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REGULAR ARTICLE

Is the dynamical polarization a significant part of the contribution of the triples to the correlation energy?

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Abstract One may call dynamical polarization of doubly excited configurations the energy lowering of these configurations under the response of the other electrons to the so-created fluctuation of the electric field. This contribution of triply excited configurations may be identified and calculated through a computation that only requires a computation time proportional to the sixth power of the number of molecular orbitals (MOs), instead of the seventh power for the total contribution of the triples. Its amplitude depends on the choice of the MOs and becomes important when localized MOs are used.

Keywords Dynamic polarization · Correlation energy · Triple excitations

1 Introduction

In the so-called closed shell systems, where a single determinant may be considered as a good approximation of the wave function, or a satisfactory zero-order reference to build a correlated description, the main part of the correlation energy is brought by the action of the double excitations on the top of the self-consistent determinant. This may be done through a configuration interaction of singles and doubles (CISD) [1]. This approach suffers a size-consistency problem, which can be easily corrected through coupled electron pair approximations (CEPA) [1–4] of various degrees of sophistication, depending on the way the exclusion principle violating (EPV) effects are taken into account, from full neglect (CEPA-0) [1–4] to full account [(SC)^{2}CISD] [5, 6]. The coupled cluster (CC) [7, 8] expansion involving single and double excitation operators (CCSD) [9] also introduce the linked effects of the quadruply excited determinants and a minor part of the effect of the triply excited ones. Actually, due to the Brillouin's theorem, the coefficients of the singly excited determinants are of 2nd order only, and the coefficients of the triply excited determinants in the CCSD wave function are only of 3rd order. In a perturbative expansion of the wave function, the triply excited determinants appear at the 2nd order, through their interaction with the doubly excited ones, and their effect on the energy is a fourth-order one. Their numerical impact is sometimes significant, and a widely used procedure, called CCSD (T) [10], consists in taking into account the perturbative correction of the triples in a CCSD scheme. The computational cost of CISD or CCSD scales as the 6th power of the number of electrons or molecular orbitals (MOs), while the perturbative treatment of the triples requires a N^7 (N being the basis set size) step. This is a severe increase in the computational cost, which limits the applicability of the method. The present paper examines the possible role of a fraction of the effect of the triples, the computation of which would only require a N^6 computational cost. Heully and one of us (JPM) have recently suggested [11] that this might be the leading contribution of the triples. It concerns the so-called

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Dedicated to Professor Vincenzo Barone and published as part of the special collection of articles celebrating his 60th birthday.

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dynamical polarization effect, the definition of which will be recalled in the next section, together with a discussion of its physical significance and the reasons why one might expect that its role is important. Numerical tests will be presented in Sect. 3, followed by a brief conclusion.

2 The dynamical polarization of the doubles

2.1 Recall

While in the mean field approximation each electron moves in a static field, the electronic correlation phenomenon introduces a fluctuation of the electric field. When a double excitation takes place on the top of the self-consistent zero-order determinant Φ_0, promoting two electrons from the occupied spin orbitals i and j to the vacant spin orbitals r and s, the other electrons feel an instantaneous field that is modified with respect to the mean field relative to Φ_0. One may call dynamical polarization the response to the fluctuation of the electric field.

In many problems, the dynamical polarization is an important phenomenon. For instance in magnetic systems, where two unpaired electrons are essentially localized in two distant magnetic orbitals a and b, the triplet configuration remains purely neutral, in the sense of valence bond (VB) theory [12, 13], $\Psi_T = |\text{core}\,ab|$ for the $M_s = 1$ component, or $\Psi_T = \left|\text{core}\,(a\bar{b} - b\bar{a})/\sqrt{2}\right|$ for the $M_s = 0$ component. On the contrary in the singlet state, two ionic components A^-B^+ and A^+B^- appear in the wave function,

$$\Psi_S = \lambda\left|\text{core}\,\left(a\bar{b} + b\bar{a}\right)/\sqrt{2}\right| + \mu\left|\text{core}\,\left(a\bar{a} + b\bar{b}\right)\right|/\sqrt{2}, \tag{1}$$

which introduces the non-dynamical (or valence left–right) correlation.

