



On the calculation of $\Delta\langle\hat{S}^2\rangle$ for electronic excitations in time-dependent density-functional theory

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ARTICLE INFO

Article history:

Received 28 March 2016

Received in revised form

6 November 2016

Accepted 19 December 2016

Available online 4 January 2017

Keywords:

Time-dependent density-functional theory (TDDFT)

Excited states

Open-shell molecules

Spin-contamination

ABSTRACT

Excited states are often treated within the context of time-dependent (TD) density-functional theory (DFT), making it important to be able to assign the excited spin-state symmetry. While there is universal agreement on how $\Delta\langle\hat{S}^2\rangle$, the difference between $\langle\hat{S}^2\rangle$ for ground and excited states, should be calculated in a wave-function-like formalism such as the Tamm–Dancoff approximation (TDA), confusion persists as to how to determine the spin-state symmetry of excited states in TD-DFT. We try to clarify the origins of this confusion by examining various possibilities for the parameters (σ_1, σ_2) in the formula

$$\Delta\langle\hat{S}^2\rangle = \left[\Delta\langle\hat{S}_{\text{TDA}}^2\rangle(\vec{X}) + \Delta\langle\hat{S}_{\text{TDA}}^2\rangle(\vec{Y}^*) + \sigma_1\Delta\langle\hat{S}_{\text{mixed}}^2\rangle(\vec{X}, \vec{Y}^*) \right] / (\vec{X}^\dagger\vec{X} + \sigma_2\vec{Y}^\dagger\vec{Y}),$$

where \vec{X} is the particle–hole part and \vec{Y} is the hole–particle part of the response theory vector. A first principles derivation leads directly to $(\sigma_1, \sigma_2) = (+1, -1)$ which we argue is the best simple formula linking spin with energy, albeit approximately. On the other hand, if the desire is to recover wave-function-like values of $\Delta\langle\hat{S}^2\rangle$, then we argue that the choice $(\sigma_1, \sigma_2) = (+1, +1)$ should be made. Additional examples are offered to justify that the choice of $\sigma_1 = 0$ should also be made when seeking wave-function-like values of $\Delta\langle\hat{S}^2\rangle$.

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1. Introduction

One of the historical roles of theoretical chemical physics has been to assign – and hence to give meaning to – experimental spectra by simulation. Response theory is one of many ways to simulate electronic absorption spectra and, as it is based upon the response of the density to an applied time-dependent (TD) electric field, response theory lends itself particularly well to the calculation of spectra from a wave-function-free theory, such as TD density-functional theory (DFT). (See Refs. [1–4] for further information on TD-DFT.) The difficulty of how to assign excited-state symmetries in TD-DFT was identified early-on and termed the “assignment problem” [1]. It is actually a double problem. In the first instance, DFT is formally wave-function free. However excited-state symmetries may be assigned in the same way that they are done for linear response TD Hartree–Fock (TD–HF, also referred to as the

random phase approximation or RPA). In some sense, this amounts to basing symmetry assignments on the zero-order Kohn–Sham system of non-interacting electrons. The second part of the problem is that response theory provides excitation energies and transition moments but not direct access to excited-state wave functions. The problem is nevertheless not too difficult for simple spatial symmetries and for spin symmetry in spin restricted same-orbitals-for-different-spin (SODS) calculations. The situation is more difficult for spin unrestricted different-orbitals-for-different-spin (DODS) calculations. This is why tools [5–8] were specifically developed to calculate the difference in the expectation value of \hat{S}^2 in the I th excited state and the ground state ($I = 0$),

$$\Delta\langle\hat{S}^2\rangle_I = \langle\hat{S}^2\rangle_I - \langle\hat{S}^2\rangle_0. \quad (1.1)$$

During the course of our and other’s work on this problem, it has become apparent that there are several intentional or accidental variations on the original implementation [6] which may appear to give better agreement with the value of $\Delta\langle\hat{S}^2\rangle_I$, intuitively expected based upon wave-function theory, than does the original implementation. The present article reports our investigation of a number of these variations and their pragmatic value is discussed.

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The original RPA-like formulation of linear response TD-DFT [1] was quite general as it could include energy- (frequency-) dependent exchange–correlation kernels, fractional occupation numbers, and there was nothing preventing direct application to open-shell molecules within a DODS formalism. [The open-shell method originally described in Ref. [1] has been implemented and tested in the semiempirical TD density-functional tight-binding (TD-DFTB) method [9].] The method was timely and so rapidly implemented in a number of programs, including the popular GAUSSIAN program with its large user base, albeit without automatic assignment of spin symmetry [10]. This opened up the possibility of both the use and abuse of what was at first a relatively new and not always well understood method. Good agreement with experiment not infrequently was claimed on the basis of excitation energies and oscillator strengths alone, without the possibility of careful investigation of spin symmetry.

A particularly interesting claim emerged from the Head-Gordon group who found that TD-DFT provided an optimal simple description of the excited states of radicals [11]. Investigation based upon calculation of $\Delta\langle\hat{S}^2\rangle_I$ showed that the good agreement holds for one-particle/two-hole (1p2h) states where \hat{S}^2 is a good quantum number [6,7]. Many other studies (which discretion prevents us from citing) claimed spin assignments which are simply not possible within the TD-DFT approach used. This was particularly the case for transition metal complexes in which open-shell ground states are common. An as yet unpublished, but readily accessible, study (in French) applies the calculation of $\Delta\langle\hat{S}^2\rangle_I$ to the problem of separating physical from nonphysical TD-DFT excitations in the complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ [12]. Recent work has also focused on the problem of fully spin-coupled TD-DFT excited state calculations or spin-projected TD-DFT beginning with a spin-restricted reference state [13–21]. (See also Ref. [22].) However many workers treat open-shell systems by a symmetry-broken spin-unrestricted different-orbitals-for-different-spin (DODS) formalism. In light of this, the fundamental importance of a formula for $\Delta\langle\hat{S}^2\rangle_I$ for DODS calculations seems indeed evident and it would be good if everyone could agree to use the same formula.

That, however is not the case. One reason was alluded to above, namely that TD-DFT provides only partial information on excited states in the form of transition moments. Several different and nonequivalent formulae for $\Delta\langle\hat{S}^2\rangle_I$ thus are imaginable on the basis of the available limited information [7]. In contrast there is universal agreement on how $\Delta\langle\hat{S}^2\rangle_I$ should be calculated within the TD-DFT Tamm–Dancoff approximation (TDA) [23]. The problem is that, once we go beyond the TDA, particle–hole (X terms) and hole–particle (Y terms) mix and there are different ways to treat the mixing. Those ways are examined in more detail in the next section.

The rest of this article is organized as follows: The next section provides a review of the basic formula for $\Delta\langle\hat{S}^2\rangle_I$ and discusses some possible variations. Section 3 provides a brief formal application to some two-orbital two-electron models. After a brief section giving computational details (Section 4), our computational results are presented in Section 5. The concluding discussion is in Section 6.

2. Formal theory

We review the basic theory for calculating $\Delta\langle\hat{S}^2\rangle_I$ within a DODS framework. Note that the theory applied to TD-DFT is actually derived within a linear response TD–HF framework [6–8]. Hence we will be using the TD–HF model. The section begins with some basic notation and review of the ground-state formalism in order to set the stage. We then look at excitation energies

($\omega = \Delta\langle\hat{H}\rangle$), and the spin difference of excited state and ground-state ($\Delta\langle\hat{S}^2\rangle_I$). While the formulae for excitation energies may be considered to be “well known”, at least “by those who know about such things”, we will show in some detail why the formulae for the spin of excited states are open to discussion.

2.1. Ground-state formalism

We will use the common molecular orbital (MO) index convention,

$$\underbrace{a, b, c, \dots}_{\text{unoccupied}}, \underbrace{h, i, j, k, l, m, n}_{\text{occupied}}, \underbrace{o, p, q, \dots, z}_{\text{free}}, \quad (2.1)$$

where “free” means that the MO may be occupied or unoccupied. The ground-state determinant is designated by Φ . We will begin with a simple spin orbital notation in which spin is implicit, but soon will need to make spin explicit.

We will use a super-operator equation-of-motion (EOM) formalism to enter rapidly into our subject, but the interested reader will find the explicit connection with linear response theory nicely explained in Ref. [24]. Our hamiltonian in second-quantized notation over the underlying set of Hartree–Fock (HF) MOs is,

$$\hat{H} = \sum_{p,q} h_{p,q} p^\dagger q + \frac{1}{2} \sum_{p,q,r,s} (pq|rs) p^\dagger r^\dagger s q. \quad (2.2)$$

Here and elsewhere we use a “lazy notation” in which $p^\dagger = \hat{a}_p^\dagger$ designates a creation operator and $q = \hat{a}_q$ designates an annihilation operator. This hamiltonian is “spin-free” in the sense of containing no spin-operators, but the hamiltonian does contain the electron repulsion integral,

$$(pq|rs) = \int \int p^*(1) q(1) \frac{1}{r_{12}} r^*(2) s(2) d1 d2, \quad (2.3)$$

which we express in Mulliken “charge cloud” notation. The corresponding HF ground-state energy is,

$$E_{\text{HF}} = \sum_i h_{i,i} + \frac{1}{2} \sum_{i,j} [(ii|jj) - (ij|ji)]. \quad (2.4)$$

[Note the use of the MO labeling convention (2.1) which limits the sums in Eq. (2.4) to occupied MOs.]

Following Löwdin [25], we suppose that Φ is a DODS HF determinant solution of the ground-state problem and we seek to calculate the expectation value of the spin operator \hat{S}^2 ,

$$\langle\hat{S}^2\rangle_0 = \langle\Phi|\hat{S}^2|\Phi\rangle. \quad (2.5)$$

We first introduce second-quantized expressions for the spin operators,

$$\begin{aligned} \hat{n}_\alpha &= \sum_r r_\alpha^\dagger r_\alpha, \quad \hat{n}_\beta = \sum_r r_\beta^\dagger r_\beta \\ \hat{S}_z &= \frac{1}{2} (\hat{n}_\alpha - \hat{n}_\beta) \\ \hat{S}_+ &= \sum_r r_\alpha^\dagger r_\beta, \quad \hat{S}_- = \sum_r r_\beta^\dagger r_\alpha \\ \hat{S}^2 &= \hat{S}_+ \hat{S}_- + \hat{S}_z (\hat{S}_z - 1) \\ &= \hat{P}_{\alpha\leftrightarrow\beta} + \hat{n}_\alpha + \hat{S}_z (\hat{S}_z - 1), \end{aligned} \quad (2.6)$$

where the spin-permutation operator,

$$\hat{P}_{\alpha\leftrightarrow\beta} = \sum_{r,s} r_\beta^\dagger s_\alpha^\dagger s_\beta r_\alpha. \quad (2.7)$$

Next we take explicit account of differences between spin α MOs (which will be represented *without* an overbar) and spin β MOs (represented *with* an overbar) by introducing the spin-transfer matrix,

$$\Delta_{r,\bar{s}} = \langle r | \bar{s} \rangle. \quad (2.8)$$

This may be used to transform between the two MO basis sets,

$$r_\alpha^\dagger = \sum_s \bar{s}_\alpha^\dagger \Delta_{r,\bar{s}}^*, \quad (2.9)$$

$$\bar{r}_\beta^\dagger = \sum_s s_\beta^\dagger \Delta_{s,\bar{r}}.$$

As single determinants always are eigenfunctions of \hat{n}_α and \hat{n}_β , we arrive at Löwdin's formula [25] for the ground state expectation value of a DODS determinant without too much trouble,

$$\langle \hat{S}^2 \rangle_0 = - \sum_{i,j} |\Delta_{j,\bar{i}}|^2 + \frac{n_\alpha + n_\beta}{2} + \left(\frac{n_\alpha - n_\beta}{2} \right)^2, \quad (2.10)$$

where

$$n_\sigma = \langle \Phi | \hat{n}_\sigma | \Phi \rangle, \quad (2.11)$$

and $\sigma = \alpha, \beta$.

2.2. Excitation energies

Now let us look at the problem of calculating excitation energies. Consider the EOM,

$$\tilde{L}(\hat{H})\hat{O}^\dagger = \omega \hat{O}^\dagger. \quad (2.12)$$

Here the tilde indicates a superoperator (i.e., an operator that acts on an operator) and

$$\tilde{L}(\hat{A})\hat{B} = [\hat{A}, \hat{B}]. \quad (2.13)$$

When $\hat{A} = \hat{H}$ is the hamiltonian operator, then $\tilde{L}(\hat{A}) = \tilde{L}(\hat{H})$ is the Liouville superoperator or Liouvillian. Note that the EOM has both excitation and de-excitation solutions,

$$\hat{O}^\dagger = |I\rangle\langle 0|, \quad \omega = E_I - E_0$$

$$\hat{O} = |0\rangle\langle I|, \quad \omega = E_0 - E_I. \quad (2.14)$$

(In Hartree atomic units, $\hbar = m_e = e = 1$, so $\Delta E = \hbar\omega = \omega$.) To solve the equation, we introduce an expansion in mono-excitation and mono-de-excitation operators,

$$\hat{O}^\dagger = \sum_{ia} \hat{e}_{ai}^\dagger X_{ai} + \sum_{ia} \hat{e}_{ai} Y_{ai}, \quad (2.15)$$

where

$$\hat{e}_{ai}^\dagger = a^\dagger i, \quad (2.16)$$

which can be written more compactly as,

$$\hat{O}^\dagger = (\vec{\epsilon}^\dagger \quad \vec{\epsilon}) \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \vec{T}^\dagger \vec{Z}. \quad (2.17)$$

Of course, the limitation to mono-excitation ($\vec{\epsilon}_1^\dagger$) and mono-de-excitation ($\vec{\epsilon}_1$) operators is arbitrary. We could easily imagine supplementing the operator basis with double- and higher-excitation and de-excitation operators,

$$\hat{O}^\dagger = (\vec{\epsilon}_1^\dagger \quad \vec{\epsilon}_2^\dagger \quad \cdots \quad \vec{\epsilon}_1 \quad \vec{\epsilon}_2 \cdots) \begin{pmatrix} \vec{X}_1 \\ \vec{X}_2 \\ \vdots \\ \vec{Y}_1 \\ \vec{Y}_2 \\ \vdots \end{pmatrix} = \vec{T}^\dagger \vec{Z}. \quad (2.18)$$

Note however that, while this more general basis set is useful for formal manipulations, the truncated mono-excitation and mono-de-excitation basis is what is used in practice.

This operator basis allows us to transform the EOM (2.12) into a matrix equation using the metric,

$$(\hat{A}|\hat{B}) = \langle \Phi | [\hat{A}^\dagger, \hat{B}] | \Phi \rangle, \quad (2.19)$$

defined for any two operators \hat{A} and \hat{B} . The wave function Φ is still the single determinant HF solution of the ground-state problem. The matrix form of the EOM is then,

$$(\vec{T}^\dagger |\tilde{L}(\hat{H})| \vec{T}^\dagger) \vec{Z} = \omega (\vec{T}^\dagger | \vec{T}^\dagger) \vec{Z}, \quad (2.20)$$

where we have followed the usual practice of introducing a “dummy bar”, $(\vec{T}^\dagger |\tilde{L}(\hat{H})| \vec{T}^\dagger) = (\vec{T}^\dagger | \tilde{L}(\hat{H}) \vec{T}^\dagger)$, to make the equations more symmetric. In particular,

$$\begin{aligned} (\vec{T}^\dagger | \vec{T}^\dagger)_{ai,bj} &= (a^\dagger i | b^\dagger j) \\ &= \langle \Phi | [i^\dagger a, b^\dagger j] | \Phi \rangle = \delta_{ij} \delta_{a,b} \\ (\vec{T}^\dagger | \vec{T}^\dagger)_{ai,jb} &= (a^\dagger i | j^\dagger b) \\ &= \langle \Phi | [i^\dagger a, j^\dagger b] | \Phi \rangle = 0 \\ (\vec{T}^\dagger | \vec{T}^\dagger)_{ia,bj} &= (i^\dagger a | b^\dagger j) \\ &= \langle \Phi | [a^\dagger i, b^\dagger j] | \Phi \rangle = 0 \\ (\vec{T}^\dagger | \vec{T}^\dagger)_{ia,jb} &= (i^\dagger a | j^\dagger b) \\ &= \langle \Phi | [a^\dagger i, j^\dagger b] | \Phi \rangle = -\delta_{ij} \delta_{a,b} \\ (\vec{T}^\dagger | \tilde{L}(\hat{H}) | \vec{T}^\dagger)_{ai,bj} &= (a^\dagger i | \tilde{L}(\hat{H}) | b^\dagger j) \\ &= \langle \Phi | [i^\dagger a, [\hat{H}, b^\dagger j]] | \Phi \rangle \equiv A_{ai,bj} \\ (\vec{T}^\dagger | \tilde{L}(\hat{H}) | \vec{T}^\dagger)_{ai,jb} &= (a^\dagger i | \tilde{L}(\hat{H}) | j^\dagger b) \\ &= \langle \Phi | [i^\dagger a, [\hat{H}, j^\dagger b]] | \Phi \rangle \equiv B_{ai,bj} \\ (\vec{T}^\dagger | \tilde{L}(\hat{H}) | \vec{T}^\dagger)_{ia,bj} &= (i^\dagger a | \tilde{L}(\hat{H}) | b^\dagger j) \\ &= \langle \Phi | [a^\dagger i, [\hat{H}, b^\dagger j]] | \Phi \rangle = B_{ai,bj}^* \\ (\vec{T}^\dagger | \tilde{L}(\hat{H}) | \vec{T}^\dagger)_{ia,jb} &= (i^\dagger a | \tilde{L}(\hat{H}) | j^\dagger b) \\ &= \langle \Phi | [a^\dagger i, [\hat{H}, j^\dagger b]] | \Phi \rangle = A_{ai,bj}^*. \end{aligned} \quad (2.21)$$

This gives the RPA equation,

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix}, \quad (2.22)$$

where

$$\begin{aligned} A_{ai,bj} &= \delta_{i,j} f_{a,b} - \delta_{a,b} f_{j,i} + (ai|jb) - (ab|ji) \\ B_{ai,bj} &= (aj|bi) - (ai|bj), \end{aligned} \quad (2.23)$$

and,

$$f_{p,q} = h_{p,q} + \sum_k [(pq|kk) - (pk|kq)], \quad (2.24)$$

denotes a matrix element of the Fock operator. Eq. (2.22) has paired excitation and de-excitation solutions,

$$\begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} \leftrightarrow \omega$$

$$\begin{pmatrix} \vec{Y}^* \\ \vec{X}^* \end{pmatrix} \leftrightarrow -\omega, \quad (2.25)$$

just as does the original EOM [Eq. (2.13)]. This pairing property will also show up in the calculation of spin properties.

