Qualitative breakdown of the unrestricted Hartree-Fock energy

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The stretching of closed-shell molecules is a qualitative problem for restricted Hartree-Fock that is usually circumvented by the use of unrestricted Hartree-Fock (UHF). UHF is well known to break the spin symmetry at the Coulson-Fischer point, leading to a discontinuous derivative in the potential energy surface and incorrect spin density. However, this is generally not considered as a major drawback. In this work, we present a set of two electron molecules which magnify the problem of symmetry breaking and lead to drastically incorrect potential energy surfaces with UHF. These molecules also fail with unrestricted density-functional calculations where a functional such as B3LYP gives both symmetry breaking and an unphysically low energy due to the delocalization error. The implications for density functional theory are also discussed.

I. INTRODUCTION

The restricted Hartree-Fock method (RHF) is one of the cornerstones of quantum chemistry for the description of closed-shell molecules. However, RHF breaks down when a bond in a closed shell system is stretched. One way around this problem, that works in many cases, is to use the unrestricted Hartree-Fock method (UHF), which allows different spatial orbitals for the α and β electrons and avoids the error of RHF by breaking the spin symmetry. For the prototypical example of the H₂ molecule, UHF gives the same description as RHF around equilibrium, and as the bond is stretched well beyond the minimum, it goes through the Coulson-Fischer point [1] at which the spin symmetry breaks to dissociate into an unrestricted solution with the correct energy and one α electron on one hydrogen and one β electron on the other hydrogen.

Due to the breaking of the spin symmetry there is a discontinuous derivative of the energy with respect to geometry at the Coulson-Fischer point. Furthermore, the UHF broken symmetry solution is not an eigenstate of the total spin operator and can give not just spin densities, but total densities, that do not obey the overall symmetry of the Hamiltonian. This has been observed in many cases; from non-spherical atomic densities for open shell p atoms [2, 3], symmetry breaking in the uniform electron gas and related systems [4–6] and stretched He₆⁺ [7]. However, for the purposes of this paper, we will assume that none of these is a major issue. In H₂, the Coulson-Fischer point is well after the equilibrium geometry, but in molecules such as F₂ [8, 9] and O₂²⁺ [10], it can occur at much shorter bond lengths and even before the RHF minimum. Symmetry breaking also plays an important role in the calculation of antiferromagnetic exchange couplings that are important in transition metals complexes [11]. In this case, a simple model often used, which also shows a symmetry breaking early in its binding curve, is the stretching of HHeH [12].

There is still the open question of whether symmetry breaking is a good idea or it is just avoiding an error of the RHF method in stretching bonds [13]. This is true for perturbation theory [10, 14, 15] but is also a particularly important question in relation to density functional theory (DFT). In this paper, we want to show a set of two-electron systems which reveal a clear qualitative breakdown in the total energy of restricted Kohn-Sham DFT (RKS), unrestricted Kohn-Sham DFT (UKS) and, remarkably, also UHF.

Figure 1: The geometries of H₄/H₄²⁺ studied in this paper. Several different rectangles are considered, each with a different factor. Increasing d leads to a uniform stretching of all of these molecules.
II. RESULTS AND DISCUSSION

Simple molecules of hydrogen atoms as in Fig. 1 are studied. All calculations are carried out using Gaussian09 [16] and the cc-pVQZ basis set [17]. The optimization of the wavefunction is done using the standard DIIS procedure checking for wavefunction instabilities [18] as well as the quadratic convergent SCF method [19]. We have also independently checked all the results by comparing with our own code based on the direct minimization of the total energy imposing orbital orthonormality [20, 21], to try and ensure that we have found the best SCF orbitals at each geometry. The full configuration interaction (FCI) calculations are carried out using the fci code of Knizia and Chan developed in their work on density matrix embedding theory [22].

First, in Fig. 2a, consider the linear H\textsubscript{4} chain and its stretching, with an equal spacing between the hydrogen atoms. The neutral system with four electrons has very similar binding curves to the well known H\textsubscript{2} molecule. Fig. 2a shows the usual behavior of RHF, with a large static correlation error, and UHF following RHF beyond equilibrium up to around 2 bohr until a Coulson-Fischer point, where it breaks the spin symmetry to give the correct dissociation limit compared to FCI. Consider now a square geometry for H\textsubscript{4} with four electrons and look at the uniform stretching (Fig. 2b). The behavior of RHF and UHF is markedly different. In this case RHF is massively wrong at nearly all geometries and consequently UHF breaks the spin symmetry at all distances and gives good agreement with FCI, although missing the dynamical correlation, to reach the correct energy at stretching. Here, although the spin density is wrong, the total density and energy are acceptable. UB3LYP performs reasonably in both cases (Fig 2a and 2b).

