Does Unrestricted Møller−Plesset Perturbation Theory for Low Spin Converge When the System Has a Triplet Ground State?

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The unrestricted Hartree−Fock UHF method is often advocated for “singlet” diradicals. Here, we examine the behavior of unrestricted Møller−Plesset (UMP) for the case where the spin along the “up” direction, M, is zero when the “triplet” is the true ground state. In this case, the UMP result should try to approximate the triplet energy, but the UMP series for $M = 0$ shows no sign of converging to the value obtained using $M = 1$. The O_2 and CH_2 molecules are treated as examples.

Introduction

Various methods of computational chemistry allow theoretical determination of the properties of molecules. Because we deal with very approximate wave functions, the calculation of a specific molecular property involves selection of the method which is expected to yield the most accurate result. Generally, the more sophisticated the method, the greater the range of properties it is expected to get correct and the more limited the range of molecules for which the calculation can actually be done. The simplest ab initio methods use a single Slater determinant as a starting point. The spin-restricted Hartree−Fock (RHF) model assigns pairs of electrons to the same space orbital and is a good model for the ground state of most molecules near the equilibrium geometry.[1] The spin-restricted open-shell Hartree−Fock method (ROHF)[2,3] allows singly as well as doubly occupied space orbitals in a simple linear combination of Slater determinants with coefficients completely determined by spin coupling to form an eigenfunction of $\hat{S}^2$ and $\hat{S}_z$. Such a ROHF calculation will give the same energy for each eigenvalue, M, of $\hat{S}_z$ and a set of wave functions related by step-up and step-down operators.

The unrestricted Hartree−Fock model (UHF) allows the use of different orbitals for different spin in a single Slater determinants.[4,5] A “maximal spin” state of a system may be defined as one where the natural orbital occupations are close to two, one, or zero and the value of S is $n/2$ where n is the number of orbitals with occupation near to one. For “maximal spin” systems, UHF with $S \approx M$ is usually a superior alternative to ROHF because it is more convenient to use in gradient optimizations, Møller−Plesset perturbation expansions (MP), etc. Even though the wave function is not an eigenfunction of $\hat{S}^2$, the potential energy surface is often more free from artefacts than the ROHF result.

“Nonmaximal spin” states of a system are those where S is less than $n/2$. Convenient, completely flexible, and accurate methods for describing electrons in nonmaximal spin systems still do not exist. Methods such as complete active space self-consistent field (CASSCF) or its restricted open-shell special case provide better approximations to the wave function but are often still in error for the energy.[6,7] One of the most challenging problems for computational chemistry concerns the relative energetics of low-spin states compared to high-spin states. These problems arise in estimating the energy gaps between states of different multiplicity.[8] In addition, the classification of maximal or nonmaximal spin is only defined in limiting situations and is not rigorous. For a fixed value of S, “maximal spin” systems may change to “nonmaximal spin” away from the equilibrium geometry as more electrons become unpaired. Theoretical predictions of transition states for photochemical or thermal reactions, “bond-breaking” reactions, and properties of diradicals all involve evolution between maximal and nonmaximal spin regions as the molecule walks across the potential energy surface. It is very unsatisfactory to switch between methods appropriate for maximal spin and methods appropriate for nonmaximal spin in various regions of the potential surfaces.[9,10] The use of CASSCF is less subject to this arbitrary switching of methods, but it requires a similarly arbitrary initial choice of active space appropriate to every point of interest on the potential surface and every state of interest.

Wave functions from UHF are only appropriate for the maximal spin case $S = n/2 \approx M$. If all of the S values that can be formed from a given set of spin-restricted orbitals in the corresponding ROHF calculation give nearly degenerate energies, then any average of them will also have the same energy. The UHF energy for $M < n/2$ corresponds approximately to such an average and so, in the quasi-degenerate case, it will be close to the same energy for each S in the range $M \leq S \leq n/2$. Thus, UHF energies may seem reasonable even when the wave function is not. Other properties derived from these wave functions may not be reasonable. In particular, the spin density is very different for each S, so the weighted average implicit in a UHF wave function will be very different from the value for the state with S equal to M when $M < n/2$.

