) | \Phi_0 \rangle \quad (18a)$$

$$C_{ij}^{ab} \Delta E = \langle D_{ij}^{ab} | H_N (1 + C_1 + C_2 + C_3 + C_4) | \Phi_0 \rangle \quad (18b)$$

$$C_{ijk}^{abc} \Delta E = \langle D_{ijk}^{abc} | H_N (C_1 + C_2 + C_3 + C_4' + C_5') | \Phi_0 \rangle \quad (18c)$$

where $C_4' = C_4 - T_4$ and $C_5' = C_5 - T_5 - T_1T_4$. No additional terms can contribute since H_N only has one- and two-particle operators, limiting the contributing matrix elements to those that differ by no more than two excitations. Equation 18 provides a closed set of coupled equations which are nonlinear in the t coefficients. They can be written into a convenient form for iterative solution³⁵ as shown at the end of this section.

The *variational* CI equations limited to single, double, and triple excitations (CISDT) are exactly the same except for C_4' and C_5' , but these are disconnected products of only T_1 , T_2 , and T_3 . The former's lead term, $T_2^2/2$, is responsible for most of the effect of quadruple excitations in calculations and all through the fourth-order energy in MBPT. Such disconnected terms like $T_2^2/2$, T_1T_2 , and T_2T_3 in C_5' are also responsible for ensuring size extensivity by eliminating the so-called "unlinked diagrams" as discussed below.

In the form of eq 18 the CCSDT equations may also be viewed as arising from a *decoupling* of the CI equations where C_4 and C_5 , which would be in a CISDTQP method, are replaced by the primed quantities. Unlike the CI quadruple and pentuple excitations, the fact that C_4' and C_5' are disconnected products of only T_1 , T_2 , and T_3 obviates the need to solve for the quadruple (C_4 , an $\sim n^{10}$ procedure) and pentuple (C_5 , an $\sim n^{12}$ procedure) excitation coefficients, greatly simplifying computation.

(34) Meunier, A.; Levy, B.; Berthier, G. *Int. J. Quantum Chem.* **1976**, *10*, 1061.

(35) Kucharski, S. A.; Bartlett, R. J. *Adv. Quantum Chem.* **1986**, *18*, 281.

Notice what else is different in CI compared to CC theory. Before projecting eq 16, we could have multiplied from the left by $\exp(-T)$. This is just a manipulation that does not change the equations but puts them into the slightly different form commonly used in CC theory, where the Schrödinger equation becomes $\exp(-T)H_N \exp(T)|\Phi_0\rangle = [H_N \exp(T)]_C|\Phi_0\rangle = \Delta E|\Phi_0\rangle$ and the C indicates a restriction to "connected" diagrams (which are a subset of the linked diagrams). The detailed terminology is unimportant to the present discussion. It simply means we have cancelled all possible terms from eq 18. It then follows that projection by some category of excitations would have given zero by orthogonality on the left of eq 18 instead of ΔE times a coefficient. To take just eq 18b as an example, we have

$$0 = \langle D_{ij}^{ab} | [H_N(1 + T_2 + T_1 + T_3 + T_2^2/2 + T_1T_2 + T_1T_3 + T_1^2/2 + T_1^2T_2/2 + T_1^3/3! + T_1^4/4!)]_C |\Phi_0\rangle \quad (18d)$$

That is, there is *no* ΔE dependence in the CC equations (but there would be in the CISDT equations because C_4' and C_5' would not be there), and this has underlying significance.

Remember that, for our noninteracting example, ΔE^L is given by eq 6 for any M , and since it is easy to show (via the iterative solution of eq 18d outlined below) that the $t_{ij}^{ab\dots}$ and consequently $C_{ij}^{ab\dots}$ coefficients have a similar dependence on the energy of the separated units of M (or higher), the products on the left of eq 18 then scale at least as $\sim M^2$. But in a proper theory, the equations have to scale linearly with M . In CC theory these erroneous terms cancel as in eq 18d, but in a truncated CI they would remain. In many-body language, the terms that arise from $\Delta EC_{ij}^{ab\dots}$ correspond to the so-called "unlinked" diagrams,^{33,36} and the linked diagram theorem tells us they are not in the correct wave function or energy. Their erroneous dependence on the number of separated pairs M^2 , M^3 , etc., is responsible for the failure of any truncated CI to be extensive, necessitating the use of unlinked diagram corrections³⁷ which are based upon some approximate consideration of terms like C_4' and which are routinely added to high-accuracy CI calculations today.³⁸ Furthermore, the CC equations are independent of ΔE (i.e., they form a set of algebraic equations), but the CI equations depend on ΔE (i.e., they are eigenvalue equations and the ΔE dependence is part of the reason that CI results for the energy are variational). Until the full CI is reached, usually a choice has to be made whether to use an extensive method or a variational method. Since the CC equations have eliminated all erroneous (unlinked diagram terms) from the beginning by virtue of the exponential wave function choice, any approximation made to the CC equations like stopping with finite-order MBPT (see below), or limiting to a subset of cluster operators like T_1 and T_2 as in CCSD, or even some subset of the possible T_1 , T_2 , T_3 contributions like the CCSDT-1 method,¹⁹ is extensive as it already benefits from the unlinked diagram cancellation. Hence, we have now come full circle. The rationale of correct scaling is manifest in the CC/MBPT equations.

Also, it should be recognized that *only an exponential* has the correct multiplicative factors in its expansion to fully eliminate all unlinked terms. The so-called quadratic CI method (QCI)³⁹ (which is an unfortunate name because it is not CI as it is not an eigenvalue equation, or variational; nor does it include all quadratic terms) would appear to be more properly viewed as an approximation to the CC equations where some quadratic, cubic,

TABLE I: Mean Absolute Error of Correlation Energies (kcal/mol) for CC Methods and Other Single-Reference (RHF) Correlated Methods Compared to Full CI^{a,b}

			FH(DZP), BH(DZP), H ₂ O(DZ), H ₂ O(DZP)		
	F ⁻	Ne	R _c	1.5R _c	2.0R _c
CISD ^c	8.4	4.8	5.5	14.1	34.2
CISDT ^c	6.5	3.2	4.3	9.4	21.6
CISDTQ ^{c,d}	0.4	0.1	0.2	0.5	1.7
LCCD	6.1	0.7	0.8	1.1	11.2
CCD	7.1	1.6	1.7	5.9	16.5
CCSD	3.8	1.8	1.9	4.4	8.6
MBPT(4)	3.2	0.4	1.1	3.1	7.8
MBPT(5) ^e	-	-	0.8	2.6	9.2
MBPT(5) + [2,1]Padé ^e	-	-	0.3	1.1	8.3
CCSD + T(CCSD)	0.7	0.1	0.2	0.4	3.2
CCSDT-1	0.7	0.1	0.3	0.7	1.3
CCSDT	0.4	0.1	0.2	0.6	0.9

