

LETTERS TO THE EDITOR

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COMMUNICATIONS

Some reasons not to use spin projected density functional theory

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Spin unrestricted calculations using density functional theory can yield wave functions with spin contamination. In conventional post Hartree–Fock calculations (such as Møller–Plesset perturbation theory), spin projection can ameliorate some of the problems caused by spin contamination. However, spin projection can seriously degrade the quality of potential energy surfaces calculated by density functional methods, just as spin projection can yield poor results for Hartree–Fock potential energy surfaces. © 1996 American Institute of Physics. [S0021-9606(96)03039-5]

In conventional *ab initio* electronic structure methods, unrestricted Hartree–Fock theory¹ (UHF) is convenient for treating radicals and exploring potential energy surfaces for open shell systems. However, spin unrestricted methods are not eigenfunctions of S^2 . Contamination of the wave function by higher energy, higher spin states can seriously distort potential energy surfaces, especially if electron correlation is added by perturbative methods. For unrestricted Møller–Plesset perturbation theory (UMPn), this problem can be partially overcome by spin projection and annihilation techniques.^{2–4} Density functional theory⁵ (DFT) is rapidly gaining favor as a method for exploring potential energy surfaces that is more accurate than Hartree–Fock theory but not much more expensive. Spin unrestricted methods are needed for a qualitatively correct treatment of surfaces for radicals and for homolytic bond cleavage. If the exact density functionals were known for the Schrödinger Hamiltonian, they would yield calculations without spin contamination since the exact wave functions are eigenfunctions of S^2 . However, the approximate DFT methods currently used are affected by spin contamination. If the contamination is large, the surface could be significantly distorted, and spin projection might improve its shape. Recently, it has been reported that spin projection improves the agreement with experiment for barrier heights calculated by spin unrestricted DFT methods.⁶ In this short note we explore the effect of spin projection on some simple bond dissociation potentials and come to the conclusion that one should not use spin projected DFT.

The calculation of S^2 for density functional methods is not entirely straightforward.⁷ In the noninteracting system, the DFT wave function is a Slater determinant of Kohn–Sham orbitals, and S^2 can be calculated by the same formula as for UHF. For the interacting system, S^2 can be computed from the two particle density, which can be written in terms

of one particle densities and hole functions.⁷ Examples given by Becke and co-workers⁷ indicate that the values for S^2 for the interacting system are slightly larger than for the noninteracting system, which are in turn larger than the exact values. For calculational simplicity, we use S^2 calculated for the noninteracting Kohn–Sham orbitals, keeping in mind that the correct S^2 for the interacting system could be larger.

One approach to spin projected UHF and Møller–Plesset perturbation theory (MPn) expands the projected wave function and energy in terms of a spin projection operator,^{8,9} \hat{P}_s , or annihilation operator, \hat{A}_{s+1} and excited determinants, ψ_i ,

$$\hat{P}_s = \prod_{k \neq s} [\hat{S}^2 - k(k+1)] / [s(s+1) - k(k+1)],$$

$$\hat{A}_{s+1} = [\hat{S}^2 - (s+1)(s+2)] / [s(s+1) - (s+1)(s+2)],$$

TABLE I. Comparison of S^2 for some radicals and open shell transition states.^a

Structure	UHF/6-31G(d)	BLYP/6-31G(d)	B3LYP/6-31G(d)
CN	1.1272	0.7536	0.7568
CO ⁺	0.9300	0.7586	0.7631
phenyl	1.4330	0.7551	0.7582
phenoxy	1.3876	0.7628	0.7913
benzyl-planar	1.3915	0.7594	0.7720
-perp.	0.7664	0.7532	0.7541
H+H ₂ CO ts	0.9494	0.7605	0.7718
H+C ₂ H ₂ ts	0.9987	0.7608	0.7695
HO+C ₂ H ₂ ts	1.1538	0.7636	0.7842
HO+C ₂ H ₄ ts	1.0449	0.7637	0.7864

^aComputed with the noninteracting formula at the UHF/6-31G(d) geometry.

