Electron Correlation Theories and Their Application to the Study of Simple Reaction Potential Surfaces

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Abstract

This paper serves two purposes. The first is to describe an implementation of the coupled cluster theory with double substitutions (CCD) previously developed by Cizek. The second is to apply this method and closely related fourth-order perturbation methods to some simple molecules and reaction potential surfaces. These studies show that CCD theory gives results close to those of a Møller–Plesset perturbation treatment to fourth order in the space of double and quadruple substitutions MP4(DQ). Addition of contributions from single substitutions at fourth order makes little change in predicted relative energies. Preliminary results on the potential surfaces for 1,2-hydrogen shifts in C_2H_2, HCN, CH_2O, and N_2H_2 are discussed and compared with previous studies.

1. Introduction

It is well recognized that refinement of molecular-orbital (MO) techniques proceeds in two distinct directions. One is extension of the set of basis functions used for expansion of the MOs and the other is the development of methods for taking account of correlation between electron motions that are neglected in the simplest, single-configuration Hartree–Fock (HF) treatment. In this second area, a wide variety of methods have been proposed and some are now widely used in practical applications. However, there are very few studies that compare the effectiveness of these methods in a systematic manner.

To be satisfactory as a general computational technique, a MO theory of electronic energy should ideally have the following features:

(a) It should be size consistent. This means that when applied to an assembly of isolated molecules, the results should be the sum of the energies calculated by applying the same method to the molecules individually. If this condition is not satisfied, the theory is unlikely to give a good description of the relative energies of molecules of different sizes.

(b) It should be invariant under transformations within a set of degenerate MOs. Since the specific forms of degenerate orbitals are usually partly arbitrary in molecules of high symmetry, clearly the results of an energy calculation should be independent of such choices.

(c) It should have the variational property of giving an upper bound to the energy that would be obtained by exact solution of the electronic Schrödinger equation.

Few theories satisfy all three of these conditions, even for molecular ground states. HF theory, in its spin-unrestricted form (UHF) with an atom-centered set of basis functions, usually satisfies all three but takes no account of the correlation between electrons of opposite spin. Complete configuration interaction (CI) within a given basis would satisfy all three but this is only practicable for the very smallest systems. There is a clear need for practical theories at an intermediate level that take some account of electron correlation.

One possible approach is truncated configuration interaction. If the HF single determinant Ψ_0 is used as a starting point, this is conveniently done by limiting the many-electron basis to Ψ_0 and those determinants that are obtained from Ψ_0 by double substitutions of occupied spin orbitals by unoccupied (virtual) spin orbitals. (Single substitutions are usually unimportant if the HF orbitals are properly optimized.) This method of *configuration interaction with double substitutions* (CID) is practical and satisfies conditions b and c. However, it fails to satisfy the important size-consistency condition (a), since it fails to account for *simultaneous* double substitutions in different molecules.

A second approach is the perturbation method, initiated by Møller and Plesset [1]. Here the HF problem is treated as the unperturbed wave function and the residual part of the Hamiltonian is treated as a perturbation. Expansion in a perturbation series can then be truncated at any order. These methods are practical to third order [2, 3] or partial fourth order [4, 5] and have been applied quite extensively. They satisfy conditions a and b but not c. Their principal deficiency is that the rate of convergence of the perturbation series may be inadequate in systems where the effects of electron correlation are large.

A third possible approach is the coupled cluster (CC) method. First introduced in nuclear physics [6], this approach has been formulated in molecular terms by Cizek and others [7, 8]. The *coupled cluster method with double substitutions* (CCD) uses a wave function that allows for all double substitutions, including the simultaneous substitutions that are omitted in CID theory. Cizek refers to this method as the coupled pair many-electron theory (CPMET). It satisfies size-consistency condition (a) and also the invariance condition (b). However, it does not have the variational property (c). Further, it can be applied more reasonably than perturbation theory if the correlation energy correction is large. For a two-electron system, it becomes equivalent to CID.

An area in which inclusion of electron correlation is likely to be important is in the study of reaction potential surfaces. It is well known that correlation makes a major contribution to the strength of electron-pair bonds, so it is probable that the theoretical energies predicted for partial bond breaking, as in the transition states (or transition structures) of simple reactions, will be influenced by the level of correlation theory. It is also reasonable to expect that the truncated CI methods, such as CID, will have deficiencies in describing some reaction potential surfaces because of the lack of size consistency. However, both the perturbation and CC methods are free from such criticism and merit serious comparison.

This paper has two objectives. The first is to report on an implementation of the CCD method completed recently by Krishnan. The second is to apply this

method and perturbation methods (up to partial fourth order) to certain simple unimolecular reactions, seeking both the energy change from reactant to product and the activation energy. The reactions we examine are the 1,2 proton transfers:

$$HCCH \rightarrow H_2CC$$
$$HCN \rightarrow CNH$$
$$H_2CO \rightarrow HCOH$$
$$HNNH \rightarrow H_2NN$$
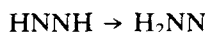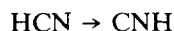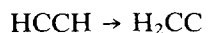
The first two have been the subject of previous *ab initio* studies, with which we will make comparisons [9, 10].