^aReference 38. ^bBasis sets for F⁻ are (4s3p1d), (4s3p2d), (5s4p2d). Basis sets for Ne are (4s2p1d), (6s4p1d), (5s3p2d). Molecules listed are studied at three geometries, their respective equilibrium values R_e, and with the bond(s) stretched to 1.5R_e and 2.0R_e. A DZ basis means 4s2p contracted atomic orbitals on the heavy atom and 2s on H. A DZP basis adds a set of d functions on the heavier atom and a set of p functions on H, i.e., (4s2p1d/2s1p). ^cCI results do not include BH at 1.5R_e and 2.0R_e or at R_e for CISDT. ^dCISDTQ results do not include H₂O(DZP), which has the largest error for the other CI methods. ^eResults exclude FH.

and higher product terms are excluded.⁴⁰

I should briefly comment on the iterative solution of eq 18d to indicate how MBPT approximations arise.³⁵ Separating H_N into a one-electron f_N and two-electron part W_N , in the canonical SCF case we would get $\langle D_{ij}^{ab} | f_N T_2 |\Phi_0\rangle = (\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j) t_{ij}^{ab}$; taking this term to the left-hand side (similar terms $(\epsilon_a - \epsilon_i) t_i^{ab}$ and $(\epsilon_a + \epsilon_b + \epsilon_c - \epsilon_j - \epsilon_k) t_{ijk}^{abc}$ would occur in eq 18a and 18c), we can initiate an iterative solution by evaluating $(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b) t_{ij}^{ab} = \langle D_{ij}^{ab} | W_N |\Phi_0\rangle$ to obtain an initial approximation to t_{ij}^{ab} . Inserting this approximation into eq 17 gives the MBPT(2) energy, while using its value in another iteration of eq 18d gives an updated t_{ij}^{ab} , whose corresponding energy is MBPT(3). Initiating the single- and triple-excitation equations and the $T_2^2/2$ contribution from eq 18d with the first approximation to t_{ij}^{ab} leads to the MBPT(4) energy, while continued iterations of all these equations gives convergence to the CCSDT result.³⁵ Hence, in examples where convergence is good, MBPT(4) \approx CCSDT, but the latter method will be much better for difficult cases as we will see in the next section.

Numerical Examples

The above discussion of the rationale for CC theory is nice formally, but does it buy us any real improvement in accessible computational accuracy? The answer is yes, which I hope to demonstrate with several examples in the following.

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(40) The following equations are programmed in QCISD:³⁸ (i) $\langle i | H_N (T_1 + T_2 + T_1 T_2) | 0 \rangle = \Delta E t_i^a$; (ii) $\langle ij | H_N (1 + T_1 + T_2 + T_2^2/2) | 0 \rangle = \Delta E t_{ij}^{ab}$, where T_n are the cluster operators as defined here, not the CI₂ operators C_n . In CCSD-1⁴¹ the $T_1 T_2$ term in (i) is not included, but the $T_1^2/2$ part of the energy formula is. In CPMET(C),¹⁴ the $T_1 T_2$ term is included in (i) and (ii). The $T_1 T_2$ in (ii) contributes in fifth-order MBPT for an SCF reference, while in (i) it contributes only in sixth order. Other contributing quadratic terms would be $T_1^2/2$ which would contribute first in sixth-order MBPT. CCSD would also include $T_1^3/3!$ in (i) and $T_1^2 T_2/2$ and $T_1^4/4!$ in (ii), which would be numerically unimportant for ordinary SCF cases but can become quite important for non-SCF cases.⁴² However, all terms including the quartic terms require no more than an $\sim n^6$ computational procedure, as do the other terms. Consequently, QCISD is an approximation to CCSD that should be satisfactory for nonpathological SCF reference examples. Similarly, QCISD(T) is similar to CCSD + T(CCSD).⁴³ The differences are that QCISD(T) deletes the higher order terms in CCSD, adds a single-excitation term to the triple-excitation expectation value, and excludes the $T_2^2/2$ contribution to the energy.

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A. Comparison with Model Exact Solutions. The best that can be done in a given basis set is the "full" CI, which for N electrons includes in its wave function all possible N -fold excitations. The full CI is size extensive; it gives a variational upper bound to the exact nonrelativistic energy, and it is independent of the particular choice of molecular orbitals. The degree of agreement with experiment depends on the AO basis set for the problem, but agreement with full CI (not experiment) is the mathematically consistent goal of any correlated ab initio method. If we can obtain the full CI solution in a basis that is *able to describe the experimental phenomena accurately* (and if relativistic corrections are small), the result has to give excellent agreement with *correct* experimental values.

The full CI solution cannot be obtained except for comparatively small examples (small molecules and small basis sets) since otherwise the number of configurations, proportional to the number of basis functions as $\sim n^N$, is exorbitant. Consequently, any comparisons with full CI could be criticized as being potentially different than would occur in large basis or large molecule applications. However, many of the recent full CI results,³⁸ with up to 28 million determinants and done mostly at NASA Ames on the CRAY-2, use a Gaussian (AO) basis set of at least double- ζ plus polarization (DZP) quality. This means having 4s2p1d AO's on C, O, N, F and 2s1p on H, a level of basis that is frequently used today in many correlated, chemical applications. Hence, the comparisons *on average* should be indicative of the comparative quality of the methods that would be obtained even in much larger basis sets. The detailed comparisons with full CI are presented elsewhere,^{20,44} but they may be summarized as in Table I. R_e represents the equilibrium internuclear distance, with $1.5R_e$ and $2.0R_e$ corresponding to stretched bonds.

The largest error occurs when bonds are stretched to twice their equilibrium distance, $2.0R_e$. There is a reason for this behavior. In each of the examples listed, a restricted HF (RHF) calculation is used as the reference for the correlated wave function. For molecules that separate into open-shell fragments, it is well-known that an RHF function does not separate correctly into neutral fragments but instead into an average of ionic states (e.g., F^- and H^+ for FH) that is much higher in energy than for the neutral atoms. Hence, the RHF function is *qualitatively wrong* at large separation, causing the correlated wave function to have to attempt to overcome this erroneous behavior. This places extreme demands on the correlated method compared to the results obtained for atoms or for molecules at R_e . When two or more determinants are equally important (the two determinants $|(core)3\sigma_g^2|$ and $|(core)3\sigma_u^2|$ enable FH to properly separate into neutral atoms so they are equally important at large separations), there is an ambiguity as to which to use as the reference function for the problem. This "multireference" situation manifests itself in causing poor convergence of the CC equations. Finite-order MBPT and linearized (LCCD) energies in particular can tend toward minus infinity at large internuclear distances.^{15,45} Bond-breaking problems of this type, and certain other cases where several determinants are essential to a correct zeroth-order description of some molecular states, like in O_3 , frequently require multireference (MR) based CC techniques as discussed later. Also, unrestricted Hartree-Fock (UHF) single-determinant references may be used which will frequently separate correctly, but as discussed elsewhere,^{44,45} UHF based CC results are generally no better for these examples than are the RHF-CC results shown.

One observation from Table I is that even a linearized (LCCD) approximation frequently offers energies much closer to full CI than CISD. This is mostly because of the cancellation of unlinked diagrams in eq 18d. The LCCD approximation corresponds to the wave function $(1 + T_2)\Phi_0$, where the $\{t_{ij}^{ab}\}$ amplitudes would be obtained from eq 18d with all $T_n = 0$ except for T_2 , and the $T_2^2/2$ term is also not considered in the equation. However, LCCD is not CID, since unlike the CID equations, eq 18d has no *unlinked*

terms in it. This makes LCCD an extensive approximation. A rough measure of the value of the extensivity error is the difference in energy between LCCD and CISD. Table I shows that for small molecules the values of the unlinked diagrams, which, remember, do not contribute to the "right" answer (i.e., the full CI), severely hurt the accuracy of CISD, being ~ 20 kcal/mol in the worst case and ~ 4 kcal/mol even for Ne.