Now, examine the same systems but with two electrons removed, that is H\textsubscript{2}\textsuperscript{+} linear chain and square geometries. Again, quite different performance is observed. RHF exhibits the usual behavior in the square geometry, whereas it is completely wrong at all distances in the chain structure. In these cases, UHF either agrees well with FCI (H\textsubscript{2}\textsuperscript{+} chain, Fig. 2c) or has the usual Coulson-Fischer symmetry breaking (H\textsubscript{2}\textsuperscript{+} square, Fig 2d). Although this
Figure 3: Stretching of a set of rectangular geometries of H$_4^{2+}$. Factor is the ratio between the two sides, and is constant as the distance is varied. The inset shows a magnified view of the UHF minimum for the rectangle with factor 1.27.

Coulson-Fischer symmetry breaking is not appealing, the potential energy curves are reasonable. The poor performance of both RB3LYP and UB3LYP for H$_4^{2+}$ in these geometries must be noted, which is due to the delocalization error [23], related to the non-integer number of electrons on each atom.

The behaviors of RHF and UHF seen in the stretching of the chain and square in Figs. 2c and 2d are somewhat limiting cases (a tetrahedron is also similar to the square). We can consider ways to go smoothly in between the two types of behavior if we take H$_4^{2+}$ in a rectangular geometry where the ratio between the two sides is a constant factor as the system is stretched. A factor of 1.0 corresponds to the square geometry and a factor of 2.0 leads to the same nearest neighbor and next nearest neighbor distances as the linear chain. Fig. 3 shows a range of factors between 1.0 and 2.0. First, it should be noted the similar nature of the FCI curves between the plots, which indicates that for real electrons there is not a great deal of difference between the different geometries. Also for RHF there is not much difference between the different ratios. It is only for UHF that the curves depend greatly on the ratio. For example, for a ratio of 1.27, the symmetry breaking Coulson-Fischer point is near the minimum of the RHF curve. This leads to a very poor UHF curve that has fundamental problems. It gives a minimum with a very large qualitative error, and calculations with smaller basis sets can even give curves with double minima.

The nature of the symmetry breaking of the orbitals is shown in Fig. 4. At short distances the $\alpha$ and $\beta$ orbitals are equal and both over all the atoms, then at the Coulson Fischer point the symmetry breaks along the longer distance such that the $\alpha$ electron is on the two right atoms and the $\beta$ electron is on the two left atoms, and finally at longer distance a further symmetry breaking occurs along the shorter distance so that in the limit of large $d$ UHF gives the $\alpha$ electron on one of the right two atoms and the $\beta$ electron diagonally opposite. Fig. 4 shows the orbitals for H$_4^{2+}$ with factor 1.27, but the same behavior is present in all H$_4^{2+}$ with factors 1 to 2, as the nature of the UHF symmetry breaking is the
III. CONCLUSIONS

Overall, this paper presents simple systems where the UHF total energy has a very poor behavior compared to FCI upon stretching. For example, the $H_4^{2+}$ rectangular molecule with a ratio of 1.27 gives a qualitatively incorrect potential energy surface with UHF due to symmetry breaking at the RHF minimum. This gives rise to a badly predicted shallow minimum around 2.4 bohr in comparison with the FCI minimum at 2.1 bohr. This analysis is also very relevant for DFT, where despite the problems for the stretching of odd electron systems like $H_2^+$ or $He_2^+$ [24, 25], there is a prevailing view that UKS is a good practical solution to the problem of stretching closed shell molecules [26]. This has been phrased as the symmetry dilemma [27, 28]. In $H_4^{2+}$ there is not even the possibility of a dilemma as UKS calculations are just incorrect due to the delocalization error. Therefore, although symmetry breaking is a useful practical tool in many molecules it should be noted that it can have large failures in some systems. The observed qualitative breakdown of UHF and the simple nature of the molecules in which it is found poses a difficult challenge for all unrestricted methodologies, and hopefully sheds light on the difficult nature of stretching bonds and related challenges for electronic structure methods.

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