In this study, we examine the results of some standard maximal spin methods such as UHF, unrestricted Møller−Plesset perturbation theory (UMP), and spin-unrestricted density functional theory (UDFT) when applied to nonmaximal spin wave functions. This was inspired by the observation that UMP should converge toward the ground state if it converges at all. Hence, in diradical molecules ($n = 2$) with triplet ground states, the $M = 0$ UMP series should be trying to approximate $S = 1$ and not $S = 0$. In such cases, it is of interest to compare the $M = 1$ and $M = 0$ results. This might also shed some light on the convergence in the similar diradical case where $S = 0$ happens to be the ground state.

Diradical Example

It is well-known that restricted Hartree−Fock (RHF) calculations for singlet diradicals are often unstable to spin localization to give a lower energy UHF results.[9,10] In the simplest case, this occurs for a wave function of the form

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$$|\Psi\rangle \approx C_a|...a^2\rangle - C_b|...b^2\rangle \qquad (1)$$

where a and b are natural orbitals and C_b/C_a is close to unity. The more general two-electron/two-orbital CASSCF wave function of this form (with orthonormal molecular orbitals) can be written as

$$2^{1/2}|\Psi\rangle = A(|...a^2\rangle + |...b^2\rangle) + B(|...a^2\rangle - |...b^2\rangle) + C(|...a\alpha b\beta\rangle - |...a\beta b\alpha\rangle) \qquad (2)$$

A unitary transformation of the orbitals has one free coefficient. This coefficient can always be chosen to put the wave function into natural orbital form with $C = 0$ or into the alternative special form with $B = 0$. The value of A is unchanged by this unitary transformation and diradicals are characterized by a "small" value of A.

When A is small, the form with $B = 0$ looks like the singlet spin coupling of an open-shell system with two singly occupied orbitals. In this case, one would expect to have a triplet state of similar energy using a similar pair of singly occupied orbitals. For the triplet, the form of the wave function is invariant to a unitary transformation between these orbitals since there is only one configuration in the CASSCF. Conventionally, the triplet calculation would be done for $M = 1$ with both singly occupied orbitals having α spin, but CASSCF would give the same energy for either $M = 1$ or $M = 0$. A UHF calculation, on the other hand, might treat the $M = 1$ case reasonably but might give a result resembling $|...a\alpha b\beta\rangle$ for $M = 0$ (with orbitals like those giving $B = 0$). This would be neither singlet nor triplet and would have $\langle\hat{S}^2\rangle$ close to 1. If the triplet is the ground state, this is the expected UHF result. Alternatively, when the singlet is the ground state and A is not too small, $M = 0$ UHF might give a result resembling $|...a^2\rangle$ (with orbitals like those giving $C = 0$).

Now consider a simple model for the UMP correction to the UHF wave function. To be specific, consider a two-electron, two-orbital model with $M = 0$. Then we will have an occupied α orbital ϕ_1 and virtual orbital ϕ_2. We will also have an occupied β orbital η_1 and virtual orbital η_2. The UMP1 wave function associated with the UMP2 energy is just

$$|\Psi\rangle = |\phi_1\alpha, \eta_1\beta\rangle - (K/\Delta\epsilon)|\phi_2\alpha, \eta_2\beta\rangle \qquad (3)$$

where K *is* the integral $\langle\phi_1\eta_1||\phi_2\eta_2\rangle$ and $\Delta\epsilon$ is the excitation energy. The sign of $\Delta\epsilon$ is definitely positive.