It is also useful to look at the TDA which consists of setting $\mathbf{B} = \mathbf{0}$ and solving,

$$\mathbf{A}\vec{X} = \omega\vec{X}. \quad (2.26)$$

This is equivalent to configuration interaction singles (CIS) in the basis of HF MOs because of Brillouin's theorem. In CIS, the excited-state wave function is,

$$\Psi_I = \Phi C_0 + \sum_{i,a} a^\dagger_i \Phi X_{ai}, \quad (2.27)$$

and the CIS matrix problem is,

$$\begin{bmatrix} E_{\text{HF}} & 0 \\ 0 & \mathbf{A} + E_{\text{HF}}\mathbf{1} \end{bmatrix} \begin{pmatrix} C_0 \\ \vec{X} \end{pmatrix} = E \begin{pmatrix} C_0 \\ \vec{X} \end{pmatrix}. \quad (2.28)$$

The zeros come from Brillouin's theorem (see, e.g., pp. 364–365 of Ref. [26]). Comparing with Eq. (2.26), we see that $\omega = E - E_{\text{HF}}$. Henceforth when referring to the TDA we will assume Eq. (2.27) with $C_0 = 0$ (which must be the case, for a nondegenerate ground state in this model, whenever $E \neq E_{\text{HF}}$). The expectation value of an operator within the TDA wave function formalism is straightforward.

2.3. Excited-state spin contamination

Let us now look at the spin operator \hat{S}^2 for excited states. It may be useful to begin with the basics by which we mean recalling that spin is interesting because the commutation property,

$$[\hat{H}, \hat{S}^2] = \hat{0}, \quad (2.29)$$

means that spin is a “good quantum number” in the sense that there must be simultaneous eigenfunctions of \hat{H} and of \hat{S}^2 . Using the Jacobi identity,

$$[\hat{A}, [\hat{B}, \hat{C}]] + [\hat{B}, [\hat{C}, \hat{A}]] + [\hat{C}, [\hat{A}, \hat{B}]] = 0, \quad (2.30)$$

we have (for arbitrary \hat{A})

$$\begin{aligned} [\tilde{L}(\hat{H}), \tilde{L}(\hat{S}^2)]\hat{A} &= [\hat{H}, [\hat{S}^2, \hat{A}]] - [\hat{S}^2, [\hat{H}, \hat{A}]] \\ &= [[\hat{H}, \hat{S}^2], \hat{A}] = 0, \end{aligned} \quad (2.31)$$

or

$$[\tilde{L}(\hat{H}), \tilde{L}(\hat{S}^2)] = \tilde{0}. \quad (2.32)$$

This means that $\tilde{L}(\hat{H})$ and $\tilde{L}(\hat{S}^2)$ should have simultaneous eigenoperators and that spin should be a good quantum number. Introducing a complete operator basis set [Eq. (2.18)], the commutator relationship reads,

$$\begin{aligned} (\tilde{T}^\dagger |\tilde{L}(\hat{H})| \tilde{T}^\dagger) (\tilde{T}^\dagger |\tilde{T}^\dagger|)^{-1} (\tilde{T}^\dagger |\tilde{L}(\hat{S}^2)| \tilde{T}^\dagger) \\ = (\tilde{T}^\dagger |\tilde{L}(\hat{S}^2)| \tilde{T}^\dagger) (\tilde{T}^\dagger |\tilde{T}^\dagger|)^{-1} (\tilde{T}^\dagger |\tilde{L}(\hat{H})| \tilde{T}^\dagger) \end{aligned} \quad (2.33)$$

and there are simultaneous eigenvectors satisfying the matrix equations,

$$(\tilde{T}^\dagger |\tilde{L}(\hat{H})| \tilde{T}^\dagger) \vec{Z} = \Delta(\hat{H}) (\tilde{T}^\dagger |\tilde{T}^\dagger) \vec{Z} \quad (2.34)$$

and

$$(\tilde{T}^\dagger |\tilde{L}(\hat{S}^2)| \tilde{T}^\dagger) \vec{Z} = \Delta(\hat{S}^2) (\tilde{T}^\dagger |\tilde{T}^\dagger) \vec{Z}. \quad (2.35)$$

Unfortunately this beautiful theory is only approximate when the operator basis set [Eq. (2.18)] is truncated to mono-excitations and mono-de-excitations [Eq. (2.17)]. At the fundamental level, this is the reason why there are different propositions for estimating the expectation value of \hat{S}^2 for excited states.

The most direct approach for estimating the expectation value of \hat{S}^2 for excited states is just to use the eigenvalue equations (2.34) and (2.35). Thus,

$$\Delta(\hat{H}) = \frac{\tilde{Z}^\dagger (\tilde{T}^\dagger |\tilde{L}(\hat{H})| \tilde{T}^\dagger) \vec{Z}}{\tilde{Z}^\dagger (\tilde{T}^\dagger |\tilde{T}^\dagger) \vec{Z}}. \quad (2.36)$$

Here, of course,

$$\Delta(\hat{H})_I = \langle \hat{H} \rangle_I - \langle \hat{H} \rangle_0 \quad (2.37)$$

for an excitation and

$$\Delta(\hat{H})_I = \langle \hat{H} \rangle_0 - \langle \hat{H} \rangle_I \quad (2.38)$$

for a de-excitation. Analogously,

$$\Delta(\hat{S}^2) = \frac{\tilde{Z}^\dagger (\tilde{T}^\dagger |\tilde{L}(\hat{S}^2)| \tilde{T}^\dagger) \vec{Z}}{\tilde{Z}^\dagger (\tilde{T}^\dagger |\tilde{T}^\dagger) \vec{Z}}. \quad (2.39)$$

Also

$$\Delta(\hat{S}^2)_I = \langle \hat{S}^2 \rangle_I - \langle \hat{S}^2 \rangle_0 \quad (2.40)$$

for an excitation and

$$\Delta(\hat{S}^2)_I = \langle \hat{S}^2 \rangle_0 - \langle \hat{S}^2 \rangle_I \quad (2.41)$$

for a de-excitation.

The evaluation of these expressions means that we need to evaluate the equivalent of the RPA matrix elements for the \hat{S}^2 problem,

$$\begin{bmatrix} \mathbf{C} & \mathbf{D} \\ \mathbf{D}^* & \mathbf{C}^* \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix}. \quad (2.42)$$

Here, after quite a bit of algebra, we find that

$$\begin{aligned} C_{ai,bj}^{\alpha,\alpha} &= (a_\alpha^\dagger i_\alpha | \tilde{L}(\hat{S}^2) | b_\alpha^\dagger j_\alpha) = (a_\alpha^\dagger i_\alpha | [\hat{S}^2, b_\alpha^\dagger j_\alpha]) \\ &= \delta_{a,b} \sum_k \Delta_{ik}^* \Delta_{jk} - \delta_{ij} \sum_k \Delta_{bk}^* \Delta_{ak} \\ C_{ai,bj}^{\alpha,\beta} &= (a_\alpha^\dagger i_\alpha | \tilde{L}(\hat{S}^2) | \bar{b}_\beta^\dagger \bar{j}_\beta) = (a_\alpha^\dagger i_\alpha | [\hat{S}^2, \bar{b}_\beta^\dagger \bar{j}_\beta]) \\ &= -\Delta_{ij}^* \Delta_{a\bar{b}} \\ C_{\bar{a}i,\bar{b}j}^{\beta,\alpha} &= (\bar{a}_\beta^\dagger \bar{i}_\beta | \tilde{L}(\hat{S}^2) | b_\beta^\dagger j_\beta) = (\bar{a}_\beta^\dagger \bar{i}_\beta | [\hat{S}^2, b_\beta^\dagger j_\beta]) \\ &= -\Delta_{\bar{b}a}^* \Delta_{ji} \\ C_{\bar{a}i,\bar{b}j}^{\beta,\beta} &= (\bar{a}_\beta^\dagger \bar{i}_\beta | \tilde{L}(\hat{S}^2) | \bar{b}_\beta^\dagger \bar{j}_\beta) = (\bar{a}_\beta^\dagger \bar{i}_\beta | [\hat{S}^2, \bar{b}_\beta^\dagger \bar{j}_\beta]) \\ &= \delta_{\bar{a},\bar{b}} \sum_k \Delta_{kj}^* \Delta_{ki} - \delta_{i,j} \sum_k \Delta_{k\bar{a}}^* \Delta_{k\bar{b}}, \end{aligned} \quad (2.43)$$

and

$$\begin{aligned} D_{ai,bj}^{\alpha,\alpha} &= (a_\alpha^\dagger i_\alpha | \tilde{L}(\hat{S}^2) | j_\alpha^\dagger b_\alpha) = (a_\alpha^\dagger i_\alpha | [\hat{S}^2, j_\alpha^\dagger b_\alpha]) \\ &= 0 \\ D_{ai,bj}^{\alpha,\beta} &= (a_\alpha^\dagger i_\alpha | \tilde{L}(\hat{S}^2) | \bar{j}_\beta^\dagger \bar{b}_\beta) = (a_\alpha^\dagger i_\alpha | [\hat{S}^2, \bar{j}_\beta^\dagger \bar{b}_\beta]) \\ &= \Delta_{ib}^* \Delta_{aj} \end{aligned}$$

$$\begin{aligned}
D_{\bar{a}i, \bar{b}j}^{\beta, \alpha} &= (\bar{a}_\beta^\dagger \bar{i}_\beta | \tilde{L}(\hat{S}^2) | j_\alpha^\dagger b_\alpha) = (\bar{a}_\beta^\dagger \bar{i}_\beta | [\hat{S}^2, j_\alpha^\dagger b_\alpha]) \\
&= \Delta_{\bar{j}\bar{a}}^* \Delta_{\bar{b}i} \\
D_{\bar{a}i, \bar{b}j}^{\beta, \beta} &= (\bar{a}_\beta^\dagger \bar{i}_\beta | \tilde{L}(\hat{S}^2) | j_\beta^\dagger \bar{b}_\beta) = (\bar{a}_\beta^\dagger \bar{i}_\beta | [\hat{S}^2, j_\beta^\dagger \bar{b}_\beta]) \\
&= 0.
\end{aligned} \tag{2.44}$$

Eq. (2.39) then reads,

$$\begin{aligned}
\Delta \langle \hat{S}^2 \rangle_I &= \frac{\bar{X}^\dagger \mathbf{C} \bar{X} + \bar{X}^\dagger \mathbf{D} \bar{Y} + \bar{Y}^\dagger \mathbf{D} \bar{X} + \bar{Y}^\dagger \mathbf{C}^* \bar{Y}}{\bar{X}^\dagger \bar{X} - \bar{Y}^\dagger \bar{Y}} \\
&= \frac{\bar{X}^\dagger \mathbf{C} \bar{X} + \bar{Y}^\dagger \mathbf{C}^* \bar{Y} + \sigma_1 2\Re \bar{X}^\dagger \mathbf{D} \bar{Y}}{\bar{X}^\dagger \bar{X} + \sigma_2 \bar{Y}^\dagger \bar{Y}},
\end{aligned} \tag{2.45}$$

with $(\sigma_1, \sigma_2) = (+1, -1)$ taking into account that \bar{X} , \bar{Y} , \mathbf{C} , \mathbf{D} are real valued. The reason for introducing the factors σ_1 and σ_2 soon will be evident.

Let us now turn to the TDA formula. This is easily obtained from Eq. (2.45) by setting $\bar{Y} = \vec{0}$ and $\bar{X}^\dagger \bar{X} = 1$. Straightforward algebra gives,

$$\begin{aligned}
\Delta \langle \hat{S}^2 \rangle_I^{\text{TDA}}(\bar{X}) &= \sum_{i,j,a} X_{ai\alpha}^* \left(\sum_{\bar{k}} \Delta_{ik}^* \Delta_{j\bar{k}} \right) X_{aj\alpha} \\
&+ \sum_{i,j,\bar{a}} X_{\bar{a}i\beta}^* \left(\sum_{\bar{k}} \Delta_{k\bar{j}}^* \Delta_{k\bar{i}} \right) X_{\bar{a}j\beta} \\
&- \sum_{i,a,b} X_{ai\alpha}^* \left(\sum_{\bar{k}} \Delta_{b\bar{k}}^* \Delta_{a\bar{k}} \right) X_{bi\alpha} \\
&- \sum_{\bar{i},\bar{a},\bar{b}} X_{\bar{a}i\beta}^* \left(\sum_{\bar{k}} \Delta_{k\bar{a}}^* \Delta_{k\bar{b}} \right) X_{\bar{b}i\beta} \\
&- 2\Re \sum_{i,a,j,\bar{b}} X_{ai\alpha}^* \Delta_{ij}^* \Delta_{a\bar{b}} X_{\bar{b}j\beta}.
\end{aligned} \tag{2.46}$$

The result is the same as taking the wave-function expectation value with the usual normalization [5].

Evaluating the various parts of Eq. (2.45) results in,

$$\begin{aligned}
\Delta \langle \hat{S}^2 \rangle_I &= \frac{\Delta \langle \hat{S}^2 \rangle_I^{\text{TDA}}(\bar{X}) + \Delta \langle \hat{S}^2 \rangle_I^{\text{TDA}}(\bar{Y}^*) + \sigma_1 \Delta \langle \hat{S}^2 \rangle_I^{\text{mixed}}(\bar{X}, \bar{Y}^*)}{\bar{X}^\dagger \bar{X} + \sigma_2 \bar{Y}^\dagger \bar{Y}},
\end{aligned} \tag{2.47}$$

with $(\sigma_1, \sigma_2) = (+1, -1)$ and the cross term,

$$\begin{aligned}
\Delta \langle \hat{S}^2 \rangle_I^{\text{mixed}}(\bar{X}, \bar{Y}^*) &= \Delta \langle \hat{S}^2 \rangle_I^{\text{mixed}}(\bar{Y}^*, \bar{X}) \\
&= 2\Re \sum_{i,j,a,\bar{b}} X_{ai\alpha}^* \Delta_{ib}^* \Delta_{aj} Y_{\bar{b}j\beta} + 2\Re \sum_{i,j,\bar{a},\bar{b}} X_{\bar{a}i\beta}^* \Delta_{j\bar{a}}^* \Delta_{bi} Y_{\bar{b}j\alpha}.
\end{aligned} \tag{2.48}$$

This formula appeared previously in Refs. [6–8]. Note how this captures the pairing property [Eq. (2.25)]: When we make the transformation $(\bar{X}, \bar{Y}) \rightarrow (\bar{Y}^*, \bar{X}^*)$, then the numerator remains invariant but the denominator changes sign, as would be expected when changing between an excitation and a de-excitation,

$$\Delta \langle \hat{S}^2 \rangle_I = \begin{cases} \langle \hat{S}^2 \rangle_I - \langle \hat{S}^2 \rangle_0 \\ \langle \hat{S}^2 \rangle_0 - \langle \hat{S}^2 \rangle_I. \end{cases} \tag{2.49}$$

Moreover Eq. (2.47) reduces to the expected TDA formulae when $\bar{X} = \vec{0}$ or $\bar{Y} = \vec{0}$. Thus the theory seems straightforward and internally consistent, albeit tedious to derive.

Table 1

Variants of formula (2.47) tested in this work. Note that setting $\sigma_2 = 0$ makes no sense unless $\bar{Y} = \vec{0}$ (i.e. the TDA).