In Sec. 2, we give a brief presentation of the CCD theory following Hurley [11] and its relation to the perturbation method. This is followed in Sec. 3 by preliminary application of the CCD techniques to simple AH_n molecules (A being a first-row atom) using a large uncontracted basis. This parallels previous studies using perturbation [3, 5] and CI [12] methods. Section 4 then gives the results and discussion of applications to the proton-shift reactions listed above.

2. CCD Theory and Its Relation to Perturbation Theory

Let Ψ_0 be the HF determinantal wave function,

$$\Psi_0 = (n!)^{-1/2} |\chi_1 \chi_2 \cdots \chi_n| \tag{1}$$

where $\chi_1 \cdots \chi_n$ are spin orbitals occupied by n electrons. These are eigenfunctions of the Fock operator, the corresponding eigenvalues being $\varepsilon_1 \cdots \varepsilon_n$. For a finite basis, there will be a finite number of unoccupied (virtual) spin orbitals χ_{n+1}, etc. We shall use labels $i, j, k, l, \ldots$, to denote occupied spin orbitals and $a, b, c, d, \ldots$, for virtual ones.

Now introduce a double substitution operator $\hat{t}_{ij}^{ab}$ such that $\hat{t}_{ij}^{ab} \Psi_0$ is a single determinant function Ψ_{ij}^{ab} in which χ_i is replaced by χ_a and χ_j is replaced by χ_b. Clearly $\hat{t}_{ij}^{ab}$ is antisymmetric in both pairs (ij) and (ab). Then a complete double substitution operator can be set up as

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} a_{ij}^{ab} t_{ij}^{ab} \tag{2}$$

where a_{ij}^{ab} is an array (antisymmetric in occupied and virtual indices) with elements to be determined.

The CID method uses an unnormalized trial wave function

$$\Psi_{CID} = (1 + \hat{T}_2) \Psi_0$$
$$= \Psi_0 + \frac{1}{4} \sum_{ijab} a_{ij}^{ab} \Psi_{ij}^{ab} \tag{3}$$

and treats the a_{ij}^{ab} as variational parameters. The CCD theory, on the other hand, uses a trial function Ψ_{CCD} defined by

$$\Psi_{CCD} = e^{\hat{T}_2}\Psi_0$$

$$= \Psi_0 + \tfrac{1}{4} \sum_{ijab} a_{ij}^{ab} \hat{t}_{ij}^{ab} \Psi_0 + \tfrac{1}{32} \sum_{ijab} \sum_{klcd} a_{ij}^{ab} a_{kl}^{cd} \hat{t}_{ij}^{ab} \hat{t}_{kl}^{cd} \Psi_0 + \cdots \qquad (4)$$

The product of operators $\hat{t}_{ij}^{ab}\hat{t}_{kl}^{cd}$ is treated as zero if there are any coincidences among the eight labels. If not, it leads to a quadruple substitution and Eq. (4) becomes

$$\Psi_{CCD} = \Psi_0 + \tfrac{1}{4} \sum_{ijab} a_{ij}^{ab} \Psi_{ij}^{ab} + \tfrac{1}{32} \sum_{ijab} \sum_{klcd} a_{ij}^{ab} a_{kl}^{cd} \Psi_{ijkl}^{abcd} + \cdots \qquad (5)$$

The explicit equations for the a coefficients are obtained by taking the function

$$(\mathcal{H} - \mathcal{E})\Psi_{CCD} \qquad (6)$$

which would be identically zero if Ψ_{CCD} were the exact wave function, and requiring that its projection on Ψ_0 and all Ψ_{ij}^{ab} is zero. Thus

$$\langle \Psi_0 | \mathcal{H} - \mathcal{E} | \Psi_{CCD} \rangle = 0 \qquad (7)$$

$$\langle \Psi_{ij}^{ab} | \mathcal{H} - \mathcal{E} | \Psi_{CCD} \rangle = 0 \qquad (8)$$

These equations suffice to determine the energy $\mathcal{E}$ and the unknown coefficients a_{ij}^{ab}.

If the full expression [Eq. (5)] is substituted for Ψ_{CCD} the matrix elements can be reduced to integrals involving one or two electrons. Thus Eq. (7) becomes

$$\mathcal{E} = \mathcal{E}_{HF} + \tfrac{1}{4} \sum_{ijab} (ij||ab)a_{ij}^{ab} \qquad (9)$$

where $\mathcal{E}_{HF}$ is the HF energy $\langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle$ and we have adopted the integral notation

$$(pq||rs) = \int \int \chi_p^*(1) \chi_q^*(2) (1/r_{12})[\chi_r(1)\chi_s(2) - \chi_s(1)\chi_r(2)] \, d\tau_1 \, d\tau_2 \qquad (10)$$

integration being over all coordinates of electrons 1 and 2. Substitution of Eq. (5) in Eq. (8) leads to the more complex equations given by Hurley [11],

$$(ab||ij) + \Delta_{ij}^{ab} a_{ij}^{ab} + u_{ij}^{ab} + v_{ij}^{ab} = 0 \qquad (11)$$

where

$$\Delta_{ij}^{ab} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j \qquad (12)$$