Let us examine this corrected wave function to see whether the correction has made it more like $S = 0$ or more like $S = 1$. In this simple model, the β orbitals can be expressed as a unitary transform of the α orbitals:

$$\eta_1 = c\phi_1 + s\phi_2$$

$$\eta_2 = -s\phi_1 + c\phi_2 \qquad (4)$$

with $c^2 + s^2 = 1$. Inserting this into the expression for $|\Psi\rangle$ gives

$$|\Psi\rangle = c|\psi_1\rangle + s|\psi_2\rangle$$

$$|\psi_1\rangle = |\phi_1\alpha, \phi_1\beta\rangle - (K/\Delta\epsilon)|\phi_2\alpha, \phi_2\beta\rangle$$

$$|\psi_2\rangle = |\phi_1\alpha, \phi_2\beta\rangle - (K/\Delta\epsilon)|\phi_1\beta, \phi_2\alpha\rangle \qquad (5)$$

The $|\psi_1\rangle$ term is purely singlet. The $|\psi_2\rangle$ term is not pure spin unless $(K/\Delta\epsilon)$ is $+1$, in which case it is a singlet, or $(K/\Delta\epsilon)$ is -1, in which case it is a triplet. In any case, the sign of K determines whether the perturbation correction enhances the singlet or triplet character of the second term. Expanding K in the same way gives

$$K = cs\,T_1 + (c^2 - s^2)T_2$$

$$T_1 = \langle\phi_1\phi_2||\phi_2\phi_2\rangle - \langle\phi_1\phi_2||\phi_1\phi_1\rangle$$

$$T_2 = \langle\phi_1\phi_1||\phi_2\phi_2\rangle \qquad (6)$$

In the extreme case that the UHF calculation actually converges to RHF, c will be 1 and K will be T_2, which is positive. The perturbation corrected wave function (5) in this case will consist of only the first term and will be a pure singlet. In the other extreme where the UHF spin-up and spin-down orbitals are actually orthogonal, the true ground state of the molecule is likely to be triplet. In this case, $c = 0$, $s = 1$, and K is $-T_2$. The wave function (5) in this case will consist only of the second term and will have an enhanced triplet character relative to the UHF function. Since there is only one triplet configuration possible in this two-electron, two-orbital model, if the ground state is triplet, the infinite-order wave function must sum to

$$|\Psi\rangle = |\phi_1\alpha, \eta_1\beta\rangle + |\phi_2\alpha, \eta_2\beta\rangle + (c/s)|\phi_1\alpha, \eta_2\beta\rangle - (c/s)|\phi_2\alpha, \eta_1\beta\rangle \qquad (7)$$

if the perturbation series converges. The correction to the UHF wave function in this case is independent of $K/\Delta\epsilon$. In any case, the average value of $\hat{S}^2$, correct to first order, for the UMP1 wave function is $\langle\hat{S}^2\rangle = s^2(1 - 2K/\Delta\epsilon)$. Because the integrals occurring in T_1 are generally larger than those in T_2, it is difficult to predict the sign of K when both c and s are non-zero. For stretched H_2, for example, c is quite small, but K is positive at every internuclear distance.

If the perturbation series converges at all, it should converge to the ground state of the molecule. Thus, for triplet ground states, the UMP series beginning from $M = 0$ UHF should lead to the triplet state and should give the same energy as the $M = 1$ series. Both, of course, should be the same as the full configuration interaction (CI) ground state energy with the same basis set. As we will see below, the energy through fourth order shows no sign of approaching this limit.

Illustrative Calculations

Two simple model molecules, CH_2 and O_2, have been chosen to illustrate the UMP convergence for $M = 0$ states. For both molecules, the triplet state is the true ground state. Hence, for both molecules, the RHF and spin-restricted density functional theory (RDFT) calculation for the singlet is unstable and a lower energy $M = 0$ UHF (or UDFT) solution can be found. All calculations reported here were performed with the 6-31G* basis set. The calculation on O_2 was done at the experimental bond lengthen[11] of 1.207 Å. The bond lengths have been separately optimized for each computational method for the curves of energy versus bond angle for CH_2. In addition to CASSCF calculations with HONDO,[12] restricted and unrestricted self consistent field (SCF), MP4[13,14], MP5[15], and DFT calculations were done with GAUSSIAN 94.[16] For the CH_2 molecule, the "singly occupied" orbitals in the $M = 1$ triplet calculation were of different symmetry (a_1 and b_1 in C_{2v}). Two different $M = 0$ UHF solutions were found. In one of these solutions, symmetry orbitals were used so that the $M = 0$ state was a symmetry-constrained mixture consisting primarily of $^1B_1$ and $^3B_1$. This solution was unstable to symmetry breaking for CH_2. In the other calculation, the sum and difference of these a_1 and