If one returns to the VB way of thinking, one understands easily that in one of these ionic components, say A^-B^+, two phenomena will take place:

- The doubly occupied orbital a is no longer adapted to a double occupancy, the orbital would prefer to be more diffuse and to hybrid in the direction of the positive center B^+. This is the so-called orbital breathing of the active orbitals [12, 13].
- The electrons of the core would tend to polarize in order to react to the field created by the active electrons in the instantaneous dipolar distribution A^-B^+.

Both effects are known to be responsible for a dramatic lowering of the effective energy of the ionic VB components of the wave function. The energy difference U between the neutral and ionic components of the wave function is typically reduced by a factor 3, going from 25 to 7 eV in copper dimer complexes [14, 15]. In a multireference configuration interaction (MRCI) picture, these effects are brought by single excitations on the complete active space (CAS of 2 electrons in 2 MOs) determinants.

2.2 Formal derivation of the dynamical polarization of the doubles

The electronic correlation problem for closed shell molecules, starting from the single-determinantal approximation Φ_0, is somewhat different, but in the doubly excited determinant $a_r^+ a_s^+ a_j a_i \Phi_0$, the field created by the electrons in the spin orbitals i and j is now replaced by that created by these electrons in the virtual MOs r and s. The response of the other electrons to the fluctuation of the electric field, created by the double excitation, may be considered as brought by the single excitations $a_t^+ a_k$ on the top of the double excitation.

Let us make explicit the corresponding correction to the energy, which is of fourth-order character and only requires a sextuple summation, three on the occupied MO indices, i, j and k, three on the virtual MOs r, s and t. The interaction between a doubly excited determinant Φ_{ij}^{rs} and a triply excited determinant Φ_{ijk}^{rst} (which only differ by a single excitation $a_t^+ a_k$) is

$$\left\langle \Phi_{ij}^{rs} \middle| H \middle| \Phi_{ijk}^{rst} \right\rangle = \left\langle k \middle| J_r + J_s - J_i - J_j \middle| t \right\rangle, \tag{2}$$

where the coulomb operators J_p incorporate the exchange counterpart K_p when the spins of the spin orbitals k and t are the same as the spin of the orbital p. The contribution to the correlation energy $\varepsilon^{(4)}_{\text{pol}\,T}$ is given by

$$\varepsilon^{(4)}_{\text{pol}\,T} = \sum_{i,j,k,r,s,t} \left(c_{ij}^{rs}\right)^2 \frac{\left\langle k \middle| J_r + J_s - J_i - J_j \middle| t \right\rangle^2}{\langle \Phi_0 | H | \Phi_0 \rangle - \left\langle \Phi_{ijk}^{rst} \middle| H \middle| \Phi_{ijk}^{rst} \right\rangle}, \tag{3}$$

where c_{ij}^{rs} is the coefficient of the doubly excited determinant Φ_{ij}^{rs}. This expression is based on the Epstein–Nesbet definition of the zero-order Hamiltonian [16]. It is worth noticing that this effect may be treated as an effective dressing of the diagonal energies of the doubly excited determinants

$$\left\langle \Phi_{ij}^{rs} \middle| H^{\text{eff}} \middle| \Phi_{ij}^{rs} \right\rangle = \left\langle \Phi_{ij}^{rs} \middle| H \middle| \Phi_{ij}^{rs} \right\rangle + \sum_{k \neq i,j,\, t \neq r,s} \frac{\left\langle k \middle| J_r + J_s - J_i - J_j \middle| t \right\rangle^2}{\langle \Phi_0 | H | \Phi_0 \rangle - \left\langle \Phi_{ijk}^{rst} \middle| H \middle| \Phi_{ijk}^{rst} \right\rangle}. \tag{4}$$

The sums may be calculated before the diagonalization of the CISD matrix, for each set of values of the indices i, j, r and s, and the resulting matrix may be diagonalized once for all. More efficient implementations are conceivable and will be evoked below.