The CCD method, $\psi_{CCD} = \exp(T_2)\Phi_0$, means we only use eq 18d with $T_1 = T_3 = 0$, and, now, the $T_2^2/2$ part remains. The change from LCCD to CCD is fairly large and because of error cancellation LCCD can be fortuitously better. Table I does not show that LCCD results sometime overestimate the correlation effects (i.e., its errors are sometimes negative),^{9b} while CCD results tend to lie above the full CI.¹⁵

CCSD which means $T_3 = 0$, with T_1 and T_2 determined from eq 18a and 18b, offers a further improvement, and the CC/MBPT methods that include triple excitations are much better. The inclusion of triple excitations adds at least an $\sim n^7$ step. CCSD + T(CCSD)⁴³ means that, following a CCSD calculation, we perturbatively perform a single evaluation of triple excitations using the converged CCSD coefficients. This noniterative procedure has an $\sim n^6 N_{ITS}$ (the number of iterations) dependence for CCSD followed by a single $\sim n^7 T(CCSD)$ step. CCSDT-1¹⁹ means that the contribution of triple excitations is approximated by the largest perturbation theory contribution in eq 18c, which comes from T_2 . This in turn defines the T_3 amplitudes which contribute to the T_1 and T_2 parts of eq 18a and 18b. Continuing the iterations until convergence gives CCSDT-1, an $\sim n^7 N_{ITS}$ procedure. The full CCSDT model²⁰ means eq 18 (after all cancellations as illustrated by eq 18d) is solved without any approximation. Its asymptotic dependence is $\sim n^8 N_{ITS}$. The average error compared to full CI is less than a kcal/mol for CCSDT for these examples.

Comparing the CISDT model with any of the CC methods shows that even the inclusion of triple excitations in CI only offers modest improvement over CISD. Once again, the reason lies mainly in the unlinked diagrams remaining in CISDT.

Only when extended to CISDTQ (an $\sim n^{10} N_{ITS}$ procedure) does the ordinary CI method become competitive with the CC methods that include triples. The reason is that once the quadruples are introduced in CI, we introduce $T_2^2/2$ along with T_4 and the other disconnected terms in C_4 in eq 15. $T_2^2/2$ effects the cancellation of the numerically most important unlinked diagrams. For large enough molecules, however, even CISDTQ will fail to be a good approximation because of the unlinked diagrams that could only be cancelled by disconnected pentuple, hextuple, and higher excitations. Hence, CCSDT would be expected to become considerably better for large molecules, in addition to its superior $\sim n^8$ versus $\sim n^{10}$ dependence. (I might add, we have shown that the largest effects of T_4 can actually be added to CCSDT with only an $\sim n^6$ dependence.³⁵)

The $\sim n^{10}$ computational dependence of CISDTQ arises because coefficients for *all* $\sim n^8$ quadruple excitations would be computed. This is not generally the best use of configurations. The preferable CI approach is to define a multireference (MR) set of several important configurations and, typically, take all single and double excitations from that set. Instead of including *all* excitations like quadruples from one reference, this introduces a selected set of excitations, some of which would be "quadruple" relative to a single reference. This procedure is superior to a straightforward CISDTQ because there are fewer configurations in the MR-CI, and the multireference space will normally include the other configurations important for bond breaking, ensuring a correct zeroth-order description as a function of internuclear separation, unlike the RHF functions discussed above. We refer to such MR corrections as "nondynamical" correlation to distinguish the MR effect from the "dynamical" correlation introduced so effectively in CC/MBPT theory to keep electrons apart. For the examples in Table I, and *for sufficiently large MR spaces*, such MR-CI methods can obtain results very close to full CI that are as good as the CCSDT results are in equilibrium situations and will often do better at stretched geometries.³⁸ However, MR-CI is still not rigorously size extensive and in practice is usually still augmented

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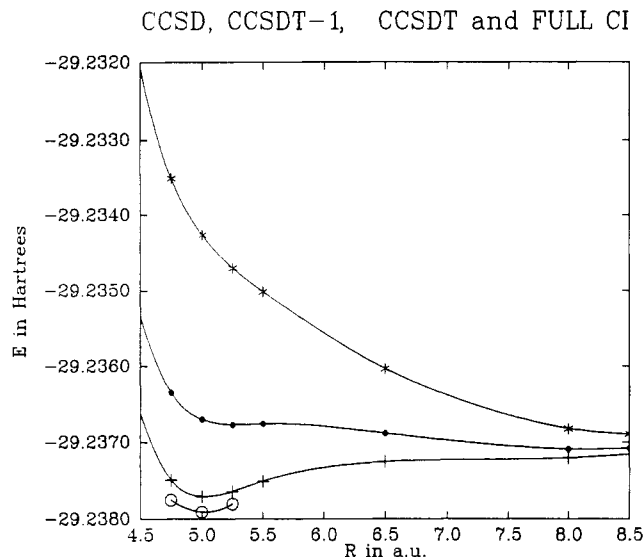


Figure 1. CCSD (*), CCSDT-1 (●), CCSDT (+), and full CI (○) curves for the $1\Sigma_g^+$ ground state of Be_2 .

by some unlinked diagram corrections.³⁷ MR methods will have similar advantages in CC theory. (See sections E and F for MR-coupled cluster examples.)

We might ask if the very sophisticated CCSDT method provides observable improvements over the simple CCSDT-1 and CCSD + T(CCSD) approaches. We might even ask, How important are the connected T_4 terms that are not in CCSDT? Clearly, for small molecules at least, these terms are numerically small since the full CI contains all such terms plus T_5 , T_6 , ... up to the number of electrons, and in all examples shown in Table I, these amount to <1 kcal/mol. For one ab initio example, however, we have a definitive and observable measure of the full effect of T_3 and T_4 . This is provided by the very interesting Be_2 molecule. Theory predicted⁴⁶ and experiment verified⁴⁷ that Be_2 was not just a van der Waals molecule but had a potential well at ~ 5 bohrs of ~ 2 kcal/mol that could support several vibrational levels. Many theoreticians studied the Be_2 curve, but depending upon the sophistication of the approach, the inner well could be too deep or not appear at all.^{19a,48}

In Figure 1 are shown CC results at three levels⁴⁸ obtained in a modest (7s3p1d) basis compared to full CI.⁴⁹ The molecule is treated as a four-electron system by keeping the $\text{Be}(1s^2)$ electrons frozen, so the full CI is the CISDTQ result in this case, indicated by open circles. In this basis, the full CI well depth is 0.7 kcal/mol. (In the real world, to obtain the well depth of ~ 2 kcal/mol would require a much larger basis (see section B), but the current full CI comparison is sufficient for our purposes.)