u_{ij}^{ab} is the linear array

$$u_{ij}^{ab} = \tfrac{1}{2} \sum_{cd} (ab||cd)a_{ij}^{cd} + \tfrac{1}{2} \sum_{kl} (kl||ij)a_{kl}^{ab}$$

$$+ \sum_{kc} \{-kb||jc)a_{ik}^{ac} + (ka||jc)a_{ik}^{bc} - (ka||ic)a_{jk}^{bc} + (kb||ic)a_{jk}^{ac}\} \qquad (13)$$

and v_{ij}^{ab} the quadratic array

$$v_{ij}^{ab} = \tfrac{1}{4} \sum_{klcd} (kl||cd)\{a_{ij}^{cd}a_{kl}^{ab} - 2(a_{ij}^{ac}a_{kl}^{bd} + a_{ij}^{bd}a_{kl}^{ac})$$

$$- 2(a_{ik}^{ab}a_{jl}^{cd} + a_{ik}^{cd}a_{jl}^{ab}) + 4(a_{ik}^{ac}a_{jl}^{bd} + a_{ik}^{bd}a_{jl}^{ac})\} \tag{14}$$

In the linearized CCD method, the v array is omitted. The procedure then remains size consistent but fails to coincide with the CID method for a two-electron system. We may note that the CID method itself replaces Eq. (11) by

$$(ab||ij) + (\Delta_{ij}^{ab} + \mathscr{E}_{HF} - \mathscr{E})a_{ij}^{ab} + u_{ij}^{ab} = 0 \tag{15}$$

Equations (11) may be solved iteratively in the form

$$a_{ij}^{ab} = -(\Delta_{ij}^{ab})^{-1}\{(ab||ij) + u_{ij}^{ab} + v_{ij}^{ab}\} \tag{16}$$

using u and v arrays from the previous iteration, starting with $u = v = 0$. The main computational effort is required for evaluation of u_{ij}^{ab} and v_{ij}^{ab} at each iteration. Methods of handling u_{ij}^{ab} have been discussed previously [12]. If N is the size of the basis, the three parts of Eq. (13) require $O(n^2N^4)$, $O(n^4N^2)$, and $O(n^3N^3)$ steps, respectively.

All of the parts of the expression [Eq. (14)] for v_{ij}^{ab} can be evaluated efficiently by using intermediate arrays. If we define

$$(kl|X_1|ij) = \sum_{cd} (kl||cd)a_{ij}^{cd} \tag{17}$$

$$(b|X_2|c) = \sum_{kld} (kl||cd)a_{kl}^{bd} \tag{18}$$

$$(k|X_3|j) = \sum_{lcd} (kl||cd)a_{jl}^{cd} \tag{19}$$

$$(il|X_4|ad) = \sum_{kc} (kl||cd)a_{ik}^{ac} \tag{20}$$

then Eq. (14) can be written

$$v_{ij}^{ab} = \tfrac{1}{4} \sum_{kl} (kl|X_1|ij)a_{kl}^{ab} - \tfrac{1}{2}\sum_{c} \{(b|X_2|c)a_{ij}^{ac} + (a|X_2|c)a_{ij}^{cb}\}$$

$$- \tfrac{1}{2}\sum_{k} \{(k|X_3|j)a_{ik}^{ab} + (k|X_3|i)a_{kj}^{ab}\}$$

$$+ \sum_{kc} \{(ik|X_4|ac)a_{jk}^{bc} + (ik|X_4|bc)a_{kj}^{ac}\} \tag{21}$$

Evaluation of the contributions of X_1, X_2, X_3, and X_4 involves $O(n^4N^2)$, $O(n^2N^3)$, $O(n^3N^2)$, and $O(n^3N^3)$ steps, respectively. In line with this, the X_4 execution is the most time-consuming part of our program for evaluation of the v

array. Nevertheless, the whole operation [Eqs. (17)–(21)] involves slightly less time than the evaluation of the u array [Eq. (13)]. Hence each iteration in the CCD method can be performed involving computer times approximately twice that of a CID iteration. However, this is efficient enough for reasonably extensive applications.

It is illustrative to consider the relation between the CCD method and the Møller–Plesset perturbation expansion. In the latter technique, the full Hamiltonian $\mathcal{H}$ is replaced by

$$\mathcal{H}_\lambda = \mathcal{H}_0 + \lambda V = \sum_p F_p + \lambda V \qquad (22)$$

where F_p is the one-electron Fock operator and V is the remaining part $(\mathcal{H} - \mathcal{H}_0)$. λ is an expansion parameter so that $\lambda = 0$ gives the many-electron Fock Hamiltonian $\mathcal{H}_0$ and $\lambda = 1$ gives the correct Hamiltonian $\mathcal{H}$. The Møller–Plesset procedure is to expand the lowest eigenvalue of $\mathcal{H}_\lambda$ in powers of λ,

$$\mathcal{E}_\lambda = \mathcal{E}^{(0)} + \lambda \mathcal{E}^{(1)} + \lambda^2 \mathcal{E}^{(2)} + \cdots \qquad (23)$$

terminate this series at some finite order, and then put $\lambda = 1$. The resulting expressions for $\mathcal{E}^{(0)}$, $\mathcal{E}^{(1)}$, $\mathcal{E}^{(2)}$, etc., show that up to third order, only double-substitution determinants are involved. At fourth order, single (S), double (D), triple (T), and quadruple (Q) substitutions contribute.