2.3 Physical content of the dynamical polarization of doubles and its dependence to the MO choice

It is important now to consider the physical content of the dynamical polarization of doubles. It reflects a polarization of an occupied spin-orbital k, by mixing with a spin-orbital t, under the effect of a double excitation from i and j to r and s. This effect is not invariant under the unitary transformations of the orbitals of the same class (occupied between themselves, virtual between themselves). The amplitude of the coulomb operators decrease when the orbitals delocalize, and the effect is expected to be more pronounced when localized occupied MOs are used. Let us illustrate this point by considering a diatomic problem, with a covalent bond orbital k, an antibonding valence MO t and one lone pair on each atom, labeled a and b, respectively. From these localized orbitals, one may define a pair of delocalized MOs g and u

$$g = (a + b)/\sqrt{2}, \tag{5}$$

$$u = (a - b)/\sqrt{2}. \tag{6}$$

The ground-state determinant may be written $\Phi_0 = \left|k\bar{k}g\bar{g}u\bar{u}\right| = \left|k\bar{k}a\bar{a}b\bar{b}\right|$. Let us consider excitations from the MOs a and b or g and u to virtual rather diffuse MOs, r and s, whose coulomb operators J_r and J_s are weaker than those relative to the valence MOs. The single excitation $a_t^+ a_k$ is of u symmetry. Consider for instance the doubly excited determinant $\Phi_{gg}^{rs} = \left|k\bar{k}r\bar{s}u\bar{u}\right|$. The corresponding interaction with the triply excited determinant

$$\left\langle \Phi_{gg}^{rs} | H | \Phi_{ggk}^{rst} \right\rangle = \langle k | J_r + J_s - 2J_g | t \rangle \tag{7}$$

is zero for symmetry reasons, and this will remain true for the effect of the single excitations $a_t^+ a_k$ acting on the doubly excited determinants involving the other pairs of symmetry-adapted MOs, uu or gu. In the localized approach, the corresponding interactions, for instance,

$$\langle \Phi_{aa}^{rs} | H | \Phi_{aak}^{rst} \rangle = \langle k | J_r + J_s - 2J_a | t \rangle, \tag{8}$$

are important. Actually, the same effect is involved in the symmetry-adapted approach, but it is no longer through a single excitation operator but a simultaneous change of hole and single excitation. Actually,

$$\left\langle \Phi_{g\bar{g}}^{r\bar{s}} | H | \Phi_{g\bar{u}k}^{r\bar{s}t} \right\rangle = (kt, gu) \approx \langle k | (J_a - J_b)/2 | t \rangle \tag{9}$$

The effect that is clearly a polarization effect in the localized picture appears through a coupling of dipolar distributions and a 2 hole − 1 particle process in the delocalized picture. The physical effect is the same, but it is not located in the same place when one goes from localized to delocalized MOs. The preceding discussion suggests that it will be more easily harvested in a localized approach.