$\sigma_1 \backslash \sigma_2$	−1	0	+1
+1	Original formula (recommended)	Nonsense	Ipatov's variation
0	Also tested	Nonsense	Revised formula (recommended)
−1	DEMON2K	Nonsense	GAUSSIAN09

2.4. Alternative excited-state spin contamination formulae

As we shall see in the next section, simple application of the formula above [Eq. (2.47)] with $(\sigma_1, \sigma_2) = (+1, -1)$ to the two-orbital two-electron model reveals the disturbing fact that this formula does not give the expected values of $\Delta \langle \hat{S}^2 \rangle_I$ in simple model cases. The origin of the problem may ultimately be traced back to the noncommutation of the matrices of $\tilde{L}(\hat{H})$ and $\tilde{L}(\hat{S}^2)$ in a truncated operator basis set. We will look at this again in greater detail in Section 5 in the context of a minimal basis set broken symmetry calculation on H_2 . In the meantime, we note that the denominator of Eq. (2.47) with $\sigma_2 = -1$ may become small in magnitude or even zero if the excitation (\bar{X}) and de-excitation (\bar{Y}) become imbalanced. However usually either $\bar{X} \approx \vec{0}$ or $\bar{Y} \approx \vec{0}$ and Eq. (2.47) provides a convenient and rapid way to assign spin states [8].

But we may still ask if we could find a better formula, more in line with what we would expect by looking at explicit spin-coupling or at the TDA. Such thinking has prompted several *ad hoc* suggestions. For example, during the course of the initial work [6,8] Andrei Ipatov suggested that $(\sigma_1, \sigma_2) = (+1, +1)$ be used instead of $(\sigma_1, \sigma_2) = (+1, -1)$. This may be heuristically argued by returning to the equation-of-motion formalism and using the *ansatz* that,

$$\hat{O}^\dagger = |I\rangle \langle 0|X + |0\rangle \langle I|Y. \tag{2.50}$$

Then for any operator \hat{M} ,

$$\langle 0 | [\hat{O}, [\hat{M}, \hat{O}^\dagger]] | 0 \rangle = (|X|^2 + |Y|^2) (\langle I | \hat{M} | I \rangle - \langle 0 | \hat{M} | 0 \rangle). \tag{2.51}$$

(See Ref. [27] for a similar but more careful analysis.) Also the expectation value of the anticommutator is:

$$\langle 0 | [\hat{O}, \hat{O}^\dagger]_+ | 0 \rangle = |X|^2 + |Y|^2. \tag{2.52}$$

Thus,

$$\Delta \langle \hat{M} \rangle_I = \frac{\langle 0 | [\hat{O}, [\hat{M}, \hat{O}^\dagger]] | 0 \rangle}{\langle 0 | [\hat{O}, \hat{O}^\dagger]_+ | 0 \rangle}. \tag{2.53}$$

Note that we have lost the expected excitation / de-excitation symmetry of response theory [Eq. (2.49)]; retaining only $\Delta \langle \hat{S}^2 \rangle_I = \langle \hat{S}^2 \rangle_I - \langle \hat{S}^2 \rangle_0$. This $(\sigma_1, \sigma_2) = (+1, +1)$ formula is essentially the one implemented in GAUSSIAN09 [28]. Unfortunately some confusion actually led to the implementation of $(\sigma_1, \sigma_2) = (-1, +1)$ in GAUSSIAN09 and of $(\sigma_1, \sigma_2) = (-1, -1)$ in DEMON2K. As we shall see, in practice, the sign of σ_1 rarely is important (though broken symmetry H_2 is a notable exception!). Yet another possibility is suggested by the lack of cross-terms in Eq. (2.52), namely $(\sigma_1, \sigma_2) = (0, +1)$. Table 1 summarizes the combinations which we will examine in the next sections: four previously used (σ_1, σ_2) pairings plus two others that arise from consideration of insensitivity to σ_1 .

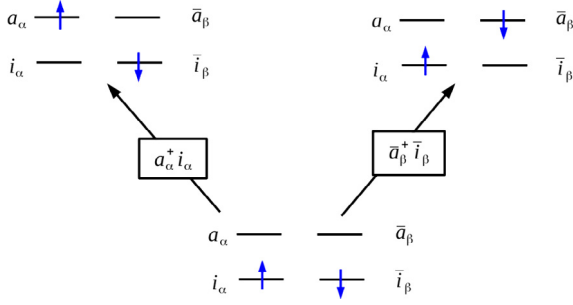


Fig. 1. The two-orbital two-electron model (TOTEM).

3. Two-orbital two-electron model

In this section, we analyze the different formulae of Table 1 in the context of the two-orbital two-electron model (TOTEM) shown in Fig. 1. The advantage of the TOTEM is that most of the calculations may be done as a paper and pencil exercise, so that the reader can fully appreciate the intricacies of the problem. The danger, of course, is that the TOTEM may be too simple to describe typical real calculations. Only two cases will be considered in this section. The first case is the normal SODS case, $\bar{i} = i$ and $\bar{a} = a$. The second case is the simplest DODS case, $\bar{i} = a$ and $\bar{a} = i$. We continue to work within the TD-HF formalism.

The general formulae for the \mathbf{A} and \mathbf{B} matrices in the frozen orbital approximation are,

$$\mathbf{A} = \begin{bmatrix} \epsilon_a^\alpha - \epsilon_i^\alpha + (ai|ia) - (aa|ii) & (ai|\bar{i}\bar{a}) \\ (\bar{a}\bar{i}|ia) & \epsilon_a^\beta - \epsilon_i^\beta + (\bar{a}\bar{i}|\bar{i}\bar{a}) - (\bar{a}\bar{a}|\bar{i}\bar{i}) \end{bmatrix} \quad (3.1)$$

and

$$\mathbf{B} = \begin{bmatrix} 0 & -(ai|\bar{a}\bar{i}) \\ -(\bar{a}\bar{i}|ai) & 0 \end{bmatrix}. \quad (3.2)$$

We will assume real orbitals, so that $\mathbf{A} + \mathbf{B}$ is diagonal. The paired eigenvalues $\pm\omega$ are then given by solving the 2×2 matrix eigenvalue equation,

$$\Omega \bar{F} = \omega^2 \Omega, \quad (3.3)$$

where,

$$\Omega = (\mathbf{A} + \mathbf{B})^{+1/2} (\mathbf{A} - \mathbf{B}) (\mathbf{A} + \mathbf{B})^{+1/2}, \quad (3.4)$$

and,

$$\bar{F} = (\mathbf{A} + \mathbf{B})^{-1/2} (\bar{X} - \bar{Y}). \quad (3.5)$$

Typical eigensolvers use the normalization, $\bar{F}^\dagger \bar{F} = 1$. We may also solve Eq. (2.22) for \bar{X} and \bar{Y} in terms of \bar{F} :

$$\begin{aligned} \bar{X} &= \frac{1}{2} [\omega (\mathbf{A} + \mathbf{B})^{-1/2} + (\mathbf{A} + \mathbf{B})^{+1/2}] \bar{F} \\ \bar{Y} &= \frac{1}{2} [\omega (\mathbf{A} + \mathbf{B})^{-1/2} - (\mathbf{A} + \mathbf{B})^{+1/2}] \bar{F}. \end{aligned} \quad (3.6)$$

Imposing the usual equation-of-motion normalization,

$$\bar{X}^\dagger \bar{X} - \bar{Y}^\dagger \bar{Y} = \pm 1, \quad (3.7)$$

means renormalizing so that, $\bar{F}^\dagger \bar{F} = \pm 1/\omega$, where the plus sign refers to an excitation and the minus sign to a de-excitation.

3.1. Case I: $\bar{i} = i$ and $\bar{a} = a$

This case represents what is often seen in typical closed-shell molecules. In this case, the spin-transfer matrix [Eq. (2.8)] is unity,

$$\Delta = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \quad (3.8)$$

The ground-state is the closed-shell singlet $\Phi = |i\alpha, i\beta\rangle$. According to the Löwdin formula,

$$\begin{aligned} \langle \hat{S}^2 \rangle_0 &= - \sum_{ij} |\Delta_{ij}|^2 + \frac{n_\alpha + n_\beta}{2} + \left(\frac{n_\alpha - n_\beta}{2} \right)^2 \\ &= -1 + 1 + 0 = 0. \end{aligned} \quad (3.9)$$

Before going to the excited-state problem, it is useful to have a look at the MO energies in the frozen orbital approximation,

$$\begin{aligned} \epsilon_i^\alpha &= \epsilon_i^\beta = \epsilon_i^0 + (ii|ii) \\ \epsilon_a^\alpha &= \epsilon_a^\beta = \epsilon_a^0 + 2(ii|aa) - (ia|ai), \end{aligned} \quad (3.10)$$

where the superscript zero indicates the neglect of electron repulsions. Hence we may drop the spin superscript on the MO energies,

$$\begin{aligned} \epsilon_i &= \epsilon_i^\alpha = \epsilon_i^\beta \\ \epsilon_a &= \epsilon_a^\alpha = \epsilon_a^\beta. \end{aligned} \quad (3.11)$$

Let us first solve the excited-state problem in the TDA. Then,

$$\mathbf{A} = \begin{bmatrix} \Delta\epsilon + (ai|ia) - (aa|ii) & (ai|ia) \\ (ai|ia) & \Delta\epsilon + (ai|ia) - (aa|ii) \end{bmatrix}, \quad (3.12)$$

where,

$$\Delta\epsilon = \epsilon_a - \epsilon_i. \quad (3.13)$$

By symmetry we have two solutions:

$$\begin{aligned} \omega_T &= \Delta\epsilon - (aa|ii) \\ \bar{X}_T &= 2^{-1/2} \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \end{aligned} \quad (3.14)$$

and

$$\begin{aligned} \omega_S &= \Delta\epsilon + 2(ai|ia) - (aa|ii) \\ \bar{X}_S &= 2^{-1/2} \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \end{aligned} \quad (3.15)$$

We may now apply the TDA formula (Eq. (2.46)),

$$\Delta \langle \hat{S}^2 \rangle_I = |X_{ai\alpha}|^2 + |X_{ai\beta}|^2 - 2\Re X_{ai\alpha} X_{ai\beta}, \quad (3.16)$$

to obtain,

$$\begin{aligned} \Delta \langle \hat{S}^2 \rangle_T &= 2(2^{-1/2})^2 + 2(2^{-1/2})^2 = 1 + 1 = 2 \\ \Delta \langle \hat{S}^2 \rangle_S &= 2(2^{-1/2})^2 - 2(2^{-1/2})^2 = 1 - 1 = 0. \end{aligned} \quad (3.17)$$

Since $\langle \hat{S}^2 \rangle_T = \Delta \langle \hat{S}^2 \rangle_T + \langle \hat{S}^2 \rangle_0 = 2$ and $\langle \hat{S}^2 \rangle_S = \Delta \langle \hat{S}^2 \rangle_S + \langle \hat{S}^2 \rangle_0 = 0$, we conclude that T corresponds to the triplet state and S corresponds to the singlet state.

We now turn to the RPA equation. In this case,

$$(\mathbf{A} + \mathbf{B}) = [\Delta\epsilon + (ai|ia) - (aa|ii)] \mathbf{1}, \quad (3.18)$$

is a multiple of the 2×2 unit matrix. As

$$\begin{aligned} \Omega &= [\Delta\epsilon + (ai|ia) - (aa|ii)] \\ &\times \begin{bmatrix} \Delta\epsilon + (ai|ia) - (aa|ii) & 2(ai|ia) \\ 2(ai|ia) & \Delta\epsilon + (ai|ia) - (aa|ii) \end{bmatrix}, \end{aligned} \quad (3.19)$$

we again find two solutions:

$$\omega_T = \sqrt{[\Delta\epsilon + (ai|ia) - (aa|ii)][\Delta\epsilon - (ai|ia) - (aa|ii)]}$$

$$\vec{F}_T = 2^{-1/2} \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad (3.20)$$

and,

$$\omega_S = \sqrt{[\Delta\epsilon + (ai|ia) - (aa|ii)][\Delta\epsilon + 3(ai|ia) - (aa|ii)]}$$

$$\vec{F}_S = 2^{-1/2} \begin{pmatrix} 1 \\ 1 \end{pmatrix}. \quad (3.21)$$

What can we say about spin in this case? From the diagonal form of $\mathbf{A} + \mathbf{B}$ [Eq. (3.18)] and from the relation (3.6) between \vec{F} and \vec{X} and \vec{Y} , we can say that each component \vec{X} and \vec{Y} will have the same general symmetry properties as $\vec{F} \propto (1, \pm 1)$ but we cannot say much more. So let us just write

$$\vec{X}_T = 2^{-1/2} X \begin{pmatrix} 1 \\ -1 \end{pmatrix}, \quad \vec{Y}_T = 2^{-1/2} Y \begin{pmatrix} 1 \\ -1 \end{pmatrix} \quad (3.22)$$

and

$$\vec{X}_S = 2^{-1/2} X \begin{pmatrix} 1 \\ +1 \end{pmatrix}, \quad \vec{Y}_S = 2^{-1/2} Y \begin{pmatrix} 1 \\ +1 \end{pmatrix}. \quad (3.23)$$

Notice that $\vec{X}^\dagger \vec{X} = X^2$ and $\vec{Y}^\dagger \vec{Y} = Y^2$. Ignoring for the moment the denominator in Eq. (2.47) and focusing only on the numerator, we find that

$$\Delta\langle\hat{S}^2\rangle_T^{\text{num}} = 2(X^2 + Y^2) \quad (3.24)$$

and

$$\Delta\langle\hat{S}^2\rangle_S^{\text{num}} = 0. \quad (3.25)$$

The value of σ_1 is unimportant in this case because there are no cross terms. However we immediately see the importance of σ_2 . If we set $\sigma_2 = +1$ then we arrive at the expected values of $\Delta\langle\hat{S}^2\rangle_T = 2$ for the triplet state and $\Delta\langle\hat{S}^2\rangle_S = 0$ for the singlet state. However if we use the first principles value of $\sigma_2 = -1$, then we arrive at $\Delta\langle\hat{S}^2\rangle_S = 0$ for the singlet state but at,

$$\Delta\langle\hat{S}^2\rangle_T = 2 \frac{X^2 + Y^2}{X^2 - Y^2}, \quad (3.26)$$

whose value can easily exceed the expected value of two for $X^2 > Y^2$, although it will typically be close to two in the normal case where the de-excitation component (Y) is small. While it could be argued that the RPA calculation is flawed unless one component (X or Y) dominates over the other [8] and so should be treated with the utmost care, nevertheless this example provides a pragmatic argument for using $(\sigma_1, \sigma_2) = (+1, +1)$ rather than the first principles $(\sigma_1, \sigma_2) = (+1, -1)$.

3.2. Case II: $\vec{i} = a$ and $\vec{a} = i$

This is the simplest open-shell DODS case that we can treat. The spin-transfer matrix is,

$$\mathbf{A} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}. \quad (3.27)$$

The ground-state is neither a singlet nor a triplet but rather the mixed symmetry state $\Phi = |\alpha\alpha, a\beta|$. This is confirmed by using the Löwdin formula,

$$\langle\hat{S}^2\rangle_0 = -\sum_{ij} |\Delta_{ij}|^2 + \frac{n_\alpha + n_\beta}{2} + \left(\frac{n_\alpha - n_\beta}{2}\right)^2$$

$$= 0 + 1 + 0 = 1. \quad (3.28)$$

The possible excited states from this reference are both closed-shell singlets with $\langle\hat{S}^2\rangle_I = 0$: $|\alpha\alpha, i\beta|$ and $|\alpha\alpha, a\beta|$.

The MO energies in the frozen orbital approximation are:

$$\begin{aligned} \epsilon_i^\alpha &= \epsilon_i^0 + (ii|aa) \\ &= \epsilon_i + (ii|aa) - (ii|ii) \\ \epsilon_i^\beta &= \epsilon_i^0 + (ii|aa) + (ii|ii) - (ia|ai) \\ &= \epsilon_i + (ii|aa) - (ia|ai) \\ \epsilon_a^\alpha &= \epsilon_a^0 + (aa|ii) + (aa|aa) - (ai|ia) \\ &= \epsilon_a + (aa|aa) - (aa|ii) \\ \epsilon_a^\beta &= \epsilon_a^0 + (ii|aa) \\ &= \epsilon_a + (ia|ai) - (ii|aa), \end{aligned} \quad (3.29)$$

where the quantities ϵ_i and ϵ_a have the same formulae as in case I. This emphasizes that the MOs are spin-dependent.