We may now enquire about the corresponding perturbation series for the CCD method. How far does the corresponding CCD expansion agree with the full expansion [Eq. (23)]? In other words, to what order in λ is $\mathcal{E}$ (CCD) correct? This point is examined in the Appendix where it is shown that the CCD expansion is correct to third order but for fourth order includes only correct contributions from double (D) and quadruple (Q) substitutions. Thus, in fourth order, the energy is equivalent to the Møller–Plesset fourth-order energy in the limited subspace of double and quadruple substitutions, which we may denote by $\mathcal{E}$ (MP4(DQ)) rather than the full energy to fourth order which would be $\mathcal{E}$(MP4(SDTQ)). Thus, no account is taken of single or triple substitutions.

3. Preliminary Applications

As a first study of the CCD method and its performance relative to the perturbation technique, we have carried out calculations on a series of AH_n molecules ($n = 0, 1, 2$) that has been studied previously with several electron correlation techniques. These computations use a moderately large uncontracted Gaussian basis (841/41) and molecular geometries optimized with this same basis at the second-order Møller–Plesset level [3]. Table I gives the resulting correlation energies at the fourth-order MP4(DQ) level, the truncated configuration interaction CID level, and the linear and full CCD levels.

The following features of the results are noteworthy:

(1) The full CCD values are always lower in energy than CID. This is clearly due to neglect of simultaneous double substitutions in the CID method. The absolute

TABLE I. Correlation energies (mH) using the (841/41) basis.

Molecule[a]	MP4 (DQ)	CID	Linearized CCD	CCD
Li	-32.7	-32.8	-32.9	-32.8
$Be(^1S)$	-74.7	-75.3	-82.6	-77.7
$Be(^3P)$	-38.1	-38.2	-38.5	-38.3
$B(^2P)$	-93.2	-93.6	-100.2	-95.5
$B(^4P)$	-48.3	-48.4	-48.8	-48.6
$C(^3P)$	-112.8	-112.3	-117.6	-114.1
$C(^5S)$	-65.1	-64.9	-65.7	-65.3
N	-132.6	-130.9	-134.8	-132.6
O	-168.9	-166.2	-171.0	-169.1
F	-210.4	-206.4	-212.1	-210.6
Ne	-256.0	-250.4	-257.0	-256.1
H_2	-35.3	-35.8	-36.4	-35.8
LiH	-62.5	-62.3	-64.0	-63.1
BeH	-72.2	-72.0	-74.2	-72.9
BH	-122.4	-120.5	-131.3	-125.3
$CH(^2\Pi)$	-145.4	-142.8	-151.9	-147.2
$CH(^4\Sigma^-)$	-117.2	-115.6	-119.7	-117.5
NH	-169.6	-166.0	-173.1	-170.0
OH	-216.0	-210.4	-219.3	-216.4
FH	-265.9	-257.8	-268.1	-266.0
BeH_2	-102.3	-100.6	-104.8	-103.0
BH_2	-124.7	-122.2	-128.0	-125.3
$CH_2(^3B_1)$	-155.4	-151.7	-159.0	-155.8
$CH_2(^1A_1)$	-179.0	-173.6	-187.7	-181.1
NH_2	-210.7	-203.9	-215.2	-211.1
OH_2	-265.3	-255.2	-269.0	-265.5

[a] Electronic ground state unless otherwise specified.

energy difference between these levels is greatest in the ten-electron systems (10.3 mH for water) and should increase further for systems with more electrons.

(2) The linearized CCD method appears to overestimate the correlation energy in all these cases (the maximum difference being 6.6 mH for singlet methylene). This parallels the finding of Cizek, who gave an example with a semiempirical Hamiltonian in his original paper.

(3) The fourth-order perturbation results (MP4(DQ)) are close to the full CCD numbers. The maximum difference is 3.0 mH for ground-state beryllium, but agreement is much closer for the rest of the atoms and molecules. Since MP4(DQ)

is the result of a Møller–Plesset expansion of CCD to fourth order, this indicates rapid convergence and suggests that not too much change is to be anticipated if we proceed from the fourth-order theory into the full CCD treatment.

4. Applications to 1,2-Hydrogen-Shift Reaction Potential Surfaces

As indicated in Sec. 1, these methods have been applied to several surfaces involving hydrogen shifts of the type

$$H_m ABH_n \rightarrow H_{m-1}ABH_{n+1} \tag{24}$$
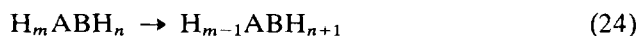
The systems considered are C_2H_2, HCN, H_2CO, and N_2H_2. In all four cases, we have found local minima corresponding to structures on the left- and right-hand sides of Eq. (24) together with an intermediate saddle point corresponding to the transition structure connecting them. The geometries of these structures were determined at the HF level using programs that explicitly calculate the energy derivative with respect to nuclear coordinates.