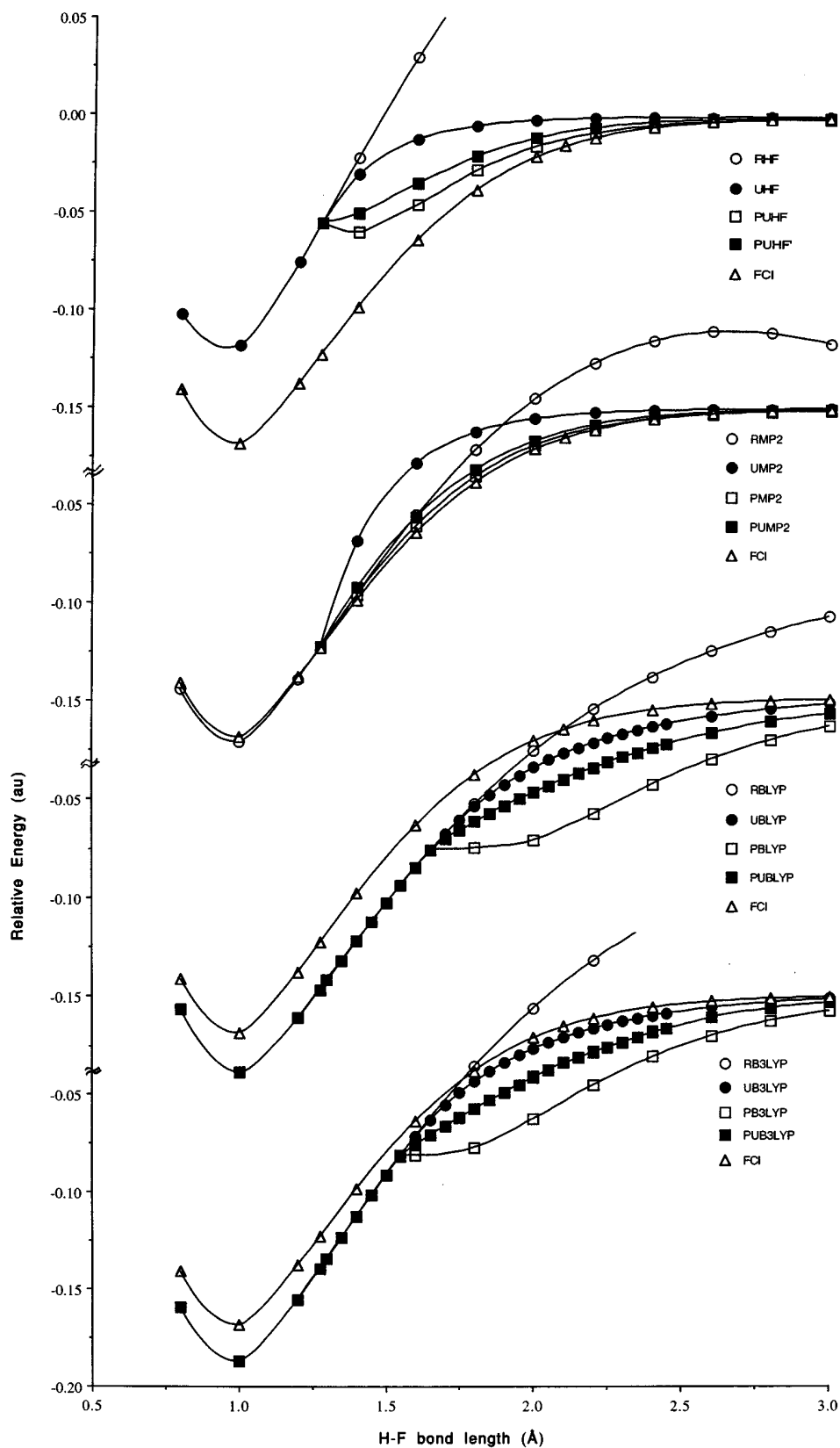


FIG. 1. Comparison of various levels of theory with full CI for the relative bond dissociation potential of hydrogen fluoride computed with the 6-31 G basis.

$$E_{\text{proj}} = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \sum_{i \neq 0} \langle \Psi_0 | \hat{H} | \psi_i \rangle \langle \psi_i | \hat{P}_s | \Psi_0 + \Psi_1 \dots \rangle / \langle \Psi_0 | \hat{P}_s | \Psi_0 + \Psi_1 \dots \rangle. \quad (1)$$

Almlöf and co-workers¹⁰ have suggested that the Kohn-Sham orbitals can be used to construct excited determinants and that the ordinary Schrödinger Hamiltonian can be used to compute the necessary matrix elements. As in Ref. 10, we

