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Totally dressed SDCI calculations: An application to HF and F_2

J. Sánchez-Marín[1], I. Nebot-Gil[1], D. Maynau[2], J.P. Malrieu[2]

[1] Departament de Química Física. Facultat de Química. Universitat de València. Dr. Moliner, 50. E-46100 Burjassot, València, Spain

[2] Laboratoire de Physique Quantique. Université Paul Sabatier, 118, route de Narbonne, F-31062 Toulouse Cedex, France

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Summary. A previously proposed procedure including the linked and unlinked contributions due to Triple and Quadruple excitations into a size-consistent SDCI-like model has been applied to HF and F_2 single-bond systems. The procedure is a non-iterative approximation to the more general total dressing model, which is based on the intermediate Hamiltonians theory. Three basis sets have been employed: the correlation consistent cc-pVTZ basis, a similar one including $3d1f$ polarization functions, and another including one set of g polarization functions. Excellent agreement with experiment and high-quality calculations is obtained for both equilibrium distances and spectroscopic constants. The possibilities of the method in treating single-bond breaking are also demonstrated. Finally, the Linked and Non-Linked contributions from Triple and Quadruple excitations are analysed separately and it is suggested that the addition of the linked triples to the size-consistent SDCI is sufficient to have quantitatively correct spectroscopic properties in going from the size-consistent SDCI to nearly experimental values.

Key words: Intermediate Hamiltonians – Total dressing – Size-consistent configuration interactions – Linked and unlinked diagrams – Spectroscopic constants

Introduction

A procedure has been recently proposed [1] to achieve the elimination of the so-called unliked diagrams effects [2] in any multi- or single reference SDCI, rendering it size-extensible (and even separable, provided that localized MO's be used) [1, 3]. The method derives from the intermediate Hamiltonian formalism [4] and goes through an appropriate dressing of the SDCI matrix. This dressing consists in adding to the SDCI matrix elements some terms which will cancel, after diagonalization, the undesired unlinked effects. The dressing terms themselves depend on the SDCI function coefficients so that an iterative procedure converging into a self-consistent solution must be built. The method has been called Self-Consistent Size-Consistent SDCI and labelled as (SC) ^{2}SDCI [1].

Correspondence to: J. Sánchez-Marín, Fax: + 34-6-386 4564

$(SC)^2$SDCI provides a great improvement both in energy and formal properties in the (projected to the SD space) wave function at the moderate cost of a few SDCI-like matrix diagonalizations. Results comparable to CCSD can be obtained at a very moderate cost [1].

$(SC)^2$SDCI method suppresses all the unlinked contributions of Triple and Quadruple excitations and takes into account to all orders the most relevant Exclusion Principle Violating diagrams [5], so that it can be considered as an exact CEPA approach [1, 6, 7].

A *total dressing* self-consistent procedure which would treat linked and unlinked Triples and Quadruples contributions in a similar way as $(SC)^2$SDCI does with unlinked ones is under development [8]. However, it is a new iterative procedure, more expensive than $(SC)^2$SDCI, and in view of the good quality of the $(SC)^2$SDCI wave functions, one may wonder whether starting from this wave function, one could not calculate the linked effects of Triples and Quadruples in a non-iterative way.

In a previous paper [9], an approximated non-iterative procedure has been proposed which estimates the linked contributions of Triples and Quadruples, by means of a suitable dressing operator Δ'. The mean value of the $(SC)^2$SDCI function (hereafter noted as $\tilde{\Psi}$) is then obtained as

$$\Delta E^{L}_{TQ} = \langle \tilde{\Psi} | \Delta' | \tilde{\Psi} \rangle .$$

The Δ' operator, itself, depends on the c_α coefficients of Triple and Quadruple excitations in the exact function Ψ (intermediate normalization is assumed)

$$\Psi = \phi_0 + \sum_{i}^{S,D} c_i \phi_i + \sum_{\alpha}^{T,Q} c_\alpha \phi_\alpha + \cdots , \tag{1}$$

where the index i runs over the space of Singles and Doubles while index α runs over the Triples and the Quadruples. Of course, the c_α coefficients are not known a priori and they must be estimated from the set of $\tilde{c}_i$ coefficients of the $\tilde{\Psi}$ function:

$$\tilde{\Psi} = \phi_0 + \sum_{i}^{S,D} \tilde{c}_i \phi_i . \tag{2}$$

A number of versions of this mean-value total dressing method (MVTD) can be conceived depending on the way of estimating c_α. Following the notation of Ref. [9], we will denote henceforth the most elaborated version of MVTD method as (mv)td-2. A closely related (mv)td-2′ version will also be mentioned (See further details below).