The first thing to notice is that the CCSD result is totally repulsive, although it will give the exact result for two Be atoms at large separation, since CCSD is exact for two electrons. However, the error in the vicinity of the inner well where we actually have four electrons interacting is 2.2 kcal/mol, washing out the well. Using CCSDT-1 which adds T_3 partly via its effect on T_2 amplitudes at least leads to a plateau near 5 au, but still no well. Yet the full inclusion of T_3 , which unlike CCSDT-1 permits T_3 to have an opportunity to directly affect the T_3 amplitudes in the coupled equation (18c),²⁰ now gives binding. Since the only remaining contribution in the full CI that is not in CCSDT is the effect of T_4 , the difference in the two curves provides that value. This difference amounts to 0.18 kcal/mol at the minimum.

For metallic systems there is evidence that T_4 will be large⁵⁰ and perhaps even comparable to $T_2^2/2$, despite T_4 being of higher

order in perturbation theory; but for most small molecules, T_4 and higher connected cluster terms should be comparatively unimportant as long as the reference function chosen is a "reasonable" approximation. For a poor Φ_0 , T_4 and higher terms will have to be large to overcome the unrealistic starting point, and this can happen in some pathological (probably multireference) cases when a single-reference function is used.

B. Basis Sets and Approach to Exact Coupled-Cluster Results. The above examples compared to full CI demonstrate that single-reference CC methods with triples are capable of obtaining the *basis set limit* correlation energy to within a few kcal/mol, at least for small molecules. Most of the remaining error comes from the choice of (AO) basis set. Although not the subject of this article, the interplay between basis set and electron correlation is important to predictive quantum chemistry and in assessing the accuracy of CC theory.

To illustrate with an interesting molecule consider C_4 . The transient C_4 molecule has been thought to exist in an open-shell ($3\Sigma_g^-$) cumulene-like linear structure, $:\text{C}=\text{C}=\text{C}=\text{C}:$.⁵¹ However, accurate calculations have shown that a closed-shell rhombus ($1A_{1g}$) state is close in energy.^{52,53} In a DZP (4s2p1d) basis at the (UHF) SCF level, the linear form is lower by 20 kcal/mol, yet once correlation is included at even MBPT(2), the rhombus is preferred by almost as much. Going to higher order MBPT(4) favors the rhombus by 10.8 kcal/mol. Yet a higher-order CCSD + T(CCSD) calculation reduces this difference to 4.5 kcal/mol.^{53a} Expanding the basis set to (5s3p1d), the linear form is 26 kcal/mol more stable at the SCF level, but MBPT(4) now favors the rhombus by only 5.6 kcal/mol and CCSD + T(CCSD) reverses the stability to be in favor of the linear isomer, but by only 1.3 kcal/mol.^{53b} This is a change in relative energy with basis set of about 6 kcal/mol. A systematic further extension of the basis may eventually permit an extrapolation to the basis set limit, but the basis dimension would be sufficiently large to seldom make that practical. Of course, other properties than the energy, like moments, polarizabilities, field gradients, etc., can be much more sensitive to basis set effects.

The pervasive basis set problem in quantum chemistry could be eliminated in principle by solving the Schrödinger equation numerically. A variety of quantum Monte Carlo methods⁵⁴ take steps in that direction, but they have other problems. At least for diatomic molecules, by exploiting the elliptical coordinate system⁵⁵ or by performing two-dimensional numerical integrations,⁵⁶ purely numerical Hartree-Fock and multiconfiguration Hartree-Fock (MCHF) calculations are now possible. Clearly, progress in numerical solutions is being made, but for the foreseeable future, the vast majority of quantum chemical applications will have to continue to use some form of basis sets. Adamowicz and I have investigated one way to attempt to transcend the limitations of conventional basis sets in CC/MBPT to attempt to approach the *exact* result, by using a basis set of *numerical orbitals*.

Solving the HF equations for diatomics numerically^{55,57} provides us with Hartree-Fock limit results for the occupied orbitals, and

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TABLE II: Percent ΔE Obtained by Numerical Orbital CC/MBPT Results (au)^a

	MBPT(2)	MBPT(3)	MBPT(4)	CCSD	CCSD + T(CCSD)
Ne (28 σ ,24 π ,17 δ ,7 ϕ)	94.5	94.2	96.6	94.4	96.0
LiH (30 σ ,24 π ,16 δ ,12 ϕ)	85.2	95.2	97.7	98.6	98.8
FH (45 σ ,40 π ,26 δ ,8 ϕ)	96.6	96.0	99.1	96.4	98.7 ^b
FH (19 σ ,21 π ,17 δ ,5 ϕ)	94.2	93.9	96.9	94.3	96.6
F ⁻ (19 σ ,21 π ,17 δ ,5 ϕ)	93.7	90.7	96.0	91.8	94.8
F (19 σ ,21 π ,17 δ ,5 ϕ)	93.4	96.7	98.4	94.0	95.7

^aAll results are from the papers in ref 57–60. ^b99.7 extrapolate m .

solving a series of MCHF equations (discussed elsewhere⁵⁵) provides us with a set of unoccupied orbitals enabling us to describe electron correlation in the usual framework. Insofar as this set of orbitals is nearly complete (there is no mathematical proof!) and a CC calculation using them should be close to the full CI in that basis, we should be close to the exact solution of the (nonrelativistic) Schrödinger equation. Some results using this method are illustrated in Table II.

The basis sets are defined for each system. Since the numerical program is for diatomics, the designation uses diatomic symmetry even for atoms. The first observation is that on average about 95% of the “experimental” correlation energy is obtained. This should be contrasted with ~95–99% of the *basis set limit* correlation energy for the examples shown in Table I; yet the DZP bases there would offer only ~60% of the experimental correlations energy. Hence, these numerical basis results are among the most accurate obtained for molecules and attest to the accuracy of CC/MBPT methods with excellent basis sets.

Two FH calculations are presented. The smaller but very extensive basis of 105 functions is also used for F and F⁻ to permit the evaluation of a highly accurate dissociation energy for FH and electron affinity of F, both classic, long-term objectives of ab initio quantum chemistry. The residual correlation energy error for these species of 3–5% is about 8 kcal/mol although most of the error would be expected to cancel in evaluating the energy differences for dissociation and electron attachment. The D_e of 141.8 kcal/mol agrees exactly with experiment,⁵⁹ but this is partly accidental since there is a potential change of a few kcal/mol for further extensions even in this high level of calculation. The electron affinity obtained for F is 3.37 eV compared to an experimental value of 3.41. Notice that MBPT(4) gives poorer results of 146.2 kcal/mol and 3.65 eV, respectively.

The other very extensive basis FH calculation ($n = 193$)⁵⁸ uses a hybrid numerical and Slater orbital basis and our optimized virtual orbital space (OVOS) method.⁵⁹ With extrapolation we obtain almost the exact result, but the main point to make here is the slow convergence with basis set of the correlation energy. Even increasing n from 105 to 193 gains only a couple of percent of the correlation energy, reducing the error to 3.1 kcal/mol. Extrapolation for contributions of functions with $m > 3$ affects the result by another 2–3 kcal/mol. We have used numerical orbital CC methods to correctly describe highly diffuse dipole bound anions including some excited states,⁶⁰ since more conventional basis sets would not generally be appropriate.