3 Numerical tests

In order to assess the performance of the dynamic polarization to the effect of triples, we first apply it to calculate the equilibrium properties of some small molecules, including the energies, bond lengths and harmonic vibrational frequencies. We also test its performance on the dissociation of single bonds and the symmetrical stretching of triangular Be_3 cluster. As described in Sect. 2.3, the results of the dynamic polarization of doubles depend on the choice of MOs. So in the energy calculations around equilibrium geometries, we examine all four possible combinations of MOs, that is, canonical occupied and virtual MOs ([CMO, CMO]), localized occupied and canonical virtual MOs ([LMO, CMO]), canonical occupied and localized virtual MOs ([CMO, LMO]) and localized occupied and virtual MOs ([LMO, LMO]). Then, we choose the MO combination of giving the largest part of the effect of triples to the remaining calculations. In all calculations, the CISD is carried out in the first stage through GAMESS package [17, 18], and then, the effect of the dynamic polarization is obtained by adding them to the diagonal elements of CISD matrix and diagonalizing the dressed matrix (named as CISD [t]) in the modified GAMESS program. The localized MOs (LMOs) are obtained through Pipek–Mezey localization method [19]. Notice that the CISD calculations are not size consistent, but we think that the present evaluation of the amplitude of the dynamical polarization effect would be approximately the same in a CCSD (T) approach.

3.1 Equilibrium properties

We examine the effect of dynamic polarization on the energetics for C_2, HF, F_2, Be_3, O_3 and C_4H_{10} molecules, in which the effect of triples plays an important role even around equilibrium geometries. The results are compared to the energy differences between CCSD [9] and CCSD (T) [10], which is a full fourth-perturbation treatment, as listed in Table 1. We also give the ratio of the correlation energy brought by the triples compared with the part due to the singles and doubles only for both the CI and CC methods (the last two columns in Table 1). At a first glance, the [LMO, CMO] combination gives the largest estimate of the full fourth-perturbation treatment, except HF molecule, in which the canonical occupied MOs are

Table 1 The numerical values (in a.u.) and percentages (under the numbers) retrieved by dynamical polarization to the effect of triples obtained through full fourth-perturbation treatment [the energy difference between CCSD (*T*) and CCSD]

Molecule	[CMO, CMO]	[LMO, CMO]	[CMO, LMO]	[LMO, LMO]	Ref.[a]	E_{corr} (T)/E_{corr} (SD)	
						CI[b] (%)	CC (%)
C_2[c]	−0.001725	−0.005237	−0.003454	−0.003970	−0.028569	1.8	8.9
	(6.0%)	(18.3%)	(12.1%)	(13.9%)			
HF[d]	−0.001808	−0.001689	−0.000786	−0.000637	−0.002060	0.8	1.0
	(87.8%)	(82.0%)	(38.2%)	(30.9%)			
F_2[e]	−0.000704	−0.005526	−0.003310	−0.001333	−0.009322	1.4	2.3
	(7.5%)	(59.3%)	(35.5%)	(14.3%)			
Be_3[f]	−0.001494	−0.003163	−0.002457	−0.001870	−0.013370	2.1	8.2
	(11.2%)	(23.7%)	(18.4%)	(14.0%)			
O_3[g]	−0.005225	−0.013418	−0.009072	−0.005252	−0.033831	2.4	5.4
	(15.4%)	(39.7%)	(26.8%)	(15.5%)			
C_4H_{10}[h]	−0.001472	−0.009625	−0.003039	−0.002480	−0.016401	1.7	2.5
	(9.0%)	(58.7%)	(18.5%)	(15.1%)			

All electrons are correlated, and Cartesian basis functions are used

[a] Energy difference between CCSD (*T*) and CCSD

[b] The ratio of correlation energy contributed by triples and that from singles and doubles for [LMO, CMO]

[c] Calculated with a cc-pVDZ basis set and at the equilibrium bond length of 1.27276 Å [21]

[d] Calculated with a cc-pVDZ basis set and at the equilibrium bond length of 0.92025 Å [21]

[e] Calculated with a cc-pVDZ basis set and at the equilibrium bond length of 2.66816 Bohr [22]

[f] Calculated with the ANO basis set [23] and at the distance of one Be atom to the center of mass of the equilateral triangle of 1.312998 Å [24]

[g] Calculated with a cc-pVDZ basis set and at the equilibrium bond length of 1.272 Å and bond angle of 116.8° [25]

[h] Calculated with a 6-31G* basis set [26, 27] and the equilibrium geometry from [28]

already localized. If we concentrate only on the use of [LMO, CMO], it appears that the dynamic polarization does not represent a systematic fraction of the total energy brought by the triples. For example, the dynamic polarization can retrieve as large as 82.0% of the total effect of triples for HF molecule with a cc-pVDZ basis set [20], but obtain only 18.3% of the total effect of triples for C_2 molecule. The largest fractions are obtained for HF, F_2 and C_4H_{10} molecules, in which more than half of the effect of triples is captured.