Two basis sets were used. The first is the split-valence 4-31G set and the second is 6-31G*, which also includes d-type polarization functions on non-hydrogen atoms. The resulting geometries are summarized in Tables II and III (geometrical specifications are given in Fig. 1). The calculations including correlation were carried out at these HF geometries. With the smaller 4-31G basis,
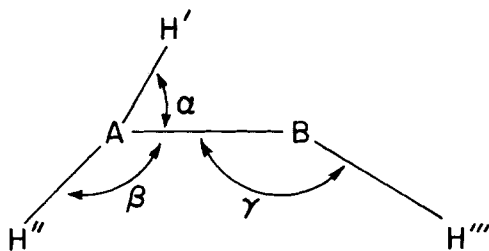

Figure 1. Geometrical specifications.

these were taken to the full CCD level. With the 6-31G* basis, they were terminated at fourth order, although the effects of single substitutions (S) were also included giving both MP4(DQ) and MP4(SDQ) energies. The total energies are given in Tables IV and V, followed by computed relative energies in Tables VI and VII. Only the valence electron correlation was used in these studies (frozen-core approximation).

Results at the 4-31G level again indicate that the full CCD method gives results close to its fourth-order equivalent MP4(DQ). The relative energies listed in Table VI change by no more than 1 kcal/mol in this comparison. This suggests that the use of fourth-order energy is a good approximation in studies of this sort. The more time-consuming 6-31 G* studies were therefore limited to fourth order.

TABLE II.   HF structures (4-31G basis).[a]

	A B	AH'	BH'	AH''	BH'''	α	β	γ
HCCH	1.190	1.051	-	-	1.051	180.0	-	180.0
HC(H)C	1.247	1.423	1.220	1.056	-	-	177.8	-
H_2CC	1.296	1.074	-	1.074	-	120.8	120.8	-
HCN	1.140	1.051	-	-	-	180.0	-	-
C(H)N	1.183	1.210	1.394	-	-	-	-	-
CNH	1.162	-	-	-	0.979	-	-	180.0
H_2CO	1.206	1.081	-	1.081	-	121.8	121.8	-
HC(H)O	1.305	1.260	1.187	1.086	-	-	116.7	-
HCOH(trans)	1.329	1.098	-	-	0.952	103.4	-	114.2
HCOH(cis)	1.326	-	-	1.112	0.957	-	107.5	121.5
HNNH(trans)	1.225	1.012	-	-	1.012	110.5	-	110.5
HNNH(cis)	1.224	-	-	1.019	1.019	-	116.1	116.1
HN(H)N	1.279	1.158	1.28 4	1.008	-	-	121.8	-
H_2NN	1.242	1.002	-	1.002	-	122.5	122.5	-

[a] Refer to Figure 1 for geometrical specifications.

Here the relative energies (Table VII) suggest fairly good convergence of the perturbation sequence probably to within 2 kcal/mol.

Turning to the individual molecular systems, the results may be compared with previous work by Pearson et al. [9]. They used CI with a somewhat larger basis and obtained 14.6 kcal/mol for the energy of HNC relative to HCN and 34.9 kcal/mol for the activation energy from HNC. These are in reasonable agreement with our MP4(SDQ)/6-31G* values of 16.8 and 34.4 kcal/mol, respectively. The convergence from left to right in Table VII indicates that second-order theory overestimates the change in the isomerization energy from HF theory. This "overshoot" at second order and subsequent correction at third and fourth is a common feature of most entries in Table VII.

The final results for the acetylene–vinylidene system also show good agreement with a previous theoretical study by Dykstra and Schaefer. Using the

TABLE III. HF structures (6-31G* basis)[a]

	AB	AH'	BH'	AH''	BH'''	α	β	γ
HCCH	1.185	1.057	-	-	1.057	180.0	-	180.0
HC(H)C	1.237	1.459	1.170	1.062	-	-	180.4	-
H_2CC	1.294	1.078	-	1.078	-	120.2	120.2	-
HCN	1.133	1.059	-	-	-	180.0	-	-
C(H)N	1.169	1.155	1.454	-	-	-	-	-
CNH	1.154	-	-	-	0.985	-	-	180.0
H_2CO	1.184	1.092	-	1.092	-	122.2	122.2	-
HC(H)O	1.270	1.219	1.175	1.095	-	-	115.9	-
HCOH(trans)	1.300	1.099	-	-	0.951	103.0	-	109.4
HCOH(cis)	1.298	-	-	1.107	0.953	-	107.1	116.1
HNNH(trans)	1.216	1.015	-	-	1.015	107.6	-	107.6
HNNH(cis)	1.215	-	-	1.018	1.018	-	113.1	113.1
HN(H)N	1.251	1.113	1.286	1.021	-	-	120.2	-
H_2NN	1.216	1.015	-	1.015	-	122.8	122.8	-

[a] Refer to Figure 1 for geometrical specifications.

self-consistent electron-pairs method, they obtain 40.0 kcal/mol for the vinylidene–acetylene energy difference and 8.6 kcal/mol for the activation energy from vinylidene. Our values are 42.0 and 8.1 kcal/mol respectively.

