A full coupled-cluster singles and doubles model: The inclusion of disconnected triples

George D. Purvis, and Rodney J. Bartlett

A full coupled-cluster singles and doubles model: The inclusion of disconnected triples

George D. Purvis III and Rodney J. Bartlett

Quantum Theory Project, Department of Chemistry, University of Florida, Gainesville, Florida 32611
(Received 13 August 1981; accepted 19 October 1981)

The coupled-cluster singles and doubles model (CCSD) is derived algebraically, presenting the full set of equations for a general reference function explicitly in spin–orbital form. The computational implementation of the CCSD model, which involves cubic and quartic terms, is discussed and results are reported and compared with full CI calculations for H_2O and BeH_2. We demonstrate that the CCSD exponential ansatz sums higher-order correlation effects efficiently even for BeH_2, near its transition state geometry where quasidegeneracy efforts are quite large, recovering 98% of the full CI correlation energy. For H_2O, CCSD plus the fourth-order triple excitation correction agrees with the full CI energy to 0.5 kcal/mol. Comparisons with low-order models provide estimates of the effect of the higher-order terms $T_1 T_2$, $T_1^2 T_2$, T_1^3, and T_1^4 on the correlation energy.

I. INTRODUCTION

Recently, a number of applications of many-body perturbation theory (MBPT)[1-4] and coupled-cluster methods (CCM)[5-8] to the *ab initio* calculation of the electronic structure of molecules have been reported.[9] These applications have restricted the full MBPT/CCM model to a fixed level of perturbation [e.g., third or fourth order as in D–MBPT(3) and SDQ–MBPT(4)] or to including all orders of the class of double excitation cluster operators as in coupled-cluster doubles (CCD), or (poorer) the linearized L-CCD[=D–MBPT(∞)] form. The methods implemented usually presume the use of Hartree–Fock orbitals, although this is not necessary.

Here we report the derivation and the computational implementation of the the full CCSD model. The method, as implemented, uses any orthogonal set of orbitals and is not restricted to Hartree–Fock orbitals. In particular, it is possible to use symmetrically orthogonalized bond orbitals instead of Hartree–Fock orbitals and to take advantage of the concomitant reduction in the number of molecular integrals in large molecules which results from the more localized structure of the bond orbitals. Additional applications for non-Hartree–Fock orbitals, such as optimizing orbitals so that the energy becomes stationary, are easily envisioned.

There are a number of reasons to recommend the development of the CCSD method as a basis for what Pople calls a "theoretical model chemistry."[10,11] These criteria propose that a method(1) should be "size extensive," which means it scales properly with molecular size; (2) applicable to a wide range of problems within a single framework; (3) invariant to classes of unitary transformations; (4) efficient; and (5) able to correctly separate a molecule into its fragments.

CCSD is a many-body method built upon the linked-diagram theorem. Hence, it is size extensive and, in particular, CCSD gives the correct result for the characteristic problem of separated electron-pair bonds

as in a lattice of N noninteracting H_2 molecules. As long as a single determinant is a reasonable starting point, which need not be a restricted or unrestricted Hartree–Fock function, CCSD is applicable to most problems without modification or special symmetry conditions.

Furthermore, CCSD is invariant to any transformation among the excited orbitals or the occupied orbitals, respectively. CCSD is not generally invariant to transformations that mix occupied and unoccupied orbitals among themselves. However, for the special case of noninteracting separated electron pairs, it is even invariant to such general transformations. This follows from the fact that CCSD is the "full" CI (i.e., all possible contributing n-tuple excitations of n electrons) for such a model problem. Since interpretations of chemistry are largely based upon the concept of separated electron-pair bonds, this is a very desirable aspect of the CCSD model. In a real molecule, different choices of the molecular orbitals will give different energies, but we would expect a smaller effect due to such transformations for CCSD than in less complete models. It will be interesting to see if localized orbital models will be approximately invariant.

The condition of efficiency also recommends CCSD since the treatment of the electron correlation effect grows no more rapidly than the sixth power of the number of basis functions, M^6. Thus, CCSD involves no more coefficients than the configuration interaction single and double excitation model, SD–CI; and, in principle, it is no more time consuming. This is true, even though CCSD includes contributions of quadruple excitations, as well as additional parts of the triple and higher excitations that arise due to disconnected products of single and double excitations. Any attempt to exceed the CCSD model by including higher categories of excitation operators, such as the connected triple excitations T_3, will invariably result in a model where the number of operations would asymptotically rise more rapidly than M^6.

The condition of correct separation depends upon the reference function as well as the degree of correlation included, and generally requires the resolution of degeneracy problems. Full CI with a single reference

function obviously separates correctly even for poor choices of reference function. For less complete correlation models, the relative importance of the reference function and the correlation corrections is not yet determined, often recommending multireference techniques. A single UHF function will, in general, separate correctly, though it can suffer from large amounts of spin contamination causing an erroneous behavior of a potential energy surface. With any choice of reference function, CCSD will certainly go farther toward achieving correct separation than SD–CI, so we might expect a higher level of applicability. For example, CCD is known to correctly handle some severely degenerate problems, [12,13] and in this paper, CCSD is similarly shown to resolve two highly degenerate problems without resorting to multireference function techniques. Consequently, CCSD offers a potentially attractive model for a "theoretical model chemistry" that can often even achieve correct separation or resolve some kinds of degeneracies despite employing a single reference configuration.

In the following section we will review coupled-cluster theory and the singles and doubles approximation. Section III summarizes the CCSD equations and Sec. IV sketches the method of implementation. Finally, Sec. V compares CCSD calculations at the double zeta level on H_2, H_2O, and BeH_2 with full-CI calculations.

II. THE SINGLE AND DOUBLE EXCITATION APPROXIMATION IN COUPLED—CLUSTER THEORY

Coupled cluster (CC), many-body perturbation theory (MBPT), and configuration interaction (CI) are methods designed to solve the Schrödinger equation, and consequently, all can be interrelated. The primary difference is in how higher order excitation configurations are handled, with the consequence that many-body methods are size extensive.[9] In particular, CC theory can be viewed as a way to sum certain categories of many-body perturbation theory diagrams to all orders. While such a viewpoint has advantages, we will discuss the CCSD approximation from the viewpoint of an exponential representation of the exact wave function. That is, we will write the exact solution to the Schrödinger equation as an exponential of the cluster operator operating on a reference function[7]

$$\Psi_{exact} = \Psi_{CC} = e^{\hat{T}} \Phi_0 , \tag{1}$$

where Φ_0 is a single determinant and $\hat{T}$ is a cluster operator which is usually separated into one-body, two-body, etc. cluster contributions as follows:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots \tag{2}$$