To solve the TDA problem we need to evaluate the \mathbf{A} matrix:

$$\mathbf{A} = \begin{bmatrix} \Delta\epsilon^\alpha + (ai|ia) - (aa|ii) & (ai|ai) \\ (ia|ia) & -\Delta\epsilon^\beta + (ia|ai) - (ii|aa) \end{bmatrix}, \quad (3.30)$$

where,

$$\begin{aligned} \Delta\epsilon^\alpha &= \epsilon_a^\alpha - \epsilon_i^\alpha \\ &= \Delta\epsilon + (ii|ii) + (aa|aa) - 2(ii|aa) \\ \Delta\epsilon^\beta &= \epsilon_a^\beta - \epsilon_i^\beta \\ &= \Delta\epsilon + 2(ia|ai) - 2(ii|aa). \end{aligned} \quad (3.31)$$

The form of the \mathbf{A} matrix is no longer simple, so we can only write that

$$\vec{X} = \begin{pmatrix} X_\alpha \\ X_\beta \end{pmatrix}, \quad (3.32)$$

with,

$$\vec{X}^\dagger \vec{X} = 1. \quad (3.33)$$

We may use the well-established TDA formula to calculate the spin of the excited states:

$$\Delta\langle\hat{S}^2\rangle_I = -|X_\alpha|^2 - |X_\beta|^2 = -\vec{X}^\dagger \vec{X} = -1. \quad (3.34)$$

So

$$\langle\hat{S}^2\rangle_I = \Delta\langle\hat{S}^2\rangle_I + \Delta\langle\hat{S}^2\rangle_0 = 1 - 1 = 0, \quad (3.35)$$

and we have verified that the excited states are indeed singlets.

Now let us look at the RPA equation. It can, in fact, be reduced to a 2×2 matrix equation in various ways, but none of them gives much insight into the exact form of the solution. This means that the best we can do is to write:

$$\vec{X} = \begin{pmatrix} X_\alpha \\ X_\beta \end{pmatrix}, \quad \vec{Y} = \begin{pmatrix} Y_\alpha \\ Y_\beta \end{pmatrix}. \quad (3.36)$$

We may now turn to the spin problem. Ignoring the denominator in Eq. (2.29) and focusing only on the numerator, we find that

$$\begin{aligned} \Delta\langle\hat{S}^2\rangle_I^{\text{num}} &= -|X_\alpha|^2 - |X_\beta|^2 - |Y_\alpha|^2 - |Y_\beta|^2 \\ &\quad + 2\sigma_1 \Re X_\alpha^* Y_\beta + 2\sigma_1 \Re X_\beta^* Y_\alpha \\ &= -(\vec{X}^\dagger \vec{X} + \vec{Y}^\dagger \vec{Y}) + 2\sigma_1 (\Re X_\alpha^* Y_\beta + \Re X_\beta^* Y_\alpha). \end{aligned} \quad (3.37)$$

It is difficult to make sense of this unless we cancel the cross terms (i.e., set $\sigma_1 = 0$) and divide by $\vec{X}^\dagger \vec{X} + \vec{Y}^\dagger \vec{Y}$ (i.e., set $\sigma_2 = +1$). The choice $(\sigma_1, \sigma_2) = (0, +1)$ then gives the expected value of $\Delta\langle\hat{S}^2\rangle_I = -1$.

We have thus arrived at the *ad hoc* $(\sigma_1, \sigma_2) = (0, +1)$ formula,

$$\Delta\langle\hat{S}^2\rangle_I = \frac{\Delta\langle\hat{S}^2\rangle_I^{\text{TDA}}(\vec{X}) + \Delta\langle\hat{S}^2\rangle_I^{\text{TDA}}(\vec{Y}^*)}{\vec{X}^\dagger\vec{X} + \vec{Y}^\dagger\vec{Y}}, \quad (3.38)$$

specifically designed to fit the examples described in this section. Nevertheless, it should be noted that there is something simple and satisfying about the form of Eq. (3.38) in that it will always hold if,

$$\Delta\langle\hat{S}^2\rangle_I^{\text{TDA}}(\vec{X}) = \vec{X}^\dagger\vec{X}\Delta\langle\hat{S}^2\rangle_I, \quad (3.39)$$

and,

$$\Delta\langle\hat{S}^2\rangle_I^{\text{TDA}}(\vec{Y}^*) = \vec{Y}^\dagger\vec{Y}\Delta\langle\hat{S}^2\rangle_I. \quad (3.40)$$

That is, the $(0, +1)$ formula expresses the degree to which the excitation (X) and de-excitation (Y) have the same spin properties. [See also Eq. (3.6) which shows how \vec{X} and \vec{Y} are both derivable from the same \vec{F} via the matrix $\mathbf{A} + \mathbf{B}$ and the eigenvalue ω .]

4. Computational details

The calculations reported in this paper were done using two different programs, namely GAUSSIAN09 [29] and the Grenoble version of DEMON2K [30]. Two types of calculations were carried out. One of these, consisting of minimal STO-3G basis set [31] broken symmetry calculations on H_2 , was done because of its important pedagogical value. The other one consists of more realistic calculations on a set of small molecules using more extensive basis sets.

The DEMON2K calculations used the Sadlej pVTZ (polarized valence triple zeta) orbital basis set [32–36] (from the EMSL Basis Set Library [37,38]) and 6d functions and DEMON2K's automatically generated GEN-A3* auxiliary density fitting basis. The numerical grid used for evaluating exchange–correlation integrals was set with the keywords FIXED and FINE. Only the local density approximation (LDA) was used with the usual Vosko–Wilk–Nusair parameterization of the electron gas correlation energy density [39].

That choice corresponds to the SVWN5 functional in GAUSSIAN09. GAUSSIAN09 calculations also used the Sadlej pVTZ orbital basis set with 5d functions and tight SCF (self-consistent field) convergence. Extensive use was made of defaults. Note that the orbital basis sets used in the DEMON2K and in the GAUSSIAN09 calculations are not exactly the same because of the respective choices of 6d and 5d sets.

Regarding the more realistic calculations on a set of small molecules: Unless otherwise stated, calculations were done at the same geometries as in Ref. [40]. Specifically the experimental bond lengths were used for diatomics. These were taken from Huber and Herzberg [41] and are: $r(\text{BeH}) = 1.3426 \text{ \AA}$, $r(\text{BeF}) = 1.3610 \text{ \AA}$, $r(\text{CN}) = 1.1718 \text{ \AA}$, $r(\text{CO}^+) = 1.1151 \text{ \AA}$, and $r(\text{N}_2^+) = 1.1164 \text{ \AA}$. Note that the bond length of BeF was given incorrectly in Ref. [40]. The geometry used for CH_2O^+ is planar with $r(\text{CO}) = 1.2078 \text{ \AA}$, $r(\text{CH}) = 1.1161 \text{ \AA}$, and $\angle\text{HCO} = 116.57^\circ$.

LDA orbital orderings for the molecules treated here at their equilibrium geometries are as follows:

$$\begin{aligned} \text{BeH} &: \dots 2\sigma^2 | 3\sigma^1 | 1\pi^0 4\sigma^0 5\sigma^0 \dots \\ \text{BeF, CN, CO}^+ &: \dots 4\sigma^2 1\pi^4 | 5\sigma^1 | 2\pi^0 \dots \\ \text{N}_2^+ &: \dots 2\sigma_u^2 1\pi_u^4 | 3\sigma_g^1 | 1\pi_g^0 \dots \\ \text{CH}_2\text{O}^+ &: \dots 1b_1^2 5a_1^2 | 2b_2^1 | 2b_1^1 5a_1^0 3b_2^0 \dots \end{aligned} \quad (4.1)$$

The vertical bars separate the singly-occupied molecular orbitals (SOMOs) from the doubly-occupied molecular orbitals and from the empty molecular orbitals.

5. Results

In this section, we present the results of computational tests of the behavior of the different spin-contamination formula alternatives given in Table 1. We will use the notation (σ_1, σ_2) to denote the different alternatives and remind the reader that the choice $(+1, -1)$ corresponds to the recommended first principles formula. It is the correct choice according to the response theory arguments given in this and previous papers [6,8]. However the $(-1, -1)$ choice is the present default in DEMON2K and $(-1, +1)$ is the choice used in GAUSSIAN09. Note that the $\sigma_1 = -1$ choice is incorrect in the sense that it is difficult, if not impossible, to justify, but it is the one that has been used for many years now because of its presence in these two programs.

Many of the results presented below are for the same molecules treated in earlier papers. This allows us to make a few comments on how the present DEMON2K results compare with the results of earlier similar calculations [8,40]. This is done in the Appendix.

However the main purpose of this section is to see in practice how much difference the various formulae make. From this point of view, we begin with the very important example of broken symmetry H_2 in a minimal STO-3G basis set which brings out several points about how to interpret $\langle\hat{S}^2\rangle_I$ in TD-DFT calculations. We then go on to compare $\langle\hat{S}^2\rangle_I$ calculated with the different formulae for single point geometries, analogous to what was done in earlier work [8]. The main conclusion here is how small the actual differences among the formulae are in practice. The section is completed by an examination of excited-state spin contamination for N_2^+ at different bond distances. This is a realistic example which, like broken symmetry minimal basis H_2 , does show significant differences when different formulae are used for $\langle\hat{S}^2\rangle_I$.

5.1. Broken symmetry minimal basis H_2

In the broken symmetry minimal basis H_2 model, there is a single s -type atomic orbital (AO) s_L on the left hydrogen and a single s -type AO s_R on the right hydrogen in H_L-H_R . Without symmetry breaking we have the usual *gerade* molecular orbital (MO),

$$\sigma_g = \frac{1}{\sqrt{2(1+S)}}(s_L + s_R), \quad (5.1)$$

and *ungerade* MO,

$$\sigma_u = \frac{1}{\sqrt{2(1-S)}}(s_L - s_R), \quad (5.2)$$

where

$$S = \langle s_L | s_R \rangle \quad (5.3)$$

is the AO overlap matrix. Eqs. (5.1) and (5.2) are the minimum energy MOs when the H–H bond distance is below the Coulson–Fischer point. Once the H–H bond distance exceeds the Coulson–Fischer point, then the broken symmetry MOs shown in Fig. 2 produce a lower energy single determinant solution. Fig. 3 shows how the ground-state potential energy curves compare with and without symmetry breaking.

Note that the amount of symmetry breaking is parameterized by θ (Fig. 2),

$$\begin{aligned} \psi_1^\alpha &= \cos(\theta)\sigma_g + \sin(\theta)\sigma_u \\ \psi_2^\alpha &= \sin(\theta)\sigma_g - \cos(\theta)\sigma_u \\ \psi_1^\beta &= \cos(\theta)\sigma_g - \sin(\theta)\sigma_u \\ \psi_2^\beta &= \sin(\theta)\sigma_g + \cos(\theta)\sigma_u. \end{aligned} \quad (5.4)$$

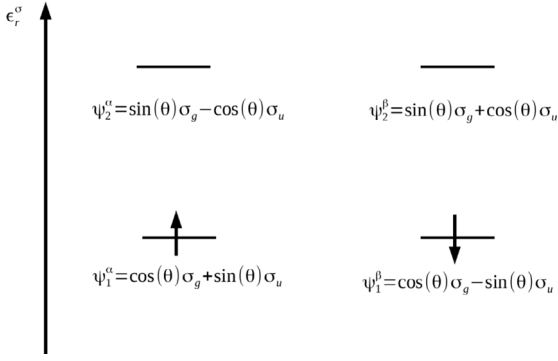


Fig. 2. The four-orbital two-electron broken symmetry minimal basis H_2 problem.

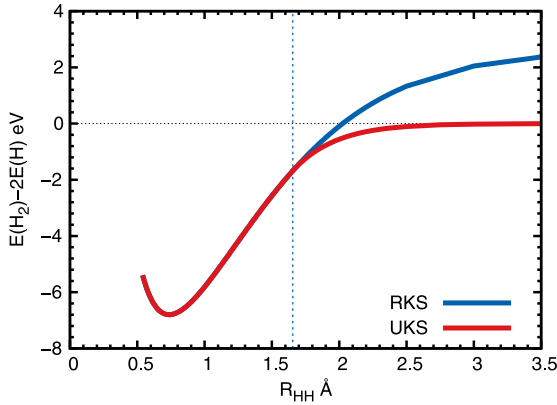


Fig. 3. (Color online) Ground-state minimal basis LDA H_2 potential energy curves with and without symmetry breaking. The spin-restricted curve and the spin-unrestricted curves are identical up to the Coulson–Fischer point at about 1.6 Å where symmetry breaking occurs for the spin-unrestricted calculation [42,43].

When there is no symmetry breaking, then $\theta = 0$ and

$$\begin{aligned}\psi_1^\alpha &= \sigma_g \\ \psi_2^\alpha &= -\sigma_u \\ \psi_1^\beta &= \sigma_g \\ \psi_2^\beta &= \sigma_u.\end{aligned}\quad (5.5)$$

In particular, $\psi_2^\alpha \rightarrow -\sigma_u$ not $\psi_2^\alpha \rightarrow +\sigma_u$.

As the spin-transfer matrix is

$$\begin{aligned}\Delta &= \begin{bmatrix} \langle \psi_1^\alpha | \psi_1^\beta \rangle & \langle \psi_1^\alpha | \psi_2^\beta \rangle \\ \langle \psi_2^\alpha | \psi_1^\beta \rangle & \langle \psi_2^\alpha | \psi_2^\beta \rangle \end{bmatrix} \\ &= \begin{bmatrix} \cos(2\theta) & \sin(2\theta) \\ \sin(2\theta) & -\cos(2\theta) \end{bmatrix},\end{aligned}\quad (5.6)$$

then Löwdin's formula yields

$$\langle \hat{S}^2 \rangle_0 = \sin^2(\theta) \quad (5.7)$$

for the ground-state spin contamination. Fig. 4 shows the calculated LDA result. At shorter bond distances than the Coulson–Fischer point, we have a pure singlet [$S(S+1) = 0$], while at larger bond distances we approach a 50/50 mixture of a singlet [$S(S+1) = 0$] and a triplet [$S(S+1) = 2$]. The spin-broken wave function,

$$|\psi_1^\alpha \alpha, \psi_1^\beta \beta\rangle = \Psi_{0,0} + \Psi_{1,0}, \quad (5.8)$$

may be resolved into a singlet component,

$$\begin{aligned}\Psi_{0,0} &= (\cos^2(\theta) \sigma_g(1) \sigma_g(2) - \sin^2(\theta) \sigma_u(1) \sigma_u(2)) \\ &\times \left[\frac{1}{\sqrt{2}} (\alpha(1) \beta(2) - \beta(1) \alpha(2)) \right],\end{aligned}\quad (5.9)$$

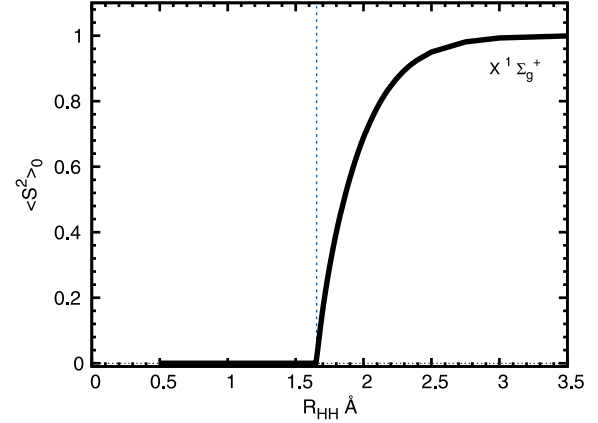


Fig. 4. Ground-state spin contamination in the symmetry broken minimal basis LDA H_2 problem.

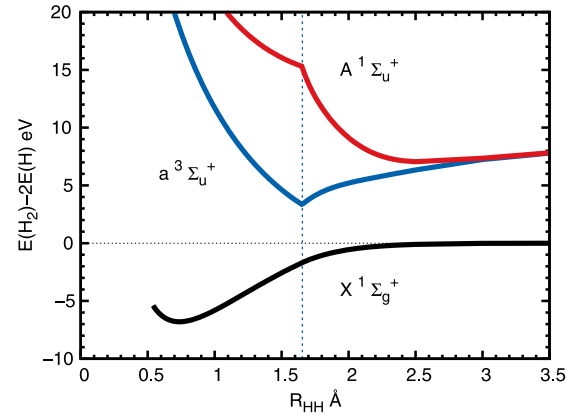


Fig. 5. (Color online) TDA potential energy surfaces for the singlet and triplet excitations in the symmetry broken minimal basis LDA H_2 problem.

and a triplet component,

$$\begin{aligned}\Psi_{1,0} &= \sqrt{2} \sin(\theta) \cos(\theta) \left[\frac{1}{\sqrt{2}} (\sigma_u(1) \sigma_g(2) - \sigma_g(1) \sigma_u(2)) \right] \\ &\times \left[\frac{1}{\sqrt{2}} (\alpha(1) \beta(2) + \beta(1) \alpha(2)) \right].\end{aligned}\quad (5.10)$$

In the dissociation limit, this becomes the mixed-symmetry state $|s_L \alpha, s_R \beta\rangle$. At intermediate distances, $0 \leq \theta \leq \pi/2$ may be calculated from

$$\theta = \sin^{-1} \sqrt{\langle \hat{S}^2 \rangle_0}, \quad (5.11)$$

and from the data in Fig. 4.