For the 16-electron systems CH_2O and N_2H_2, some new features are found. The 1,2-forms are nonlinear and exist as *cis* and *trans* isomers. For both systems, the *trans* forms are predicted to be most stable. For CH_2O, the theory predicts *trans*-hydroxy methylene to be 56.6 kcal/mol less stable than formaldehyde, with an activation barrier of 31.6 kcal/mol toward rearrangement. For N_2H_2, the H_2NN form is predicted to be 25.4 kcal/mol less stable than *trans*-diazene, HNNH, the activation barrier being as high as 57.6 kcal/mol.

TABLE IV. Total energies (H) (4-31G basis)

	HF	MP2 [a]	MP3 [a]	MP4(DQ) [a]	CCD [a]
HCCH	-76.71141	-76.89365	-76.89833	-76.90360	-76.90619
HC(H)C	-76.61001	-76.78717	-76.79357	-76.79837	-76.79948
H_2CC	-76.65171	-76.80566	-76.82110	-76.82604	-76.82872
HCN	-92.73193	-92.94194	-92.93291	-92.94061	-92.94168
C(H)N	-92.62502	-92.82885	-92.82313	-92.83030	-92.83030
CNH	-92.71678	-92.90629	-92.90374	-92.90980	-92.91046
H_2CO	-113.69262	-113.91077	-113.90989	-113.91677	-113.91761
HC(H)O	-113.51697	-113.75162	-113.74140	-113.75151	-113.75143
HCOH(trans)	-113.61107	-113.80714	-113.81228	-113.81888	-113.82054
HCOH(cis)	-113.60005	-113.79707	-113.80248	-113.80915	-113.81097
HNNH(trans)	-109.81269	-110.03537	-110.03912	-110.04504	-110.04648
HNNH(cis)	-109.79884	-110.02416	-110.02771	-110.03379	-110.03526
HN(H)N	-109.66670	-109.90882	-109.90176	-109.91037	-110.91056
H_2NN	-109.79981	-110.00296	-110.00937	-110.01464	-110.01584

[a] With frozen-core.

The energies of the saddle-point structures for CH_2O and N_2H_2 are so high that some doubt must be expressed as to whether they represent the true transition structures. At the HF/4-31G level, the total energy of HC(H)O, given in Table V, is higher than that of HCO + H, provided that UHF theory is used for the radicals. This suggests that a lower-energy rearrangement path exists in which a hydrogen atom is removed from one end of the molecule, taken to large distances, and then returned to the other end. A similar situation arises for N_2H_2 where the HN(H)N energy at the HF/4-31G level is higher than N_2H + H. Clearly, more work on the location of the true transition structures is needed in both these systems.

TABLE V.   Total energies (H) (6-31G* basis)

	HF	MP2 [a]	MP3 [a]	MP4(DQ) [a]	MP4(SDQ) [a]
HCCH	- 76.81783	- 77.06457	- 77.07502	-77.07652	- 77.07995
HC(H)C	- 76.73717	- 76.98034	- 76.99381	- 76.99541	- 77.00009
H_2CC	- 76.76340	- 76.98518	- 77.00704	- 77.00983	- 77.01299
HCN	- 92.87520	- 93.15461	- 93.15701	-93.15980	- 93.16376
C(H)N	- 92.79195	- 93.06709	- 93.07371	- 93.07639	- 93.08213
CNH	- 92.85533	- 93.12306	- 93.13082	- 93.13301	- 93.13707
H_2CO	-113.86633	-114.16523	-114.17168	-114.17529	-114.17947
HC(H)O	-113.69964	-114.01801	-114.01823	-114.02333	-114.03024
HCOH(trans)	-113.78351	-114.06882	-114.08153	-114.08553	-114.08925
HCOH(cis)	-113.77449	-114.05987	-114.07280	-114.07683	-114.0805?
HNNH(trans)	-109.99476	-110.31108	-110.32275	-110.32576	-110.32863
HNNH(cis)	-109.98350	-110.30097	-110.31267	-110.31571	-110.31873
HN(H)N	-109.84629	-110.18300	-110.18641	-110.19048	-110.19641
H_2NN	-109.96357	-110.26728	-110.28098	-110.28401	-110.28817

[a] With frozen-core.

5. Conclusions

The conclusions from this work are as follows:

(1) The CC method with double substitutions (CCD) is a feasible computational scheme using an iterative procedure. At the end of the first such iteration, the results are sufficient to obtain the Møller–Plesset fourth-order result in the space of double and quadruple substitutions (MP4(DQ)).

(2) Preliminary applications to systems AH_n with one heavy (nonhydrogen) atom indicate that total correlation energies calculated by these two methods are close. Similar conclusions follow from studies on some two-heavy-atom systems with the smaller 4-31G basis. It therefore appears that fourth-order theory is an adequate approximation for many purposes.