Previous test calculations with these total dressing models [9] and, in particular, on the single-bond dissociation curves of HF and F_2 have been performed employing DZP basis sets for which very accurate solutions are available [10–12]. Some conclusions from these previous calculations were:

a) In the well region, the td-2 results compare very well with results from CC methods which include Triples (CCSD + T(CCSD), CCSD(T) or even better). An improvement of one order of mangitude in the energy error is obtained when one goes from the $(SC)^2$SDCI to the td-2 model. Errors less than 1 mhartree for HF with respect to full-CI and for F_2 with respect to CCSDT-1 were obtained in this region as well as reliable equilibrium distances and other spectroscopic properties.

b) Despite the single referential nature of the model space and some perturbative steps involved in the method (see below and Ref. [9] for details), it does not diverge at long bond distances where quasi-degenerate $\sigma^2 \rightarrow \sigma^{*2}$ diexcitations occur. A little hump appears at intermediate bond distances but the estimates of dissociation energy D_e obtained from differences between long-range distance energies and the minimum are good (5.8 vs 6.128 eV (experiment) [13] for HF, 1.2 vs 1.66 (experiment) [13] for F_2). Taking apart this artifact, (mv)td-2 energies follow very close (less than 1 mhartree) the CCSDT values for HF and CCSDT-1 or MR-LCCM values for F_2 at medium range and even long-range distances.

Dressing matrix methods are not variational in the sense of satisfying the Variational Principle, but they share this defect with their MBPT and CC competitors. They are not (in general) invariant under rotation of the MO's, but this is not a defect, in our mind, since the MO-dependence of the energy provides a supplementary information. One advantage is that they can be formulated as Hermitian eigenvalue equations [8] and rest on the very efficient algorithms available for the diagonalization of symmetrical real matrices. Besides this, they do not diverge neither in quasi-degenerate multireference situations [8] nor for dissociating single bonds where CC methods could not converge. We present here results on HF and F_2 with extended basis sets taking now as a reference the experimental values. Both the $(SC)^2$SDCI and, mainly, the (mv) td-2 procedures are tested in this sense. Some insight on the origin of the small hump occurring at long distances as well as its behavior with the basis set changes is obtained. Finally the relative role of linked and non linked Triples and Quadruples is discussed.

Method of calculation

1) Three basis sets have been used in the Hartree-Fock step. The first one is the correlation consistent cc-pVTZ basis set of Dunning [14], which contraction is $(10s5p)/\langle 4s\,3p\rangle + (2d1f)$ for F atoms, and $(5s)/\langle 3s\rangle + (2p1d)$ for H. The $(5s)/\langle 3p\rangle$ contraction was that from van Duijneveldt [15]. The second basis set is similar, but $(3d1f)$ polarization functions have been used for F, while the valence contraction was the widely used $(9s5p)/\langle 4s3p\rangle$ Huzinaga–Dunning contraction [16, 17]. This choice allows to eliminate of the correlation space the highest virtual MO's which remain quasi-purely s in nature. The third basis set has a contraction $(10s6p)/\langle 5s4p\rangle + (3d2f1g)$ for the F atoms which is basically the standard cc-pVQZ basis set of Dunning [14] but for the s AO's. For the H atom the standard $(6s)/\langle 4s\rangle + (3p2d1f)$ cc-pVQZ basis set has been used [14]. The highest virtual MO's were switched off in the $3d1f$ calculations only, but the two core electrons of each F were frozen in all correlation calculations.

The details, origin and implementation of both (SC) ^{2}SDCI and td-2 methods have been discussed in Refs. [1, 9]. Hence, only an outline of the main details follows here.

2) $(SC)^2$SDCI step: An intermediate Hamiltonian

$$\tilde{H} = P(H + \tilde{V})P \tag{3}$$

is built, where P is the projector operator onto the space spanned by the closed shell single reference ϕ_0 and all its Single- and Double-excitation determinants:

$$P = |\phi_0\rangle\langle\phi_0| + \sum_i^{\mathrm{S,D}} |\phi_i\rangle\langle\phi_i| \tag{4}$$

and $\tilde{V}$ is the dressing operator on the same space. $\tilde{V}$ is purely diagonal and, hence, Hermitian (other options can be considered [3]) and defined as

$$\langle \phi_i | \tilde{V} | \phi_i \rangle = \sum_{\substack{j \\ D_j^+ \phi_i \neq 0}} \tilde{c}_j \langle \phi_0 | H | \phi_j \rangle , \tag{5}$$

where D_j^+ is the double excitation $\hat{X}_{ab}^{rs}$ operator that creates a Double configuration ϕ_j from ϕ_0 and $\tilde{c}_j$ is the coefficient of ϕ_j in Eq. (2). The expected value of operator $\tilde{H}$ is then obtained as

$$\tilde{E} = \langle \tilde{\Psi} | \tilde{H} | \tilde{\Psi} \rangle = \langle \tilde{\Psi} | H + \tilde{V} | \tilde{\Psi} \rangle \tag{6}$$

by diagonalization of $\tilde{H}$. As Eq. (5) shows, the operator $\tilde{V}$ depends on the $\tilde{c}_j$ coefficients, so that an iterative procedure is undertaken which converges to the self-consistent solution. In the following steps, such self-consistent solutions are assumed to have been reached. It can be shown [1] that $\tilde{V}$ incorporates the unlinked effects of Triples (on Singles) and Quadruples (on Doubles) which are required to cancel the undesired unlinked terms brought by the truncation of the CI space. Moreover, the converged $\tilde{\Psi}$ and $\tilde{E}$ incorporate to all orders the most relevant EPV diagrams.