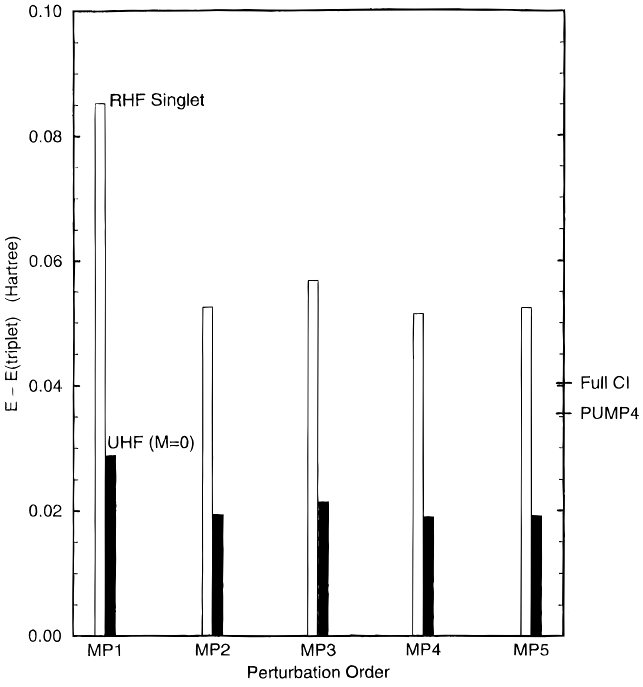

Figure 1. Convergence of the calculated energy difference from the $^3\Sigma_g^-$ state for O_2 as a function of perturbation order.

b_1 orbitals were used in the initial guess. For CH_2, this gave a lower energy UHF solution with broken symmetry. This solution was primarily a mixture of $^1A_1$ and $^3B_1$. Interestingly, not all symmetry was lost and the spin-up and spin-down densities were mirror images of each other when reflected in the molecular plane. Consequently, the spin density in the molecular plane was zero.

The O_2 molecule is a special case that illustrates the problem with diradicals. The ground state, calculated using D_{2h} symmetry adapted orbitals, is $^3(\pi_{gx}, \pi_{gy})\ ^3\Sigma_g^-$. The first singlet state is $^1\Delta_g$, which may be computed as $^1(\pi_{gx}, \pi_{gy})$ or $(\pi_{gx}^2 - \pi_{gy}^2)$ using CASSCF. Using UHF, the first of these forms with $M = 0$ should be viewed as a poor approximation to the triplet state. A RHF calculation using the first term in the second form would give a poor approximation to $^1\Delta_g$. If the calculation is done without D_{2h} symmetry, then the second form may be rewritten exactly using "broken symmetry" orbitals $\pi_{g\pm} = \pi_{gx} \pm \pi_{gy}$ as $^1(\pi_{g+}, \pi_{gu-})$. A $M = 0$ UHF calculation starting from this way of writing the second form leads to the same energy as the first form, but with broken symmetry orbitals. Figure 1 shows the result of MP calculations of various order beginning from these SCF solutions. The series based on the RHF solution seems to quickly approach an energy relative to the triplet energy in the range 0.050−0.055 hartrees in spite of the enormous error in the initial wave function. Even though the UMP series for $M = 0$ should converge to the same result as the one for $M = 1$, this tendency is not apparent in Figure 1, and the series probably does not converge at all. Thus, in spite of the fact that this UMP series appears to approach a constant energy difference from both $^3\Sigma_g^-$ and the RMP approximation to $^1\Delta_g$, it is not a valid approximation to any state of O_2. Annihilation of the $S = 1$ component gives a projected MP (PMP4)[17] energy of 0.035 hartrees that is in fair agreement with our best estimate, 0.0405 hartrees, of the full-CI $^1\Delta_g - {}^3\Sigma_g^-$ energy difference for this basis set. Thus, neither the RMP4 or UMP4 result is close to the correct energy. The PMP4 result is surprisingly good since the corrections to the UHF wave functions are trying to make it more like $S = 1$, but the projection has annihilated the $S = 1$ components to obtain a "$S = 0$" energy. The full-CI result with this modest basis set is in only fair agreement with the experimental value of T_e, 0.036 hartrees.[11]