The calculated fraction also depends on the size of basis sets. For HF for instance when the cc-pVDZ basis set (totally 20 basis functions) is used, the dynamic polarization effect obtained with [LMO, CMO] can retrieve 82.0% of the effect of triples as listed in Table 1, but the percentage decreases to 54.8% when the cc-pVTZ basis set (with 50 basis functions) is used.

We also evaluate the equilibrium bond lengths and harmonic vibrational frequencies of HF and C_2 molecules (Table 2), as examined in [21]. Since [LMO, CMO] gives the best estimate of the effect of triples, the following tests used only such MO combination. The results are consistent with those of Table 1. The dynamic polarization retrieving the largest part of effect of triples for HF gives a great improvement for the bond length and harmonic vibrational frequencies, CISD [*t*] compares well with CCSD. But for C_2 molecule, the improvement is very limited, and the difference between bond lengths of CISD and CISD [*t*] is about 0.001 Å. CISD [*t*] gives an improvement of about 13 cm^{-1} to the harmonic vibrational frequency compared to CISD.

3.2 The dissociation of single bonds

3.2.1 *HF*

The full potential curves are investigated by considering the dynamic polarization effect with a 6-31G** basis set [26, 27]. The results are displayed in Fig. 1, along with the results of CCSD, CCSD (*T*) and full CI (FCI) [29]. CISD [*t*] does not present a divergent behavior in bond-breaking regions, although the dynamic polarization effect is incorporated by a dressing of perturbative character. CCSD (*T*) presents divergence when the bond length is longer than 1.8 Å. The dynamic polarization effect gives largest part of the effect of triples at 1.1 Å, amounting to 84.0%. This percentage decreases gradually when the bond length becomes larger than 1.1 Å, but generally the dynamic polarization effect can obtain no <50% of the total effect of triples when the bond length is no more than 1.8 Å.

Table 2 The equilibrium bond lengths (r_e) in Å and harmonic vibrational frequencies (ω_e) in cm^{-1} of HF and C_2 molecules obtained by fitting a polynomial using points around equilibrium bond length

	HF		C_2	
	r_e	ω_e	r_e	ω_e
CISD	0.91661	4212.1	1.26065	1899.3
CISD [*t*]	0.91884	4168.9	1.26143	1886.2
CCSD[a]	0.91895	4169.0	1.26616	1861.5
CCSD (*T*)[a]	0.91988	4150.2	1.27045	1828.1

The cc-pVDZ basis set and harmonic components of *d* orbitals are used. The frozen core approximation is adopted in post-Hartree–Fock calculations

[a] From [21]

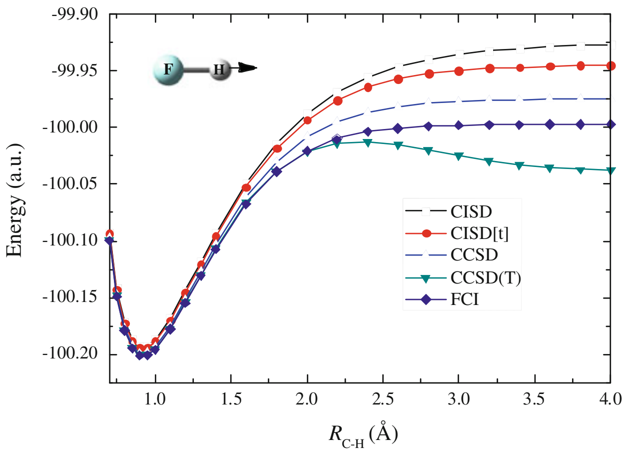

Fig. 1 The potential *energy curves* of HF molecule

The absolute value represented by dynamic polarization effect increases gradually from 1.225 m hartree (at 0.7 Å) to 17.899 m hartree (at 4.0 Å).