The various parts of the cluster operators are represented as expansions of second quantized excitation operators and the problem of determining $\hat{T}$ is reduced to the problem of finding the expansion coefficients of the second quantized operators. For $\hat{T}_1$ and $\hat{T}_2$, the expansions are

$$\hat{T}_1 = \sum_{i,a} t_i^a a_a^\dagger a_i \tag{3}$$

and

$$\hat{T}_2 = \sum_{\substack{i > j \\ a > b}} t_{ij}^{ab} a_a^\dagger a_i a_b^\dagger a_j , \tag{4}$$

where we have adopted the convention that the lower case roman subscripts (superscripts) i, j, k, l, ... (a, b, c, d, ...) refer to orbitals which are occupied (unoccupied) in the reference determinant. The undetermined coefficients are $\{t_i^a\}$ and $\{t_{ij}^{ab}\}$ while $\{a_a^\dagger a_i\}$ and $\{a_a^\dagger a_i a_b^\dagger a_j\}$ are second quantized sets of single and double excitation operators, and t_{ij}^{ab} is antisymmetric (i.e., $t_{ij}^{ab} = -t_{ji}^{ab} = -t_{ij}^{ba} = t_{ji}^{ba}$).

The chief advantage of CC over CI can be easily demonstrated by using the expansion of an exponential operator

$$e^{\hat{T}} = 1 + \hat{T} + \tfrac{1}{2}\hat{T}^2 + \tfrac{1}{6}\hat{T}^3 + \cdots \tag{5}$$

to bring the CC cluster operators into a formal correspondence with the CI excitation operators. In the CI method, the exact wave function can be written as a linear combination of excitations from a reference determinant.

$$\Psi_{exact} = \Psi_{CI} = (1 + \hat{C}_1 + \hat{C}_2 + \cdots \hat{C}_N)\Phi_0 , \tag{6}$$

where $\hat{C}_i$ is a sum of i-fold excitations with coefficients which must be determined. The correspondence between $\hat{C}_i$'s and $\hat{T}_i$'s is established by using Eqs. (2) and (5) in Eq. (1) to produce an expanded equation

$$\Psi_{exact} = (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_3$$
$$+ \cdots + \tfrac{1}{2}\hat{T}_1^2 + T_1 T_2 + \tfrac{1}{2}\hat{T}_2^2 + \cdots)|\Phi_0\rangle . \tag{7}$$

Terms with the same total excitation level are collected together and equated to the CI coefficient of the same excitation level. For example, the CI quadruple excitations $\hat{C}_4\Phi$ correspond to the following sum:

$$\hat{C}_4 = \hat{T}_4 + \tfrac{1}{2}\hat{T}_2^2 + \hat{T}_1\hat{T}_3 + \tfrac{1}{2}\hat{T}_1^2\hat{T}_2 + \frac{1}{4!}\hat{T}_1^4 . \tag{8}$$

Thus, CC can be regarded as a way to decompose CI coefficients into other, possibly more physically meaningful terms.[14] In the case of quadruples, a substantial body of work has indicated that the largest component of $\hat{C}_4$ comes from $\tfrac{1}{2}\hat{T}_2^2$ in Eq. (8).[14-16] From a computational point of view, this is an important observation because the effects of $\hat{T}_2^2$ can be included using algorithms where the work is proportional only to the sixth power of the basis set size instead of proportional to the eighth power.

The CCSD method is an approximate CC method in which the exact wave function [cf. Eq. (1)] is approximated by truncating the expansion of $\hat{T}$ [cf. Eq. (2)] after $\hat{T}_2$. Thus,

$$\Psi_{exact} \approx \Psi_{CCSD} = \exp(\hat{T}_1 + \hat{T}_2)\Phi_0 . \tag{9}$$

The coefficients which must be determined are just those given in Eqs. (3) and (4), and the number of unknown coefficients in the CCSD approximation equals the number of coefficients in SD–CI. Thus, the level of computational effort required in the CCSD model is expected to be comparable to the level of effort required for the SD–CI model. However, as indicated in Eq. (8), the CCSD approximation incorporates parts of the CI quadruple excitation terms, namely, $\tfrac{1}{2}\hat{T}_2^2$, $\tfrac{1}{2}\hat{T}_1^2\hat{T}_2$, and

$(1/4!)\hat{T}_1^4$, and it does so more economically and compactly than a SDQ–CI calculation can. There is evidence based upon perturbation theory, previous calculations, and physical grounds that the single missing term $\hat{T}_4$ is usually not needed to achieve accurate calculations. [14-16] In addition to including the effects of CI-type quadruple excitations, the CCSD model also incorporates some of the effects of triple excitations. Relating $\hat{C}_3$ to cluster terms, we find

$$\hat{C}_3 = \hat{T}_3 + \hat{T}_1 \hat{T}_2 + \frac{1}{3!}\hat{T}_1^3 . \tag{10}$$

Thus, the CCSD model incorporates the $\hat{T}_1\hat{T}_2$ and $\hat{T}_1^3$ components of CI-type triple excitations. Unfortunately, when Hartree–Fock orbitals are used, perturbation theory indicates that the dominant contribution to $\hat{C}_3$ usually comes from $\hat{T}_3$, [9,16-18] which is not included in the CCSD method. On the other hand, if non-Hartree–Fock orbitals are used, so that $\hat{T}_1$ is large, then the dominant contributions to $\hat{C}_3$ can come from $\hat{T}_1\hat{T}_2$ and $\hat{T}_1^3$. In practice, we have found that these terms do become important in bond breaking processes which one is usually tempted to describe with a multireference approach. They seem to remain unimportant for simple closed-shell molecules at their minimum energy geometries. As in the case of the $\hat{C}_4$ components inherent in CCSD, the disconnected $\hat{C}_3$ components can be computed with algorithms in which the work is proportional to the sixth power of the size of the basis set.