The numerical orbital technique is currently only possible for diatomic molecules. To study polyatomic systems more accurately than before requires other approaches. Two worth mentioning are the atomic natural orbital techniques⁶¹ and our complementary OVOS method.⁵⁹ For example, using OVOS we were able to reduce a benzene basis from 105 virtual orbitals to only 30 and still retain 97% of the full basis CC correlation energy with a hybrid method.⁵⁹

C. Vibrational Frequencies. In CC theory we are not just interested in energies but also in the shape of potential energy surfaces. To raise the question of how well CC theory can treat such problems, we can take the example of the H₂O molecule.

TABLE III: Errors in Fundamental Frequencies for H₂O vs Experiment (cm⁻¹)

	$\Delta\omega_1$	$\Delta\omega_2$	$\Delta\omega_3$
SCF	300	123	293
CISD	98	54	93
CCSD	34	40	32
MBPT(4)	-9	25	6
CCSDT-1	-2	28	-3

In a series of papers,⁶² CI, MBPT, and CC results for the quartic force field of H₂O were determined. This was done by evaluating the energy at 36 geometries (symmetric and asymmetric) in the vicinity of the equilibrium geometry using an extended Slater orbital basis. By fitting these points and solving the vibrational Schrödinger equation, we obtained the fundamental frequencies, a series of overtone frequencies corresponding to levels accessible by a few quanta, and the constants X_{ij} which characterize low-order anharmonicity in the potential energy function.

The errors in the fundamental frequencies compared to experiment for SCF, CISD, and various CC/MBPT methods are shown in Table III. The CISD result improves upon SCF by close to a factor of 3 in the two stretching modes and somewhat less for the bending mode. CCSD improves upon CISD by another factor of 3, attesting to the important effect of the unlinked diagrams left in CISD compared to CCSD. Once triple excitations are included via the CCSDT-1 model, excellent agreement is obtained for the two stretch modes, but somewhat poorer results are obtained for the bend. The constancy of the error in the latter tends to suggest a basis set deficiency that preferentially affects that mode.

Bowman et al.⁶³ fit our CCSDT-1 surface and found the average error in the predicted frequencies for 18 vibrational states to be less than 18 cm⁻¹. By making an adjustment in the bending force constant which attempted to correct for the observed basis set error, he reduced the average error in the set of frequencies to only 6 cm⁻¹.

Of course, the best way to study energy surfaces is not to compute a series of energies at different geometries and fit the surface but to analytically compute first, second, and eventually higher derivatives. However, we are still a long way from doing that for a quartic force field at a correlated level. (Cubic SCF derivatives have been done, however.⁶⁴) On the other hand, great progress has recently been made in analytical first derivatives in CC/MBPT which permits frequency calculations from finite differences of gradients, and analytical second derivatives have been implemented for the simplest correlated model, MBPT(2).⁶⁵ Soon I expect general CC second and third derivatives will be available.

The theory for CC analytical derivatives, which has MBPT as a special case, has been presented.²⁷ The basic idea is straight-

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TABLE IV: FH₂ Barrier and Transition-State Geometry

method	basis	geometry, au		barrier, kcal/mol
		R _{FH}	R _{HH}	
MR-CI ^a	7s5p3d2f/4s3p2d	2.80	1.46	3.43
MBPT(4) ^b	11s7p5d3f/7s5p3d	2.72	1.46	3.68
MR-CI ^c	8s5p3d1f/3s1p1d	2.81	1.46	3.69
MR-CI ^c	8s5p3d1f/3s1p1d	3.07	1.43	1.59 ^f
UHF-CCSDT-1 ^d	8s5p3d1f/3s1p1d	2.78	1.46	2.50
QRHF-CCSDT-1 ^d	8s5p3d1f/3s1p1d	2.78	1.46	2.02
MR-CI ^e	5s5p3d2f1g/4s3p2d	2.88	1.45	2.89
MR-CI	5s5p3d2f1g/4s3p2d	2.91	1.44	2.14 ^g
MR-CI	5s5p3d2f1g/4s3p2d	2.91	1.44	1.86 ^h

^a Reference 72b. ^b Reference 72a. ^c Reference 71. ^d Reference 75 and this work. Transition-state geometry determined by the CCSD + T(CCSD) method. ^e Reference 77. ^f Scaled. ^g Plus *Q* correction. ^h Plus *Q* and adiabatic correction.

forward. Since the energy and coefficients are computed in eq 17 and 18, differentiation of these equations with respect to some atomic displacement for an atom, X_α , gives a set of equations for ΔE^α and C_n^α which may be solved simultaneously to provide the first derivatives. Proceeding in this brute force fashion is not recommended, however, since that would require the solution of $\sim 3N$ (linearized) CC equations, one for each possible X_α . Fortunately, we were able to show that the CC gradient problem could be formulated such that only a single linearized CC-like equation needed to be solved²⁷ and that this could be readily accomplished in what we term a "relaxed" density formulation that avoids all derivative integral transformations. Our initial implementation for CCD²⁸ did not make use of this efficient density approach, but subsequently, the density approach was implemented by Scheiner et al.²⁹ at the CCSD level. They have now presented results for harmonic vibrational frequencies of small molecules with great success.⁶⁶ The average CCSD error is 2.2% compared to 3.7% for CISD and 9.1% for SCF. MBPT(3) and MBPT(4) gradients have also been implemented by using the relaxed density method.⁶⁷ In addition, CCSDT-1 analytical gradients have been reported by Scuseria and Schaefer,^{68a} demonstrating the high accuracy we observed for the H₂O molecule, for a wider class of small molecules. They also observe some important changes for frequencies of multiply bonded systems like CO between CCSDT-1 and CCSDT,^{68b} analogous to the Be₂ binding energy example above. A bonus from the analytical gradient theory is that the correlated relaxed density is obtained as a byproduct. This permits the facile evaluation of *all one-electron properties* like moments, field gradients, etc.,^{68c} plus density plots for qualitative studies of the effects of electron correlation.⁶⁹

D. Activation Barrier. Another example of great interest and controversy is the classical barrier of the extensively studied reaction $F + H_2 \rightarrow FH + H$, recently reviewed by Schaefer.⁷⁰ In essence, the best ab initio calculations had predicted 3–4 kcal/mol for this barrier, but the experimental value is believed to be 1–1.2 kcal/mol. Pertinent results are summarized in Table IV. Schwenke et al.⁷¹ performed a large basis MR-CI calculation which gave a computed barrier of 3.69 kcal/mol but then introduced some empirical scale factors based upon requiring the

correct results at the noninteracting limit, which reduced their result to 1.6 kcal/mol. Schaefer, however, concludes that all the quality calculations indicate the barrier must be greater than 2.35 kcal/mol. Quantum chemistry is being pushed to agonize over a difference of ~ 1 kcal/mol, but in this reaction, as in Be₂, it is an important 1 kcal/mol.

Several very thorough MR-CI studies, with very extended bases, consistently find a barrier higher than 3.43 kcal/mol. However, since the size-extensive property of CC/MBPT is particularly important in getting correct relative energies as in an activation barrier, might we expect some potential improvement from such methods? A very large basis UHF-MBPT(4) study was performed by Frisch et al.,⁷² resulting in values of 3.24 and 3.68 kcal/mol, depending on the geometry choice. This is an extensive method, so it tends to support the MR-CI results. However, a UHF reference suffers from spin contamination which might artificially increase the value of the UHF-MBPT(4) barrier due to quartet and higher spin states.

