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Density functional theory: excited states and spin annihilation

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Abstract

A spin-annihilation technique for a single determinant formed from Kohn–Sham orbitals is described for the calculation of excited state singlet energies. This procedure accurately calculates the $1^1B_u \leftarrow 1^1A_g$ vertical transition for *s*-trans-1,3-butadiene using the Becke–Lee–Yang Parr (BLYP) functional. For this system, extrapolating from triplet and 50:50 B_u state energies gives poor results at either the UHF or BLYP levels; spin-annihilated Hartree–Fock theory is similarly unsuccessful.

1. Introduction

Spin annihilation is often used to improve determinantal wavefunctions that are not eigenfunctions of the total spin operator, and is frequently used in connection with unrestricted Hartree–Fock (UHF) theory. However, in the formalism of density functional theory (DFT) electronic energies are calculated not from a determinantal wavefunction, but rather from an electronic (or spin-) density. This density is usually expressed by means of orbitals, the Kohn–Sham (KS) orbitals, which to a casual observer appear similar to Hartree–Fock orbitals. It must be kept in mind that these KS orbitals are purely a mathematical construct to facilitate solution of the KS self-consistent field (SCF) procedure. With such a formal perspective, a many-electron wavefunction is not defined in DFT, and spin-annihilation technology has no applicability.

However, one may take a somewhat different view of the KS SCF methodology. In particular, one may regard it as a method to generate approximate molecular orbitals (MOs). They differ from HF MOs

insofar as the exact exchange operator in the Hartree–Fock (HF) Hamiltonian has been modified in some rational fashion based on properties of an inhomogeneous electron gas. These orbitals are then often used in a manner more typically associated with MOs derived from HF or configuration interaction calculations. For instance, Löwdin [1] has discussed the relationship between $X\alpha$ [2] MOs and natural orbitals. More recently, Duffy et al. [3] have discussed the use of KS orbitals to approximate Dyson orbitals in calculations of electron-momentum-spectroscopy cross sections. Extending this philosophy, the KS MOs may be employed to form a determinantal ‘wavefunction’ wherefrom expectation values for various one- and two-electron properties may be calculated. This was done by Slater [4], and later more explicitly by Ziegler et al. [5], in discussions concerning multiplet energies for excited electronic configurations.

By the variational nature of the HF procedure, it is clear that if a conventional Schrödinger Hamiltonian is used the Kohn–Sham determinant will not provide as good an expectation value of the elec-

tronic energy as the HF determinant does. However, for the evaluation of other quantities it is of interest to determine whether a determinant formed from KS orbitals produces molecular properties that are superior to the HF determinant, and what effect spin annihilation will have on those properties.

In this spirit, we have defined a spin-projected DFT electronic energy in a fashion similar to that more conventionally associated with unrestricted Hartree–Fock (UHF) theory. Our generalization allows for an obvious extension to wavefunctions obtained from hybrid DFT/HF operators, like the popular B3LYP operator [6,7].

This Letter describes spin annihilation of DFT wavefunctions to calculate properties for excited-state singlet energies (the theory is generalizable to other multiplets under appropriate conditions). The theory is described in Section 2 and the methods in Section 3. To illustrate the utility of the method, calculation of the first excited singlet and triplet energies of $B_{u,s}$ -trans-1,3-butadiene (corresponding to a $\pi \rightarrow \pi^*$ promotion) is performed in Section 4. Some brief conclusions may be found in Section 5.

2. Theory

2.1. General

In 1964, Hohenberg and Kohn proved that for the non-degenerate ground state of a system the energy was calculable as a functional of the electronic probability density [8]. Gunnarsson and Lundqvist later extended this proof to include the lowest energy configuration within each irreducible representation of the molecular point group [9]. No formal prescription exists, however, for calculating the energies of higher-lying multiplets.