In the TDA, the excitation energies (Fig. 5) are obtained as the eigenvalues of the matrix,

$$\mathbf{A} = \begin{bmatrix} \epsilon_2^\alpha - \epsilon_1^\alpha & (\psi_2^\alpha \psi_1^\alpha | \psi_1^\alpha \psi_2^\alpha) \\ +(\psi_2^\alpha \psi_1^\alpha | \psi_1^\alpha \psi_2^\alpha) & \epsilon_2^\beta - \epsilon_1^\beta \\ -(\psi_2^\alpha \psi_2^\alpha | \psi_1^\alpha \psi_1^\alpha) & +(\psi_2^\beta \psi_1^\beta | \psi_1^\beta \psi_2^\beta) \\ (\psi_2^\beta \psi_1^\beta | \psi_1^\alpha \psi_2^\alpha) & -(\psi_2^\beta \psi_2^\beta | \psi_1^\beta \psi_1^\beta) \end{bmatrix}. \quad (5.12)$$

Note that the molecular symmetry means that the two diagonal elements are equal and that the two off-diagonal elements are equal. Similarly for $\langle \hat{S}^2 \rangle_I$,

$$\mathbf{C} = \begin{bmatrix} \cos(4\theta) & \cos^2(2\theta) \\ \cos^2(2\theta) & \cos(4\theta) \end{bmatrix}, \quad (5.13)$$

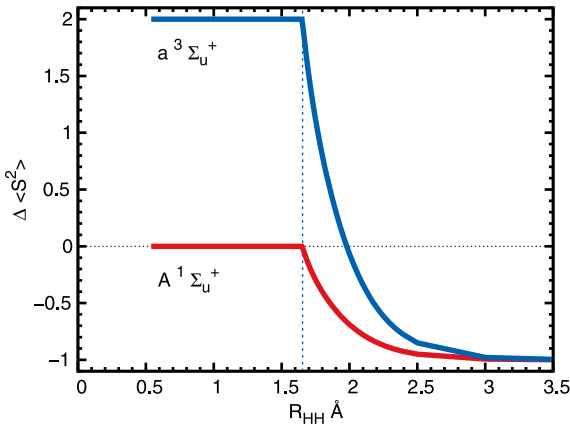


Fig. 6. (Color online) TDA $\Delta\langle\hat{S}^2\rangle$ for the singlet and triplet excitations in the symmetry broken minimal basis LDA H_2 problem.

As any two matrices of the form

$$\begin{bmatrix} a & b \\ b & a \end{bmatrix} \quad (5.14)$$

commute, we conclude that **A** and **C** have simultaneous eigenvectors and so $\Delta[S(S+1)]$ is a good quantum number for the excitation problem. Note that we do not expect this to hold in general for the TDA because single excitations are not expected to be a sufficiently nearly complete basis set to calculate matrix elements of the two-electron operator \hat{S}^2 . However it does work out in this toy problem (Fig. 6). We thus have two solutions, namely

$$\begin{aligned} \vec{X}_+ &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ \omega_+ &= \epsilon_2^\alpha - \epsilon_1^\alpha + (\psi_2^\alpha \psi_1^\alpha | \psi_1^\alpha \psi_2^\alpha) \\ &\quad + (\psi_2^\alpha \psi_1^\alpha | \psi_1^\beta \psi_2^\alpha) - (\psi_2^\alpha \psi_2^\alpha | \psi_1^\alpha \psi_1^\alpha) \\ \Delta\langle\hat{S}^2\rangle_+ &= 2\cos^2(\theta) - \sin^2(\theta) \\ \langle\hat{S}^2\rangle_+ &= \langle\hat{S}^2\rangle_0 + \Delta\langle\hat{S}^2\rangle_+ = 2\cos^2(2\theta), \end{aligned} \quad (5.15)$$

which reduces to the triplet excitation $[S(S+1) = 2]$ in the limit of no symmetry breaking, and

$$\begin{aligned} \vec{X}_- &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \\ \omega_- &= \epsilon_2^\alpha - \epsilon_1^\alpha + (\psi_2^\alpha \psi_1^\alpha | \psi_1^\alpha \psi_2^\alpha) \\ &\quad - (\psi_2^\alpha \psi_1^\alpha | \psi_1^\beta \psi_2^\alpha) - (\psi_2^\alpha \psi_2^\alpha | \psi_1^\alpha \psi_1^\alpha) \\ \Delta\langle\hat{S}^2\rangle_- &= -\sin^2(\theta) \\ \langle\hat{S}^2\rangle_- &= \langle\hat{S}^2\rangle_0 + \Delta\langle\hat{S}^2\rangle_- = 0, \end{aligned} \quad (5.16)$$

which reduces to the singlet excitation $[S(S+1) = 0]$ in the limit of no symmetry breaking. Notice how the sum of $\langle\hat{S}^2\rangle_0$ and $\Delta\langle\hat{S}^2\rangle_i$ neatly corrects the symmetry errors for the singlet in this case because

$$\begin{aligned} \Psi_- &= \frac{1}{\sqrt{2}} (|\psi_2^\alpha \alpha, \psi_1^\beta \beta\rangle + |\psi_1^\alpha \alpha, \psi_2^\beta \beta\rangle) \\ &= -\frac{1}{\sqrt{2}} (|\psi_g^\alpha \alpha, \psi_u^\beta \beta\rangle + |\psi_u^\alpha \alpha, \psi_g^\beta \beta\rangle) \end{aligned} \quad (5.17)$$

is exactly the expected open-shell singlet solution.

We now turn to the symmetry broken minimal basis response problem. Here we have to include the matrix,

$$\mathbf{B} = \begin{bmatrix} 0 & -(\psi_2^\alpha \psi_1^\alpha | \psi_2^\beta \psi_1^\beta) \\ -(\psi_2^\beta \psi_1^\beta | \psi_2^\alpha \psi_1^\alpha) & 0 \end{bmatrix}, \quad (5.18)$$

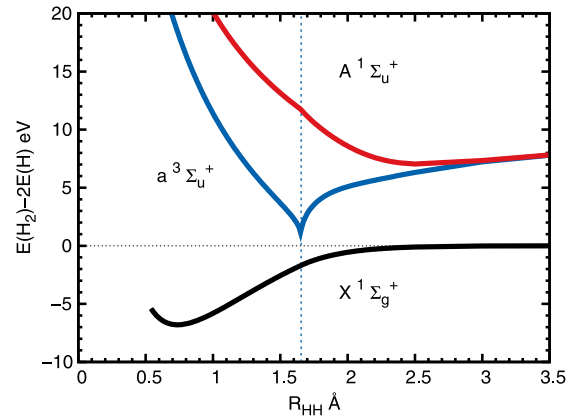


Fig. 7. (Color online) TDLDA potential energy surfaces for the singlet and triplet excitations in the symmetry broken minimal basis LDA H_2 problem.

in the excitation energy problem and the matrix,

$$\mathbf{D} = \begin{bmatrix} 0 & \sin^2(\theta) \\ \sin^2(\theta) & 0 \end{bmatrix}, \quad (5.19)$$

in the spin problem. The eigenvalues of the spin matrix problem can be worked out and found to be,

$$\begin{aligned} \Delta\langle\hat{S}^2\rangle_+ &= \pm 2\cos(4\theta)\sqrt{\cos(4\theta)} \\ &= \pm 2\cos^2(2\theta)\sqrt{1 - \frac{\sin^2(2\theta)}{\cos^2(2\theta)}} \\ &\approx \pm 2\cos^2(2\theta) \left(1 - \frac{\sin^2(2\theta)}{2\cos^2(2\theta)}\right) \\ &= \pm (2\cos^2(2\theta) - \sin^2(2\theta)) \quad (\text{TDA solution}) \end{aligned}$$

$$\Delta\langle\hat{S}^2\rangle_- = 0 \quad (\text{doubly degenerate}). \quad (5.20)$$

At first glance, it is very pleasing to see $\Delta\langle\hat{S}^2\rangle_- = 0$ as this is what would be expected for a singlet \rightarrow singlet transition and the TDA form of $\langle\hat{S}^2\rangle_+$ may be viewed as an approximate form of the more general response expression for $\langle\hat{S}^2\rangle_+$. However the real problem is that

$$\begin{aligned} &(\vec{T}^\dagger | \tilde{L}(\hat{H}) | \vec{T}^\dagger) (\vec{T}^\dagger | \vec{T}^\dagger)^{-1} (\vec{T}^\dagger | \tilde{L}(\hat{S}^2) | \vec{T}^\dagger) \\ &= \begin{bmatrix} \mathbf{AC} - \mathbf{BD} & \mathbf{AD} - \mathbf{BC} \\ \mathbf{BC} - \mathbf{AD} & \mathbf{BD} - \mathbf{AC} \end{bmatrix} \\ &\neq (\vec{T}^\dagger | \tilde{L}(\hat{S}^2) | \vec{T}^\dagger) (\vec{T}^\dagger | \vec{T}^\dagger)^{-1} (\vec{T}^\dagger | \tilde{L}(\hat{H}) | \vec{T}^\dagger) \\ &= \begin{bmatrix} \mathbf{CA} - \mathbf{DB} & \mathbf{CB} - \mathbf{DA} \\ \mathbf{DA} - \mathbf{BC} & \mathbf{DB} - \mathbf{CA} \end{bmatrix}, \end{aligned} \quad (5.21)$$

even though the individual submatrices (**A**, **B**, **C**, and **D**) commute. This means that the spin is no longer a rigorously good quantum number for labeling the energy states.

Nevertheless we may solve the response energy problem to obtain \vec{X} and \vec{Y} as in Fig. 7 and use these solutions to calculate $\Delta\langle\hat{S}^2\rangle$. One very remarkable thing about Fig. 7 is the form of the triplet excited state curve. From Refs. [42] and [43], we know the spin-restricted triplet excitation energy should go to zero at the Coulson–Fischer point and then become imaginary at bond distances longer than the Coulson–Fischer point. Fig. 7 shows that the triplet excitation energy goes to zero (or would show if the points were calculated sufficiently densely in that region) but thereafter remains real and actually increases. This is an indication that something is wrong – specifically, that the LDA

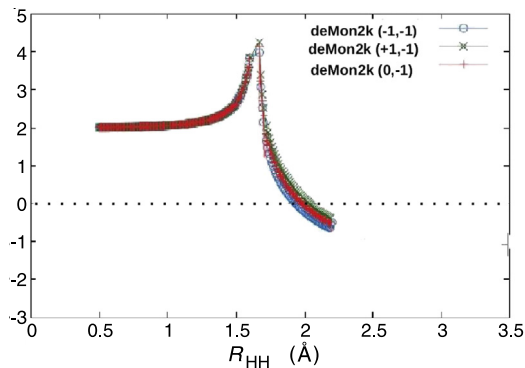


Fig. 8. (Color online) TDLDA $\Delta\langle\hat{S}^2\rangle$ for the triplet excitations in the symmetry-broken minimal basis LDA H_2 problem calculated with different values of $(\sigma_1, \sigma_2) = (\sigma_1, -1)$.

description of the ground state is insufficiently accurate for a response theory calculation of the triplet excited state near and beyond the Coulson–Fischer point.

A very important question now arises – indeed a question which is central to the present article – namely, how we judge whether $\Delta\langle\hat{S}^2\rangle$ is a reasonable representation of the underlying physics. Here there are two choices.

The first choice is based upon the hope that $\Delta\langle\hat{S}^2\rangle$ provides at least an approximate quantum number for labeling the excitation energy. It will not be exact because of the failure of the energy-spin commutation condition, but we might at least hope that the behavior of $\Delta\langle\hat{S}^2\rangle$ provides an indication of what happens with the excitation energies. In particular, since we know that the triplet excitation energy goes to zero too quickly approaching the Coulson–Fischer from short bond distances and then becomes imaginary, that some similar aberration should be seen in the value of $\Delta\langle\hat{S}^2\rangle$ around the Coulson–Fischer point in response theory calculations. Fig. 8 shows that the triplet state curve for $\Delta\langle\hat{S}^2\rangle$ at $(\sigma_1, \sigma_2) = (\sigma_1, -1)$ for the original recommended $\sigma_1 = -1$ as well as for $\sigma_1 = 0$ and for $\sigma_1 = +1$. Notice also that the value of σ_1 does not make a dramatic difference for the triplet excited state $\Delta\langle\hat{S}^2\rangle$. For all the values, the curves start at small bond lengths at the expected value of $\Delta\langle\hat{S}^2\rangle = 2$ and end up for large bond lengths at the expected value of $\Delta\langle\hat{S}^2\rangle = -1$ (compare with Fig. 6 for the TDA). However $\Delta\langle\hat{S}^2\rangle$ becomes alarmingly large around the Coulson–Fischer point. From the present philosophical choice, this is a reassuring positive point in the sense that it is indicating that there is indeed something very wrong in the triplet response energy solution around the Coulson–Fischer point that is being used to calculate $\Delta\langle\hat{S}^2\rangle$.

Fig. 9 shows the results of using various different values of (σ_1, σ_2) for calculating $\Delta\langle\hat{S}^2\rangle$ for the singlet excited state. Notice that, in this case, the choice of the value of σ_2 does not make much difference for a given value of σ_1 . However the value of σ_1 does make an important difference for the singlet excited state. For the singlet state, $\Delta\langle\hat{S}^2\rangle = 0$ as expected at shorter bond distances than the Coulson–Fischer point and goes to the expected value of $\Delta\langle\hat{S}^2\rangle = -1$ at large bond lengths (compare also with Fig. 6 for the TDA). In between, however, the value σ_1 makes a significant difference, with the $\sigma_1 = +1$ curve lying above the $\sigma_1 = 0$ curve which lies above the $\sigma_1 = -1$ curve.

The second reasonable choice that we might make is to judge the physical value of $\Delta\langle\hat{S}^2\rangle$ on the basis of whether it gives results similar to the wave-function approach. In this case, we would like to see values of $\Delta\langle\hat{S}^2\rangle$ which are similar to those obtained in the TDA. Fig. 10 shows that the simple trick of setting $\sigma_2 = +1$ brings the response theory curves into much better agreement with the

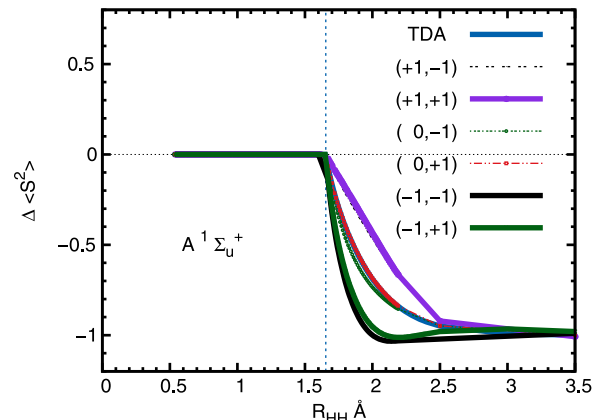


Fig. 9. (Color online) $\Delta\langle\hat{S}^2\rangle$ for singlet excitations in the symmetry broken minimal basis LDA H_2 problem calculated with different values of (σ_1, σ_2) .

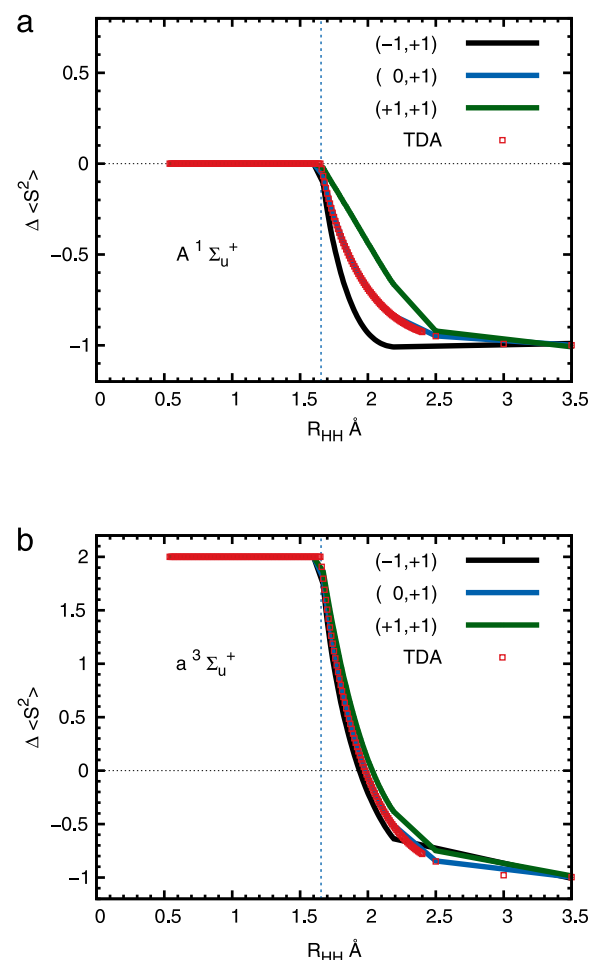


Fig. 10. (Color online) TDLDA $\Delta\langle\hat{S}^2\rangle$ with $\sigma_2 = +1$ for the (a) singlet and (b) triplet excitations in the symmetry broken minimal basis LDA H_2 problem.