3.2.2 F_2

The dynamic correlation plays a significant role in F_2 molecule, especially the triples has an important effect on the correlation energy, which has been investigated by various types of CC methods [22]. The results calculated with a cc-pVDZ basis set are listed in Table 3, together with the results of CCSDT, CCSD and CCSD (*T*) taken from [22]. Different from HF molecule, CCSD (*T*) shows an overshooting behavior even at 1.25 R_e. The dynamic polarization captures 60.0% of the effect of triples at 1 R_e. The absolute numbers obtained by the dynamic polarization effect range from 4.324 m hartree (at 0.75 R_e) to 6.589 m hartree (at 1.5 R_e). It remains almost constant around 6.0 m hartree at large interatomic distances, while the full treatment of the triples in CCSDT recovers up to 50 m hartree at 5 R_e.

3.3 Triangular Be_3 cluster

The effect of connected triples plays an essential role in the triangular Be_3 cluster due to its obvious multireference character caused by the relatively small energy differences between the atomic 2 *s* and 2*p* orbitals [30]: CCSD cannot satisfactorily reproduce the binding energy, but CCSD (*T*) treatment gives greatly improved result [31, 32]. Although the dynamic polarization gives only 18.3% of the effect of total triples in Table 1, it is interesting to investigate its behavior in symmetrical stretching of three Be atoms. The ANO basis set [23] in a [3*s*2*p*1*d*] contraction was used for this system. The frozen core approximation was employed in all post-Hartree–Fock calculations. The results are displayed in Fig. 2, together with the results of CCSD, CCSD (*T*) and FCI [24]. Surprisingly, the CISD [*t*] indeed reproduces the symmetrical stretching process qualitatively (without the spurious hump of CCSD), although the dynamic polarization retrieves only about one-fifth of the effect of triples around equilibrium geometries. The dissociation energies from FCI, CCSD (*T*) and CCSD are 17.2, 14.5 and 6.4 kcal/mol, respectively. CISD [*t*] and CISD give values of 11.1 and 9.5 kcal/mol, respectively. Figure 3 displayed the percentages retrieved by the dynamic polarization effect relative to the energy difference between CCSD (*T*) and CCSD, which increase monotonically except the first two points.

Table 3 The total energy of F_2 molecule calculated by CCSDT and energy differences between other correlation methods and CCSDT at several geometries ($R_e = 2.66816$ Bohr)

Methods	0.75 R_e	1 R_e	1.25 R_e	1.5 R_e	1.75 R_e	2 R_e	3 R_e	5 R_e
CCSDT	−198.922138	−199.102796	−199.085272	−199.065882	−199.059433	−199.058201	−199.058511	−199.058586
CISD	22.937	35.881	59.429	88.571	111.737	125.492	139.798	142.466
CISD [*t*]	18.613	30.342	53.016	81.982	105.481	119.574	133.901	136.195
CCSD	4.504	9.485	19.917	32.424	41.184	45.638	49.425	49.816
CCSD (*T*)	0.102	0.248	−0.503	−5.711	−15.133	−23.596	−35.700	−39.348

The core orbitals are frozen in the correlated methods. The CCSDT, CCSD and CCSD (*T*) energies are taken from [22]