3) Total dressing step. Besides the unlinked contributions, the linked ones due to Triples and Quadruples can be incorporated to the dressing by means of a new (also diagonal) dressing operator defined as [9]

$$\langle \phi_i | \tilde{V}' | \phi_i \rangle = \frac{1}{\tilde{c}_i} \sum_{\alpha}^{\mathrm{T,Q}} \langle \phi_i | H | \phi_\alpha \rangle c'_\alpha , \tag{7}$$

where α runs over the whole outer space made of Triple- and Quadri-excitations, ϕ_α is any Triple or Quadruple interacting with ϕ_i and the c_α coefficients are taken in intermediate normalization.

The origin of Eq. (7) can be easily understood if one considers the Schroedinger equation $H\Psi = E_0\Psi$. After cancelling on the left by ϕ_i, one can write:

$$\sum_{j \in S} c_j H_{ij} - E_0 c_i + \sum_{\alpha \notin S} c_\alpha H_{i\alpha} = 0 , \tag{8}$$

where S stands for the model space (in the present work, the space of Singles and Doubles). On the other hand, if one considers the dressed Hamiltonian eigenvalues equation

$$(H + \tilde{V}') | \Psi \rangle = E_0 | \Psi \rangle \tag{9}$$

and remembering that $\tilde{V}'$ is defined as a diagonal operator, the equivalent of Eq. (8) is,

$$\sum_{j \in S} c_j H_{ij} - E_0 c_i + c_i \langle \phi_i | \tilde{V}' | \phi_i \rangle = 0 . \tag{10}$$

Equation (7) derives from the equality of the last terms on the left-hand side of Eqs. (8) and (10).

The iterative (built $H + \tilde{V}'$ then diagonalize)-procedure would be very costly. The following alternative approach is then used: We calculate the mean value of the total dressing $H + \tilde{V}'$ operator relative to the (SC)^{2}SDCI function $\tilde{\Psi}$.

If we call $\underline{\tilde{\Psi}} = \tilde{\Psi} \times c_0$ the normalized vector $\tilde{\Psi}$, the (mv) td-n contribution is given by

$$E_{(\mathrm{mv})\,\mathrm{td-n}} = \langle \underline{\tilde{\Psi}} | H + \tilde{V}' | \underline{\tilde{\Psi}} \rangle, \tag{11}$$

where $E_{(\mathrm{mv})\,\mathrm{td-n}}$ includes all the effects carried by the $(\mathrm{SC})^2$SDCI function and the linked effects brought by $\tilde{V}'$. The practical definition of $\tilde{V}'$ requires to have an estimate of the c_α coefficients. In the model which we call td-2 the c_α coefficients (see Eqs. (1) and (7)) are approached as follows:

i) For the Triples: In a second-order perturbation theory-like way

$$c_\alpha = \frac{\langle \phi_\alpha | H | \tilde{\Psi} \rangle}{\Delta_\alpha}, \tag{12}$$

where Δ_α is the Epstein–Nesbet denominator for the Triple ϕ_α, i.e., $\Delta_\alpha = \langle \phi_0 | H | \phi_0 \rangle - \langle \phi_\alpha | H | \phi_\alpha \rangle$.

ii) For the Quadruples, we take

$$c_\alpha = \sum_{\substack{(i,j) \\ D_i^+ D_j^+ \phi_0 = \phi_\alpha}} \tilde{c}_i \tilde{c}_j \left(\frac{\Delta_i + \Delta_j}{\Delta_\alpha} \right), \tag{13}$$

where (i,j) stands for every couple of disconnected Doubles ϕ_i and ϕ_j into which the Quadruple ϕ_α can be decomposed, and Δ_i, Δ_j, and Δ_α are Epstein–Nesbet denominators.

A simpler version of td-2 which we call td-2′ is obtained by simply assuming additivity of the denominators (which would be exact in an Moller–Plesset partition of H) so that

$$c_\alpha = \sum_{\substack{(i,j) \\ D_i^+ D_j^+ \phi_0 = \phi_\alpha}} \tilde{c}_i \tilde{c}_j. \tag{14}$$

For single-bond potential curves, the results from td-2′ are expected to be very similar to those of td-2 [9] but a noticeable time-saving is obtained.