2.2. Sum method

Ziegler et al. [5] illustrated that excited-state singlet energies could be estimated by the sum method (originally referred to by Slater as the statistical exchange approximation [4]) in spin-polarized density functional theory (DFT) calculations under certain circumstances. In particular, for a system in which all orbitals are doubly occupied save for the

two highest orbitals (which are singly occupied), the $S_z = 1$ triplet configuration is

$${}^3\Psi_1 = [\varphi_a(1)\varphi_b(2) - \varphi_a(2)\varphi_b(1)][\alpha(1)\alpha(2)], \quad (1)$$

where 1 and 2 are the indices of the unpaired electrons of spin α occupying orbitals φ_a and φ_b (for simplicity in this and following expressions, the doubly occupied orbitals are not included and normalization is assumed). When the orbital occupation is specified identically except that one α spin is changed to be β , the resulting configuration is

$${}^{50:50}\Psi = [\varphi_a(1)\alpha(1)\varphi_b(2)\beta(2) - \varphi_a(2)\alpha(2)\varphi_b(1)\beta(1)]. \quad (2)$$

The 50:50 superscript emphasizes that this configuration is an equal combination of the open-shell singlet

$${}^1\Psi = [\varphi_a(1)\varphi_b(2) + \varphi_a(2)\varphi_b(1)] \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (3)$$

and the $S_z = 0$ triplet

$${}^3\Psi_0 = [\varphi_a(1)\varphi_b(2) - \varphi_a(2)\varphi_b(1)] \times [\alpha(1)\beta(2) + \alpha(2)\beta(1)] \quad (4)$$

so long as the two pure spin states are characterized by the same spatial orbitals.

When the Hamiltonian contains no spin-dependent terms, the separation

$$\begin{aligned} \langle {}^{50:50}\Psi | H | {}^{50:50}\Psi \rangle \\ = \frac{1}{2}(\langle {}^3\Psi_0 | H | {}^3\Psi_0 \rangle + \langle {}^1\Psi | H | {}^1\Psi \rangle) \end{aligned} \quad (5)$$

may be accomplished. Noting that in the absence of an external magnetic field the triplet states are degenerate, one may estimate the energy of the open-shell singlet from the expectation value of the Hamiltonian operating on the configurations of Eqs. (1) and (2). Ziegler et al. emphasize that the approximation is limited to cases where the triplet and 50:50 states are defined by single determinantal wavefunctions [5].

2.3. Spin annihilation

The sum method described above has also been explored for UHF theory, and its limitations are well

known. An alternative approach within the context of UHF theory is to apply a spin annihilation operator to the 50:50 determinant. The annihilation operator A_{s+1} is defined by [10]

$$A_{s+1} = \frac{S^2 - (s+1)[(s+1)+1]}{s(s+1) - (s+1)[(s+1)+1]}, \quad (6)$$

where S is the total spin operator, s is the desired total spin, and $s+1$ is the contaminant (next highest) spin state to be annihilated. For the following discussion, Ψ^0 is taken to be the 50:50 wavefunction described by Eq. (2) and $s=0$. The annihilated UHF energy may be calculated as [11,12]

$$E_{\text{PUHF}} = \langle \Psi^0 | H | \Psi^0 \rangle + \frac{\sum_i \langle \Psi^0 | H | \Psi^i \rangle \langle \Psi^i | A_{s+1} | \Psi^0 \rangle}{\langle \Psi^0 | A_{s+1} | \Psi^0 \rangle}. \quad (7)$$

With a UHF wavefunction satisfying Brillouin's theorem the summation runs over only double excitations; evaluation of the denominator similarly requires no consideration of higher excitations. Annihilation of higher spin contaminants may be accomplished by generalization of A_{s+1} to the full projection operator P_s , but this comes at the expense of making evaluation of the denominator in a generalized Eq. (7) more computationally demanding [10,12].

Extension of this approach to DFT is straightforward, provided one accepts the formation of a determinantal wavefunction from the KS orbitals, in particular,

$$E_{\text{PDFT}} = {}^{50:50}E_{\text{DFT}} + \frac{\sum_i \langle \Psi_{\text{KS}}^0 | H | \Psi_{\text{KS}}^i \rangle \langle \Psi_{\text{KS}}^i | A_{s+1} | \Psi_{\text{KS}}^0 \rangle}{\langle \Psi_{\text{KS}}^0 | A_{s+1} | \Psi_{\text{KS}}^0 \rangle}. \quad (8)$$