CC theory can potentially improve upon CI because of its size extensive property. It can improve upon MBPT(4) because of its infinite-order correlation corrections. Also, CC theory significantly improves upon the UHF spin multiplicity as several results have shown.⁷³ Furthermore, a theorem⁷⁴ shows that CCSD will naturally benefit from annihilation of the principal UHF contaminant, so at the level of UHF + CCSDT-1 we might expect to get a better result than the finite-order UHF-MBPT. Using the extended basis of Schwenke et al., Rittby and I did this calculation and found a barrier of 2.5 kcal/mol,⁷⁵ which is significantly lower than the unscaled MR-CI result of 3.69 kcal/mol. As this basis is comparable with that of Frisch et al.,⁷² we can expect UHF multiplicity corrections plus infinite-order correlation corrections to perhaps be as large as ~ 0.7 to ~ 1.2 kcal/mol.

An even more pervasive improvement on an erroneous UHF multiplicity is offered by a new method recently developed, which is to use a restricted open-shell Hartree-Fock reference (ROHF) or a variant we call a (quasi)-QRHF function as a starting point.⁷⁶ The latter is composed of any set of orbitals, like those for FH₂⁺, which we can then doubly occupy up to the open-shell orbital, to offer a starting point for FH₂. Unlike UHF for open shells, QRHF or ROHF offers pure doublet reference states, which aids in further eliminating spin contamination. The CC wave function is spin contaminated, but its projected value $\langle \Phi_0 | \hat{S}^2 | \psi_{cc} \rangle = S(S + 1)$ is not. Using this method and CCSDT-1, we obtain 2.0 kcal/mol for the activation barrier, closer to the scaled estimate of Truhlar in the same basis. The residual effects can be due to higher correlation corrections and to expected additional basis set deficiencies, but we also see changes as large as 0.3 kcal/mol in ROHF versus QRHF for this example. This would not happen at the full CI limit, so we can only conclude that there is good evidence that the barrier is near or below the 2.35 kcal/mol estimate of Schaefer.

A thorough study recently published by Bauschlicher et al.⁷⁷ obtains a classical barrier of 2.89 kcal/mol for MR-CI, and using a correction for unlinked diagrams reduces this value to 2.14 kcal/mol (falling between our results). The unlinked diagram estimate of 0.75 is highly significant here, as even for extremely sophisticated calculations, unlinked diagram, size-extensive corrections remain a crucial part of the final result. This should be contrasted with CC results that eliminates unlinked diagrams rigorously. Corrections to the adiabatic approximation further lower Bauschlicher et al.'s predicted barrier to 1.86 kcal/mol.⁷⁷

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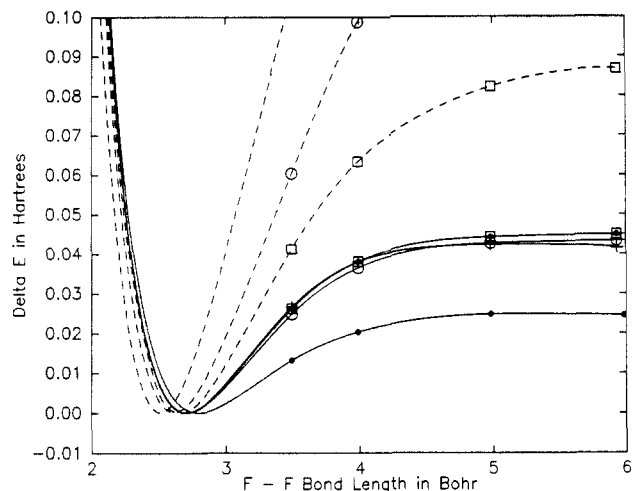


Figure 2. RHF-based SCF, CISD, CCSD and CCSDT-1, MCSCF-10, MR-CISD-10, and MR-LCCM-10 potential curves for F_2 . All potential curves are shifted such that their respective energy minima are zero. The various curves are identified as follows: (---) SCF, (○) CISD, (□) CCSD, (+) CCSDT-1, (●) MCSCF, (▣) MR-CISD, and (⊖) MR-LCCM.

The activation barrier of $F + H_2$ is an example of a problem where most corrections due to basis set, correlation, spin contamination, size-extensivity, and multireference character have effectively the same sign, which is the worst situation possible for quantum chemistry since there is little error cancellation. The fact that the spin-restricted open-shell CC methods can help resolve such delicate energy differences is an encouraging result.

Another study of an activation barrier is also informative. In the automerization of cyclobutadiene the transition state (TS) is a square that requires two important configurations to describe its wave function. A two-configuration SCF (GVB)⁷⁸ is the obvious choice. Attempting to obtain this barrier with a single configuration is difficult.⁷⁹ The correct barrier is probably about 9–10 kcal/mol.

In a DZP basis a single-configuration SCF gives 30.6 kcal/mol, attesting to the difficulty in describing the TS. CISD using the SCF as a reference would give only a modest improvement. Second- and third-order MBPT is about the same, or ~20–24 kcal/mol, but even in fourth order (19.5), MBPT misses the barrier by a factor of 2. CCSD is no better (19.8). Yet when triple excitations are introduced into the CC method, CCSD + T(CCSD) gives 14.4 kcal/mol with their more complete inclusion in CCSDT-1 providing a good answer (9.5).⁷⁹ Note that in section A triple excitations were usually required to successfully overcome the errors at stretched geometries, which is another manifestation of a multireference problem. However, GVB-CISD is a relatively simple calculation and is already quite accurate for the barrier. Even GVB itself is comparatively good.

Problems that benefit from the unambiguous use of a single-reference function *even when inappropriate* can often be accurately solved by CC theory if connected triple excitations are included. However, multireference CC variants analogous to the GVB-CI are going to be preferred for many classes of problems.

E. Single-State Multireference Coupled-Cluster Methods. Multireference CC theories fall into two categories: those that describe bond-breaking phenomena and those directed toward excitation or ionization energies. For bond breaking crude first attempts to handle this problem have been made.⁴⁵ The essential idea is to use a wave function like $\psi_i = e^T \psi_i^0$ where $\psi_i^0 = \sum_{\mu} \phi_{\mu} c_{\mu i}$ consists of a sum over a series of important determinants ϕ_{μ} weighted by $c_{\mu i}$ that introduce the "nondynamic" correlation. One realization for ψ_i^0 is a multiconfiguration (MCSCF) wave function.

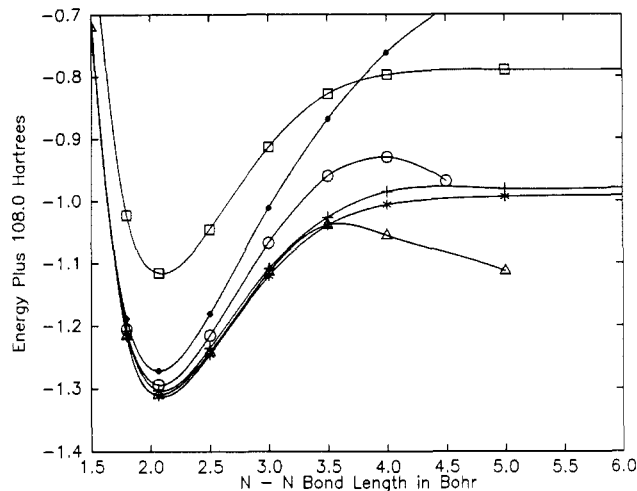


Figure 3. RHF-based CISD, CCSD and CCSDT-1, MCSCF, MR-CISD, and MR-LCCM potential curves for N_2 (absolute scale). The various curves are identified as follows: (●) CISD, (○) CCSD, (△) CCSDT-1, (□) MCSCF, (+) MR-CISD, and (*) MR-LCCM.

