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Cite as: J. Chem. Phys. **72**, 4244 (1980); https://doi.org/10.1063/1.439657
Published Online: 15 July 2008

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Contribution of triple substitutions to the electron correlation energy in fourth order perturbation theory

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(Received 15 January 1980; accepted 31 January 1980)

Many-body perturbation theory, as originally formulated by Møller and Plesset,[1] has been widely used to describe the effect of electron correlation on molecular energies. At second and third orders, it is only necessary to use configurations which involve double substitutions in a reference Hartree–Fock wavefunction.[2–4] At fourth order, single, triple and quadruple substitutions also have to be considered for a full treatment. Until recently, applications of fourth order theory[5–7] have omitted the effects of triples because they required a more time-consuming computational algorithm. It is clearly important to assess the magnitude of the triples' contribution compared to other parts of the fourth-order energy. Also it is desirable to investigate whether inclusion of triples modifies theoretical predictions of chemically important differences such as bond energies and hydrogenation energies.

A general treatment of triple substitutions has been given by Wilson and Silver[8] and applied to the neon atom.[9] We have also examined the fourth-order triples energy contribution, using a somewhat different computational technique. In this Communication, we present a preliminary assessment of the importance of these energy terms in some small molecules.

Let Ψ_0 be the spin-unrestricted Hartree-Fock determinantal wave function with n occupied spin orbitals χ_1, $\chi_1, \ldots, \chi_n$. These are eigenfunctions of the Fock operator F, the corresponding eigenvalues being $\epsilon_1, \ldots, \epsilon_n$. If there are N atomic spin orbital basis functions, there will be a finite number of unoccupied (virtual) spin orbitals $\chi_{n+1}, \ldots, \chi_N$.

In Møller–Plesset perturbation theory, the Hamiltonian $\mathcal{H}$ is written as

$$\mathcal{H} = \mathcal{H}_0 + V = \sum_p F_p + V, \tag{1}$$

where V is the perturbation. The eigenfunctions and eigenvalues of $\mathcal{H}_0$ are given by Ψ_s and E_s. These are determinants which may be classified (apart from $s = 0$) as single substitutions $i \to a$, double substitutions $ij \to ab$, ..., etc., from the Hartree–Fock determinant. Following the derivation in Ref. 5, the contribution of triple substitutions to the fourth-order energy may be expressed as

$$\mathcal{E}_T^{(4)} = -\sum_{su}^{D} \sum_{t}^{T} (E_t - E_0)^{-1} a_s V_{st} V_{tu} a_u. \tag{2}$$

Here a_s is the first-order wave function coefficient

$$a_s = (E_0 - E_s)^{-1} V_{s0}. \tag{3}$$

The summation of s and u in (2) runs over all the double substitutions D and t over all the triple substitutions T.

If we define an array w_t for all triple substitutions as

$$w_t = \sum_u^D V_{tu} a_u, \tag{4}$$

(2) may be simplified as

$$\mathcal{E}_T^{(4)} = -\sum_t^T (E_t - E_0)^{-1} \mid w_t \mid^2. \tag{5}$$

If t is the triple substitution $ijk \to abc$ and u the double substitution $lm \to de$, there must be three or more coincidences between the two indices for the matrix element V_{tu} to be nonzero. After some algebraic manipulation, the final expression for w_t may be written

$$\begin{aligned} w_{ijk}^{abc} = \sum_e^{\text{virt}} & [a_{ij}^{ae}(bc\|ek) - a_{ij}^{be}(ac\|ek) - a_{ij}^{ce}(ba\|ek) + a_{ik}^{ae}(bc\|je) - a_{ik}^{be}(ac\|je) - a_{ik}^{ce}(ba\|je) \\ & - a_{jk}^{ae}(bc\|ie) + a_{jk}^{be}(ac\|ie) + a_{jk}^{ce}(ba\|ie)] \\ + \sum_m^{\text{occ}} & [a_{im}^{ab}(cm\|jk) + a_{im}^{bc}(am\|jk) - a_{im}^{ac}(bm\|jk) - a_{jm}^{ab}(cm\|ik) - a_{jm}^{bc}(am\|ik) + a_{jm}^{ac}(bm\|ik) \\ & + a_{km}^{ab}(cm\|ij) + a_{km}^{bc}(am\|ij) - a_{km}^{ac}(bm\|ij)], \end{aligned} \tag{6}$$

 0021-9606/80/074244-02$01.00

TABLE I. Hartree–Fock and correlation energy contributions up to fourth order.[a]