TABLE VI. Relative energies (kcal/mol) (4-31G basis)

	HF	MP2 [a]	MP3 [a]	MP4(DQ) [a]	CCD[a]
HCCH	0.0	0.0	0.0	0.0	0.0
HC(H)C	63.6	66.8	65.7	66.0	67.0
H_2CC	37.5	55.2	48.5	48.7	48.6
HCN	0.0	0.0	0.0	0.0	0.0
C(H)N	67.1	71.0	68.9	69.2	69.9
CNH	9.5	22.4	18.3	19.3	19.6
H_2CO	0.0	0.0	0.0	0.0	0.0
HC(H)O	110.2	99.9	105.7	103.7	104.3
HCOH(trans)	51.2	65.0	61.3	61.4	60.9
HCOH(cis)	58.1	71.4	67.4	67.5	66.9
HNNH(trans)	0.0	0.0	0.0	0.0	0.0
HNNH(cis)	8.7	7.0	7.2	7.1	7.0
HN(H)N	91.6	79.4	86.2	84.5	85.3
H_2NN	8.1	20.3	18.7	19.1	19.2

[a] With frozen-core.

(3) Some applications to 1,2-hydrogen-shift reactions using the 6-31G* basis show good convergence at the fourth-order level MP4(DQ). Relative energies of stationary points (isomerization and activation energies) are not much changed by the inclusion of single substitutions to give MP4(SDQ) theory. Results for C_2H_2 and HCN are in good agreement with previous studies.

(4) Preliminary results for CH_2O and N_2H_2 suggest that stationary saddle points on the HF potential surface may not give the true activation energy since calculated energies relative to the minimum are higher than those of dissociated radicals at the same level of theory.

TABLE VII.   Relative energies (kcal/mol) (6-31G* basis).

	HF	MP2 [a]	MP3 [a]	MP4(DQ)[a]	MP4(SDQ)[a]
HCCH	0.0	0.0	0.0	0.0	0.0
HC(H)C	50.6	52.9	51.0	50.9	50.1
H_2CC	34.2	49.8	42.7	41.9	42.0
HCN	0.0	0.0	0.0	0.0	0.0
C(H)N	52.2	54.9	52.3	52.3	51.2
CNH	12.5	19.8	16.4	16.8	16.7
H_2CO	0.0	0.0	0.0	0.0	0.0
HC(H)O	104.6	92.4	96.3	95.4	93.7
HCOH(trans)	52.0	60.5	56.6	56.3	56.6
HCOH(cis)	57.6	66.1	62.1	61.8	62.1
HNNH(trans)	0.0	0.0	0.0	0.0	0.0
HNNH(cis)	7.1	6.3	6.3	6.3	6.2
HN(H)N	93.2	80.4	85.6	84.9	83.0
H_2NN	19.6	27.5	26.2	26.2	25.4

[a] With frozen-core.

Appendix: Expansion of the CCD Energy in Powers of the Møller–Plesset Perturbation Parameter

The Hamiltonian [Eq. (22)] is

$$\mathcal{H} = \mathcal{H}_0 + \lambda V$$

The CCD energy can be expanded in powers of the perturbation parameter λ. By truncating at a given order and putting $\lambda = 1$, we then get the various contributions. The energy expression [Eq. (9)] can now be written

$$\mathcal{E} = \mathcal{E}^{(0)} + \lambda \mathcal{E}(1) + \frac{\lambda}{4} \sum_{ijab} (ij||ab) a_{ij}^{ab} \tag{25}$$

Note that the HF energy itself is correct to first order

$$\mathcal{E}_{HF} = \mathcal{E}^{(0)} + \mathcal{E}^{(1)} \tag{26}$$

The expression for the coefficients [Eq. (16)] becomes

$$a_{ij}^{ab} = -(\Delta_{ij}^{ab})^{-1}\lambda\{(ab||ij) + u_{ij}^{ab} + v_{ij}^{ab}\} \tag{27}$$

Matrix notation can be used to simplify the equations. Let $\mathbf{c}$, $\mathbf{u}$, and $\mathbf{v}$ represent the column vectors $(ab||ij)$, u_{ij}^{ab}, and v_{ij}^{ab}. These vectors can be very large and have the same number of elements as the number of double sustitutions. Let $\mathbf{a}$ denote the coefficients a_{ij}^{ab}. Equations (27) and (25) can now be written

$$\mathbf{a} = -\lambda\Delta^{-1}(\mathbf{c} + \mathbf{u} + \mathbf{v}) \tag{28}$$

$$\mathcal{E} = \mathcal{E}^{(0)} + \lambda\mathcal{E}^{(1)} + \lambda\mathbf{c}^{\dagger}\mathbf{a} \tag{29}$$

Substituting Eq. (28) into Eq. (29)

$$\mathcal{E} = \mathcal{E}^{(0)} + \lambda\mathcal{E}^{(1)} - \lambda^2\mathbf{c}^{\dagger}\Delta^{-1}\mathbf{c} - \lambda^2\mathbf{c}^{\dagger}\Delta^{-1}\mathbf{u} - \lambda^2\mathbf{c}^{\dagger}\Delta^{-1}\mathbf{v}$$

$$= \mathcal{E}^{(0)} + \lambda\mathcal{E}^{(1)} + \lambda^2\mathcal{E}^{(2)} - \lambda^2\mathbf{c}^{\dagger}\Delta^{-1}\mathbf{u} - \lambda^2\mathbf{c}^{\dagger}\Delta^{-1}\mathbf{v} \tag{30}$$

The expression for u_{ij}^{ab} [Eq. (13)] can be represented as

$$\mathbf{u} = \bar{\mathbf{V}}\mathbf{a} \tag{31}$$

where $\bar{\mathbf{V}}$ represents a square matrix of the same dimension as $\mathbf{a}$.