III. CCSD EQUATIONS

The procedure for deriving the CCSD equations have been previously reported in diagrammatic form[7] and approximations to these equations in orbital form[16] using elegant and compact notations. In some cases, the reported equations have been restricted to Hartree–Fock orbitals or approximations were made in the equations. In this section, we present the complete set of equations satisfied by the coefficients which define $\hat{T}_1$ and $\hat{T}_2$ in the CCSD method. These equations are applicable to any set of orthonormal spin orbitals. In particular, the equations are applicable to RHF and UHF as well as non-Hartree–Fock reference determinants. The equations are derived algebraicly for this work using the conventional procedure[7] beginning with the Schrödinger equation

$$(H - E_{CCSD})\Psi_{CCSD} = (H - E_{CCSD})\exp(\hat{T}_1 + \hat{T}_2)|\Phi_0\rangle = 0 \tag{11}$$

and projecting onto a set of functions $\langle\Phi_0|$, $\{\langle^a_i|\}$, and $\{\langle^{ab}_{ij}|\}$, such that a set of equations sufficient for determining the t^a_i and t^{ab}_{ij} coefficients results as follows:

$$\langle\Phi_0|(H - E_{CCSD})|\exp(\hat{T}_1 + \hat{T}_2)\Phi_0\rangle = 0 , \tag{12}$$

$$\langle^a_i|(H - E_{CCSD})|\exp(\hat{T}_1 + \hat{T}_2)\Phi_0\rangle = 0 , \quad \text{for all } i, a , \tag{13}$$

$$\langle^{ab}_{ij}|(H - E_{CCSD})|\exp(\hat{T}_1 + \hat{T}_2)\Phi_0\rangle = 0 , \quad \text{for all } i > j, \ a > b . \tag{14}$$

Next, the exponential is expanded using Eq. (5) and using the fact that H contains no more than two-electron operators, we have

$$\langle\Phi_0|H - E_{CCSD}|1 + T_1 + T_2 + \tfrac{1}{2}T_1^2|\Phi_0\rangle = 0 , \tag{12a}$$

$$\langle^a_i|H - E_{CCSD}|(1 + T_1 + T_2 + \tfrac{1}{2}T_1^2 + T_1 T_2 + \frac{1}{3!}T_1^3)|\Phi_0\rangle = 0 , \tag{13a}$$

$$\langle^{ab}_{ij}|H - E_{CCSD}|(1 + T_1 + T_2 + \tfrac{1}{2}T_1^2 + T_1 T_2 + \tfrac{1}{2}T_2^2 + \tfrac{1}{2}T_1^2 T_2$$
$$+ \frac{1}{3!}T_1^3 + \frac{1}{4!}T_1^4)|\Phi_0\rangle = 0 . \tag{14a}$$

Evaluating Eq. (12) in terms of the amplitudes t^a_i and t^{ab}_{ij}, then gives

$$E_{CCSD} = \langle\Phi_0|H|\Phi_0\rangle + \sum_{ia} f_{ia} t^a_i + \sum_{\substack{i>j \\ a>b}} \langle ij||ab\rangle$$
$$\times (t^{ab}_{ij} + t^a_i t^b_j - t^a_j t^b_i) , \tag{15}$$

where

$$f_{ia} \equiv \langle^a_i|H|\Phi_0\rangle$$

and

$$\langle ij||ab\rangle = \int \chi_i^*(1)\chi_j^*(2) \frac{(1 - P_{12})}{r_{12}} \chi_a(1)\chi_b(2) \ d\tau_1 d\tau_2 .$$

Finally, Eq. (15) is substituted into Eqs. (13) and (14) causing terms, which would make unlinked contributions to the energy, to cancel and eliminating the explicit E dependence of the t coefficients. The other important step in the derivation is to observe that the T_1 equation may be factored from the equation for the T_2 amplitude, as discussed more fully below. Evaluating the resulting second-quantized matrix elements with KOMMUTE, [19] a computer program for determining matrix elements between determinants, and carrying out the above simplification results in the two equations satisfied by the amplitudes in $\hat{T}_1$ and $\hat{T}_2$. These are presented in Tables I, II, and III. After solving the equations of Tables I–III, the energy is given by Eq. (15).

An important aspect of the coupled-cluster equations, in general, and the CCSD equations, in particular, are their fully "connected" diagrammatic form. All unlinked diagrams (diagrams that contain a closed disconnected part) cancel with the energy in Eqs. (13)–(14), thereby ensuring the size extensivity of the model. [20,21] Disconnected diagrams (diagrams that have open disconnected parts) would still remain in the general case. However, it has been proven[22] that

---

TABLE I. CSSD equation satisifed by single excitation coupled-cluster coefficients t^a_i.

$$f_{ia} + \sum_a f_{aa} t^a_i - \sum_i f_{ii} t^a_i + \sum_{la} \langle di||la\rangle t^d_l + \sum_{la} (t^{ad}_{il} - t^a_i t^d_l) f_{ia} + \sum_{\substack{a>b \\ l}} \langle id||ab\rangle (t^{ab}_{lj} + t^a_l t^b_j - t^a_j t^b_l) - \sum_{\substack{i>j \\ a}} \langle ij||al\rangle$$

$$\times (t^{ad}_{lj} + t^a_l t^d_j - t^d_l t^a_j) - \sum_{\substack{i>j \\ ca}} \langle ij||ca\rangle t^c_i t^{da}_{lj} - \sum_{\substack{lk \\ a>b}} \langle ik||ab\rangle t^a_k t^{ab}_{li} - \sum_{\substack{kc \\ jb}} \langle jk||cb\rangle t^c_k (t^{ab}_{li} - t^a_i t^b_l) = 0 .$$

TABLE II. CCSD equation satisfied by the double excitation coefficient t_{ij}^{ab}.

$$\langle ij \| ab \rangle + \sum_d [f_{bd} t_{ij}^{ad} + f_{ad} t_{ij}^{db}] - \sum_k [f_{kj} t_{ik}^{ab} + f_{ki} t_{kj}^{ab}] - \sum_k [\langle ak \| ij \rangle t_k^b + \langle kb \| ij \rangle t_k^a] + \sum_c [\langle ab \| cj \rangle t_i^c + \langle ab \| ic \rangle t_j^c] + \sum_{c>d} \langle ab \| cd \rangle C_{ij}^{cd}$$

$$+ \sum_{k>l} \langle ij \| kl \rangle C_{kl}^{ab} - \sum_{k,d} [\langle bk \| jd \rangle \tilde{C}_{ki}^{ad} - \langle bk \| id \rangle \tilde{C}_{kj}^{ad} - \langle ak \| jd \rangle \tilde{C}_{ik}^{db} + \langle ak \| id \rangle \tilde{C}_{jk}^{db}] + \sum_d f_{kc}[- t_k^a t_{ij}^{cb} - t_k^b t_{ij}^{ac} - t_i^c t_{kj}^{ab} - t_j^c t_{ik}^{ab}] + \sum_d [\eta^{bd} t_{ij}^{ad} - \eta^{ad} t_{ij}^{bd}]$$

$$- \sum_l [\eta_{lj} t_{il}^{ab} - \eta_{li} t_{jl}^{ab}] + \sum_c [t_i^c \alpha_{ab;cj} - t_j^c \alpha_{ab;ci}] + \sum_l [t_l^a \alpha_{ij;lb} - t_l^b \alpha_{ij;la}] + \frac{1}{4} \sum_{\substack{kl \\ cd}} \langle kl \| cd \rangle [C_{ij}^{cd} C_{kl}^{ab} - 2 (t_{ij}^{ac} C_{kl}^{bd} + t_{ij}^{bd} C_{kl}^{ac})$$