TDA curves. In fact, this simple trick seems to suffice to bring the triplet excited state response $\Delta\langle\hat{S}^2\rangle$ curves into agreement with the corresponding TDA $\Delta\langle\hat{S}^2\rangle$ curve because, as noted above, the value of σ_1 is not critical in this case. On the other hand, Fig. 10 shows that the choice of σ_1 is critical for the singlet. While the original (and carefully justified) choice $\sigma_1 = +1$ leads to an overestimation of the corresponding TDA curve and the choice $\sigma_1 = -1$ leads to an underestimation of the TDA curve, the new choice $\sigma_1 = 0$ suggested in this paper leads to excellent agreement

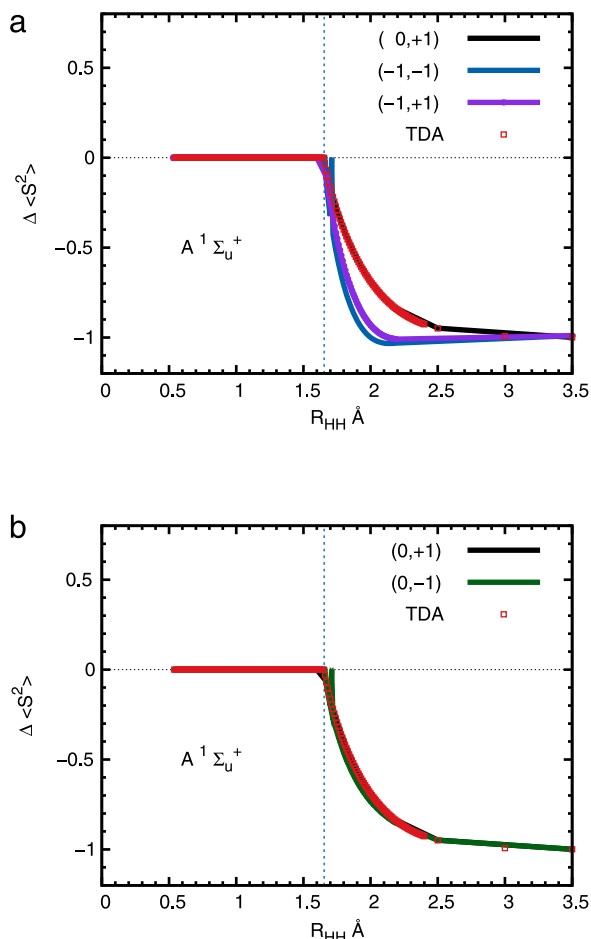


Fig. 11. (Color online) Singlet excited state TDLDA $\Delta\langle\hat{S}^2\rangle$ curves: (a) comparison of results from the recommended $(\sigma_1, \sigma_2) = (0, +1)$ formula with the $(\sigma_1, \sigma_2) = (-1, -1)$ formula currently implemented in **DEMON2K** and with the $(\sigma_1, \sigma_2) = (-1, +1)$ formula currently implemented in **GAUSSIAN09** and (b) comparison showing the relative unimportance of the value of σ_2 for calculating $\Delta\langle\hat{S}^2\rangle$ for this state.

with the TDA curve for both the singlet and the triplet. **Fig. 11** emphasizes the superiority of the $\sigma_1 = 0$ choice over the $\sigma_1 = -1$ choice now used in **GAUSSIAN09** and in **DEMON2K** for $\Delta\langle\hat{S}^2\rangle$ of the singlet excited state. [We note that we have carefully compared the **DEMON2K** and **GAUSSIAN09** programs and have thereby numerically confirmed that **GAUSSIAN09** does indeed use $(\sigma_1, \sigma_2) = (-1, +1)$.] It is particularly striking that the value of σ_1 is more important than the value of σ_2 in this case. Hence, *if the goal is to obtain $\Delta\langle\hat{S}^2\rangle$ close to those expected from the TDA, we strongly recommend taking $(\sigma_1, \sigma_2) = (0, +1)$, but note that this is not the only philosophical choice as it is somewhat easier to justify the choice $(\sigma_1, \sigma_2) = (+1, -1)$ from first principles considerations as a better reflection of the behavior of the excited state energy curves obtained from response theory.*

5.2. More realistic calculations

Although H_2 in a minimal basis set is the prototypical model of a σ bond and, as such, is important to understand, it is also important to see how our formulae for $\Delta\langle\hat{S}^2\rangle$ work in realistic calculations. We have chosen some small molecules as typical test cases. One of the interesting results is that the precise values in the couple (σ_1, σ_2) often make relatively little difference. This is illustrated in the following subsection which is then followed by a subsection mentioning a case in which we found more important differences.

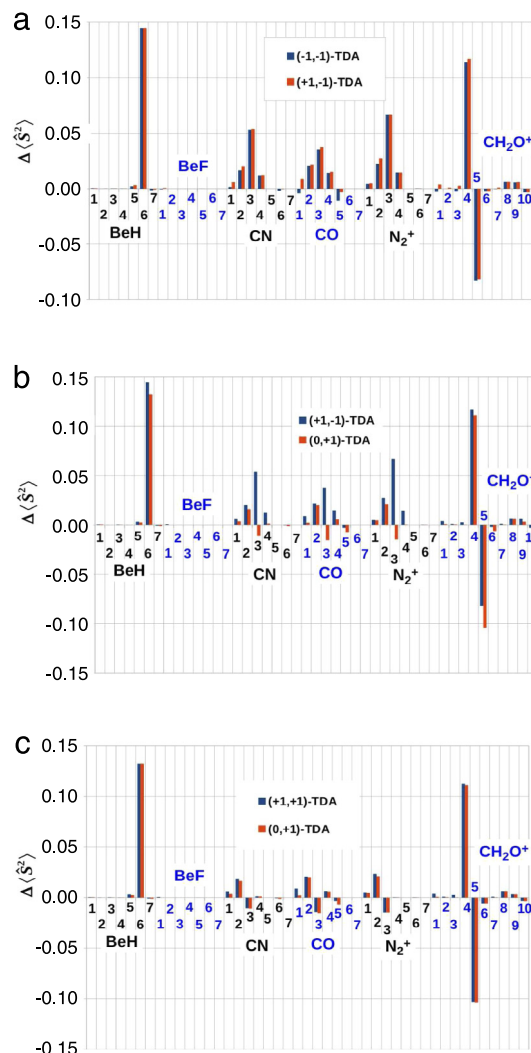


Fig. 12. (Color online) Comparison of the different choices of measure of spin contamination minus the TDA value: (a) **DEMON2K** $(-1, -1)$ with the originally proposed $(+1, -1)$, (b) $(+1, -1)$ with $(0, +1)$, and (c) $(+1, +1)$ with $(0, +1)$. The data are for the different excited states shown in **Tables 9–14**.

5.2.1. Cases where different choices give similar results

We first examine some cases in which the exact choice of spin-contamination formula seems to make little difference. These are for electronic excitations at the equilibrium geometries of the following molecules: BeH , BeF , CN , CO^+ , N_2^+ , and CH_2O^+ . As these excitations have been treated before, we may make a few comments on how the present **DEMON2K** results compare with the results of earlier similar calculations [8,40]. This is done in the **Appendix**. The main conclusion is that better results are obtained in the absence of the use of a charge conservation constraint and that the present **DEMON2K** results are in excellent agreement with those of **GAUSSIAN09** for excitation energies.

Tables 2–7 provide the results of our calculations with the different choices of measure of spin contamination. **Fig. 12** provide a graphical overview of how close each of the methods is to giving what is obtained from the TDA. For these examples, it is seen that the first principles choice $(+1, -1)$ does not differ significantly from the **DEMON2K** choice $(-1, -1)$, nor does Ipatov's $(+1, +1)$ variation give results significantly different from our revised choice $(0, +1)$. However the revised choice $(0, +1)$ does behave on average more similarly to the TDA than does the first principles choice $(+1, -1)$. At this point, if our interest is to stick to results close to wave function theory (i.e., the TDA), then the clear choice is $(0, +1)$.

Table 2
Spin contamination in BeH excited-states.

State	$\Delta\langle\hat{S}^2\rangle_i (h^2), [2S + 1] (h)$				
	TDA	TDLDA			
		(−1.0, −1.0)	(+1.0, −1.0)	(+1.0, +1.0)	(+0.0, +1.0)
7	0.0072 [2.0075]	0.0058 [2.0061]	0.0064 [2.0066]	0.0063 [2.0066]	0.0061 [2.0063]
6	1.8223 [3.3601]	1.9670 [3.4452]	1.9670 [3.4452]	1.9544 [3.4378]	1.9544 [3.4378]
5	0.0302 [2.0302]	0.0323 [2.0323]	0.0335 [2.0335]	0.0334 [2.0334]	0.0327 [2.0328]
4	0.0050 [2.0053]	0.0052 [2.0055]	0.0052 [2.0055]	0.0052 [2.0055]	0.0052 [2.0055]
3	0.0061 [2.0064]	0.0064 [2.0067]	0.0065 [2.0068]	0.0065 [2.0068]	0.0064 [2.0067]
2	0.0048 [2.0051]	0.0049 [2.0051]	0.0050 [2.0053]	0.0050 [2.0053]	0.0049 [2.0052]
1	0.0008 [2.0010]	0.0013 [2.0016]	0.0013 [2.0016]	0.0013 [2.0015]	0.0013 [2.0015]
0	0.7503 [2.0003]	0.7503 [2.0003]	0.7503 [2.0003]	0.7503 [2.0003]	0.7503 [2.0003]

Table 3
Spin contamination in BeF excited-states.

State	$\Delta\langle\hat{S}^2\rangle_i (h^2), [2S + 1] (h)$				
	TDA	TDLDA			
		(−1.0, −1.0)	(+1.0, −1.0)	(+1.0, +1.0)	(+0.0, +1.0)
7	0.0234 [2.0245]	0.0241 [2.0253]	0.0257 [2.0268]	0.0256 [2.0268]	0.0249 [2.0260]
6	0.0005 [2.0018]	0.0005 [2.0018]	0.0005 [2.0018]	0.0005 [2.0018]	0.0005 [2.0018]
5	0.0011 [2.0024]	0.0012 [2.0025]	0.0012 [2.0025]	0.0012 [2.0025]	0.0012 [2.0025]
4	0.0002 [2.0015]	0.0002 [2.0015]	0.0002 [2.0016]	0.0002 [2.0016]	0.0002 [2.0015]
3	0.0004 [2.0017]	0.0004 [2.0017]	0.0004 [2.0017]	0.0004 [2.0017]	0.0004 [2.0017]
2	0.0007 [2.0020]	0.0007 [2.0020]	0.0007 [2.0020]	0.0007 [2.0020]	0.0007 [2.0020]
1	−0.0002 [2.0011]	−0.0007 [2.0006]	0.0005 [2.0018]	0.0005 [2.0018]	−0.0001 [2.0012]
0	0.7513 [2.0013]	0.7513 [2.0013]	0.7513 [2.0013]	0.7513 [2.0013]	0.7513 [2.0013]

Table 4
Spin contamination in CN excited-states.

State	$\Delta\langle\hat{S}^2\rangle_i (h^2), [2S + 1] (h)$				
	TDA	TDLDA			
		(−1.0, −1.0)	(+1.0, −1.0)	(+1.0, +1.0)	(+0.0, +1.0)
7	0.9968 [2.8294]	0.9968 [2.8294]	0.9968 [2.8294]	0.9968 [2.8294]	0.9968 [2.8294]
6	0.0971 [2.0992]	0.0954 [2.0976]	0.0967 [2.0989]	0.0965 [2.0987]	0.0959 [2.0981]
5	0.9967 [2.8293]	0.9967 [2.8294]	0.9967 [2.8294]	0.9967 [2.8294]	0.9967 [2.8294]
4	1.9747 [3.4521]	1.9865 [3.4590]	1.9868 [3.4592]	1.9761 [3.4530]	1.9760 [3.4529]
3	1.9502 [3.4379]	2.0033 [3.4687]	2.0040 [3.4691]	1.9393 [3.4316]	1.9390 [3.4314]
2	0.0444 [2.0484]	0.0608 [2.0644]	0.0647 [2.0682]	0.0625 [2.0660]	0.0606 [2.0641]
1	0.0050 [2.0096]	0.0065 [2.0111]	0.0110 [2.0156]	0.0109 [2.0155]	0.0087 [2.0133]
0	0.7546 [2.0046]	0.7546 [2.0046]	0.7546 [2.0046]	0.7546 [2.0046]	0.7546 [2.0046]

5.2.2. Cases where different choices give different results

We have also tried to find a case where different values of the couple (σ_1, σ_2) gave dramatically different results. In particular, the 8 $\Delta\langle\hat{S}^2\rangle$ curves for the following doublet excited states of N_2^+

were examined: $1^2\Sigma_g^+$, $1^2\Sigma_u^+$, $2^2\Sigma_u^+$, $1^2\Pi_u$, $1^2\Pi_g$, $1^2\Delta_u$, $2^2\Delta_u$, $1^2\Sigma_u^-$, and $2^2\Sigma_u^-$. Only one of the potential energy curves showed any significant difference between the TDA and the $(\sigma_1, \sigma_2) = (0, +1)$, $(\sigma_1, \sigma_2) = (-1, -1)$, $(\sigma_1, \sigma_2) = (+1, -1)$, and

Table 5
Spin contamination in CO⁺ excited-states.

State	$\Delta\langle\hat{S}^2\rangle_I (\hbar^2), [2S + 1] (\hbar)$				
	TDA	TDLDA			
		(−1.0, −1.0)	(+1.0, −1.0)	(+1.0, +1.0)	(+0.0, +1.0)
7 (10)	0.9885 [2.8288]	0.9885 [2.8288]	0.9885 [2.8288]	0.9885 [2.8288]	0.9885 [2.8288]
6 (9)	0.9884 [2.8287]	0.9884 [2.8287]	0.9884 [2.8287]	0.9884 [2.8287]	0.9884 [2.8287]
5 (7,8)	0.1179 [2.1259]	0.1070 [2.1157]	0.1150 [2.1232]	0.1146 [2.1228]	0.1106 [2.1191]
4 (5,6)	1.8480 [3.3823]	1.8619 [3.3905]	1.8629 [3.3911]	1.8542 [3.3860]	1.8537 [3.3857]
3 (4)	1.9279 [3.4292]	1.9631 [3.4497]	1.9653 [3.4510]	1.9134 [3.4208]	1.9123 [3.4201]
2 (3)	0.0597 [2.0705]	0.0805 [2.0904]	0.0815 [2.0914]	0.0805 [2.0904]	0.0799 [2.0899]
1 (1,2)	0.0041 [2.0160]	−0.0003 [2.0117]	0.0128 [2.0247]	0.0128 [2.0246]	0.0063 [2.0182]
0	0.7620 [2.0120]	0.7620 [2.0120]	0.7620 [2.0120]	0.7620 [2.0120]	0.7620 [2.0120]

Table 6
Spin contamination in N₂⁺ excited-states.

State	$\Delta\langle\hat{S}^2\rangle_I (\hbar^2), [2S + 1] (\hbar)$				
	TDA	TDLDA			
		(−1.0, −1.0)	(+1.0, −1.0)	(+1.0, +1.0)	(+0.0, +1.0)
7	0.9999 [2.8293]	0.9999 [2.8293]	0.9999 [2.8293]	0.9999 [2.8293]	0.9999 [2.8293]
6	0.0007 [2.0021]	0.0010 [2.0024]	0.0010 [2.0024]	0.0010 [2.0024]	0.0010 [2.0024]
5	0.9999 [2.8293]	0.9999 [2.8293]	0.9999 [2.8293]	0.9999 [2.8293]	0.9999 [2.8293]
4	1.9939 [3.4614]	2.0082 [3.4696]	2.0082 [3.4696]	1.9943 [3.4617]	1.9943 [3.4617]
3	1.9398 [3.4300]	2.0068 [3.4689]	2.0068 [3.4689]	1.9249 [3.4213]	1.9249 [3.4213]
2	0.0585 [2.0591]	0.0810 [2.0808]	0.0858 [2.0854]	0.0819 [2.0817]	0.0796 [2.0795]
1	0.0048 [2.0062]	0.0092 [2.0106]	0.0098 [2.0112]	0.0097 [2.0111]	0.0094 [2.0108]
0	0.7514 [2.0014]	0.7514 [2.0014]	0.7514 [2.0014]	0.7514 [2.0014]	0.7514 [2.0014]

Table 7
Spin contamination in CH₂O⁺ excited-states.