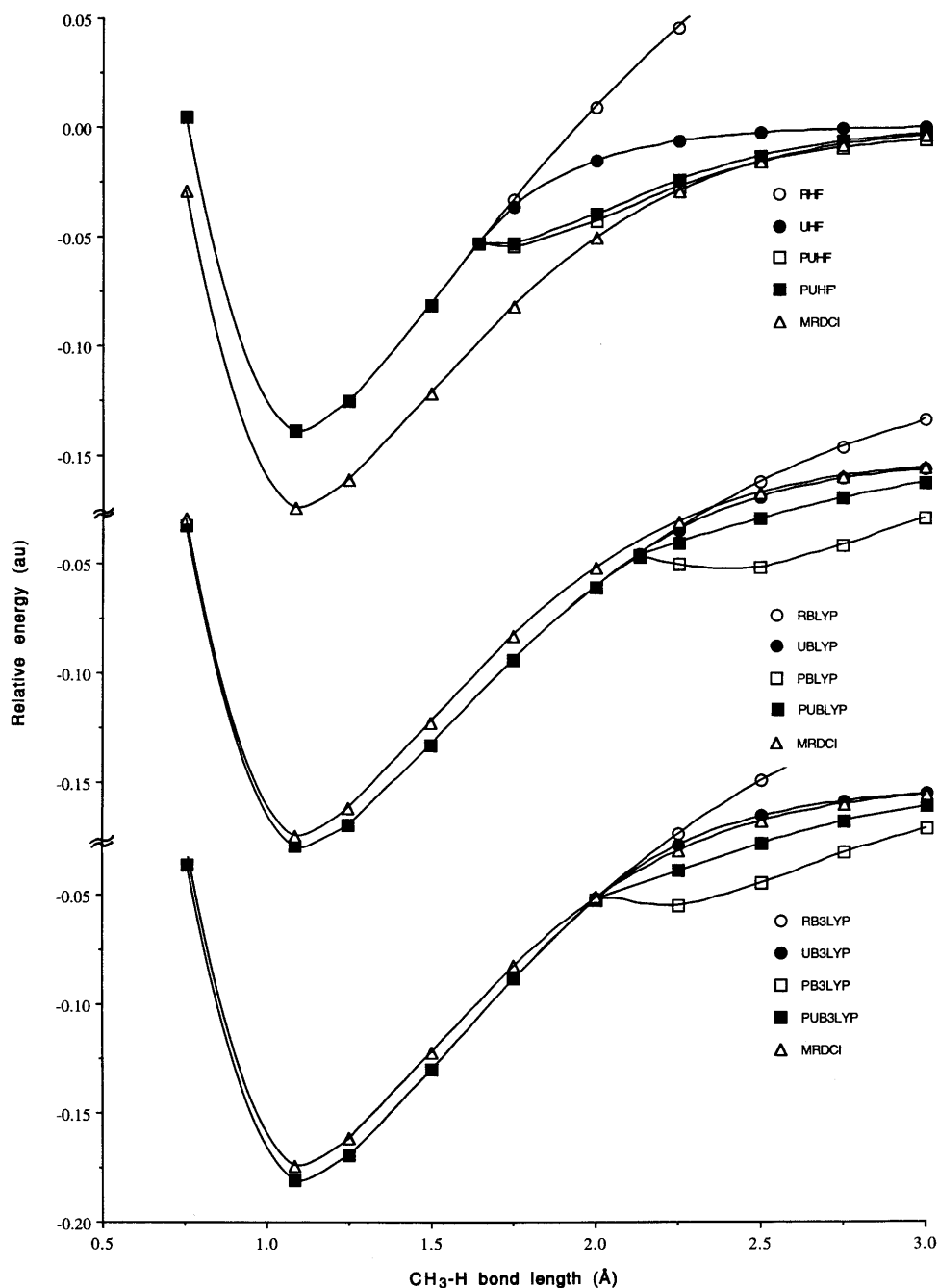


FIG. 2. Comparison of various levels of theory with MRDCI for the relative bond dissociation potential of methane computed with the 6-31G(d,p) basis.

approximate the spin projector by the single annihilator and restrict the sum to double excitations. The abbreviations PUHF, PMPn, PBLYP, and PBLYP are used for these projected energies in the present discussion.

