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On the performance of density functional theory for symmetry-breaking problems

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Abstract

Density functional theory (DFT) has been applied to three open-shell molecules (NO_3, O_4^+, and O_2^+) for which the unrestricted Hartree–Fock (UHF) wavefunction breaks spatial symmetry. In contrast to Hartree–Fock, all of the standard DFT methods we employed yielded symmetric densities for each of the molecules considered. Symmetry-broken solutions were obtained with DFT only when we used hybrid functionals including unusually large fractions of Hartree–Fock exchange. The exchange functional seems more important than the correlation functional in determining whether symmetry is preserved or broken.

1. Introduction

The possibility that an approximate wavefunction can sometimes attain a lower energy (and become better in a variational sense) by breaking symmetries present in the exact wavefunction has been called the 'symmetry dilemma' by Löwdin [1]. When the wavefunction breaks spatial symmetry (i.e., when the electronic wavefunction fails to transform as an irreducible representation of the molecular point group [2]), molecular property predictions become suspect. For example, geometry optimizations may yield artifactual lower-symmetry structures, spurious dipole moments may arise, and the computation of reliable vibrational frequencies becomes extremely difficult [3–7].

A standard approach to symmetry-breaking problems is the use of multiconfigurational self-consistent-field (MCSCF) or complete active space self-consistent-field (CASSCF) wavefunctions, which allow the proper mixings of competing, near-degenerate valence-bond structures ('non-dynamical correlation') if a sufficiently large active space is used [3,8–10]. Non-orthogonal configuration interaction [10,11] represents a similar approach. An alternative strategy is to use Brueckner orbital coupled-cluster methods [7,12], which have been found empirically to resist spatial symmetry breaking in several cases [5,7,13,14]. These methods succeed because the the effects of electron correlation are incorporated into the solution of the molecular orbitals, and part of the modeling of electron correlation in coupled-cluster approaches describes the non-dynamical correlation required to avoid symmetry breaking. Since density functional theory (DFT) also includes electron correlation effects during the optimization of the Kohn–Sham orbitals, this raises the obvious question of how DFT performs for symmetry-breaking cases. A

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review of the 'symmetry dilemma' for DFT in general terms and an alternative interpretation of spin DFT which attempts to avoid this dilemma has been given by Perdew et al. [15].

Although DFT has been applied in several chemical applications involving molecules prone to symmetry breaking [11,16–18], there has been little systematic work on the performance of DFT for symmetry-breaking molecules. One exception is a stability analysis of the closed-shell Kohn–Sham equations by Bauernschmitt and Ahlrichs [19]. These authors analyzed the dissociation curves of H_2, N_2, F_2, and C_2H_4 and found that the onset of symmetry breaking (i.e., the geometry at which a symmetry-broken solution becomes lower in energy than the symmetric solution) was in the order

$$R_{\mathrm{crit}}: \quad \mathrm{RHF} < \mathrm{B3LYP} < \mathrm{BP} < \mathrm{S\text{-}VWN}. \tag{1}$$

Although this study was limited to closed-shell molecules, another recent study by Bally and Sastry [20] finds that DFT breaks symmetry at much larger internuclear distances than unrestricted Hartree–Fock (UHF) for He_2^+.

The Hartree–Fock wavefunction of almost any molecule will eventually break symmetry if bonds are broken. Additionally, there are many radicals for which restricted open-shell Hartree–Fock (ROHF) breaks symmetry even near the equilibrium geometry. In these cases, the use of UHF often overcomes symmetry breaking near equilibrium (e.g., LiO_2 [3] and $HOOH^+$). Here, we consider $^2A'_2$ NO_3 [13,14], $^4B_{1g}$ O_4^+ [5,7,10], and $^2\Pi_g$ O_2^+, which represent the most pathological case, where even the UHF wavefunction breaks spatial symmetry near the equilibrium geometry.