Indeed, Eq. (11) can be rewritten as

$$\begin{aligned} E_{(\mathrm{mv})\,\mathrm{td-x}} &= \langle \underline{\tilde{\Psi}} | H + \tilde{V} | \underline{\tilde{\Psi}} \rangle + \langle \underline{\tilde{\Psi}} | \tilde{V}' | \underline{\tilde{\Psi}} \rangle - \langle \underline{\tilde{\Psi}} | \tilde{V} | \underline{\tilde{\Psi}} \rangle \\ &= \tilde{E} + \langle \underline{\tilde{\Psi}} | \tilde{V}' | \underline{\tilde{\Psi}} \rangle - \langle \underline{\tilde{\Psi}} | \tilde{V} | \underline{\tilde{\Psi}} \rangle. \end{aligned} \tag{15}$$

In this way, the second term on the right-hand adds the effect of linked diagrams due to triple and quadruple excitation determinants while the third term avoids the reintroduction of the unlinked effects which were in $\tilde{E}$ yet.

Our algorithm computes separately the effects due to Triples and Quadruples [9] as well as the linked and unlinked contributions, so that we can write

$$E_{(\mathrm{mv})\,\mathrm{td-x}} = \tilde{E} + \Delta E_{\mathrm{L}}^{\mathrm{Q}} + \Delta E_{\mathrm{L}}^{\mathrm{T}} - \Delta E_{\mathrm{NL}}^{\mathrm{Q}} - \Delta E_{\mathrm{NL}}^{\mathrm{T}} \tag{16}$$

and each term contribution can be analysed separately.

From the technical point of view, we have taken benefit in the present work of an algorithm recently developed by one of us (D.M.) which allows for a very efficient systematic scanning of all the Triple and Quadruple excitations interacting with the space of Single and Double excitations built on a ϕ_0 closed-shell single reference [18]. In this work the computation time increases in N^8 (N being the size of the basis set) due to the scanning of the Quadruples. However, as discussed in

Ref. [18], the intermediate information storage which reduces the computational time of CCSD to N^6 would be feasible in the treatment of the linked effects of the Quadruples; this would lead to an irreducible N^7 behaviour, as for CCSD(T). Instead, we have chosen to keep the N^8 dependence due to several reasons: 1) Our factor in the N^8 power is very low. 2) The dependence of the Triples is in fact $N_{oc}^3 N_v^4$ (N_{oc} and N_v being the number of occupied and virtual MO's respectively), quite close to the $N_{oc}^4 N_v^4$ dependence of the Quadruples so that N^6 (one would better write $N_{oc}^2 N_v^4$) dependence for the Quadruples does not ameliorates so much the global dependence, and 3). This choice allows for a much larger freedom in the choice of denominators in perturbative or perturbative-like formulations [8, 18]. Moreover, our N^8 algorithm is highly parallelizable because each individual contribution from either a Triple or a Quadruple can be computed independently of the others after a proper addressing arrangement.

Results and discussion

The HF molecule deserves very often attention from theoreticians due to the great interest involved in the hydrogen bonded $(HF)_2$ system [19–23]. Very accurate correlation calculations exists on the HF ground state potential well [9, 10, 21, 22, 24], but calculations involving *f* atomic orbitals are scarce [23, 25]. This is in part motivated by the need of comparing with extensive calculations on the dimer. Instead, high-quality calculations on a limited number of geometries ($r_e = 1.733$ a.u., $1.5r_e$, and $2r_e$) in a DZ + P basis set can be found [10, 11, 26, 27]. Benchmark calculations with systematically improved Dunning's correlation consistent basis sets have also been published and provide excellent reference results for spectroscopic properties and dissociation energies [28].

In order to compare properly with our previous results [9] on the DZ + P basis sets for which some full CI results are available, we have calculated the energies at the same set of 12 points, taken as selected multiples of $r_e = 1.733$ a.u. and ranging from $0.65r_e$ to $5r_e$. Besides this, we have stretched the single bond up to $30r_e$ (about 52 Bohr) in the largest basis set case. Our method of calculation converged easily at very large bond lengths provided that the (very poor) RHF function could be obtained.

All spectroscopic properties have been calculated with the same procedure used in previous work [29]. Our results are shown in Table 1. A very recent paper [30] reports experimental measurement of the rotational constants for the three lowest vibrational states of HF. The Hutson's method [29] that we use to estimate the spectroscopic properties works specially well to get an efficient estimate of the centrifugal distortion constants. We show in Table 2 the theoretical values for the + $3d2f1g$ basis set (mv)td-2 calculations. In spite of the absolute error in the energies of the vibrational levels which are responsible for the deviation in the estimates of ω_e and $\omega_e x_e$, the agreement in order of magnitude, sign and first figures of the rotational constants is noticeable, specially up to third order (H_v). However, the high precision of the experimental measurements remains as a permanent challenge for *ab initio* calculations.