The energy of the 50:50 state is calculated in the conventional way, i.e. according to the DFT energy expression. The spin-annihilation correction, however, is calculated using matrix elements of the Schrödinger Hamiltonian and the spin-annihilation operator expressed in the KS MO basis. One consequence of using the KS MO basis is that Brillouin's theorem no longer guarantees single-excitation ma-

trix elements to be zero. However, when the KS orbitals are similar to the HF orbitals, as is quite typical, one may reasonably expect the contribution from single excitations to be small. An upper bound to any individual single excitation contribution may be estimated from

$$|z| = \max \left\{ \left| [\mathbf{F}_\alpha^{\text{KS}}]_{ai} [\mathbf{c}_\alpha^\dagger \mathbf{S} \mathbf{c}_\beta]_{ai} \right| + \left| [\mathbf{F}_\beta^{\text{KS}}]_{ai} [\mathbf{c}_\beta^\dagger \mathbf{S} \mathbf{c}_\alpha]_{ai} \right| \right\}, \quad (9)$$

where a and i are matrix indices referring to occupied and virtual orbitals, respectively, \mathbf{F}^{KS} is the Fock matrix in the KS MO basis, \mathbf{S} is the atomic orbital (AO) overlap matrix, and \mathbf{c}_α and \mathbf{c}_β are the alpha and beta coefficient matrices for the KS orbitals in the AO basis. Similarly, an estimate of the overall magnitude of the total singles contribution is given by

$$\bar{z} = \sum_{a,i} \left\{ [\mathbf{F}_\alpha^{\text{KS}}]_{ai} [\mathbf{c}_\alpha^\dagger \mathbf{S} \mathbf{c}_\beta]_{ai} + [\mathbf{F}_\beta^{\text{KS}}]_{ai} [\mathbf{c}_\beta^\dagger \mathbf{S} \mathbf{c}_\alpha]_{ai} \right\}. \quad (10)$$

For the case of *s*-trans-1,3-butadiene discussed below, z and \bar{z} are 0.01 and -0.06 eV, respectively. This places the contribution from single-excitation matrix elements essentially within the rounding errors of the $1^1\text{B}_u \leftarrow 1^1\text{A}_g$ transition energies reported below. There is no reason, however, to expect this to be true in every case, and it is obviously straightforward to more formally include singles when appropriate.

3. Methods

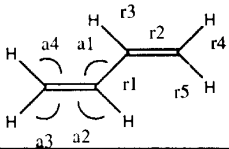
Molecular geometries of the closed-shell singlet (and triplet) states were fully optimized using the cc-pVDZ basis set [13] at the UHF, B3LYP, and BLYP levels of theory. The DFT functionals incorporate the gradient-corrected exchange functional of Becke [14] and the gradient-corrected correlation functional of Lee, Yang, and Parr [15]. Relative energies of all states were calculated at the same levels of theory using the cc-pVTZ basis set [13]. Vertical excitation energies were calculated for closed-shell singlet geometries. Closed-shell singlet and triplet geometries were verified as local minima

by analytic frequency calculations in all cases. All calculations were accomplished using the GAUSS-
IAN 92/DFT suite of programs [16].

4. Results

Optimized geometrical parameters for the C_{2h} *s*-trans conformer of 1,3-butadiene are provided in Table 1. There is little difference between the geometries calculated at different levels of theory with two exceptions: the C=C double bonds are about 0.03 Å longer at the BLYP level than at the UHF level for the 1^1A_g state and the C–C single bond is about 0.05 Å longer at the BLYP level than at the UHF level for the 1^3B_u state. This is consistent with DFT's tendency to predict slightly longer C–C bonds

Table 1
Optimized geometrical parameters for C_{2h} *s*-trans-1,3-butadiene



State/parameter	UHF	B3LYP	BLYP
1^1A_g			
r_1 (Å)	1.468	1.459	1.463
r_2 (Å)	1.326	1.343	1.355
r_3 (Å)	1.085	1.097	1.104
r_4 (Å)	1.082	1.092	1.099
r_5 (Å)	1.083	1.094	1.101
a_1 (deg)	124.1	124.4	124.6
a_2 (deg)	119.5	119.3	119.2
a_3 (deg)	121.5	121.5	121.5
a_4 (deg)	121.5	121.4	121.4
1^3B_u			
r_1 (Å)	1.333	1.361	1.376
r_2 (Å)	1.469	1.456	1.462
r_3 (Å)	1.086	1.097	1.104
r_4 (Å)	1.080	1.091	1.097
r_5 (Å)	1.082	1.092	1.099
a_1 (deg)	124.6	125.0	125.2
a_2 (deg)	116.5	116.8	116.7
a_3 (deg)	120.7	120.8	120.8
a_4 (deg)	120.7	120.6	120.7

Table 2
 $\langle S^2 \rangle$ values for different electronic states of C_{2h} *s*-trans-1,3-butadiene

State	UHF	B3LYP	BLYP
1^3B_u	2.021	2.006	2.005
$50:50^3B_u$	1.005	1.001	1.000
1^1B_u	0.036	0.004	0.002

in general [7,17,18]. Table 2 presents $\langle S^2 \rangle$ values for the triplet, 50:50, and spin-annihilated singlet states. While by no means severe, contamination from quintet and higher states is considerably larger for the UHF wavefunctions than for the B3LYP or BLYP wavefunctions. This tendency for DFT wavefunctions to exhibit minimal spin contamination has been noted elsewhere [19–21].