Equation (30) now gives

$$\mathcal{E} = \mathcal{E}^{(0)} + \lambda\mathcal{E}^{(1)} + \lambda^2\mathcal{E}^{(2)} - \lambda^2\mathbf{c}^{\dagger}\Delta^{-1}\bar{\mathbf{V}}\mathbf{a} - \lambda^2\mathbf{c}^{\dagger}\Delta^{-1}\mathbf{v} \tag{32}$$

Substituting Eq. (28) into Eq. (32) we get,

$$\mathcal{E} = \mathcal{E}^{(0)} + \lambda\mathcal{E}^{(1)} + \lambda^2\mathcal{E}^{(2)} + \lambda^3\mathbf{c}^{\dagger}\Delta^{-1}\bar{\mathbf{V}}\Delta^{-1}\mathbf{c} + \lambda^3\mathbf{c}^{\dagger}\Delta^{-1}\bar{\mathbf{V}}\Delta^{-1}\mathbf{u}$$

$$+ \lambda^3\mathbf{c}^{\dagger}\Delta^{-1}\bar{\mathbf{V}}\Delta^{-1}\mathbf{v} - \lambda^2\mathbf{c}^{\dagger}\Delta^{-1}\mathbf{v} \tag{33}$$

This expression is sufficient to get the contributions to CCD up to fourth-order after just one iteration.

We start with $u = v = 0$. Equation (28) gives

$$\mathbf{a} = -\lambda\Delta^{-1}\mathbf{c} = \lambda\mathbf{a}^{[1]} \tag{34}$$

where $\mathbf{a}^{[1]}$ represents the vector of the first-order wave function coefficients.

$\mathbf{u}$ and $\mathbf{v}$ may now be given

$$\mathbf{u} = \lambda\mathbf{u}^{[1]} = \lambda\bar{\mathbf{V}}\mathbf{a}^{[1]}$$

and

$$\mathbf{v} = \lambda^2\mathbf{v}^{[1]} \tag{35}$$

Here $\mathbf{u}^{[1]}$ and $\mathbf{v}^{[1]}$ can be calculated by substituting $\mathbf{a}^{[1]}$ in Eqs. (13) and (14).

Using Eqs. (34) and (35) in Eq. (33) we get all the terms that contribute to the energy up to fourth-order [5].

$$\mathcal{E} = \mathcal{E}^{(0)} + \lambda\mathcal{E}^{(1)} + \lambda^2\mathcal{E}^{(2)} + \lambda^3[\mathbf{a}^{[1]\dagger}\mathbf{u}^{[1]}] + \lambda^4[-\mathbf{u}^{[1]\dagger}\Delta^{-1}\mathbf{u}^{[1]} + \mathbf{a}^{[1]\dagger}\mathbf{v}^{[1]}]$$

$$+ \text{(higher order terms)}$$

$$= \mathcal{E}^{(0)} + \lambda\mathcal{E}^{(1)} + \lambda^2\mathcal{E}^{(2)} + \lambda^3\mathcal{E}^{(3)} + \lambda^4[-\mathbf{u}^{[1]\dagger}\Delta^{-1}\mathbf{u}^{[1]} + \mathbf{a}^{[1]\dagger}\mathbf{v}^{[1]}] \tag{36}$$

From Eq. (36) it is seen that the CCD energy is correct to third order. The fourth-order contribution to the CCD energy is given by

$$\mathscr{E}_{CCD}^{(4)} = -\mathbf{u}^{[1]\dagger}\boldsymbol{\Delta}^{-1}\mathbf{u}^{[1]} + \mathbf{a}^{[1]\dagger}\mathbf{v}^{[1]} \tag{37}$$

It has been shown previously [5] that the expression for the full $\mathscr{E}^{(4)}$ may be given as

$$\mathscr{E}^{(4)} = \mathscr{E}_R^{(4)} + \mathscr{E}_S^{(4)} + \mathscr{E}_D^{(4)} + \mathscr{E}_T^{(4)} + \mathscr{E}_Q^{(4)} \tag{38}$$

$\mathscr{E}_R^{(4)}$ is the renormalization term and the other terms are the contributions of single, double, triple, and quadruple substitutions to $\mathscr{E}^{(4)}$.

It is easily seen that the first term on the right-hand side of Eq. (37) is the same as $\mathscr{E}_D^{(4)}$ and the second term is equal to the sum $\mathscr{E}_R^{(4)} + \mathscr{E}_Q^{(4)}$. Comparing Eq. (37) and (38) it is seen that we get all the contributions to $\mathscr{E}^{(4)}$ except $\mathscr{E}_S^{(4)}$ and $\mathscr{E}_T^{(4)}$. Hence the CCD energy is correct to fourth order in the space of double and quadruple substitutions.

Acknowledgment

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