The increase of basis set quality in going from DZ + P to extended sets is well reflected in the improvement of the calculated values corresponding to the (mean value) total dressing technique. This does not hold for the intermediate $(SC)^2$SDCI step which shows an irregular behavior in equilibrium bond lengths and only a moderate improvement in ω_e. Using canonical MO's, as we do, $(SC)^2$SDCI

Table 1. Spectroscopic properties for HF. Equilibrium distances are in Å, dissociation energies in eV and other properties in cm^{-1}

Calculation	R_e	B_e	α_e	ω_e	$\omega_e x_e$	D_e
Basis set DZ + P[a]						
(SC)^{2}SDCI[a]	0.917	20.9749	0.757	4234.8	90.6	6.28[b]
(mv) td-2′[a]	0.919	20.8963	0.767	4216.8	92.0	5.75[b]
Basis set 4*s*3*p*3*d*1*f*/3*s*2*p*1*d*						
(SC)^{2}SDCI	0.912	21.0564	0.716	4218.9	82.0	6.79[b]
(mv)td-2	0.915	20.9544	0.724	4183.2	84.0	6.07[b]
(mv)td-2′	0.916	20.9414	0.730	4178.9	84.1	6.03[b]
Basis set cc-pVTZ						
(SC)^{2}SDCI	0.914	21.0018	0.712	4210.5	81.9	6.74[b]
(mv)td-2	0.917	20.9015	0.725	4172.5	83.6	6.03[b]
(mv)td-2′	0.917	20.8886	0.726	4169.1	83.8	5.98[b]
Basis set 5*s*4*p*3*d*2*f*1*g*/4*s*3*p*2*d*1*f*						
(SC)^{2}SDCI	0.912	21.0526	0.711	4196.9	80.5	6.94[c]
(mv)td-2	0.915	20.9383	0.724	4156.3	82.4	6.12[c]
(mv)td-2′	0.916	20.9203	0.725	4150.7	82.5	6.07[c]
(mv)td-2 (Linked Triples only)	0.915	20.9667	0.726	4164.4	82.6	6.01[c]
Other works[d]						
FCI[e]	0.9203			4143.1	91.3	5.49
MRD-CI[f]	0.9127	21.45	0.8494	4181.0	88.78	6.09
SCEP/CEPA[g]	0.919	20.8	0.780	4131	89	
MCSCF[g]	0.917	20.9	0.762	4181	86	
SDCI/CASSCF[h]	0.9152	21.029	0.7912	4167.2	88.6	6.01
Experiment[i]	0.9168	20.9557	0.798	4138.32	89.88	6.128

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[a] Ref. [9]. Results for td-2 method are slightly worse but for B_e and D_e

[b] Estimate of D_e from the difference of energies at $5r_e$ and r_e with $r_e = 1.733$ a.u.

[c] Estimate of D_e from the difference of energies at $30r_e$ and r_e

[d] Other results from literature are: $R_e = 0.9194$ Å, $B_e = 20.84\ cm^{-1}$, $\omega_e = 4135\ cm^{-1}$ (method: CPF, basis set: 8*s*6*p*2*d*/4*s*1*p*), Ref. [22]; $R_e = 0.9218$ Å, $\omega_e = 4167.4\ cm^{-1}$, $\omega_e x_e = 85.1\ cm^{-1}$ (method: (A)CCD, basis set, 6*s*4*p*1*d*/4*s*1*p*), Ref. [21];$R_e = 0.9198$ Å, $\omega_e = 4202.4\ cm^{-1}$, $\omega_e x_e = 82.2\ cm^{-1}$ (method: SCEP, same basis set), Ref. [21]; $R_e = 0.917$ Å (method: CCSD(T), basis set: 4*s*3*p*2*d*1*f*/3*s*2*p*1*d*), Ref. [23]; $R_e = 0.9198$ Å, $\omega_e = 4202.4\ cm^{-1}$. $D_e = 6.07$ eV (method: MP4 + counter Poise, basis set: 7*s*5*p*2*d*1*f*/5*s*2*p*1*d* + (3*s*3*p*2*d*) at midpoint), Ref. [41]

[e] Ref. [28]. Basis set cc-pVDZ

[f] Ref. [24]. Basis set 6*s*4*p*3*d*/5*s*2*p*1*d* + (3*s*, 2*p*) at midpoint

[g] Ref. [25]. Basis set 12*s*8*p*3*d*1*f*/7*s*2*p*1*d*

[h] Ref. [28]. Basis set aug-cc-pV5Z

[i] Ref. [13]

dissociates very high in energy when the basis set is improved; (mean value) td-2 and td-2′ correct in the good sense these tendencies, and predict R_e with an error lesser than 0.002 Å with the three extended basis sets, reducing the error in ω_e to less than $18\ cm^{-1}$ (0.44%). Our largest basis set results compare well with the internally contracted multireference CI (CASSCF + 1 + 2) spectroscopic properties of Peterson et al. [28] in spite of the very different ways of including dynamical and non-dynamical correlation effects. The approach to the dissociation limit also

Table 2. Centrifugal distortion constants for the first three vibrational levels of HF in cm^{-1}