Table 3 presents the relative energies of the 1^1A_g , 1^3B_u , and 1^1B_u states calculated for the ground-state geometry, i.e. corresponding to vertical excitation. Comparison to experiment [22–24] indicates that all levels of theory do well in predicting the relative energy of the 1^3B_u state. This is at first glance unsurprising since both the 1^1A_g state and the 1^3B_u state are well described by single-determinantal wavefunctions. However, while not indicated in Table 3, we note that the relative energy of the 1^3B_u state at its *optimized* geometry is 1.8, 2.6, and 2.6 eV at the UHF, B3LYP, and BLYP levels, respectively. This large discrepancy between UHF and DFT, which is probably related to the sizable difference between the two theories for the predicted length of the C–C single bond, cannot be resolved by the present spectral data. Given the results described below, however, it appears likely that the DFT relative energies and structures are the more trustworthy.

At the UHF level, the sum method predicts considerably too high an energy for the 1^1B_u state, arguably because of the failure to account for significant non-dynamic correlation in the open-shell singlet. Spin annihilation at the UHF level corrects the relative energy in the proper direction, but the error remains on the order of 1 eV. At the BLYP level, on the other hand, the sum method predicts too low an energy for the 1^1B_u state. Spin annihilation, however, predicts an excitation energy in excellent agreement with experiment. This number is moreover in

Table 3

Absolute energy (au) of 1^1A_g ground state and relative energies (eV) for excited states of C_{2h} *s*-trans-1,3-butadiene calculated at the ground state geometry

State	UHF	B3LYP	BLYP	Exp.
1^1A_g	-154.97829	-156.05526	-155.97087	
1^3B_u	3.0	3.2	3.1	3.2 [22]
${}^{3,5,7}B_u$	5.6	4.2	3.8	
1^1B_u				
stat. exch.	8.2	5.1	4.5	
spin annihil.	7.1	6.3	6.1	5.9 [22–24]

close agreement with the best available results from multireference configuration interaction (6.2 eV) [25] and perturbation theory (6.2 eV) [26]. The broadness of the observed absorption band together with the general tendency for theoretical predictions to overestimate the energy of the 1^1B_u state has been interpreted to imply that the maximal Franck–Condon overlap (and by inference the absorption maximum) may correspond to an excitation energy roughly 0.3 eV lower than vertical excitation from the equilibrium geometry [25,27]. Serrando-Andrés et al. [26], however, ascribe the theoretical discrepancies to too much Rydberg character in reference wavefunctions, which fails to be removed by correlation treatments.

The B3LYP functional also performs well overall with respect to spin annihilation, although the incorporation of some Hartree–Fock exchange increases the energy of the 1^1B_u state marginally. While this warrants further investigation, it appears that wavefunctions derived from pure DFT functionals will be more useful for spin annihilation purposes. Of the three Hamiltonians, the sum method works best for the B3LYP functional (although it continues to considerably underestimate the 1^1B_u state energy), but it is clear that this is simply a fortuitous cancellation of errors upon inclusion of a small amount of Hartree–Fock exchange.

We have examined this methodology for the prediction of excited-state singlet energies in several other molecules, including methylene, silylene, formaldehyde, formalimine, diazene [28], and *s*-cis-1,3-butadiene. For most of these cases, the sum method delivers reasonable results; spin annihilation gives either similar or improved state energies in every case. These results will be reported in detail elsewhere.

5. Conclusions

We have described an extension of spin annihilation to DFT (or, more rigorously, approximate single-determinantal Hartree–Fock) wavefunctions. This methodology agrees well with both experiment and multiconfigurational treatments with respect to the energy of the 1^1B_u excited state of *s*-trans-1,3-butadiene. The time required to accomplish the calculation is only slightly more than that required for a standard DFT calculation, that being considerably faster than more rigorous multiconfiguration calculations. Although developed here only for annihilation of the $s+1$ spin contaminant, this theory is easily generalized to more complete projection schemes like those presently in use for unrestricted many-body perturbation theory [29,30].