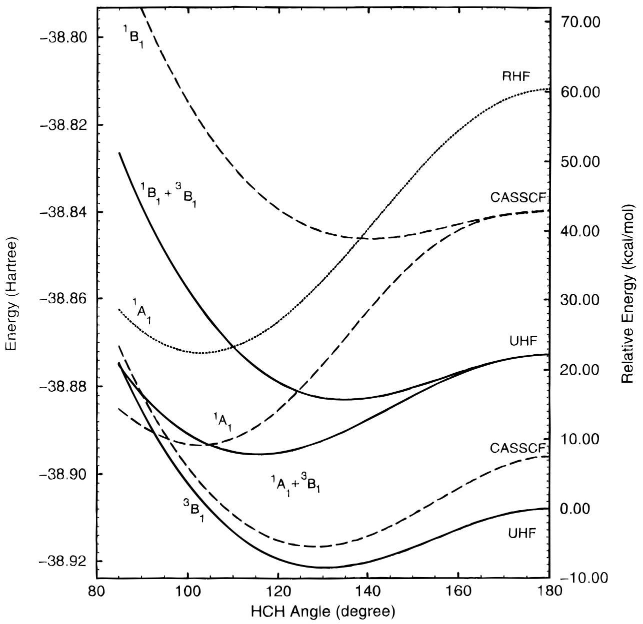

Figure 2. Behavior of restricted and unrestricted energies compared with CASSCF(2,2) for CH_2 as a function of bond angle.

The CH_2 molecule presents similar difficulties. In fact, the linear molecule has the same states as O_2 with the same difficulties. As the molecule is bent, the degeneracy of the π orbital is removed and the $^1\Delta$ state splits into ^1A_l and $^1B_1$. Figure 2 shows the results from the two-electron, two-orbital CASSCF calculation compared with RHF and UHF methods. It is well-known that CASSCF produces a reasonable singlet−triplet gap and reasonable bond angles for this molecule. The RHF method for the singlet leads to much too high a singlet−triplet gap. The UHF results are less well-known. For the triplet, UHF gives a lower barrier to linearity than ROHF (identical to CASSCF). Because the triplet is the ground state, the $M = 0$ ROHF results for $^1B_1$ and $^1A_1$ are unstable. As mentioned above, it is possible to obtain both symmetry-constrained and symmetry-unconstrained $M = 0$ UHF solutions. These are not very good approximations to any state of CH_2 and their existence is not usually recognized.

Figure 3 shows the UMP4 and projected PMP4 results. The $M = 1$ UMP4 curve has a minimum at 132°. The PMP4 result for the triplet is very similar to UMP4, although the difference is indicative of lack of convergence. Traditionally,[18,19] the UMP results for $M = 1$ have been compared with the restricted MP4 result for $M = 0$. The $M = 0$ UMP4 result is remarkably similar to the UHF result over the whole range of bond angles, and it clearly shows no tendency to converge to either the $S = 0$ or $S = 1$ energy. By default, the GAUSSIAN program assumes that the UMP series for $M = 0$ is approximating the $S = 0$ state, so the $S = 1$ component is annihilated. In spite of the fact that the $M = 0$ UMP4 energy should be regarded as an approximation to the triplet state, spin annihilation of $S = 1$ appears to be very effective since the PMP4 energy is very similar to the CASSCF energy. Projection also had a large effect on the position of the minima in the $M = 0$ curves. The $^1A_1$ and $^1B_1$ minima were shifted from 115° to 102° and from 135° to 140°, respectively. Below about 95° where $^1A_1$ is the lowest state, projecting out the higher energy $S = 1$ contamination lowers the energy, but above this angle, projection increases the energy. For reference, the experimental bond angles are 136° for $^3B_1$,