	$v = 0$		$v = 1$		$v = 2$	
Constant	Calc.[a]	Exp.[b]	Calc.[a]	Exp.[b]	Calc.[a]	Exp.[b]
$G(v)$	—	—	3994	3961.42	7816	7750.8
B_v	20.62	20.5597	19.85	19.7874	19.10	19.0349
$D_v \times 10^3$	2.11	2.1199	2.05	2.0637	1.99	2.0100
$H_v \times 10^7$	1.61	1.6350	1.56	1.5845	1.51	1.5301
$L_v \times 10^{11}$	− 1.48	− 1.4978	− 1.64	− 1.432	− 0.88	− 1.351
$M_v \times 10^{15}$	1.54	1.049	1.81	0.68	3.33	—

[a] From (mv)td-2 curve and the $+3d2f1g/+3p2d1f$ basis set
[b] From Ref. [30]

takes place at energies which compare well with the experiment, so that the inclusion of linked effects of Triples and Quadruples strongly correct the deficiencies of $(SC)^2$SDCI and provide reliable estimates of D_e. As stated in the DZ + P calculations, td-2′ provides results which lie very near to those of the td-2 method, and rest as a good choice for extensive calculations because it is cheaper in time. The D_e estimates from the largest basis set and very long distances are very reliable for HF, and clearly show that our total dressing procedures do not diverge at single bond dissociation distances.

The ground state of the F_2 molecule is an excellent test problem for theoretical calculations on a highly correlated single bond, and, consequently, has merited a great number of high quality calculations, all of them including f functions in the basis set [31–35], and even g ($l = 4$) AO's [32, 36–38]. Benchmark calculations by Peterson et al. are also available for F_2 [39]. We have performed calculations of the potential curves on a set of 16 points ranging from 2.0 to 10.0 a.u., and the spectroscopic constants have been calculated in the same conditions that they were in the DZ + P basis set [9]. Our results, along with a number of reference values taken from the literature, are shown in Table 3. The (mv)td-2′ values for both + df basis sets are not reported but they show little differences with the (mv)td-2 results. It must be noticed that spectroscopic constants, and particularly the vibrational ones, calculated from (mv)td-2 and (mv)td-2′ (cc-pVTZ basis set calculations) are in very good agreement with experiment. As was shown by Ahlrichs and coworkers [32], the angular incompleteness of the basis set can be responsible for errors larger than 0.01 a.u. in R_e even for highly correlated methods (e.g., MR-CI(SD)). Our smallest errors with + df basis sets (0.003 Å) seem to overpass the possibilities of the basis set and could be the result of fortunate error cancellations.

As reported in Table 3, the errors in ω_e are less than 2 cm^{-1} (0.22%) and this would confirm the reliability of the (mean value) total dressing approaches to treat the well region of the potential and its capability to correct the bad trends in the $(SC)^2$SDCI energies at stretched bond lengths. The dissociation energies estimated from differences in (mv)td energies at long and equilibrium distances are also very reliable when compared with spectroscopic measurements. Moreover, the method converged fairly well for homoatomic F_2 at a bond distance of 100 a.u. and the D_e estimate for the + dfg basis set agrees remarkably with the CCSD(T) estimates using cc-pVQZ basis set [33].

Table 3. Spectroscopic properties for F_2. Equilibrium distances are in Å, Dissociation energies in eV and other properties in cm^{-1}

Calculation	R_e	B_e	α_e	ω_e	$\omega_e x_e$	D_e
Basis set DZ + P[a]						
(SC)^{2}SDCI[a]	1.437	0.8653	0.0197	829.7	17.1	2.33[b]
(mv)td-2′[a]	1.433	0.8669	0.0169	849.0	14.7	1.15[b]
Basis set 4*s*3*p*3*d*1*f*						
(SC)^{2}SDCI	1.393	0.9147	0.0112	982.1	7.1	2.90[b]
(mv)td-2	1.417	0.8858	0.0141	909.0	11.7	1.52[b]
Basis set cc-pVTZ						
(SC)^{2}SDCI	1.392	0.9167	0.0112	996.5	7.6	2.87[b]
(mv)td-2	1.415	0.8890	0.0142	918.5	11.6	1.50[b]
Basis set 5*s*4*p*3*d*2*f*1*g*						
(SC)^{2}SDCI	1.389	0.9206	0.0109	1004.2	7.7	3.05[c]
(mv)td-2	1.413	0.8904	0.0135	915.2	10.4	1.59[c]
(mv)td-2′	1.413	0.8912	0.0134	916.0	10.1	1.59[c]
(mv)td-2 (Linked Triples only)	1.409	0.8961	0.0137	913.4	9.6	1.47[c]
Other works[d]						
MCSCF[e]	1.4115					1.638
MP4[f]	1.422			906		1.641
MR-SDCI + Q[g]	1.417			930		1.658
CMRCI[h]	1.4130	0.889	0.0109	934.4	16.57	1.65
ACPF[h]	1.4158	0.885	0.0113	924.4	17.30	1.55
QD-VPT[h]	1.4161	0.885	0.0112	927.4	17.16	1.57
CEPA(0)[h]	1.4211	0.879	0.0116	911.5	17.70	
CCSD(T)[i]	1.4130			921		1.589
QCISD(T)[j]	1.4266			903		1.51
SDQ[k]	1.404			957		1.98
SDCI/CASSCF[l]	1.4128	0.889	0.0135	899.9	12.4	1.59
Experiment[m]	1.4119	0.8902	0.0141	917	11.2	1.659