2. Calculations

We used the geometry of Stanton et al. [21] for NO_3, Sherrill et al. [7] for O_4^+, and Huber and Herzberg [22] for O_2^+. Employing the 6-31G* basis of Pople and co-workers [23,24], we started from the symmetry-broken UHF guess orbitals and applied various popular DFT methods: the local spin density approximation with Slater exchange [25] and the correlation functional of Vosko, Wilk, and Nusair [26] (denoted S-VWN); the generalized gradient approximation (GGA) methods which pair Becke's 1988 exchange functional [27] with the correlation functionals of Lee, Yang, and Parr [28] (BLYP) and of Perdew [29] (BP86), along with the PW91 method of Perdew [30]; and the hybrid [31] gradient-corrected functionals which mix in Hartree–Fock exchange, B3LYP [32] and B3PW91 [31]. Additionally, we have used the EDF1 method of Adamson et al. [33] in conjunction with its associated 6-31+G* basis set. To gain additional insight, we have also employed the unusual combination of pure Hartree–Fock exchange with the LYP correlation functional, which we denote HFLYP. Spatial symmetry breaking was diagnosed by the presence of non-equivalent Mulliken atomic charges for atoms which are symmetry equivalent (equivalent charges agree to at least 0.0001 a.u. when we use a fine grid with 100 radial nodes and 302 angular points per node). Computations were performed using the Q-Chem program package [34].

Tables 1–3 give the total energies, expectation values of $\hat{S}^2$, and Mulliken charges for NO_3, O_4^+, and O_2^+. Each entry in these tables is labeled either 'sym' or 'asym', indicating that the charges are symmetric or asymmetric for the symmetry-equivalent atoms. The lowest-energy UHF solution is asymmetric in each case (for NO_3 and O_4^+, we found two distinct asymmetric solutions below the symmetric solution). For each molecule, all of the popular DFT methods considered here, namely, BLYP, B3LYP, BP86, PW91, B3PW91, S-VWN, and EDF1, all yield symmetric solutions even when given the symmetry broken UHF solutions as an initial guess (the EDF1 Mulliken charges for NO_3 differ substantially from the other DFT charges simply because EDF1 uses the 6-31+G* basis rather than the 6-31G* basis). However, the unconventional procedure of using pure Hartree–Fock exchange in conjunction with the LYP correlation functional, denoted HFLYP, *does* break symmetry; indeed, it yields solutions which mimic the UHF solutions as judged by the charges and by $\langle \hat{S}^2 \rangle$. This suggests that the success of the standard DFT methods lies not in the inclusion of correlation but in the use of non-Hartree–Fock exchange, a result consistent with the ordering in Eq. (1).

Further support for this idea is given in Table 4, in which the components of the UHF and B3LYP

Table 1
Total energies, spin expectation values, and Mulliken charges (a.u.) for NO_3 [a]

Method		Energy	$\langle \hat{S}^2 \rangle$	Charges			
				N	O_1	O_2	O_3
UHF	sym	−278.757 840	0.783	0.8970	−0.2990	−0.2990	−0.2990
UHF	asym	−278.774 819	0.800	0.8445	−0.0867	−0.3789	−0.3789
UHF	asym	−278.811 463	1.348	0.6901	−0.3420	−0.1740	−0.1740
BLYP	sym	−280.218 687	0.752	0.7268	−0.2423	−0.2423	−0.2423
B3LYP	sym	−280.100 057	0.755	0.7578	−0.2526	−0.2526	−0.2526
BP86	sym	−280.261 211	0.752	0.7250	−0.2416	−0.2416	−0.2416
PW91	sym	−280.168 807	0.752	0.6567	−0.2189	−0.2189	−0.2189
B3PW91	sym	−280.105 925	0.754	0.7606	−0.2535	−0.2535	−0.2535
EDF1	sym	−280.324 239	0.753	0.0107	−0.0036	−0.0036	−0.0036
S-VWN	sym	−278.248 418	0.751	0.6514	−0.2171	−0.2171	−0.2171
HFLYP	sym	−279.889 068	0.779	0.8800	−0.2933	−0.2933	−0.2933
HFLYP	asym	−279.903 040	0.791	0.8275	−0.0839	−0.3718	−0.3718
HFLYP	asym	−279.935 785	1.303	0.6915	−0.3481	−0.1717	−0.1717

[a] The DZP QRHF CCSD D_{3h} optimized geometry $r_{NO} = 1.236$ Å of Stanton et al [21]. was used, with a 6-31G* basis set (6-31 + G* for EDF1).