T , here, has to be suitably defined to generate nonredundant classes of excitations from all the determinants in the MCSCF. This is a *single, but multiconfiguration, reference* approach. It may be generalized by introducing an effective Hamiltonian matrix (see section F) whose eigenvectors are the $\{c_{\mu i}\}$,⁴⁵ but in a first approximation the coefficients are fixed at their MCSCF values.

Building upon some work of Paldus,^{30e} we have solved these MR-CC equations in a linear approximation, $\sim(1 + T)\psi_i^0$ termed MR-LCCM,⁴⁵ but this is still quite informative. Results for the F_2 and N_2 molecule are shown in Figure 2 and 3. For F_2 the minima of the curves are superimposed while for N_2 absolute locations are shown.

The RHF result for F_2 shows the erroneous separation characteristic previously discussed. The MCSCF for F_2 , which consists of 10 configurations, is qualitatively correct but leads to a substantially wrong D_e . For N_2 the MCSCF consists of 176 configurations, and though it separates correctly, it too underestimates the dissociation energy. As long as a reference function is qualitatively right, however, the exponential operator even linearized introduces much of the dynamic correlation. In this case, the T operator generates the other single and double excitations relative to all the references. The analogue in CI is known as complete active space CASSCF-CI or FORS-CI.⁸⁰ In both F_2 and N_2 , a single and a triple bond, MR-CISD and MR-LCCM give curves that separate correctly. With a couple of exceptions, all the single-reference CI, CC, or MBPT methods fail. For F_2 , where only a single bond is broken, the CCSDT-1 method even with an RHF reference provides a good curve all the way to 6 bohrs. This should be contrasted with the same method for N_2 , where CCSDT-1 is fine until about 3.5 bohrs, but fails beyond that. In other words, additional corrections, possibly due to more complete inclusion of T_3 plus T_4 , T_5 , or T_6 , might be important to correctly describe N_2 when using an incorrectly separating RHF reference. Since UHF correctly separates for N_2 , UHF-CC curves shown elsewhere⁴⁵ are much improved as they benefit from the spin annihilation inherent in CCSD and CCSDT-1 but are still not as accurate as the MR-LCCM results. Much work remains to be done in developing rigorous, accurate MR-CC methods for potential energy surfaces.

F. Multistate Multireference Coupled-Cluster Theory. So far, we have mostly limited ourselves to CC methods directed toward the ground state (or lowest state of a given symmetry). However, we obviously need to be able to treat excited, ionized, and electron attached states equally well. In this regard, the CC theory offers some new ideas. These ideas have their origin in

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a "universal" (wave) operator $\Omega^{81,82}$ that will take a reference function into the exact solution for the Schrödinger equation. In the standard theory $\Omega = \exp(T)$ and the "model" or reference function is Φ_0 , an independent particle solution like SCF. For other kinds of states, we want to define an MR model function, $\psi_m^0 = \sum_\mu \phi_\mu c_{\mu m}$, where $\{\phi_\mu\}$ are a set of important configurations, as above. However, Ω will still take ψ_m^0 into the exact solution of the Schrödinger equation, $\psi_m = \Omega \psi_m^0$. However, unlike the approach in section E, here we do not care how many electrons are being described by ψ_m . That is, one and only one "universal" Ω will be able to take an appropriately chosen ψ_m^0 into the exact solution for ionization processes ($N - 1$), electron affinities ($N + 1$), or excited states (N). Similarly, we can describe double ionization ($N - 2$), as is important to Auger spectroscopy, and many other phenomena. In mathematical language we say we are now working in Fock space instead of Hilbert space, since in Fock space we can change the number of electrons.

An example might make this discussion more concrete. For an eight-electron system we have $\Phi_0 = |\bar{i}\bar{i}j\bar{j}k\bar{k}l\bar{l}|$, the determinant of four spatial (eight spin) orbitals. We perform a CC calculation to define the ground-state energy and wave function $\exp(T)\Phi_0$. We will assume k and l correspond to inner shell electron pairs which are of less interest, while i and j correspond to the valence orbitals. The latter will be said to be active. Similarly, we have a set of unoccupied orbitals labeled as a, b, c, \dots of which we will assume a and b are the unoccupied orbitals chosen to be active. To describe an ionization from the occupied orbital i or j , we would define a doublet model function $\psi_m^1 = c_i^1 |\bar{i}j\bar{j}k\bar{k}l\bar{l}| + c_j^1 |\bar{i}i\bar{j}k\bar{k}l\bar{l}|$. We now require two things: To get the exact solution we require that all possible new correlation effects (i.e., the distinct excitations from the two $N - 1$ electron determinants) be introduced by the wave operator Ω , and we need to know the values of c_i^1 and c_j^1 . The excitations that we can now have involve the orbitals i and j , since they are empty in one or the other determinants, and we can now excite an electron from k and l into i or j . Since this cannot happen in the ground state, we have new coefficients (amplitudes) for these processes which we term $S^{(0,1)}$.

Our universal wave operator⁸⁰ becomes $\Omega = \{\exp(T) \exp(S^{(0,1)})\}$. (The "normal ordering" signified by $\{\}$ ²⁴ is important to avoid ambiguity in the definition but is not essential to the concepts we are describing.) All terms in $S^{(0,1)}$ expanded in terms of the cluster operators $S_n^{(0,1)}$ would give zero when applied to Φ_0 , so Ω is correct for the ground state and now also for the ionized states. Inserting Ω into the Schrödinger equation and subtracting the ground-state energy, we obtain the ionization energies $\{\omega_m\}$ and coefficients from the effective Hamiltonian equation, $\mathbf{H}_{\text{eff}}\mathbf{C} = \mathbf{C}\omega$, $\mathbf{H}_{\text{eff}} = \langle \underline{\phi} | \Omega^{-1} H \Omega | \underline{\phi} \rangle$ for $\underline{\phi}$ the ($N - 1$) electron functions that span the reference space. Analogous to the single-reference case, the coefficients in the operator $S^{(0,1)}$ are obtained from projecting the Schrödinger equation onto the set of $N - 1$ electron determinants that are orthogonal to the reference determinants. T is known from the ground-state solution.

At the next stage in this hierarchy, we would define a model space of $N + 1$ electron determinants $|\bar{i}\bar{i}j\bar{j}k\bar{k}l\bar{l}a|$ by adding additional active unoccupied orbitals. The same procedure will lead to an $S^{(1,0)}$ operator for the new excitations we can now introduce by virtue of exciting from the new occupied orbital, a . Now our universal operator becomes $\Omega = \{\exp(T) \exp(S^{(0,1)}) \exp(S^{(1,0)})\}$, and the eigenvalues of the \mathbf{H}_{eff} constructed in the $N + 1$ electron space give the electron affinities.