[a] Ref. [9]. Results for td-2 method are similar or slightly worse but for $B_e = 0.8674\ cm^{-1}$

[b] Estimate of D_e from the difference of energies at $R = 10$ a.u and $R = 2.70$ a.u.

[c] Estimate of D_e from the difference of energies at $R = 100$ a.u. and $R = 2.70$ a.u.

[d] Other selected results from the literature are: $R_e = 1.4323$ Å, $\omega_e = 911\ cm^{-1}$, $D_e = 1.61$ eV (method: CCD(ST), basis set: 5*s*3*p*2*d*1*f*), Ref. [34]; $R_e = 1.4158$ Å, $\omega_e = 920\ cm^{-1}$, $D_e = 1.507$ eV (method: CCSD(T), basis set: cc-pVTZ), Ref. [33]; $R_e = 1.414$ Å, $D_e = 1.310$ eV (method: CPF, basis set: 6*s*4*p*2*d*1*f*), Ref. [32]; $R_e = 1.412$ Å, $\omega_e = 948\ cm^{-1}$, $D_e = 1.673$ eV (method: CASSCF, basis set: 5*s*4*p*3*d*2*f*1*g*, ANO's), Ref. [37]

[e] Ref. [32]. Basis set: 7*s*5*p*3*d*3*f*1*g*

[f] Ref. [41]. Basis set: 7*s*5*p*2*d*1*f* + (3*s*3*p*2*d*) at midpoint. Counter Poise correction

[g] Ref. [37]. Basis set: 5*s*4*p*3*d*2*f*1*g*, ANO's

[h] Ref. [38]. Basis set: 13*s*8*p*3*d*2*f*1*g*

[i] Ref. [33]. Basis set: cc-pVQZ.

[j] Ref. [34]. Basis set: 5*s*3*p*2*d*1*f*.

[k] Ref. [35]. Basis set: 6*s*4*p*3*d*2*f* (STO's)

[l] Ref. [39]. Basis set: cc-pV5Z.

[m] Ref. [13].

Linked and non-linked contributions from Triples and Quadruples

As was indicated above (see Eq. (16)), we proceed to a separate evaluation of the contributions to the correlation energy by means of independent summations over the linked and unlinked diagrams which relate every Triple and Quadruple excitation which the model space of Singles and Doubles. Of course, all fourth-order diagrams implying Triples and Quadruples have been taken into account, but some diagrams, including the most relevant EPV ones, have been also summed to infinite order and enter in the evaluation of the (mv)td energies because they are included in the self-consistent $\tilde{c}_j$ coefficients.

We have plotted in Figs. 1, 2 the values of the four contributions (Linked Triples, Linked Quadruples and the respective Non-Linked terms) at each point of the potential curves of the homoatomic bond F_2 and the heteroatomic bond HF. It must be remembered that the Non-Linked contributions have the important role of insuring size-consistency. As Figs. 1,2 show, the role of the NL Quadruples term is very important in both molecules at equilibrium distances and its importance increases severely as the bond is stretched. In contrast, the role of NL Triples contribution shows a marked difference in HF and F_2. While it contributes less than a mHartree at bond distances in F_2 and remains two orders of magnitude lesser than the NL Quadruples for long distances, its role in HF is very relevant at long distances. This behaviour evidences the increasing weight of Single excitations in the correlated wave function in the heteroatomic case.

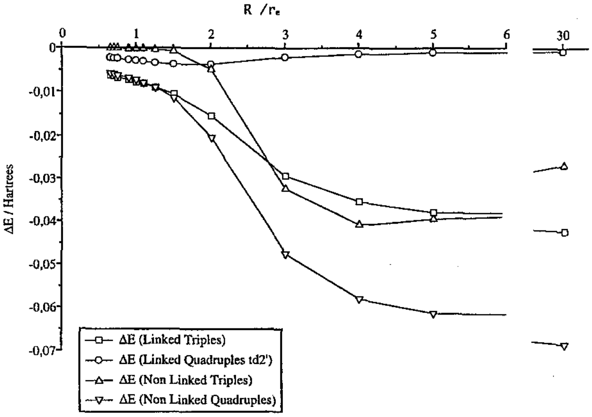

Fig. 1. Linked and Non-Linked contributions from Triples and Quadruples to the mv(td)-2′ correlation energy in hartrees calculated with the largest basis set from Triples and Quadruples along the dissociations curve of HF. Units of bond length are $r_e = 1.733a_0$