$$- 2 (t_{ik}^{ab} C_{jl}^{cd} + t_{jl}^{ab} C_{ik}^{cd}) + 4 (\tilde{C}_{ki}^{ac} \tilde{C}_{lj}^{bd} + \tilde{C}_{ki}^{bd} \tilde{C}_{lj}^{ac}) - 8 t_i^a t_k^b t_l^a t_j^c] = 0 .$$

in coupled-cluster theory, only connected diagrams need be considered for the various T_n amplitudes. This feature becomes transparent in the direct algebraic derivation presented here, since all disconnected diagrams obtained in the straightforward evaluation of Eq. (14) correspond to a single particle amplitude, t_i^a multiplied by the T_1 equation of Table I, which, of course, vanishes. Diagrammatically, these disconnected terms are of the form
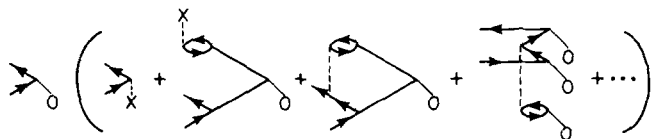
where a T_1 amplitude is signified by and a T_2 amplitude by . A recent thesis by Cullen,[23] presents the diagrammatic derivation of the CCSD equations with most of the diagrams enumerated.

Several points about the expressions for the T_1 and T_2 amplitudes should be made. First, at this point we have not yet prescribed a method for solving these equations. Second, the equations are nonlinear and coupled, a feature they share with the Hartree–Fock or MCSCF equations. Third, the equations are quartic in $\hat{T}_1$ but only quadratic in $\hat{T}_2$. The quadratic nonlinearities are similar to the nonlinearity that is implicit in the CI secular problem (see Appendix). Although the quartic nonlinearity can be a problem, anyone who has solved Hartree–Fock on MCSCF problems in unlikely to be deterred by the comparatively low level of nonlinearity in the CCSD equations. A fourth feature is that the computational effort required to evaluate each amplitude grows asymptotically no more rapidly than the sixth power of the number of basis functions. In a system with n occupied orbitals and N unoccupied orbitals, the CCSD computation time for very large basis sets and many electrons will grow only as $n^2 N^4$, which is the same as for SD-CI. Enhancements to CCSD incorporating all excitations in a class of higher excitations (e.g., $\hat{T}_3$) will result in algorithms in which the time required grows as the seventh power of the size of the basis.[20]

The final point to be made concerns the form of the equations for the T_2 amplitudes in Tables II and III.

These equations have been written in a form which emphasizes the similarity between $\hat{T}_2$ and $\frac{1}{2}\hat{T}_1^2$ terms. Thus, it is possible to implement terms containing $\hat{T}_1^2$ using subroutines already written for $\hat{T}_2$ terms.[20]

IV. IMPLEMENTATION OF THE CCSD METHOD

At the time when we reported implementing the CCD model,[20] we briefly outlined the procedures we used for solving the nonlinear $\hat{T}_2$ equations. We omitted many details which we felt were self-evident; however, our subsequent experience has convinced us that a more detailed description of the algorithms should be disclosed.

First, we wish to define what we do not do. If we collect the $\hat{T}_1$ and $\hat{T}_2$ coefficients into a vector X and define the arrays A, B, C, D, and E, it is possible to write the equations in a general tensor form

$$A_i + \sum_j B_{ij} X_j + \sum_{ij} C_{ijk} X_{jk} + \sum_{jkl} D_{ijkl} X_j X_k X_l$$

$$+ \sum_{jklm} E_{ijklm} X_j X_k X_l X_m = 0 . \tag{16}$$

In principle, Eq. (16) can be solved using standard approaches after constructing the matrices A, B, C, D, and E. Although we find Eq. (16) occasionally useful in discussing properties of the coupled-cluster equations,[13] the large dimension of the B, C, D, and E arrays make implementation of practically useful algorithms predicated upon the construction and manipulation of these arrays impossible. Consequently, the programs never construct these arrays; however, it is possible to think of our programs as producing the result of B, C, D, and E operating on X without explicitly constructing the arrays.

TABLE III. Definitions of quantities in Table II.

$$A_{ij}^{ab} \equiv t_i^a t_j^b - t_j^a t_i^b , \qquad C_{ij}^{ab} \equiv t_{ij}^{ab} + A_{ij}^{ab} , \qquad \tilde{C}_{ij}^{ab} \equiv t_{ij}^{ab} + t_i^a t_j^b ,$$

$$B_{ij}^{ab} \equiv t_{ij}^{ab} + A_{ij}^{ab}/3 , \qquad \tilde{B}_{ij}^{ab} \equiv t_{ij}^{ab} + t_i^a t_j^b/3 ,$$

$$\eta^{bd} \equiv \sum_{kc} \langle bk \| dc \rangle t_k^c , \qquad \eta_{lj} \equiv \sum_{kc} \langle kl \| cj \rangle t_k^c ,$$

$$\alpha_{ab;cj} \equiv \sum_{kd} \langle bk \| cd \rangle \tilde{B}_{kj}^{ad} - \sum_{kd} \langle ak \| cd \rangle \tilde{B}_{kj}^{bd} + \sum_{k>l} \langle lk \| jc \rangle B_{kl}^{ab} ,$$

$$\alpha_{ij;lb} \equiv \sum_{kc} \langle lk \| cj \rangle \tilde{B}_{ik}^{cb} - \sum_{kc} \langle lk \| ci \rangle \tilde{B}_{jk}^{cb} + \sum_{c>d} \langle bl \| cd \rangle B_{ij}^{cd} .$$

The methods used within the programs can be most simply explained by referring to the equation in Table I as an example. The first step is to rearrange the equation into an explicit equation for the coefficient t_i^d. Based upon our experience with perturbation theory,[20,21] we usually choose the terms containing the diagonal Fock matrix elements (i. e., orbital energies) for the rearrangement of the T_1 equation. Thus, we would write

$$t_i^d = (f_{ii} - f_{dd})^{-1} \left\{ f_{id} + \sum_{a(\neq d)} f_{ad} t_i^a - \sum_{i(\neq l)} f_{il} t_l^d \right.$$
$$\left. + \sum_{ia} \langle di || la \rangle t_i^a + \sum_{ia} f_{ia}(t_{il}^{ad} - t_i^a t_l^d) + \cdots \right\} \quad . \quad (17)$$