The next stage is to consider excitation energies. A reasonable model space for most such states consists of a set of singly excited (N -particle) determinants like $|\bar{a}i\bar{j}j\bar{k}k\bar{l}l|$ where the electron in active orbital i is excited to orbital a . We now have some new correlation effects in the excited state introduced by excitations like removing electrons from orbitals a and k and putting them into i and c , e.g., that we could not previously have in T , $S^{(0,1)}$, or $S^{(1,0)}$. We call

TABLE V: Vertical Excitation Energies of N_2 and CO in DZP Basis Sets (eV)

N_2 ($R = 2.074$ au)			CO ($R = 2.132$ au)		
state	MRCC	expt	state	MRCC	expt
B $^3\Pi_g$	7.95	8.1	a $^3\Pi$	6.32	6.3
a $^1\Pi_g$	9.27	9.3	A $^1\Pi$	8.79	8.5
A $^3\Sigma_u^+$	7.60	7.8	a' $^3\Sigma^+$	8.26	8.5
B $^3\Sigma_u^-$	9.92	9.7	e $^3\Sigma^-$	9.82	9.9
W $^3\Delta_u$	8.95	8.9	d $^3\Delta$	9.18	9.4
a' $^1\Sigma_u^-$	10.12	9.9	I $^1\Sigma^-$	9.92	9.9
w $^1\Delta_u$	10.59	10.3	D $^1\Delta$	10.10	10.2

the operator composed of these amplitudes, $S^{(1,1)}$ and Ω gains a fourth exponential term. Hierarchially building upon all prior operators whose amplitudes have since been determined, we can now construct Ω and \mathbf{H}_{eff} . Its eigenvalues are the electronic excitation energies. We present results for the prototype molecules N_2 and CO in Table V. These numbers, computed with a DZP basis, included all one- and two-electron operators in the S_n operators (MR-CCSD), while the ground-state T was determined by CCD. Higher excitations can be introduced in T and S to approach the exact solution, leading to a series of approximations analogous to those already presented in the single-reference CC method.

We also obtain the ionization potentials as a step toward the excitation energies. For the first two ionizations these are 14.0 and 16.6 eV for CO compared to experimental values, 14.0 and 16.9 eV. For N_2 the same results are 15.3 and 17.0 V compared to 15.6 and 17.0 eV. These can be improved with a better basis and some consideration of triple excitations.^{22,83} The excitation energies are already quite good, however, and competitive with good CI, higher RPA, and polarization propagator results.²⁴ With a basis set appropriately chosen to be able to describe anions, electron affinities can also be quite accurate.²⁶

There is a definite philosophical difference between the Fock space approach and more conventional quantum chemistry. To get excitation energies, you have to compute ionization potentials and electron affinities whether you want them or not. On the other hand, assuming we want to know all the properties of a molecule, there is an economy and unity in performing calculations in this way. I believe the Fock space approach will be a further area of great development in quantum chemistry.

The Future in Coupled-Cluster Theory: Some Speculations

Since this article calls for speculations, I will at least risk a few comments from my personal perspective.

We have seen several examples that show how correlation effects, comparatively easily included in single-reference CC theory, permit better results to be obtained for molecules than many other methods. MR-CC should further expand the attainable accuracy. CC theory, like its finite-order MBPT approximation, lends itself to "easily used" computer programs. This has its pros and cons, but the universal application GAUSSIAN 86⁸⁴ for MBPT calculations suggests that some system like our ACES program,⁸⁵ which performed all the CC/MBPT calculations reported here, and will be released soon, could have a similar applicability for CC theory. "Quadratic CI"³⁹ which, remember, is a restricted CC theory, will be in future editions of the GAUSSIAN program system.

We have discussed single-reference and two variants of multireference CC theory. The unity of the Fock space approach for a variety of properties is appealing and will soon near a routine application level. The MR-CC approach to potential energy

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surfaces is still undergoing rapid development. The so-called "intruder state" problem, where configurations excluded from the reference space assume unusual importance, is severe for potential energy surfaces (PES). This can introduce singularities in an effective Hamiltonian method. Hence, applications to PES where very different configurations can be important at different geometries would seem to recommend a single but multideterminantal reference as discussed in section E, if such a CC theory can be formulated rigorously.

New kinds of CC approaches that maintain the size-extensive property can be envisioned. Two of these may be viewed to arise from an expectation value expression.^{6,73,86,87a}

$$\Delta E = \langle 0 | [\exp(T^\dagger) H_N \exp(T)]_C | 0 \rangle$$

or from a unitary ansatz^{87b,88}

$$\Delta E = \langle 0 | [\exp(\tau^\dagger) H_N \exp(\tau)]_C | 0 \rangle = \langle 0 | [H_N \exp(\tau)]_C | 0 \rangle$$

where $\tau = T - T^\dagger$.

Unlike the standard CC theory, these expressions lead to an infinite series of terms. However, by truncating in some way and varying ΔE with respect to the amplitudes, we obtain different equations for the amplitudes than in the standard theory, termed XCC and UCC.⁸⁷ This leads to a hierarchy of new approximations that have some computational advantages for correlation energies. Though these methods use a "variational", i.e., stationary principle, they do not result in an upper bound to the energy. However, these new methods have some properties that the standard approach does not. First, they permit the facile inclusion of T_4 in CC theory; and UCC can be used to satisfy the generalized Hellman-Feynman (GHF) theorem.⁸⁹ This ensures that the expectation value of an operator and the energy derivative of a Hamiltonian perturbed by that operator are equivalent, as is true for the exact wave function. Hence, we have an alternative way to evaluate properties like gradients and moments. Also with a *single* set of perturbed T^α operators, we can analytically evaluate second and third derivatives for force constants, for hyperpolar-

izabilities⁹⁰ that are important in nonlinear optical behavior, for magnetic susceptibilities, and for numerous other properties of interest. Other CC methods proposed with an eye toward properties are the ECCM approaches of Arponen et al.⁹¹

For polymers and other extended systems, only size-extensive ("many-body") methods are appropriate. I anticipate that substantial efforts will be directed toward coupling CC methods with translational symmetry conditions to try to obtain correlated studies of energy levels in solids and polymers. An important application today might be to high-temperature superconducting materials, where among other elements, strong pair correlations that would be ideally introduced by CC theory, might play an important role.

When translational symmetry is not present, more conventional but still "extensive" large molecule quantum chemical methods would have to be used. Any such method is likely to be based upon some localized-orbital fragment method to make the method scale no worse than quadratic with the number of electron pairs. Two such localized CC/MBPT schemes have been proposed.^{41,92}

As an effective computational tool, CI has been around for maybe 25 years, although essential multireference, unitary group advances have only been made in the past 10 years.⁹³ MBPT has been available for general applications for only about 10 years,⁸ with important developments in gradient methods only being made quite recently.⁶⁷ Computational CC theory has been similarly available for about 10 years,¹⁵ with the requisite gradient applications²⁹ and methods for excited states^{23,24} and multireference methods only now being developed.³⁰ Considering the accelerated pace of development, the fact that greater accuracy is more frequently required, plus the computer hardware advances, CC theory and its extensions should play an increasingly prominent role in the future.

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