energies are evaluated using the converged asymmetric and symmetric UHF densities for O_2^+. For both UHF and B3LYP, the one-electron and exchange terms favor the asymmetric solution while the Coulomb term favors the symmetric solution. The correlation term in B3LYP also favors the symmetric solution, but this contribution is very small compared to the others. Most importantly, for B3LYP the preference of the exchange term for the asymmetric solution is substantially reduced from that for UHF, making the overall driving force for broken symmetry smaller than the competing (Coulomb) driving force for a symmetric solution. Similar results were obtained for NO_3 and O_4^+. As an alternative test of the role of exchange versus correlation functionals in preserving or breaking spatial symmetry, we again

Table 2
Total energies, spin expectation values, and Mulliken charges (a.u.) for O_4^+ [a]

Method		Energy	$\langle \hat{S}^2 \rangle$	Charges			
				O_1	O_2	O_3	O_4
UHF	sym	−298.746 531	3.788	0.2500	0.2500	0.2500	0.2500
UHF	asym	−298.750 925	3.828	0.0541	0.0541	0.4459	0.4459
UHF	asym	−298.765 336	4.330	0.5721	0.4105	0.0287	−0.0114
BLYP	sym	−300.244 604	3.754	0.2500	0.2500	0.2500	0.2500
B3LYP	sym	−300.110 121	3.758	0.2500	0.2500	0.2500	0.2500
BP86	sym	−300.268 963	3.754	0.2500	0.2500	0.2500	0.2500
PW91	sym	−300.173 451	3.753	0.2500	0.2500	0.2500	0.2500
B3PW91	sym	−300.101 922	3.757	0.2500	0.2500	0.2500	0.2500
S-VWN	sym	−298.138 772	3.753	0.2500	0.2500	0.2500	0.2500
EDF1	sym	−300.332 872	3.755	0.2500	0.2500	0.2500	0.2500
HFLYP	sym	−299.866 543	3.784	0.2500	0.2500	0.2500	0.2500
HFLYP	asym	−299.869 735	3.787	0.0656	0.0656	0.4344	0.4344
HFLYP	asym	−299.876 056	4.257	0.5490	0.4339	0.0224	−0.0053

[a] The 6-31G* UHF CCSD D_{2h} equilibrium geometry $r_{OO} = 1.1737$, $r_{cm} = 2.3792$ Å from Sherrill et al. [7] was used, along with the 6-31G* basis set (6-31 + G* for EDF1).

Table 3
Total energies, spin expectation values, and Mulliken charges (a.u.) for O_2^+ [a]

Method		Energy	$\langle \hat{S}^2 \rangle$	Charges	
				O_1	O_2
UHF	sym	−149.158 014	0.762	0.5000	0.5000
UHF	asym	−149.166 715	1.112	0.4588	0.5412
BLYP	sym	−149.864 799	0.751	0.5000	0.5000
B3LYP	sym	−149.801 194	0.752	0.5000	0.5000
BP86	sym	−149.874 618	0.751	0.5000	0.5000
PW91	sym	−149.827 093	0.751	0.5000	0.5000
B3PW91	sym	−149.797 404	0.752	0.5000	0.5000
S-VWN	sym	−148.804 373	0.751	0.5000	0.5000
EDF1	sym	−149.910 352	0.751	0.5000	0.5000
HFLYP	sym	−149.700 255	0.761	0.5000	0.5000
HFLYP	asym	−149.704 646	1.022	0.4743	0.5257

[a] The experimental equilibrium geometry $r_e = 1.1164$ Å from Huber and Herzberg [22] was used, along with the 6-31G* basis set (6-31 + G* for EDF1).

considered O_2^+ and applied a hybrid functional mixing Hartree–Fock exchange with Becke88 exchange in varying proportions, both with and without the LYP correlation functional. Fig. 1 demonstrates that at about 63% Hartree–Fock exchange, the lowest energy solution becomes symmetry broken. As larger fractions of Hartree–Fock exchange are mixed in, the orbitals polarize further towards asymmetry. Furthermore, in accordance with Table 4 the LYP functional delays the onset of symmetry breaking to a mixing of 72% Hartree–Fock exchange.