An alternative, approximate formula expresses the spin-contaminated energy, E_c , and wave function, Ψ_c , in terms of spin pure states.¹¹ An explicit calculation of a higher spin state, Ψ_{s+1} , is used to estimate the contribution to the energy and $\langle S^2 \rangle$ of the spin contaminated calculation. Subtraction of the energy contribution of the higher spin state, E_{s+1} , from the spin contaminated energy, E_c , and renormalization yields an estimate of the energy of the desired pure spin state, E_s ,

$$\begin{aligned}\Psi_c &= (1-a)\Psi_s + a\Psi_{s+1}, \\ E_c &= (1-a)E_s + aE_{s+1}, \\ \langle S^2 \rangle_c &= (1-a)s(s+1) + a(s+1)(s+2), \\ a &= [\langle S^2 \rangle_c - s(s+1)] / 2(s+1), \\ E_s &= (E_c - aE_{s+1}) / (1-a).\end{aligned}\quad (2)$$

These approximate projected energies are designated by PUHF', PUMP2, PUBLYP, etc., in the present discussion. A third approximate method for reducing the effect of spin contamination is to project the density matrix during the SCF iterations,¹² but this approach reverts to restricted Hartree-

Fock for homolytic bond cleavage. Other approaches that apply spin projection prior to the variational step are difficult to define for DFT calculations.

Table I lists S^2 for some radicals and transition states calculated by UHF and two flavors of DFT: BLYP¹³ and B3LYP,¹⁴ calculated with GAUSSIAN94.¹⁵ Spin contamination is quite large at the UHF level but, as noted previously,¹⁶ DFT calculations on radicals have very little spin contamination. Hybrid density functionals such as B3LYP have somewhat higher spin contamination, probably because of the admixture of Hartree–Fock exchange. Even if the spin contamination calculated for the interacting system were twice as large as for the noninteracting system, the spin contamination would still be relatively small and it would be difficult to decide if spin projection were actually improving the calculations.

Another class of systems that shows the effects of spin contamination rather dramatically is homolytic bond cleavage. As a single bond is elongated, a point is reached where the UHF solution is lower in energy than the RHF solution. Beyond the onset of the RHF/UHF instability, S^2 rises rapidly to its limiting value of ca. 1 for the dissociation of a single bond (equal mixture of singlet and triplet). The effect of spin contamination and spin projection can be seen quite dramatically in this region. Figure 1 shows various potential energy curves for dissociation of hydrogen fluoride compared to full configuration interaction using the 6-31G basis set.⁴ In Fig. 2, the relative potential energy curves for C–H dissociation in methane are compared to the MRDCI calculations of Hirst.¹⁷ In each case, the RHF curve is qualitatively incorrect (dissociating to a mixture of covalent and ionic states), UHF is qualitatively correct (but with a dissociation energy that is ca. 20 kcal/mol too low compared to the full CI or MRDCI calculations), and PUHF (Eq. 1) is quite unacceptable, with a cusp at the onset of the RHF/UHF instability and a minimum just beyond.¹⁸ The PUHF' curves (Eq. 2) are not as extreme as the PUHF curves, but are still unacceptable. As discussed previously,^{2–4} the UMP2 curves are too high beyond the instability but the PMP2 and PUMP2 curves are in better agreement with the full CI and MRDCI potentials.

The qualitative behavior of the BLYP and B3LYP curves beyond the restricted/unrestricted instability compares more closely to that of the Hartree–Fock curves than the MP2 curves. The restricted curves go to the wrong dissociation limit. The onset of the instability for DFT is about midway between the Hartree–Fock and Brueckner doubles cases.⁴ The unrestricted BLYP and B3LYP potential energy curves have the correct shape when compared to the full CI and MRDCI curves (but with dissociation energies differing from the full CI and MRDCI results by up to 10 kcal/mol). The approximate projected DFT potentials obtained by Eqs. (1) and (2) are significantly below the unprojected curves, and show a discontinuity in the first derivative at the onset of the

instability. If the interacting formula were used to compute S^2 rather than the noninteracting formula, S^2 would probably be larger and the projected curves would be in even greater disagreement with the shape of full CI curve. For both projected Hartree–Fock and projected DFT computations, the problems with the potential energy surfaces arise because the projection is carried out after the variational calculation.

In summary, the qualitative behavior of the projected density functional curves and the projected Hartree–Fock curves for bond dissociation is incorrect when compared to more accurate curves. Both have a discontinuity in the first derivative at the onset of the restricted/unrestricted instability. Spin projected density functional theory, like projected Hartree–Fock theory, clearly should not be used for ground state bond dissociation potentials, and probably should not be used for ground-state radicals. The approximate functionals currently used in DFT computations appear to have much less spin contamination than unrestricted Hartree–Fock calculations. If the exact functionals were known, they would yield calculations with no spin contamination.

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