Molecule	E_{UHF}	$E^{(2)}$	$E^{(3)}$	$E_{DQ}^{(4)}$	$E_S^{(4)}$	$E_T^{(4)}$
H	−0.49823	•••	•••	•••	•••	•••
H_2	−1.13133	−26.32	−5.49	−1.30	−0.10	•••
Li	−7.43137	•••	•••	•••	•••	•••
LiH	−7.98134	−20.26	−4.58	−1.21	−0.17	•••
Be	−14.56694	−26.32	−10.50		−0.11	•••
BeH_2	−15.76691	−48.80	−10.58	−2.38	−0.17	−0.23
B	−24.52204	−36.68	−12.25	−4.45	−0.21	−0.32
BH_3	−26.39287	−93.28	−17.18	−2.84	−0.28	−1.10
C	−37.68086	−52.11	−13.39	−3.43	−0.19	−0.46
CH_4	−40.20170	−162.91	−18.22	−1.98	−0.65	−3.13
N	−54.38544	−71.57	−13.64	−2.07	−0.09	−0.45
NH_3	−56.19553	−187.42	−12.81	−1.48	−0.55	−3.23
O	−74.78393	−96.10	−13.18	−1.68	−0.38	−0.69
OH_2	−76.02357	−195.79	−6.47	−1.60	−0.68	−2.70
F	−99.36496	−122.31	−8.42	−1.03	−0.73	−1.20
FH	−100.01155	−182.96	−1.82	−1.61	−1.07	−2.30
Ne	−128.47441	−150.32	−0.04	−1.22	−1.14	−2.09
N_2	−108.94395	−304.24	+2.86	−4.04	−3.85	−13.26

[a]UHF energy in hartrees; correlation contributions in millihartree.

the sums $\sum^{virt}$ and $\sum^{occ}$ being over all virtual and occupied spin orbitals, respectively.

Then, from (5),

$$\mathcal{E}_T^{(4)} = -\frac{1}{36}\sum_{ijk}^{occ}\sum_{abc}^{virt}(\epsilon_a+\epsilon_b+\epsilon_c-\epsilon_i-\epsilon_j-\epsilon_k)^{-1}\,|\,w_{ijk}^{abc}\,|^2. \tag{7}$$

Evaluation of (6) involves $O(n^3(N-n)^3N)$ computational steps and is the dominant part of the computation. The program to evaluate $\mathcal{E}_T^{(4)}$ is based on direct evaluation of w_{ijk}^{abc} from (6) and calculation of the contributions of each triple substitution from (7).

In the initial applications of our algorithm, we have used the 6-31G** basis.[10] This is of the split valence plus polarization type and should give a reasonable account of the energy contributions of electron correlation. Molecular equilibrium geometries were obtained by the unrestricted Hartree–Fock (UHF) theory with the 6-31G* basis (without polarization functions on hydrogen).[10–12] The Møller–Plesset calculations were carried out with the "frozen-core" approximation, no substitutions involving K-shell molecular orbitals being considered.

Results for the ground states of first-row atoms, simple hydrides and the nitrogen molecule are listed in Table I. In the fourth-order energy, the contributions from double and quadruple substitutions $E_{DQ}^{(4)}$ are combined, since the separate parts involve larger and partly cancelling terms from unlinked clusters. The single and triple contributions $E_S^{(4)}$ and $E_T^{(4)}$ are presented individually. From this data, we conclude that $E_T^{(4)}$ is numerically larger than $E_S^{(4)}$ in all those systems which involve triple substitutions. $E_T^{(4)}$ is generally of a comparable order to $E_{DQ}^{(4)}$ but, for the ten-electron systems CH_4, NH_3, H_2O, and HF and for N_2, it is the largest of the three components of $E^{(4)}$. The contribution of triple substitutions to total atomization energies is always positive (increasing binding), the magnitude of the increase varying from 0.23 mhartree (0.14 kcal/mole) for BeH_2 to 12.36 mhartree (7.76 kcal/mole) for N_2. Since computed binding energies are normally less than those observed, this represents improved agreement with experiment. However, the calculated results are still too small, being generally about 10% less than observed values. The $E_T^{(4)}$ contribution to hydrogenation energy of nitrogen (energy of the reaction $N_2 + 3H_2 \rightarrow 2NH_3$) is −6.80 mhartree (−4.27 kcal/mole). Evidently the contributions of triple substitutions are important in accurate quantitative theories of chemical binding. The preliminary results on N_2 suggest that they may be most important in multiple bonds involving more than two electrons.

This work was supported in part by the National Science Foundation under Grant CHE79-01061.

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