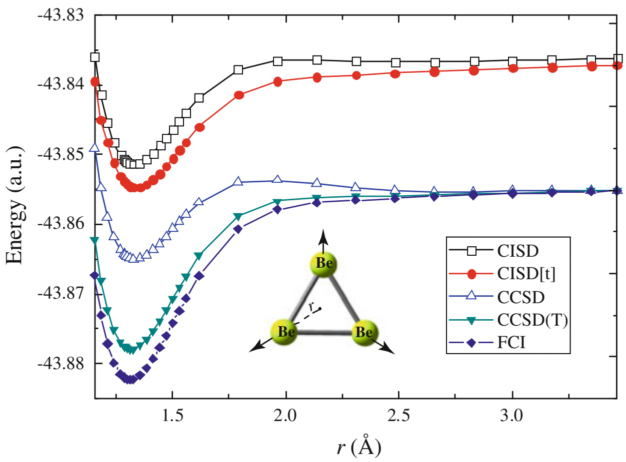

Fig. 2 The potential *curves* of the symmetrical *stretching* of *triangular* Be_3 cluster

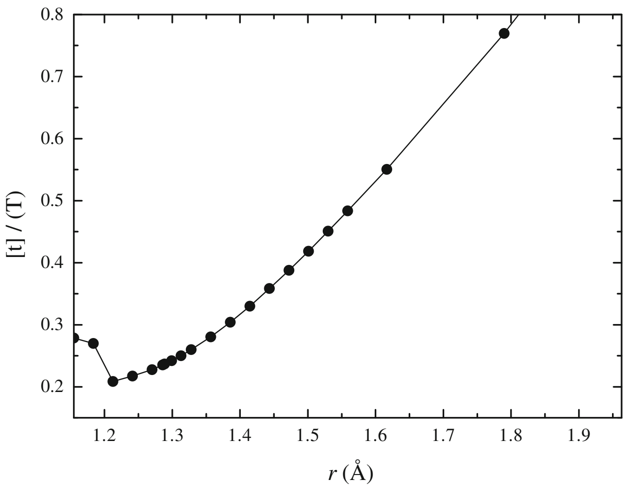

Fig. 3 The percentages retrieved by dynamic polarization effect relative to the energy difference between CCSD (T) and CCSD during the symmetrical *stretching* of *triangular* Be_3 cluster

4 Conclusion

Heully and one of us (JPM) had suggested [11] that the dynamical polarization of the doubly excited configurations might be a leading part of the contribution of the triples to the correlation energy. If this was true, one might avoid the bottleneck of CCSD (T) method, the computational cost of which scales as the 7th power of the number of electrons or MOs. This hypothesis is tested here for the first time. This work shows that the percentage of the effect of the triples brought by this effect strongly depends on the basis of occupied MOs. It is larger when LMOs are used and the reason why it is so has been clarified. The procedure we propose here, namely a dressing of the energies of the doubly excited determinants, may perfectly be employed in a CCSD formalism, which may always be expressed as a dressing of the CISD matrix [5, 6]. Moreover, the authors of [11] suggested treating this effect through the definition of energy-dependant modifications of the coulomb integrals between the pairs of spin orbitals m and n through a double summation

$$\delta J_{mn}(E) = \sum_{k,t} \frac{\langle k|J_m|t\rangle\langle t|J_n|k\rangle}{F_{kk} - F_{tt} - E}, \tag{10}$$

which might be performed before the CI process. In this case, the cost of the evaluation of the effect of the dynamical polarization of the doubles by the triples falls to N^4. The present numerical tests indicate that the so-calculated fraction of the contribution of the triples, although working in the right direction regarding the ground-state properties, is not sufficient to recover the overall effect of the triple excitations.

A surprising side result of the present work concerns the impact of the choice of the zero-order Hamiltonian. Our Epstein–Nesbet calculation goes through all the triples. The results do not exhibit a spurious overestimation of the calculated perturbative correction at large interatomic distances, in contrast with what is observed in CCSD (T) treatments, which use a Moller–Plesset zero-order Hamiltonian. Usually, the Epstein–Nesbet corrections are larger in absolute value than the Moller–Plesset ones. This point should deserve further analysis.

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