State	$\Delta\langle\hat{S}^2\rangle_I (\hbar^2), [2S + 1] (\hbar)$				
	TDA	TDLDA			
		(−1.0, −1.0)	(+1.0, −1.0)	(+1.0, +1.0)	(+0.0, +1.0)
10	0.2787 [2.2654]	0.2755 [2.2625]	0.2758 [2.2628]	0.2755 [2.2625]	0.2753 [2.2623]
9	1.6934 [3.2849]	1.6992 [3.2885]	1.6995 [3.2886]	1.6968 [3.2870]	1.6967 [3.2869]
8	0.0564 [2.0598]	0.0627 [2.0659]	0.0627 [2.0659]	0.0625 [2.0656]	0.0625 [2.0656]
7	0.0055 [2.0097]	0.0053 [2.0095]	0.0066 [2.0108]	0.0065 [2.0108]	0.0059 [2.0101]
6	1.9389 [3.4311]	1.9368 [3.4299]	1.9368 [3.4299]	1.9326 [3.4274]	1.9326 [3.4274]
5	1.7297 [3.3069]	1.6468 [3.2564]	1.6479 [3.2571]	1.6260 [3.2436]	1.6255 [3.2433]
4	0.2616 [2.2502]	0.3758 [2.3495]	0.3787 [2.3520]	0.3738 [2.3478]	0.3724 [2.3466]
3	0.0185 [2.0226]	0.0164 [2.0205]	0.0212 [2.0253]	0.0212 [2.0253]	0.0188 [2.0229]
2	0.0011 [2.0053]	0.0011 [2.0053]	0.0021 [2.0064]	0.0021 [2.0064]	0.0016 [2.0058]
1	−0.0016 [2.0027]	−0.0039 [2.0003]	0.0023 [2.0065]	0.0023 [2.0065]	−0.0008 [2.0035]
0	0.7542 [2.0042]	0.7542 [2.0042]	0.7542 [2.0042]	0.7542 [2.0042]	0.7542 [2.0042]

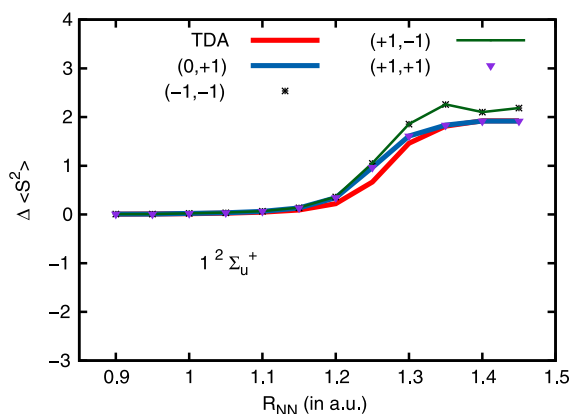


Fig. 13. (Color online) Comparison of different choices of formulae for spin-contamination for the $1^2\Sigma_u^+$ state of N_2^+ at different bond lengths.

$(\sigma_1, \sigma_2) = (+1, +1)$ values of $\Delta\langle\hat{S}^2\rangle$ is the $1^2\Sigma_u^+$ state shown in Fig. 13. We see that $(+1, -1)$ and $(-1, -1)$ are nearly identical. Also that $(+1, +1)$ and $(0, +1)$ are nearly identical and closer to the TDA result. This again leads us to recommend $(\sigma_1, \sigma_2) = (0, +1)$.

6. Conclusion

Excitations in molecules with open-shell ground states are notoriously more difficult to treat than those of molecules with closed-shell ground states. Especially in DFT, open-shell calculations are often carried out using a single-determinant DODS description of the ground state. Spin-contamination of the ground state obtained in this way is nearly universally estimated using Löwdin's formula for $\langle\hat{S}^2\rangle_0$. The extension of Löwdin's approach to excited states is straightforward in a wave function framework. Indeed Maurice and Head-Gordon have deduced just such a formula for $\Delta\langle\hat{S}^2\rangle_l^{\text{TDA}}$ of the l th excited state within the TDA [5]. The extension of their work to linear response theory calculations in the TD Hartree–Fock (TD–HF) or TD–DFT formalisms turns out to be less obvious for reasons already discussed in the introduction. Nevertheless such a formula was published about 10 years ago and has been implemented, albeit with some variations, in programs such as DEMON2K and GAUSSIAN09 [6,8]. This paper has discussed this formula and its variations in detail and complemented this discussion with illustrative calculations.

Spin is not as good a quantum number as might be desired in TD–HF calculations because the energy $(\tilde{L}(\hat{H})\hat{A} = [\hat{H}, \hat{A}])$ and spin $(\tilde{L}(\hat{S}^2)\hat{A} = [\hat{S}^2, \hat{A}])$ commutator superoperators do not commute in the truncated operator basis set. Nevertheless the energy EOM may be solved to find the eigenvector $\tilde{Z} = (\tilde{X}, \tilde{Y})$, where \tilde{X} is the particle–hole component and \tilde{Y} is the hole–particle component, and these may be used to evaluate the expectation value of $\tilde{L}(\hat{S}^2)$ to obtain the formula,

$$\Delta\langle\hat{S}^2\rangle = \frac{\Delta\langle\hat{S}^{\text{TDA}}\rangle(\tilde{X}) + \Delta\langle\hat{S}^{\text{TDA}}\rangle(\tilde{Y}^*) + \sigma_1\Delta\langle\hat{S}^{\text{mixed}}\rangle(\tilde{X}, \tilde{Y}^*)}{\tilde{X}^\dagger\tilde{X} + \sigma_2\tilde{Y}^\dagger\tilde{Y}}, \quad (6.1)$$

with $(\sigma_1, \sigma_2) = (+1, -1)$. Given the nature of the derivation, it is natural to expect that the behavior of this $\Delta\langle\hat{S}^2\rangle$ should parallel the behavior of excitation energies, and we have demonstrated by direct calculation that this does indeed seem to be the case. In particular, $\Delta\langle\hat{S}^2\rangle$ becomes abnormally large for the lowest triplet state at geometries where there is a triplet instability visible

Table 8

Ground-state spin contamination obtained from DEMON2K with the LDA functional. The spin contamination obtained from GAUSSIAN09 is identical to the number of significant figures shown.

Molecule	$\langle\hat{S}^2\rangle$	Multiplicity ($2S + 1$) ^a	Spin contamination ^b (%)
BeH	0.7503	2.0003	0.010
BeF	0.7513	2.0013	0.043
CN	0.7546	2.0046	0.150
CO ⁺	0.7620	2.0120	0.400
N ₂ ⁺	0.7514	2.0014	0.047
CH ₂ O ⁺	0.7542	2.0042	0.060

^a Calculated assuming that $\langle\hat{S}^2\rangle = S(S + 1)$.

^b Coefficient of next highest allowed spin component squared times 100%, calculated assuming that all spin contamination comes from the next highest allowed spin component.

in the excitation energy curve. *A priori* this is a good thing as the fundamental usefulness of spin is as a quantum number for describing the energy. Thus it is reassuring that $\Delta\langle\hat{S}^2\rangle$ is wrong when the excitation energy is wrong.

However there is another criterion which might be used for judging the value of a formula for $\Delta\langle\hat{S}^2\rangle$ and that is whether this formula coincides with our physical intuition regarding the value of $\Delta\langle\hat{S}^2\rangle$ which would be calculated using a wave-function-like theory such as the TDA. We have discussed how our formula for $\Delta\langle\hat{S}^2\rangle$ becomes more wave-function-like by following the common practice of setting $\sigma_2 = +1$. Indeed this is the form implemented in GAUSSIAN09 [28]. Perhaps surprisingly the effect of changing the sign of σ_2 often is only of quantitative, not qualitative, importance, with a notable exceptions being around triplet instabilities. For historical reasons which have long since been forgotten, the choice of $\sigma_1 = -1$ also was made in both DEMON2K [$(\sigma_1, \sigma_2) = (-1, -1)$] and in GAUSSIAN09 [$(\sigma_1, \sigma_2) = (-1, +1)$]. We have shown that the precise value of σ_1 is often relatively unimportant in practical calculations as the choice of values $\sigma_1 = -1, 0, +1$ gives very similar results. However there are cases where the precise choice of σ_1 does make a difference in that we find that $\sigma_1 = 0$ coincides best with wave-function-like TDA results for $\Delta\langle\hat{S}^2\rangle$.

Theory is, of course, concerned with modeling and, as such, is never completely free of philosophical choices about what makes a better model. We have argued that there are two “best” choices for the couple (σ_1, σ_2) . If $\Delta\langle\hat{S}^2\rangle$ is to be used to estimate the quality of TD–DFT excitation energies, then $(\sigma_1, \sigma_2) = (+1, -1)$ is a good choice. However if the desire is to match wave-function-based intuition regarding the spin of the excited state, then $(\sigma_1, \sigma_2) = (0, +1)$ seems a good choice. In such cases, there is no one “best” answer and so it seems reasonable that both values be calculated so as to let the user decide which is the best choice for a given application.

Acknowledgments

This work is supported, in part, by the ORGAVOLT (ORGANic solar cell VOLTage by numerical computation) grant ANR-12-MONU-0014-02 of the French Agence Nationale de la Recherche (ANR) 2012 Programme Modèles Numériques. Grenoble Centre d'Expérimentation du Calcul Intensif en Chimie (CECIC) computing resources are gratefully acknowledged as is computing help from Pierre Girard. We thank Edward Brothers and Mike Frisch for useful discussions.

Appendix. Comparison with earlier work

As a precaution and to see the evolution of the DEMON TD–DFT programs and of GAUSSIAN over time, we make a comparison

Table 9
Spin contamination in BeH excited states.

State	Excitation energy (eV) [f] ($\Delta\langle\hat{S}^2\rangle$)				TDLDA ^e	TDLDA TDA ^a	TDLDA TDA ^c	TDLDA TDA ^e	Assignment	Reference values (eV) ^f
	TDLDA ^a	TDLDA ^b	TDLDA ^c	TDLDA ^d						
<i>TDLDA spin down ionization threshold = 8.0 eV</i>										
7	5.6414 [0.1684] (0.0057)	5.6414 [0.1684] (0.0057)	5.6283 [0.1710] (0.0058)	5.418	5.4803 (0.0034)	5.6712 [0.1801] (0.0067)	5.6584 [0.1830] (0.0072)	5.5030 (0.0039)	$^2\Sigma^+$ ($3\sigma^{\text{SOMO}} \rightarrow 6\sigma$, $2\bar{\sigma} \rightarrow 3\bar{\sigma}$)	
6	5.6338 [0.0010] (1.9677)	5.6338 [0.0010] (1.9677)	5.6331 [0.0005] (1.9670)	5.671	5.1685 (2.0115)	5.6744 [0.0003] (1.9347)	5.6735 [0.0001] (1.8223)	5.2953 (1.9784)	$^1\Pi$ ($2\sigma \rightarrow 1\pi$, $1\bar{\pi} \rightarrow 2\bar{\sigma}$)	
5	5.1318 [0.0029] (0.0307)	5.1318 [0.0029] (0.0307)	5.1257 [0.0021] (0.0323)	5.129	4.8049 (0.0297)	5.1765 [0.0018] (0.0307)	5.1703 [0.0011] (0.0302)	4.8676 (0.0303)	$^2\Sigma^+$ ($2\bar{\sigma} \rightarrow 3\bar{\sigma}$)	
4	4.8451 [0.0043] (0.0057)	4.8451 [0.0043] (0.0057)	4.7805 [0.0036] (0.0052)	4.858	4.7047 (0.0134)	4.8463 [0.0039] (0.0047)	4.7815 [0.0033] (0.0050)	4.7104 (0.0091)	$^2\Pi$ ($3\sigma^{\text{SOMO}} \rightarrow 2\pi$)	6.31
3	4.7576 [0.0022] (0.0057)	4.7576 [0.0022] (0.0057)	4.7307 [0.0000] (0.0064)	4.771	4.6300 (0.0134)	4.7602 [0.0023] (0.0057)	4.7328 [0.0000] (0.0061)	4.6481 (0.0091)	$^2\Sigma^+$ ($3\sigma^{\text{SOMO}} \rightarrow 5\sigma$)	
<i>TDLDA spin up ionization threshold = 4.6 eV</i>										
2	4.6633 [0.0491] (0.0057)	4.6633 [0.0491] (0.0057)	4.6576 [0.0503] (0.0049)	4.593	4.5103 (0.0083)	4.6685 [0.0465] (0.0057)	4.6633 [0.0480] (0.0048)	4.5278 (0.0063)	$^2\Sigma^+$ ($3\sigma^{\text{SOMO}} \rightarrow 4\sigma$)	5.51
1	2.3657 [0.0427] (0.0003)	2.3657 [0.0427] (0.0003)	2.3637 [0.0427] (0.0013)	2.391	2.2479 (0.0060)	2.3899 [0.0495] (0.0007)	2.3879 [0.0495] (0.0008)	2.2860 (0.0011)	$^2\Pi$ ($3\sigma^{\text{SOMO}} \rightarrow 1\pi$)	2.56

^a Present work: GAUSSIAN09, D01.

^b Table 4 of Ref. [8]: GAUSSIAN03.

^c Present work: DEMON2K.

^d Table 3 of Ref. [40]: DEMON-DYNARHO.

^e Table 4 of Ref. [8]: DEMON2K.

^f See Table 4 of Ref. [8].

Table 10
Spin contamination in BeF excited states.

State	Excitation energy (eV) [f] ($\Delta\langle\hat{S}^2\rangle$)								Assignment	Reference values (eV) ^f
	TDLDA ^a	TDLDA ^b	TDLDA ^c	TDLDA ^d	TDLDA ^e	TDLDA TDA ^a	TDLDA TDA ^c	TDLDA TDA ^e		
	<i>TDLDA spin down ionization threshold = 10.3 eV</i>									
7	6.7056 [0.0256] (0.0257)	6.7268 [0.0027]	6.7246 [0.0257] (0.0241)	6.114	6.6988 (0.0155)	6.7140 [0.0300] (0.0257)	6.7320 [0.0285] (0.0234)	6.7092 (0.0114)	$^2\Pi$ ($5\sigma^{\text{SOMO}} \rightarrow 4\pi$)	
6	6.5750 [0.0000] (0.0007)	6.5432 [0.0000]	6.5775 [0.0000] (0.0005)	5.574	6.4884 (0.0011)	6.5783 [0.0000] (0.0007)	6.5810 [0.0000] (0.0005)	6.4940 (0.0009)	$^2\Sigma^+$ ($5\sigma^{\text{SOMO}} \rightarrow 8\sigma$)	
5	6.1312 [0.0729] (0.0007)	6.1070 [0.0739]	6.0928 [0.0771] (0.0012)	5.951	6.0584 (0.0031)	6.1349 [0.0720] (0.0007)	6.0970 [0.0759] (0.0011)	6.0637 (0.0024)	$^2\Delta$ ($5\sigma^{\text{SOMO}} \rightarrow 1\delta$)	
4	5.6825 [0.0001] (0.0003)	5.6536 [0.0000]	5.6338 [0.0000] (0.0002)	5.274	5.5639 (0.0003)	5.6844 [0.000] (0.0007)	5.6358 [0.0000] (0.0002)	5.5666 (0.0003)	$^2\Pi$ ($5\sigma^{\text{SOMO}} \rightarrow 3\pi$)	
3	5.6473 [0.0000] (0.0007)	5.6201 [0.0000]	5.6399 [0.0011] (0.0004)	4.929	5.5811 (0.0003)	5.6571 [0.0001] (0.0007)	5.6504 [0.0020] (0.0004)	5.5917 (0.0003)	$^2\Sigma^+$ ($5\sigma^{\text{SOMO}} \rightarrow 7\sigma$)	
	<i>TDLDA spin up ionization threshold = 5.4 eV</i>									
2	5.3723 [0.0999] (0.0007)	5.3462 [0.0977]	5.3530 [0.0945] (0.0007)	4.770	5.5264 (0.0017)	5.3762 [0.0994] (0.0007)	5.3566 [0.0935] (0.0007)	5.3314 (0.0014)	$^2\Sigma^+$ ($5\sigma^{\text{SOMO}} \rightarrow 6\sigma$)	6.345
1	4.0574 [0.1665] (0.0013)	4.0747 [0.1693]	4.0495 [0.166] (0.0007)	4.366	3.9816 (0.0000)	4.0957 [0.1905] (0.0003)	4.0886 [0.190] (-0.0002)	4.0225 (0.0005)	$^2\Pi$ ($5\sigma^{\text{SOMO}} \rightarrow 2\pi$)	4.249

^a Present work: GAUSSIAN09, D01.

^b Table 5 of Ref. [8]: GAUSSIAN03.

^c Present work: DEMON2K.

^d Table 4 of Ref. [40]: DEMON-DYNARHO.

^e Table 5 of Ref. [8]: DEMON2K.

^f See Table 5 of Ref. [8].

Table 11
Spin contamination in CN excited states.