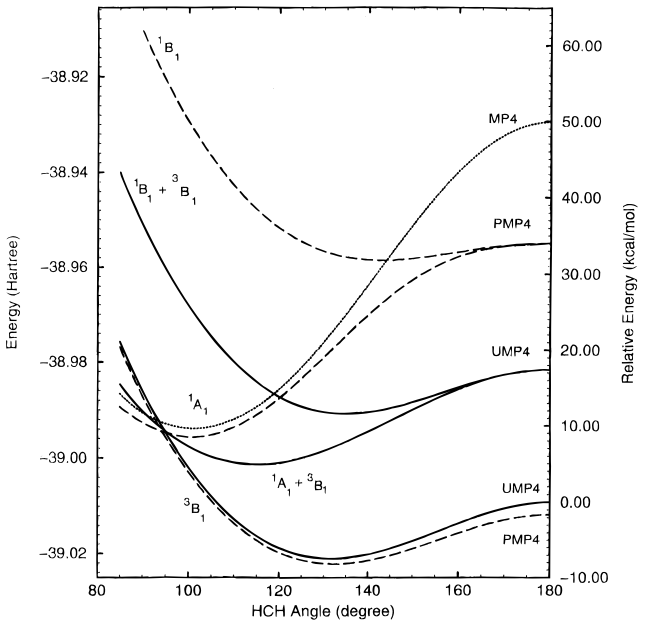

Figure 3. Fourth-order Møller−Plesset energies as a function of bond angles for CH_2.

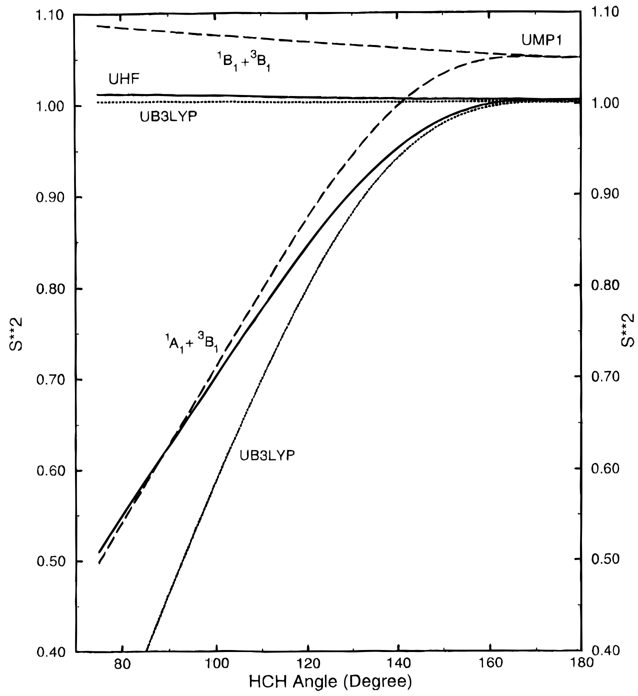

Figure 4. The average value of S^2 for CH_2 as a function of angle. Solid lines are for UHF and dashed lines are for the UMP1 wave function. Dotted lines are expectation values treating the Kohn−Sham UB3LYP determinant as though it were a wave function.

140° for $^1B_2$, and 102° for $^1A_1$. The energy gap $^1B_1 - {}^3B_1$ is 32.5 kcal/mol and $^1A_1 - {}^3B_1$ is 9.0 kcal/mol.[20,21]

Figure 4 shows the average value of $\hat{S}^2$ for the UHF and the UMP1 wave functions. As expected, the perturbation correction increases $\langle\hat{S}^2\rangle$ for most bond angles. Even though the triplet remains the ground state over most of this range of angle, the value of $\langle\hat{S}^2\rangle$ for the $^1A_1 + {}^3B_1$ UHF calculation decreases smoothly as the energy difference between $^1A_1$ and $^3B_1$ decreases. Also, below the crossing of these two energies, the UMP1 wave function has a smaller value for $\langle\hat{S}^2\rangle$ than does UHF. Even where the singlet is the ground state, the calculation gives a lower energy for UHF than for the closed-shell RHF energy of the $^1A_1$ state.