The spin-annihilation formalism is a clear improvement upon the sum method for calculation of the 1^1B_u state energy of *s*-trans-1,3-butadiene. Furthermore, while the sum method only permits calculation of an excited state energy, spin annihilation improves the DFT wavefunction and expectation values for observables other than the energy may also be calculated therefrom. We have noted elsewhere that DFT performs well in the calculation of singlet–triplet energy differences between closed-shell singlets and triplets characterized by significant non-dynamic correlation effects [21,31–33]. Spin annihilation continues to expand the range of multiplet comparisons that may be accomplished using DFT.

References

- [1] P.-O. Löwdin, Phys. Rev. 97 (1955) 1474.
- [2] J.C. Slater, Phys. Rev. 81 (1951) 385.

- [3] P. Duffy, D.P. Chong, M.E. Casida and D.R. Salahub, *Phys. Rev. A* 50 (1994) 4707.
- [4] J.C. Slater, *Advan. Quantum Chem.* 6 (1972) 1.
- [5] T. Ziegler, A. Rauk and E.J. Baerends, *Theoret. Chim. Acta* 43 (1977) 261.
- [6] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [7] B.G. Johnson, P.M.W. Gill and J.A. Pople, *J. Chem. Phys.* 98 (1993) 5612.
- [8] P. Hohenberg and W. Kohn, *Phys. Rev. B* 3 (1964) B864.
- [9] O. Gunnarsson and B.I. Lundqvist, *Phys. Rev. B* 13 (1976) 4274, 15 (1978) 6006 (E).
- [10] P.-O. Löwdin, *Phys. Rev.* 97 (1955) 1509.
- [11] T. Amos and G.G. Hall, *Proc. Roy. Soc. A* 263 (1961) 483.
- [12] I. Mayer, *Advan. Quantum Chem.* 12 (1980) 189.
- [13] T.H. Dunning, *J. Chem. Phys.* 90 (1989) 1007.
- [14] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [15] C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [16] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart, and J.A. Pople, *GAUSSIAN 92/DFT, Revision G.1* (Gaussian, Pittsburgh, 1993).
- [17] J. Andzelm and E. Wimmer, *J. Chem. Phys.* 96 (1992) 1280.
- [18] C.W. Murray, G.J. Laning, N.C. Handy and R.D. Amos, *Chem. Phys. Letters* 199 (1992) 551.
- [19] J. Baker, A. Scheiner and J. Andzelm, *Chem. Phys. Letters* 216 (1993) 380.
- [20] C.W. Murray, N.C. Handy and R.D. Amos, *J. Chem. Phys.* 98 (1993) 7145.
- [21] C.J. Cramer, F.J. Dulles and D.E. Falvey, *J. Amer. Chem. Soc.* 116 (1994) 9787.
- [22] O.A. Mosher, W.M. Flicker and A. Kuppermann, *J. Chem. Phys.* 59 (1973) 6502.
- [23] R. McDiarmid, *J. Chem. Phys.* 64 (1976) 514.
- [24] J.P. Doering and R. McDiarmid, *J. Chem. Phys.* 73 (1980) 3617.
- [25] R.J. Cave and E.R. Davidson, *J. Phys. Chem.* 91 (1987) 4481.
- [26] L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, R. Lindh and B.O. Roos, *J. Chem. Phys.* 98 (1993) 3151.
- [27] S. Shih, R.J. Buenker and S.D. Peyerimhoff, *Chem. Phys. Letters* 16 (1972) 244.
- [28] M.H. Lim, S.E. Worthington, F.J. Dulles and C.J. Cramer, in: *Density-Functional Methods in Chemistry*, ACS Symp. Ser., B.B. Laird, T. Ziegler, and R. Ross (American Chemical Society, Washington), submitted for publication.
- [29] H.B. Schlegel, *J. Phys. Chem.* 92 (1988) 3075.
- [30] P.J. Knowles and N.C. Handy, *J. Phys. Chem.* 92 (1988) 3097.
- [31] A. Ghosh and J. Almlöf, *Chem. Phys. Letters* 213 (1993) 519.
- [32] C.J. Cramer, F.J. Dulles, J.W. Storer and S.E. Worthington, *Chem. Phys. Letters* 218 (1994) 387.
- [33] C.J. Cramer and S.E. Worthington, *J. Phys. Chem.* 99 (1995) 1462.