That exchange seems more important than correlation in determining the tendency to break or preserve symmetry in density functional theory may seem surprising at first. However, there is a very simple explanation for this observation. The correlation functionals in DFT have been created to model *dynamical correlation* – arising from short-range instantaneous electron–electron repulsions – rather than *non-dynamical correlation* arising from the long-range interaction between near-degenerate configurations occurring in symmetry-breaking problems. Furthermore, Becke has claimed that DFT exchange functionals simulate non-dynamical correlation to some degree [35]. He notes that for H_2, the exchange-correlation hole for a reference point near a nucleus is localized about that nucleus, reflecting ‘left-right’ or non-dynamical correlation. Due to their local nature, popular DFT exchange functionals yield localized exchange holes and hence ‘‘this implicit locality automatically and trivially (though crudely) mimics left-right correlation’’ [35]. Pure Hartree–

Table 4
Comparison of the energy terms of UHF and B3LYP evaluated at the converged symmetric (s) and asymmetric (a) UHF wavefunctions using a 6-31G* basis for O_2^+ at $r_e = 1.1164$ Å

Component	UHF			B3LYP		
	E_a	E_s	$E_a - E_s$	E_a	E_s	$E_a - E_s$
One-electron	−258.027952	−257.966901	−0.061051	−258.027952	−257.966901	−0.061051
Coulomb	94.482041	94.331134	0.150907	94.482041	94.331134	0.150907
Exchange	−15.957013	−15.858455	−0.098557	−15.916084	−15.848910	−0.067174
Correlation	n/a	n/a	n/a	−0.635526	−0.640523	0.004997
Total	−149.166715	−149.158014	−0.008701	−149.761311	−149.788991	0.027680

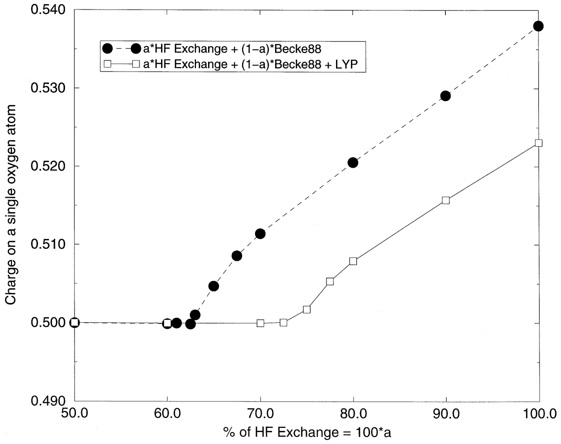

Fig. 1. Both symmetric and asymmetric solutions for O_2^+ (6-31G*) can be obtained by mixing Hartree–Fock exchange and Becke88 exchange in varying proportions. A charge of 1/2 on a single oxygen atom corresponds to a symmetric state, while deviations from 1/2 indicate an asymmetric solution. The LYP correlation functional provides a modest symmetry-preserving effect.

Fock exchange, by contrast, yields delocalized exchange holes in such circumstances and contains no description of non-dynamical correlation; hence, hybrid DFT methods will exhibit more delocalized exchange-correlation holes as greater fractions of Hartree–Fock exchange are incorporated, which may result in a less complete description of non-dynamical correlation and thus a greater tendency to break spatial symmetry. Note that there is no contradiction with the generally superior performance of hybrid DFT methods compared to pure DFT methods lacking Hartree–Fock exchange; for most molecules near equilibrium, unlike those considered here, non-dynamical correlation is unimportant.

3. Conclusions

We have provided empirical evidence that DFT methods tend to avoid artifactual spatial symmetry breaking in the equilibrium geometry region even when UHF fails. The DFT exchange functional seems to be more important than the correlation functional in providing this resistance to symmetry breaking, and hybrid functionals mixing in large fractions of Hartree–Fock exchange once again exhibit symmetry breaking. Of course the present results do not imply that DFT will always solve symmetry-breaking problems near equilibrium, and the same could be said of Brueckner coupled-cluster methods. Furthermore, even if a symmetric solution is obtained, this does not mean that vibrational frequencies are entirely free of the effects of symmetry breaking, because the higher-lying asymmetric solutions may interact strongly with the symmetric solution (the symmetric solution may exhibit near-zero eigenvalues in the molecular orbital Hessian) [3–6]. Nevertheless, based on the present results we expect that DFT methods are increasingly less likely to break spatial symmetry or yield anomalous vibrational frequencies as they incorporate smaller fractions of Hartree–Fock exchange.