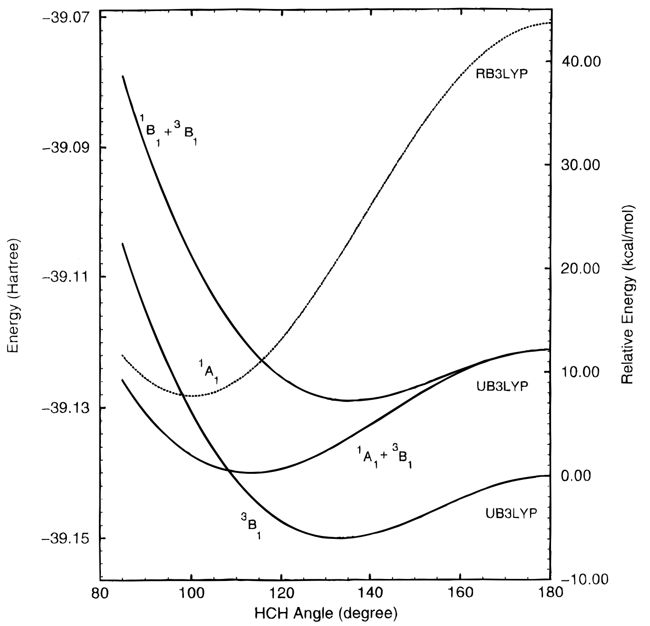

Figure 5. Density functional calculation of the energies of CH_2 as a function of bond angle.

Recently, calculations using unrestricted density functional theory with the three-parameter Becke exchange and the Lee−Yang−Parr correlation functionals (B3LYP) for $M = 1$ and restricted B3LYP for $M = 0$ have been advocated[22] as an accurate and inexpensive method for obtaining the singlet−triplet energy gap in substituted methylene molecules. Figure 5 shows the result of this approach for CH_2, along with the result obtained when the spin-instability of the $M = 0$ calculation is considered. Mixing of restricted and unrestricted results to obtain the singlet−triplet gap clearly gives a very reasonable result even though the barrier to linearity of the $^1A_1$ curve is much too high. Properly considering the spin and symmetry instabilities gives a much worse energy. Although $\langle\hat{S}^2\rangle$ computed with the Kohn−Sham determinant is not a true measure of the implicit $\langle\hat{S}^2\rangle$ of the DFT method, the value shown in Figure 4 indicates a significant problem with the spin density. Further, since $S = 1$ is the ground state, the desired value of $\langle\hat{S}^2\rangle$ is 2 and not 0, independent of angle, for angles greater than 105°. Similarly, if the exchange−correlation functionals were perfect, the energy for $M = 0$ and $M = 1$ would be identical for triplet ground states.

Conclusion

Selective use of unrestricted methods for $S = 0$ states of diradicals is often advocated in reactions involving bond breaking, whether at a transition state or during fragmentation into radical pairs. To be consistent, unrestricted methods should then be used whenever they give a lower energy than spin-restricted methods. Here, we show by example that this blanket use of unrestricted methods will lead to poor results. In particular, in regions of the potential energy surface having a triplet ground state, restricted $M = 0$ RHF calculation are always unstable, but unrestricted $M = 0$ calculations just produce a poor approximation to the triplet energy.

The original UHF papers[5] envisioned a more fully unrestricted approach where each orbital could have mixed α and β spin character like that which occurs in Fock−Dirac calculations. For the case of a triplet ground state, the $M = 0$ constrained UHF solutions are unstable to the mixing of α and β character into the same orbitals. If this mixing is allowed, then the UHF calculation will converge to the $M = 1$ solution if $M = 1$ is stable, or to an even lower energy if $M = 1$ is unstable. Hence, much of the logical and numerical difficulty with the $M = 0$ UHF or UDFT calculation discussed in this paper is due to its partially constrained nature.

A fully unconstrained calculation would give a unique optimum Slater determinant of undefined M which could approximate only the ground state. For the situation discussed in the introduction, this would generally have $S \approx M \approx n/2$. Hence, it would approximate the maximal spin state and might be able to vary smoothly with changes in molecular geometry that lead to additional pairing or unpairing of electrons.

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