Equation (17) would then be solved iteratively. Usually, but not always, we start with t_i^d initially set to 0 so that

$$t_i^d(1) = (f_{ii} - f_{dd})^{-1} f_{id} \quad (18)$$

and subsequently on the jth iteration

$$t_i^d(j+1) = (f_{ii} - f_{dd})^{-1} \left\{ f_{id} + \sum_{a(\neq d)} f_{ad} t_i^a(j) \right.$$
$$- \sum_{j(\neq l)} f_{il} t_l^d(j) + \sum_{ia} \langle di || la \rangle t_i^a(j)$$
$$\left. + \sum_{ia} f_{ia}(t_{il}^{ad}(j) - t_i^a(j) t_l^d(j)) + \cdots \right\} \quad . \quad (19)$$

Equation (19) illustrates one additional feature of the method we use to solve the CCSD equations. Namely, we usually choose to simultaneously iterate the equations for $\hat{T}_1$ and $\hat{T}_2$ coefficients so that at the end of the nth cycle we have all $t_i^d(n)$ and $t_{ij}^{ab}(n)$. Of course, it is possible to iterate separately for the $\hat{T}_1$ coefficients with frozen $\hat{T}_2$ coefficients and then iterate for $\hat{T}_2$ coefficients with fixed $\hat{T}_1$. We usually find that $\hat{T}_1$ and $\hat{T}_2$ coefficients are sufficiently coupled that such an iteration method is uneconomical.

Another point which Eq. (19) illustrates is that we retain the nonlinearity of the CC equations throughout their solution. Usually, we do not choose to solve a linear approximation before introducing the nonlinear terms. Nor do we choose to use a Newton–Raphson method to achieve rapid convergence because the N–R method requires evaluation of a gradient matrix. The size of the gradient matrix would be too large to handle conveniently. Instead, we use a reduced linear equation method to accelerate convergence.[13]

In writing down Eq. (17), we choose to use the terms containing diagonal Fock matrix elements to solve for t_i^d. This choice implies that the first few iterations of Eq. (17) beginning with $\hat{T}_1 = 0$ correspond to a perturbation solution of the CC equations using a Møller–Plesset partitioning of the Hamiltonian, which has been shown to normally have better convergence.[24] If a linear approximation to Eq. (17) is made, then all iterations can be made just as in perturbation theory. Although the Moller–Plesset partitioning has been shown to be superior for perturbation methods based upon Hartree–Fock orbitals, there are times when it is clearly inappropriate such as when RHF orbitals are used for an open-shell configuration and $f_{ii} = f_{dd}$. In that situation,

$(f_{ii} - f_{dd})^{-1}$ is indeterminant and we have a so-called "dangerous denominator." Fortunately, in this case the dangerous denominator problem is artifical and can be eliminated by electing to add an arbitrary constant times t_i^d to both sides of the T_1 equation (Table I) and then solve for t_i^d. A simple rearrangement to other forms, like the Epstein–Nesbet partitioning, for example, will not usually alleviate the denominator singularity. Of course, any circumvention does not resolve the inherently multideterminatal description implied by the dangerous denominator.

Throughout this paper, the equations have been written in spin-orbital form. However, prior to implementation in the computer program, the equations are rewritten and the spin factors are specifically included. For example, for orbitals l and d having α-spin,

$$\sum_{\substack{a>b \\ i}} \langle id || ab \rangle t_{il}^{ab} = \sum_{\substack{a_\alpha > b_\alpha \\ i_\alpha}} \langle i_\alpha d_\alpha || a_\alpha b_\alpha \rangle t_{i_\alpha l_\alpha}^{a_\alpha b_\alpha}$$
$$+ \sum_{\substack{a_\beta, b_\alpha \\ i_\beta}} \langle i_\beta d_\alpha | a_\beta b_\alpha \rangle t_{i_\beta l_\alpha}^{a_\beta b_\alpha} \quad , \quad (20)$$

since the other possible spin components vanish, i_α refers to the spatial function of the ith spin orbital and β orbitals are numbered higher than α orbitals. If $n_\alpha (n_\beta)$ is the number of occupied orbitals with $\alpha (\beta)$ spin and $N_\alpha (N_\beta)$ is the number of unoccupied orbitals with $\alpha (\beta)$ spin then the factoring by spin reduces the sum on the left side from $(n_\alpha + n_\beta)^2 (N_\alpha + N_\beta)^3$ to $n_\alpha^2 N_\alpha^2 (N_\alpha + 1)/2 + n_\alpha n_\beta N_\alpha^2 N_\beta$ operations. The equations are also analyzed to reveal simplifications which result when orbitals are spin restricted so that α and β components have the same space functions. Thus, in the spin-restricted problem, $t_{l\alpha}^{d\alpha}$ is evaluated, but $t_{l\beta}^{d\beta}$ (which equals $t_{l\alpha}^{d\alpha}$) is not evaluated. Similarly for RHF double excitations $t_{i\alpha j\alpha}^{a\alpha b\alpha} = t_{i\beta j\beta}^{a\beta b\beta}$ and $t_{i\beta j\alpha}^{a\beta b\alpha} = t_{j\beta i\alpha}^{b\beta a\alpha}$. Thus, the number of double excitation coefficients which must be evaluated in the RHF case is nearly half the number required in the UHF case. In all cases, we have been able to implement the spin-restricted sums with the same subprograms as used for the implementation of the spin-unrestricted sums by changing loop limits and inserting appropriate factors of two. As a result of explicitly treating the spin, the work involved in evaluating our equations is essentially the same as if we had adopted a spin-adapted formulation while retaining the flexibility of removing spin restrictions.

In addition to an explicit treatment of spin summations, we also factor terms containing products of three terms into intermediate partial sums containing just two terms. Thus,

$$\sum_{\substack{i>j \\ ca}} \langle ij || ca \rangle t_i^c t_{ij}^{da} = \sum_c t_i^c \sigma_{cd} \quad , \quad (21)$$

where

$$\sigma_{cd} = \sum_{\substack{i>j \\ a}} \langle ij || ca \rangle t_{ij}^{da} \quad . \quad (22)$$

The intermediate σ_{cd} is computed and stored as a partial sum before completing the evaluation by summing over the $\hat{T}_1$ terms. As a result of this factorization, the work required to evaluate the above term is reduced from $n^2(n-1)N^3/2$ operations to $n^2(n-1)N^2/2 + nN^2$ operations. This is exactly the same type of simplification required to reduce the two-electron integral transformation to an $(n+N)^5$ process from an $(n+N)^8$ process; and like the explicit spin summations, it always has been used in our MBPT/CCD programs.[20,21,24-26]

Our treatment of symmetry within the program occurs at two levels and is intertwined with the choices we made for integral and coefficient storage. Hence, a brief explanation of our integral storage technique is required. Before we adopted any storage scheme, we first proposed some design goals for the program:

(1) The storage scheme adopted should facilitate writing the program, i.e., it should be easier to write the required subroutines and easier to ensure the correctness of the routines.

(2) Every step in the evaluation of the terms required should be fully factored and no term should require more than n^2N^4, n^4N^2 or n^3N^3 operations.