State	Excitation energy (eV) [<i>f</i>] ($\Delta\langle\hat{S}^2\rangle$)								Assignment	Reference values (eV) ^f
	TDLDA ^a	TDLDA ^b	TDLDA ^c	TDLDA ^d	TDLDA ^e	TDLDA TDA ^a	TDLDA TDA ^c	TDLDA TDA ^e		
	TDLDA spin down ionization threshold = 9.5 eV TDLDA spin up ionization threshold = 9.7 eV									
7	8.3190 [0.0000] (0.9964)	8.3190 [0.0000]	8.3208 [0.0000] (0.9968)	8.626	8.3210 (0.9967)	8.3190 [0.0000] (0.9964)	8.3208 [0.0000] (0.9968)	8.3210 (0.9967)	² <i>Π</i> (5σ ^{SOMO} → 2π)	8.619
6	8.0518 [0.0027] (0.0954)	8.0518 [0.0027]	8.0509 [0.0026] (0.0954)	8.061	7.9829 (0.0948)	8.0879 [0.0030] (0.0974)	8.0872 [0.0029] (0.0971)	8.0236 (0.0964)		
5	8.0324 [0.0000] (0.9964)	8.0324 [0.0000]	8.0338 [0.0000] (0.9967)		8.0334 (0.9967)	8.0324 [0.0000] (0.9964)	8.0338 [0.0000] (0.9967)	8.0334 (0.9967)		
4	7.4325 [0.0000] (1.9764)	7.4325 [0.0000]	7.4323 [0.0000] (1.9865)	7.434	7.1807 (2.0050)	7.4826 [0.0000] (1.9754)	7.4826 [0.0000] (1.9747)	7.2699 (1.9838)	^{TC} Δ (1π → 2π, 1 $\bar{\pi}$ → 2 $\bar{\pi}$) ^{TC} Σ ⁺ (1π → 2π, 1 $\bar{\pi}$ → 2 $\bar{\pi}$)	
3	6.6326 [0.0007] (1.9524)	6.6347 [0.0008]	6.6315 [0.0007] (2.0033)	6.629	6.0967 (1.9928)	6.8576 [0.0015] (1.9504)	6.8576 [0.0015] (1.9502)	6.4792 (1.9152)		
2	3.2333 [0.0363] (0.0394)	3.2333 [0.0366]	3.2304 [0.0360] (0.0608)	3.227	2.8364 (0.1566)	3.5093 [0.0483] (0.0444)	3.5083 [0.0483] (0.0444)	3.1908 (0.0786)		
1	1.3575 [0.0029] (0.0014)	1.3576 [0.0029]	1.3566 [0.0029] (0.0065)	1.340	1.2131 (0.0160)	1.4106 [0.0038] (0.0054)	1.4098 [0.0038] (0.0050)	1.3017 (0.0084)	² <i>Π</i> (1 $\bar{\pi}$ → 5 $\bar{\sigma}$)	1.235

^a Present work: GAUSSIAN09, D01.
^b Table 6 of Ref. [8]: GAUSSIAN03.
^c Present work: DEMON2K.
^d Table 5 of Ref. [40]: DEMON-DYNARHO.
^e Table 6 of Ref. [8]: DEMON2K.
^f See Table 6 of Ref. [8].

Table 12
Spin contamination in CO⁺ excited states.

State	Excitation energy (eV) [<i>f</i>] ($\Delta\langle\hat{S}^2\rangle$)								Assignment	Reference values (eV) ^f
	TDLDA ^a	TDLDA ^b	TDLDA ^c	TDLDA ^d	TDLDA ^e	TDLDA TDA ^a	TDLDA TDA ^c	TDLDA TDA ^e		
TDLDA spin down ionization threshold = 22.2 eV TDLDA spin up ionization threshold = 21.8 eV										
7	10.3165 [0.0000] (0.989)	10.3165 [0.0000]	10.3181 [0.0000] (0.9885)	10.866	10.3175 (0.9885)	10.3165 [0.0000] (0.9890)	10.3181 [0.0000] (0.9885)	10.3175 (0.9885)		
6	9.4114 [0.0000] (0.988)	9.4114 [0.0000]	9.4134 [0.0000] (0.9884)	9.600	9.4107 (0.9884)	9.4114 [0.0000] (0.988)	9.4134 [0.0000] (0.9884)	9.4107 (0.9884)		
5	8.9870 [0.0118] (0.107)	8.9870 [0.0118]	8.9858 [0.0118] (0.1070)	8.832	8.9203 (0.0950)	9.0390 [0.0141] (0.1180)	9.0382 [0.0141] (0.1179)	8.9782 (0.1102)	² <i>Π</i> (5σ ^{SOMO} → 2π)	
4	8.8850 [0.0000] (1.853)	8.8850 [0.0000]	8.8856 [0.0000] (1.8619)	8.630	8.6319 (1.9189)	8.9361 [0.0000] (1.8480)	8.9370 [0.0000] (1.8480)	8.7202 (1.8950)	^{TC} Δ (1π → 2π, 1 $\bar{\pi}$ → 2 $\bar{\pi}$)	
3	8.0626 [0.0025] (1.919)		8.0601 [0.0024] (1.9631)	7.812		8.2990 [0.0031] (1.928)	8.2996 [0.0031] (1.9279)			
2	5.0091 [0.0176] (0.067)	5.0089 [0.0176]	5.0088 [0.0173] (0.0805)	4.982	4.6249 (0.1941)	5.1269 [0.0202] (0.060)	5.1285 [0.0202] (0.0597)	4.8274 (1.8785)	² Σ ⁺ (4 $\bar{\sigma}$ → 5 $\bar{\sigma}$)	5.965
1	3.1623 [0.0038] (0.003)	3.1623 [0.0038]	3.1629 [0.0038] (-0.0003)	2.998	2.9126 (0.0049)	3.2165 [0.0049] (0.004)	3.2174 [0.0049] (0.0041)	3.0144 (0.0074)	² <i>Π</i> (1 $\bar{\pi}$ → 5 $\bar{\sigma}$)	3.137

^a Present work: GAUSSIAN09, D01.
^b Table 7 of Ref. [8]: GAUSSIAN03.
^c Present work: DEMON2K.
^d Table 6 of Ref. [40]: DEMON-DYNARHO.
^e Table 7 of Ref. [8]: DEMON2K.
^f See Table 7 of Ref. [8].

Table 13Spin contamination in N_2^+ excited states.

State	Excitation energy (eV) [f] ($\Delta\langle\hat{S}^2\rangle$)				TDLDA ^e	TDLDA TDA ^a	TDLDA TDA ^c	TDLDA TDA ^e	Assignment	Reference values (eV) ^f
	TDLDA ^a	TDLDA ^b	TDLDA ^c	TDLDA ^d						
TDLDA spin down ionization threshold = 22.7 eV TDLDA spin up ionization threshold = 22.5 eV										
7	9.5045 [0.0000] (0.9996)	9.5045 [0.0000]	9.5050 [0.0000] (0.9999)		9.5049 (0.9999)	9.5045 [0.0000] (0.9996)	9.5050 [0.0000] (0.9999)	9.5049 (0.9999)		
6	9.2685 [0.0000] (0.0006)	9.2685 [0.0000]	9.2682 [0.0000] (0.0010)		9.1901 (0.0016)	9.3157 [0.0000] (0.0006)	9.3157 [0.0000] (0.0007)	9.2415 (0.0016)	$^2\Pi_g$ ($3\sigma_g^{\text{SOMO}} \rightarrow 1\pi_g$)	
5	9.2616 [0.0000] (0.9996)	9.2685 [0.0000]	9.2619 [0.0000] (0.9999)		9.2617 (0.9999)	9.2616 [0.0000] (0.9996)	9.2619 [0.0000] (0.9999)	9.2617 (0.9999)		
4	8.3921 [0.0000] (1.9946)	8.3921 [0.0000]	8.3921 [0.0000] (2.0082)		8.1080 (2.0207)	8.4623 [0.0000] (1.9936)	8.4623 [0.0000] (1.9939)	8.2238 (1.9965)	$^{\text{TC}}\Delta_u$ ($1\pi_u \rightarrow 1\pi_g$, $1\tilde{\pi}_u \rightarrow 1\tilde{\pi}_g$)	
3	7.3321 [0.0007] (1.9426)	7.3319 [0.0359]	7.3304 [0.0007] (2.0068)	7.729	6.7385 (0.1954)	7.6428 [0.0017] (1.9396)	7.6425 [0.0017] (1.9398)	7.2329 (0.0985)	$^{\text{TC}}\Sigma_u^+$ ($1\pi_u \rightarrow 1\pi_g$, $1\tilde{\pi}_u \rightarrow 1\tilde{\pi}_g$)	
2	3.7198 [0.0358] (0.0536)	3.7195 [0.0359]	3.7159 [0.0359] (0.0810)	3.632	3.2982 (0.1954)	4.1188 [0.0507] (0.0586)	4.1163 [0.0507] (0.0585)	3.7822 (0.0985)	$^2\Sigma_g^+$ ($2\tilde{\sigma}_u \rightarrow 3\tilde{\sigma}_g$)	5.965
1	1.4634 [0.0021] (0.0026)	1.4634 [0.0021]	1.4626 [0.0021] (0.0097)	1.598	1.3345 (0.0191)	1.5298 [0.0028] (0.0046)	1.5291 [0.0028] (0.0048)	1.4321 (0.0081)	$^2\Pi_u$ ($1\pi_u \rightarrow 3\tilde{\sigma}_g$)	1.41

^a Present work: GAUSSIAN09, D01.^b Table 8 of Ref. [8]: GAUSSIAN03.^c Present work: DEMON2K.^d Table 7 of Ref. [40]: DEMON-DYNARHO.^e Table 8 of Ref. [8]: DEMON2K.^f See Table 8 of Ref. [8].

here of the present work with work reported in Refs. [40] and [8].

We first check the amount of ground-state spin contamination obtained with DEMON2K. Table 8 shows that we get exactly the same results for the ground state contamination of several ions as was previously reported in Table 3 of Ref. [8]. This is reassuring in so far as it seems to indicate little change in the numerics of DEMON2K, at least for the ground state.

Next we examine excitation energies for several open-shell systems. Note that we do not expect results from the GAUSSIAN and DEMON calculations to agree exactly as our DEMON calculations use an auxiliary density fitting basis set to facilitate the handling of exchange–correlation (xc) while xc terms are handled by numerical integration in GAUSSIAN. As seen in Tables 9–14 GAUSSIAN03 and GAUSSIAN09 results agree perfectly – but only for BeH, CN, CO^+ , and N_2^+ , while the present GAUSSIAN09 results disagree significantly with the GAUSSIAN03 results reported in Ref. [8] for BeF and for CH_2O^+ . Overall this indicates that there was no fundamental change in the algorithm between the 2003 and 2009 releases. The most likely explanation then for the observed differences would be the use of different geometries. This is possible in the case of BeF because there is an error in the geometry reported in Ref. [40]. That geometry was used in Ref. [8]. When the geometry is corrected to be the one given explicitly in Section 4, we see that the resultant differences are small (even if numerically significant) and there is overall agreement between the present work and Refs. [40] and [8]. As the DEMON program results reported in Ref. [40] for CH_2O^+ agree satisfactorily with the present DEMON2K, we assume that there was an error in the geometry used in the calculations for that molecule reported in Ref. [8].

The implementation of TD-DFT in the DEMON family of programs predates that in the GAUSSIAN family of programs and has varied over time. Ref. [40] reports post-DEMON-KS DEMON-DYNARHO results. The orbital and auxiliary basis sets and grid were

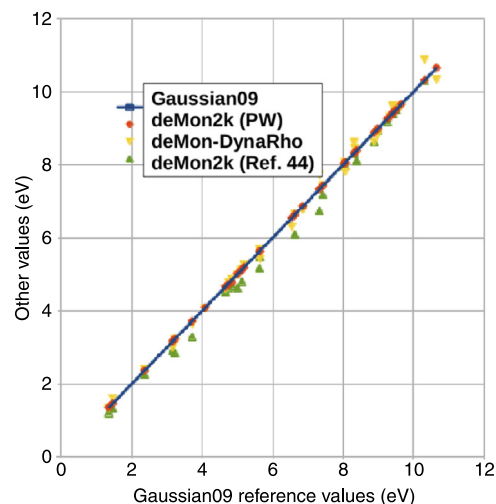


Fig. 14. (Color online) Comparison of present (PW) and previous (Ref. 44) DEMON calculations with GAUSSIAN09 TD-DFT excitation energies. The diagonal line indicates perfect agreement. Molecules: BeH (present work and Refs. [8,40]), CN (present work and Refs. [8,40]), CO^+ (present work and Refs. [8,40]), N_2^+ (present work and Refs. [8,40]), and CH_2O^+ (present work and Refs. [40]).

more elaborate than those used in the present work and there is no charge conservation constraint (CCC) used in the TD-DFT calculation. The CCC was introduced in TD-DFT in DEMON when TD-DFT was programmed in DEMON2K [44]. Although this CCC was soon abandoned and is not used in the present work, it was used in Ref. [8]. Fig. 14 shows that the present DEMON2K calculations are in better agreement with GAUSSIAN09 calculations for TD-DFT excitation energies than was ever the case before in previous DEMON program calculations.

Table 14
Spin contamination in CH₂O⁺ excited states.

State	Excitation energy (eV) [f] ($\Delta\langle\hat{S}^2\rangle$)							Assignment	Reference values (eV) ^f	
	TDLDA ^a	TDLDA ^b	TDLDA ^c	TDLDA ^d	TDLDA ^e	TDLDA TDA ^a	TDLDA TDA ^c			TDLDA TDA ^e
	TDLDA spin down ionization threshold = 17.3 eV TDLDA spin up ionization threshold = 19.8 eV									
10	9.6529 [0.0000] (1.6978)	9.9685 [0.0005] (1.6968)	9.6550 [0.0000] (1.6968)	9.603	9.9403	9.6728 [0.0000] (1.6948)	9.6750 [0.0000] (1.6934)	10.0286 (0.0067)	² A ₂ (1b ₂ → 2b ₁ , 1b ₂ → 2b ₁)	
9	9.4792 [0.0002] (0.0618)	9.7157 [0.0396] (0.0625)	9.4788 [0.0002] (0.0625)	9.554	9.7036	9.5476 [0.0001] (0.0558)	9.5471 [0.0001] (0.0564)	9.7862 (0.0367)	² A ₁ (5a ₁ → 2b ₁ , 5a ₁ → 2b ₁)	
8	9.3359 [0.0345] (0.0048)	8.6708 [0.0000] (0.0065)	9.3299 [0.0345] (0.0065)	9.318	8.3665 (2.0046)	9.4433 [0.0425] (0.0058)	9.4430 [0.0426] (0.0055)	8.5006 (1.9834)	² C _{B1} (4a ₁ → 2b ₂ , 2b ₂ ^{SOMO} → 6a ₁)	
7	8.3380 [0.0000] (1.9328)	7.9952 [0.0006] (1.9326)	8.3393 [0.0000] (1.9326)	8.462	7.8765	8.3664 [0.0000] (0.0058)	8.3678 [0.0000] (1.9389)	7.8980 (0.0047)	² A ₂ (5a ₁ → 2b ₁ , 5a ₁ → 2b ₁)	3.86, 3.84
6	6.8607 [0.0020] (1.6208)	7.9510 [0.0000] (1.6260)	6.8608 [0.0020] (1.6260)	6.768	7.8765 (1.9870)	6.9760 [0.0014] (1.7278)	6.9765 [0.0014] (1.7297)	7.8980 (1.9619)	² C _{B2} (1b ₁ → 2b ₁ , 1b ₂ → 2b ₂)	
5	6.5453 [0.0243] (0.3678)	7.5641 [0.0391] (0.3738)	6.5452 [0.0243] (0.3738)	6.299	7.5623 (0.0061)	6.6841 [0.0271] (0.2638)	6.6843 [0.0271] (0.2616)	7.7839 (0.0050)	² C _{B2} (1b ₂ → 2b ₂ , 1b ₁ → 2b ₁)	
4	5.1921 [0.0000] (0.0158)	5.4543 [0.0001] (0.0212)	5.1940 [0.0000] (0.0212)	5.266	5.1002 (0.0064)	5.2091 [0.0000] (0.0188)	5.2110 [0.0000] (0.0185)	5.2638 (1.9933)	² A ₁ (2b ₂ ^{SOMO} → 2b ₁)	
3	5.1094 [0.0001] (-0.0002)	5.1707 [0.0145] (0.0021)	5.1074 [0.0001] (0.0021)	5.089	5.0833 (2.0502)	5.1765 [0.0002] (0.0008)	5.1759 [0.0002] (0.0011)	5.1678 (0.0045)	² B ₁ (5a ₁ → 2b ₂)	
2	4.0882 [0.0000] (-0.0052)	4.7445 [0.0083] (0.0023)	4.0869 [0.0000] (0.0023)	4.062	4.6046 (0.0019)	4.1122 [0.0000] (-0.0012)	4.1110 [0.0000] (-0.0016)	4.6862 (0.0019)	² B ₁ (1b ₁ ^{SOMO} → 2b ₂)	5.30, 5.46
1		2.7014 [0.0000]			2.6439 (0.0020)			2.6669 (0.0012)		5.78, 6.46

^a Present work: GAUSSIAN09, D01.^b Table 9 of Ref. [8]: GAUSSIAN03.^c Present work: DEMON2K.^d Table 8 of Ref. [40]: DEMON-DYNARHO.^e Table 9 of Ref. [8]: DEMON2K.^f See Table 9 of Ref. [8].

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