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References

[1] P.O. Löwdin, Rev. Mod. Phys. 35 (1963) 496.
[2] E.R. Davidson, W.T. Borden, J. Phys. Chem. 87 (1983) 4783.
[3] W.D. Allen, D.A. Horner, R.L. DeKock, R.B. Remington, H.F. Schaefer, Chem. Phys. 133 (1989) 11.
[4] N.A. Burton, Y. Yamaguchi, I.L. Alberts, H.F. Schaefer, J. Chem. Phys. 95 (1991) 7466.
[5] L.A. Barnes, R. Lindh, Chem. Phys. Lett. 223 (1994) 207.
[6] T.D. Crawford, J.F. Stanton, W.D. Allen, H.F. Schaefer, J. Chem. Phys. 107 (1997) 10626.
[7] C.D. Sherrill, A.I. Krylov, E.F.C. Byrd, M. Head-Gordon, J. Chem. Phys. 109 (1998) 4171.
[8] L. Engelbrecht, B. Liu, J. Chem. Phys. 78 (1983) 3097.
[9] A.D. McLean, B.H. Lengsfield, J. Pacansky, Y. Ellinger, J. Chem. Phys. 83 (1985) 3567.
[10] R. Lindh, L.A. Barnes, J. Chem. Phys. 100 (1994) 224.
[11] P.Y. Ayala, H.B. Schlegel, J. Chem. Phys. 108 (1998) 7560.

[12] N.C. Handy, J.A. Pople, M. Head-Gordon, K. Raghavachari, G.W. Trucks, Chem. Phys. Lett. 164 (1989) 185.
[13] J.F. Stanton, J. Gauss, R.J. Bartlett, J. Chem. Phys. 97 (1992) 5554.
[14] T.D. Crawford, T.J. Lee, N.C. Handy, H.F. Schaefer, J. Chem. Phys. 107 (1997) 9980.
[15] J.P. Perdew, A. Savin, K. Burke, Phys. Rev. A 51 (1995) 4531.
[16] P.M. Kozlowski, G. Rauhut, P. Pulay, J. Chem. Phys. 103 (1995) 5650.
[17] E.F. Archibong, A. St-Amant, Chem. Phys. Lett. 284 (1998) 331.
[18] H.A. Duarte, E. Proynov, D.R. Salahub, J. Chem. Phys. 109 (1998) 26.
[19] R. Bauernschmitt, R. Ahlrichs, J. Chem. Phys. 104 (1996) 9047.
[20] T. Bally, G.N. Sastry, J. Phys. Chem. A 101 (1997) 7923.
[21] J.F. Stanton, J. Gauss, R.J. Bartlett, J. Chem. Phys. 94 (1991) 4084.
[22] K.P. Huber, G. Herzberg, Constants of Diatomic Molecules, Van Nostrand Reinhold, New York, 1979.
[23] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.
[24] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
[25] P.A.M. Dirac, Proc. Cam. Phil. Soc. 26 (1930) 376.
[26] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200.
[27] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[28] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[29] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.
[30] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[31] A.D. Becke, J. Chem. Phys. 98 (1993) 1372.
[32] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
[33] R.D. Adamson, P.M.W. Gill, J.A. Pople, Chem. Phys. Lett. 284 (1998) 6.
[34] B.G. Johnson, P.M.W. Gill, M. Head-Gordon, C.A. White, D.R. Maurice, T.R. Adams, J. Kong, M. Challacombe, E. Schwegler, M. Oumi, C. Ochsenfeld, N. Ishikawa, J. Florian, R.D. Adamson, J.P. Dombroski, R.L. Graham, A. Warshel, Q-Chem 1.1, Q-Chem, Inc., Export, PA, 1997.
[35] A.D. Becke, Exchange-correlation approximations in density-functional theory, in: D.R. Yarkony (Ed.), Modern Electronic Structure Theory, vol. 2, Advanced Series in Physical Chemistry, World Scientific, Singapore, 1995, pp. 1022–1046.