(3) Access to data, both in memory and on disk, should be sequential in the inner loops. No input/output would ever occur within the two innermost loops. Random access to records on disk would be presumed, but primarily used to position subfiles which would then be read sequentially. Because of the sequential access through memory, the program would be ideally suited for virtual memory computers.

(4) The central memory requirements, should be proportional to the square of the number of basis functions. Thus, if the computer has enough memory to solve the Hartree–Fock problem, then there should be enough memory to solve the CC problem. Unlike most CI programs, we do not assume that all of our coefficients could fit into memory. Instead, we choose to hold only a single distribution of coefficients in memory and to carefully manage the concommitant increase in input/output by working with fully ordered integrals and coefficients. Consequently, we were able to carry out frozen core CCD double zeta calculation on benzene (60 MO's) on a VAX 11-780 using a physical memory working set of 256 kbytes while paging at a relatively slow rate.[11]

(5) Symmetry zeros and accidental zeros should be treated transparently and on equal footing where possible.

Our approach to implementing these six goals centers on the observation that most terms in Tables I–III can be written as simple scalar products. For example, by combining ab, cd, and ij into single labels c, f, and k, we can rewrite

$$\sum_{cd} \langle ab||cd \rangle t_{ij}^{cd} \qquad (23)$$

as a simple matrix product $\sum_f V_{ef} T_{fk}$. If all $\langle ab||cd \rangle$ and t_{ij}^{cd} are sorted into a random access device so that

the label ab identifies a record containing $\langle ab || cd \rangle$ for all cd and the label ij identifies a record containing t_{ij}^{cd} for all cd, then the summation indicated in Eq. (23) is easy to perform, especially if the integrals are also ordered within each record. Furthermore, the sums can be set up so that only N^2 integrals of $\langle ab||cd \rangle$ type and N^2 coefficients of t_{ij}^{cd} type must be in memory to generate a given t_{ij}^{ab}. If integrals are ordered in each record, exact zeros and integrals smaller than a given threshold can be removed and a skip count indicating the distance between labels can be packed into the integrals.

As a result, to simplify programming, we opt to sort the molecular orbital integrals coming out of the two-electron transformation into antisymmetrized combinations with Dirac type labels and to store them in random access subfiles according to the number and location of occupied indices. Within each subfile, two integral labels are used to specify a record containing all integrals of that type. Zero integrals and approximately zero integrals are not stored in the records and skip counts are inserted to keep track of these integrals. While these steps introduce some inefficiency and redundancy at the N^4 level, we are willing to make these kinds of sacrifices to speed up the N^6 processes.

Returning to the treatment of symmetry, we see that at the lowest level symmetry is implemented by removing all zeros from the antisymmetrized integral and coefficient lists. While it is important to remove zeros for integral and coefficient storage, the principal benefit occurs during the construction of the scalar products where a routine like that shown in Table IV can be used to perform a sparse scalar product. Thus, the innermost loops are implemented with a sparse scalar product subroutine which is driven by the indices implicit within the antisymmetrized integral list. Since indices which are zero by symmetry never appear the loops effectively run only over symmetry indices. To avoid generating a term which is zero by symmetry, we use a symmetry template in the outermost loops. Thus, the target arrays contain a bit flag which indicates whether the sum is zero by symmetry. In effect, the outermost loops run over all orbital indices, but the inner loops are skipped altogether if the evaluation term must be zero by symmetry.

This completes the discussion of the computational considerations. The following section discusses some applications of the CCSD model to molecules.

V. EXAMPLES

Our first application of the CCSD model was to H_2 in a double zeta basis, using the $1\sigma_g^2$ configuration as the reference point. A potential curve from 0.9 through 10 a.u. was calculated with both the CCSD model and SDCI (i.e., full CI), which must necessarily give the same answer. Since at large R, the $1\sigma_g^2$ and $1\sigma_u^2$ configurations become degenerate, the single reference CCSD model demonstrates the same flexibility as full CI. Furthermore, the CCSD energy was found to be invariant to orbital transformations—including UHF

TABLE IV. A Fortran subroutine for performing a sparse scalar product.

```
         FUNCTION PAKRD (A, LA, B, LB, N)
C
C  PAKPRD PERFORMS A PACKED SCALAR PRODUCT
C            BETWEEN VECTOR A AND VECTOR B
C
C  A  : AN ARRAY OF NUMBERS WITH SKIP INDICES
C  LA : THE LENGTH OF A
C  B  : AN ARRAY OF NUMBERS WITH SKIP INDICES
C  LB : THE LENGTH OF B
C  N  : THE LENGTH OF A AND B IF THEY WERE
           UNPACKED
C

       PAKPRD = 0.
       IA = 0
       IB = 0
       NA = 0
       NB = 0

 40    IA = IA + 1
       NA = NA + (A(IA).AND.255)
 30    IB = IB + 1
       NB = NB + (B(IB).AND.255)
 50    IF (NA-NB) 10, 20, 30
 20    PAKPRD = PAKPRD + A (IA)*B(IB)
       IF (NA.LT.N) GO TO 40
       IF (NB.GT.N) CALL BOMB (NB)
       IF (IB.GT.LB) CALL BOMB (IB)
       IF (IA.GT.LA) CALL BOMB (IA)
       RETURN
 10    IA = IA + 1
       NA = NA + (A(IA).AND.255)
       GO TO 50
       END
```

TABLE V. Comparison of MBPT/CCM results with full CI for H_2O in a 14 CGTO basis set from Saxe, Schaefer, and Handy.[a]

Model	Configurations	Correlation energy	ΔE (FCI) kcal/mol
SD–CI	361	−0.140 18	4.9
SDTQ–CI	17 678	−0.147 77	0.2
FULL CI	256 743	−0.148 03	0.0
D–MBPT(2)		−0.139 48	5.4
D–MBPT(3)		−0.140 87	4.5
D–MBPT(4)		−0.143 92	2.6
DQ–MBPT(4)		−0.144 76	2.1
SDQ–MBPT(4)		−0.145 65	1.5
SDTQ–MBPT(4)[b]		−0.147 04	0.6
CCD		−0.145 44	1.6
CCD-orbital optimized		−0.146 22	1.3
CCD+ST(4)		−0.147 71	0.2
CCSD-2		−0.146 55	0.9
CCSD		−0.146 24	1.2
CCSD + T(4)[b]		−0.147 60	0.3

[a]Reference 27.   [b]Reference 28.

orbitals—which were applied to test the program.

The second application, also made to test the correctness of the program, was $2H_2$ at 100 a.u. intermolecular separation. In this problem, the CCSD energy was exactly twice the SDCI energy for a single H_2 as size extensivity requires.[20] Again, the correct relationship held for the range of H_2 intermolecular separations while keeping the intermolecular separation of the H_2's at 100 a.u.