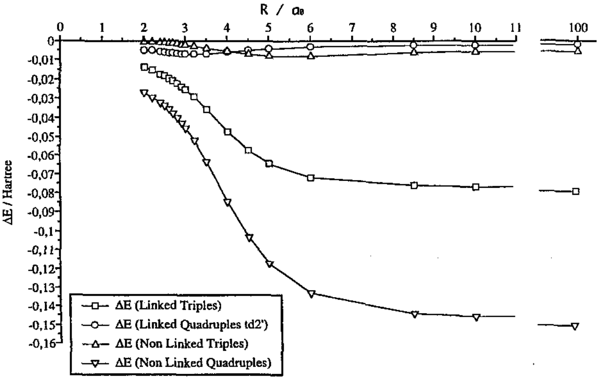

Fig. 2. Linked and Non-Linked contributions from Triples and Quadruples to the mv(td)-2′ correlation energy in hartrees calculated with the largest basis set from Triples and Quadruples along the dissociations curve of F_2. Units of bond length are a_0

In contrast to Non-Linked contributions, the linked ones do not attempt to correct the undesirable effects due to normalization in the Singles and Doubles model space. Instead, these are additional energy terms which bring actual physical contributions. A reliable calculation of these contributions all along the dissociation curve is needed to have good D_e values.

Despite the great difference in the number of Quadruple and Triple excitations (e.g., for F_2 in the + dfg basis set the number of Q amounts to about 2.5×10^9 while the number of T is about 2×10^7), their Linked contributions are very different, as evidenced in Figs. 1, 2. The weight of the LT terms is significantly greater in short bond distances and becomes increasingly important at long distances. Instead, the role of LQ remains relatively little at all distances, and never goes up of a few mHartree in both HF and F_2.

Hence, taking into account the cost in evaluating the LQ contributions, we have tried the evaluation of the spectroscopic properties from the potential curves obtained adding only LT contributions to the $(SC)^2$SDCI energy $\tilde{E}$. The results for the largest basis set are shown in Tables 1 and 3 for HF and F_2 respectively and show that the main improvements of all properties relative to the $(SC)^2$SDCI ones are obtained from Triples only. These results are consistent with the previously noticed parallelism of CCSD and $(SC)^2$SDCI results; they suggest that the $(SC)^2$SDCI plus addition of the linked Triples might be an interesting alternative to CCSD(T) since it is somewhat cheaper and better converging. This would provide a convenient algorithm with an N^7 increase of the computation time.

The present calculations show, in any case, that the results of the (mean value) total dressing technique improve in a consistent way with the angular enhancement of the basis set. The spurious behaviour at intermediate bond distances does not disappear, however, with the sole improvement of the basis set quality. In fact, a somewhat detailed analysis of the linked contributions of Triple and Quadruple excitations as estimated at td-2 level (see Table 4) reveals that Linked Triple contributions are mainly responsible for this spurious behaviour.

It is easily seen that adding the linked Quadruples (ΔE_L^Q) contribution only to the $(SC)^2$SDCI correlation energies gives − 199.177261 hartree for F_2 at 5.00 a.u. and − 199.168362 hartree at 10.00 a.u., so that the energy decreasing at long distances does not occur. A similar behaviour is found for HF and with all the basis sets. The perturbative-like way of calculating c for triples in Eq. (12) could be responsible for this behaviour. In fact, similar behaviours, but significantly more divergent, have been reported for CCSD(T) on a RHF reference in F_2 [40].

The results of (mv)td are in general similar or slightly better than for CCSD(T) in the well region, and easily obtainable and reliable at very long single bond

Table 4. Contributions to the total energy calculated at some selected distances with the (mean value) td-2 model and cc-pVTZ basis set. All data are in a.u.

Molecule	R	E^{SCF}	$E^{(SC)2SDCI}$	ΔE_L^T	ΔE_L^Q	Total energy ((mv)td-2)
F_2	2.70	− 198.758003	− 0.521463	− 0.018352	− 0.006575	− 199.296020
F_2	5.00	− 198.501833	− 0.671113	− 0.061162	− 0.004315	− 199.238423
F_2	10.00	− 198.402833	− 0.763416	− 0.072541	− 0.002113	− 199.240903
HF	$r_e = 1.733$	− 100.058009	− 0.271261	− 0.006472	− 0.002418	− 100.338160
HF	$4r_e$	− 99.644654	− 0.437953	− 0.033952	− 0.000679	− 100.115880
HF	$5r_e$	− 99.620342	− 0.461054	− 0.036264	− 0.000930	− 100.116729

distances where CC procedures do not converge. We have also shown that adding the Linked effects of Triples to the $(SC)^2$SDCI method is sufficient to obtain reliable potential curves.

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