More interesting results are the CCSD energies for H_2O and the comparison with the full CI results of Saxe, Schaefer, and Handy (Table V).[27] Our CCSD energy, in the double zeta basis at their geometry, is −76.156 077 hartree which represents an energy lowering of −0.006 062 hartree relative to their SD–CI energy of −76.150 015 hartree. The CCSD energy is 0.001 789 hartree above their full CI energy of −76.157 866 hartree. The largest part of the difference between CCSD and full CI comes from triple excitations, which have been calculated to contribute −0.001 364 hartree.[28] The CCSD energy accounts for 98.79% for 98.8% of the total correlation energy compared to 94.7% for SD–CI. Thus, the CCSD model accounts for two-thirds of the error inherent in SD–CI. As can be seen from Table V, the CCSD + T(4) model energy is only 0.1 kcal/mol above the SDTQ–CI energy. In this case, the effect of CI-type

quadruple excitations are handled accurately by the exponential ansatz.

Equally interesting is a comparison of CCSD with CCSD-2, a simplification of the full CCSD in which only the linear single excitation terms and the $1/2T_1^2$ are retained. The difference between CCSD and CCSD-2 of 0.000 31 hartree is the energy raising caused by disconnected single contributions to CI-type triple and quadruple excitations.

One of the advantages of an infinite-order model like CCSD over a finite-order perturbation approximation occurs with more difficult cases that involve some quasidegeneracy.[20] Unlike the H_2O example, where the

TABLE VI. Contracted Gaussian basis used for the ten orbital BeH_2 model problem.

		Exponent	Contraction coefficient
Be	1s	1267.07	0.001 940
		190.356	0.014 786
		43.295 9	0.071 795
		12.144 2	0.236 348
		3.809 23	0.471 763
		1.268 47	0.355 183
	1s′	5.693 880	−0.028 876
		1.555 630	−0.177 565
		0.171 855	1.071 630
	1s″	0.057 181	1.000
	2p	5.693 880	0.004 836
		1.555 630	0.144 045
		0.171 855	0.949 692
H	1s	19.240 6	0.032 828
		2.899 2	0.231 208
		0.653 4	0.817 238
	1s′	0.177 60	1.000

TABLE VII. Comparison of BeH_2 energies calculated near the transition state geometry Be(0, 0, 3 a.u.) H(0, +1.16 a.u., 0) reference configuration $a_1^2 a_1^2 a_1^2$.[a]

Model	Configurations	Total energy	ΔE(FCI) kcal/mol
SCF	1	-15.536 47	55.5
FCI	1574	-15.624 96	0.0
D-MBPT(2)		-15.584 85	25.2
D-MBPT(3)		-15.604 60	12.8
D-MBPT(4)		-15.614 37	6.6
SD-MBPT(4)		-15.614 85	6.3
DQ-MBPT(4)		-15.613 31	7.3
SDQ-MBPT(4)		-15.613 78	7.0
CCSD-2		-15.627 09	1.3
CCSD		-15.624 18	0.5

[a]CCSD expansion coefficient for $a_1^2 a_1^2 b_2^2 = -0.24$ using intermediate normalization.

Hartree-Fock reference determinant has a coefficient of 0.95 in the full CI expansion with all other coefficients very small, a quasidegenerate problem usually has two or more configurations with comparatively large coefficients, which might recommend a multi-reference approach. However, the infinite-order CCD model relative to only a single reference function has been shown to often describe even highly degenerate problems reliably.[12] Consequently, to assess the stability of the CCSD model for quasidegenerate cases, a problem involving the insertion of Be into an H_2 molecule has been considered.

Be is well-known for the quasidegeneracy between the 2s and 2p orbital that causes the $1s^2 2p^2$ configuration to be important in the CI expansion. The degree of importance of the $1s^2 2p^2$ configuration is very much a function of the choice of molecular orbitals with natural orbitals weighting it heavily. With less appropriate SCF orbitals from a large basis set, the coefficient is smaller, but still about 0.1.[20] Also, as the H_2 bond is broken, the $1\sigma_g^2$ and $1\sigma_u^2$ configurations become equally important, placing a severe burden on a method referred to only the $1\sigma_g^2$ configurations. In addition to these elements, as Be is inserted perpendicularly (C_{2v}) into H_2, there is a promotion from Be($2s^2$) to Be($2p^2$) near the critical geometry, causing the principal configuration for BeH_2 to change from $1a_1^2 2a_1^2 3a_1^2$ to $1a_1^2 2a_1^2 1b_2^2$. Since in a single reference model, one of these configurations must be treated in the complementary space, such quasidegeneracy effects should severely tax the ability of a single reference model to describe this insertion reaction. Another complication is that both RHF functions are unstable since a lower UHF solution exists. Just as in full CI, however, even a poor choice of single reference function might be used to generate the configurations, but the proper weight factors would be obtained via the diagonalization step. CCSD potentially has the same flexibility, although one must distinguish between a method containing the correct solution and the practical problem of extracting that solution numerically. In all applications reported here, the reduced linear equation method[13] and Padé approximants[24] are used to obtain the solutions.

The basis set for BeH_2 is given in Table VI, and we present the SCF, full CI, CCSD, and various lower order MBPT results in Table VII. The geometry Be(0., 0., 3.0 a.u.) and H(0. ±1.16 a.u., 0.) is near the point of crossover where the principal configuration $1a_1^2 2a_1^2 3a_1^2$ would be superseded by $1a_1^2 2a_1^2 1b_2^2$. The full CI coefficients using SCF orbitals obtained from $1a_1^2 2a_1^2 1b_2^2$ at this geometry are 0.823 and -0.294, respectively. When Be is moved to 2.75 a.u. from H_2, the respective coefficients change to -0.560 and 0.724.

Despite the large amount of potential degeneracy in this system, the agreement between the single reference CCSD model and the full CI is exceptional. Unlike the example of H_2O where fourth-order perturbation theory SDTQ-MBPT(4) is only 0.6 kcal/mol higher than the full CI, while the other fourth-order approximations are in the vicinity of 2 kcal/mol of the full CI, the error is 6-7 kcal/mol for fourth-order approximations to the correlation energy of BeH_2. The remaining error is probably due to triple excitations.

An even more extreme test example is to choose to use the less important $1a_1^2 2a_1^2 1b_2^2$ configuration as the reference determinant. Its coefficient of 0.294 corresponds to a weight of less than 10% of the full CI wave function. These results are listed in Table VIII. Notice that the SCF result is much higher and, in fact, seems to be approximating the second root of the full CI. The perturbation approximations tend to cluster in the vicinity of the second eigenvalue although they do not go below the correct answer, assuming some kind of average value between the two eigenvalues. However, the CCSD model appears to overcome the comparatively poor starting point to a large degree, getting within 5.3 kcal/mol of the full CI. This occurs despite the enormous weight of the $1a_1^2 2a_1^2 3a_1^2$ configuration (2.16 intermediately normalized) in the CCSD wave function.

In conclusion, BeH_2 has an approximately separated pair structure and the basis set is small, but this example still illustrates the large degree of flexibility inherent in the CCSD model. Other molecules without such a separated pair structure should be less accurate-

TABLE VIII. Comparison of BeH_2 energies calculated at Be(0, 0, 3 a.u.) H(0, ±1.16 a.u., 0) with reference configuration $a_1^2 a_1^2 b_2^2$.[a]

Model	Configurations	Total energy	ΔE(FCI) (kcal/mol)
SCF	1	-15.477 28	92.7
FCI root 1	1574	-15.624 96	0.0
FCI root 2	1574	-15.535 75	56.0
D-MBPT(2)		-15.519 87	65.9
D-MBPT(3)		-15.535 64	56.0
D-MBPT(4)		-15.544 22	50.7
SD-MBPT(4)		-15.544 95	50.2
DQ-MBPT(4)		-15.543 31	51.2
SDQ-MBPT(4)		-15.544 04	50.8
CCSD		-15.616 45	5.3

[a]CCSD expansion coefficient for $a_1^2 a_1^2 a_1^2 = 2.16$ using intermediate normalization.

ly described with CCSD. However, CCSD's stability, efficiency, size-extensivity, and equivalence to the full CI for the chemical pertinent problem of a group of separated electron pairs, would appear to make CCSD a very attractive model for numerous applications.

ACKNOWLEDGMENTS

The authors wish to thank Mr. Frank Brown and Dr. Ron Shepard for computing the full CI energies for BeH_2. We also are indebted to Professor Mike Zerner for a helpful discussion about the connected diagram aspect of the CCSD equation.

APPENDIX A: THE CI EIGENVALUE PROBLEM IN ENERGY INDEPENDENT FORM

Consider the problem of finding an eigenvalue satisfying

$$(H - E1)C = 0 , \qquad (A1)$$

where H is a symmetric matrix and 0 is the eigenvector corresponding to the energy eigenvalue E. One technique for solving secular equations is the partitioning method. Here we partition Eq. (A1) and renormalize it so that

$$\begin{bmatrix} H_0 - E1 & a \\ a^t & B - E1 \end{bmatrix} \begin{bmatrix} 1 \\ t \end{bmatrix} = 0 , \qquad (A2)$$

which is equivalent to two equations

$$H_0 - E1 + at = 0 \qquad (A3)$$

and

$$a^t + (B - E1)t = 0 . \qquad (A4)$$

Solving Eq. (A3) for E, we find

$$E = H_0 + at \qquad (A5)$$

which we use in Eq. (A4) to get

$$a + (B - H_0 1)t = (at1)t = 0 . \qquad (A6)$$

Equation (A6) is independent of E and equivalent to Eq. (A2). The energy corresponding to the t which satisfies Eq. (A6) is given by Eq. (A5). The quadratic dependence manifest in Eq. (A6) is different from that present in the coupled-cluster equation, since in Eq. (A6) there is a scalar product, while in the coupled-cluster equations a true tensor product $t \times t$ appears.

Equation (A6) also has an additional interesting feature in that the linearized coupled-cluster method can be derived by deleting $-(at1)t$ from Eq. (A6).

[1] K. A. Brueckner, Phys. Rev. 97, 1353 (1955); 100, 36 (1955).

[2] K. A. Brueckner, R. J. Eden, and N. C. Francis, Phys. Rev. 93, 1445 (1955); K. A. Brueckner and C. A. Levinson, ibid. 97, 1344 (1955).

[3] J. Goldstone, Proc. R. Soc. London, Ser. A 239, 267 (1957).

[4] H. P. Kelly, Adv. Chem. Phys. 14, 129 (1969).

[5] F. Coester, Nucl. Phys. 1, 421 (1958).

[6] F. Coester and H. Kümmel, Nucl. Phys. 17, 477 (1960); H. Kümmel, ibid. 22, 177 (1969).

[7] J. Čížek, J. Chem. Phys. 45, 4256 (1966); Adv. Chem. Phys. 14, 35 (1969).

[8] J. Čížek and J. Paldus, Phys. Scr. 21, 251 (1980).

[9] R. J. Bartlett, Annu. Rev. Phys. Chem. 32, 359 (1981), and references therein.

[10] J. A. Pople, J. S. Binkley, and R. Seeger, Int. J. Quantum Chem. Symp. 101, 1 (1976).

[11] R. J. Bartlett and G. D. Purvis, Ann. N. Y. Acad. Sci. 367, 62 (1981).

[12] K. Jankowski and J. Paldus, Int. J. Quantum Chem. 18, 1243 (1980).

[13] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. 75, 1284 (1981).

[14] O. Sinanoglu, J. Chem. Phys. 36, 706, 3198 (1962); Adv. Chem. Phys. 6, 315 (1964).

[15] J. Čížek, J. Paldus, and L. Sroubkova, Int. J. Quantum Chem. 3, 149 (1969).

[16] J. Paldus, J. Čížek, and I. Shavitt, Phys. Rev. A 5, 50 (1972).

[17] R. Krishnan, M. J. Frisch, and J. A. Pople, J. Chem. Phys. 72, 4244 (1980).

[18] M. J. Frisch, R. Krishnan, and J. A. Pople, Chem. Phys. Lett. 75, 66 (1980).

[19] G. D. Purvis and C. Nehrkorn, KOMMUTE program, QCPE, Bloomington, Ind.

[20] R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. 14, 561 (1978).

[21] R. J. Bartlett and G. D. Purvis, Phys. Scr. 21, 255 (1980).

[22] J. Paldus, J. Chem. Phys. 67, 303 (1977); I. Lindgren, J. Phys. B 7, 2441 (1974).

[23] J. Cullen, dissertation, Guelph University, Guelph, Ontario, Canada, 1981.

[24] R. J. Bartlett and I. Shavitt, Chem. Phys. Lett. 50, 190 (1977); 57, 157 (1978).

[25] G. D. Purvis and R. J. Bartlett, J. Chem. Phys. 68, 2114 (1978); 71, 548 (1978).

[26] R. J. Bartlett and D. M. Silver, Int. J. Quantum Chem. Symp. 8, 271 (1974); Phys. Rev. A 10, 1927 (1974).

[27] P. Saxe, H. F. Schaefer, and N. Handy, Chem. Phys. Lett. 79, 202 (1981).

[28] S. Wilson and M. F. Guest, Chem. Phys. Lett. 73, 607 (1980).