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The Hartree–Fock dissociation of F_2

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We examine the stability of the restricted Hartree-Fock (RHF) wave function for F_2 in the vicinity of the equilibrium internuclear distance ($R = R_e$) and the shape of the unrestricted Hartree-Fock (UHF) potential energy curve for the same system. The results depend on the basis set: With a split valence plus polarization basis, 6-31G(d), the RHF wave function is unstable at R_e, and the UHF potential curve is purely dissociative. When the basis is extended to 6-311+G(3d) or 6-311+G(3df), the RHF wave function becomes stable, and the UHF potential curve acquires a local maximum for R slightly ($\sim$0.02 Å) greater than R_e. The local maximum, however, is only 0.1 kcal/mol higher than the local minimum at $R = R_e$.

Key words: Electronic structure — Potential curve — Hartree-Fock stability

1. Introduction

The failure of restricted Hartree-Fock (RHF) [1] theory to properly describe the dissociation of diatomic fluorine into two fluorine atoms is well known [2, 3]: while this level of theory predicts a minimum on the F_2 surface, the minimum lies above the energy calculated by separate RHF calculations for the separated atoms, because of restrictions on the RHF wave function. Furthermore, RHF F_2 dissociates (incorrectly) to a mixture of ionic and neutral products, well above two neutral atoms in energy. As first demonstrated by Wahl [3] and later by many others [4], multi-configurational self-consistent field (MCSCF) wavefunctions may be used to correct this deficiencey, leading to proper dissociation products and to a positive bond energy.

Another way to correct RHF theory is to use the unrestricted Hartree-Fock (UHF) method [5]. Usually, UHF wave functions for closed-shell molecules near their equilibrium structures are identical to the RHF solutions, but the RHF solutions become unstable with respect to an unrestricted description as an internuclear distance is increased and the molecule is dissociated (see, e.g., the potential energy curves for the dissociation of H_2 [6] or a single C–H bond in CH_4 [7]. Furthermore, the molecular UHF wave function should dissociate correctly to a product of UHF wave functions for the dissociated atoms. Typically, therefore, one expects the UHF bond energy to be positive for dissociation of a covalent bond [8].

For F_2, however, the situation is less than clear. Since the RHF solution for two F atoms is lower in energy than the RHF energy for F_2, and the UHF F_2 energy must be equal to or less than the RHF value, the UHF potential energy curve (PEC) might contain a barrier to dissociation or it might be purely dissociative. Evidence that the latter is the case is provided by the double zeta (DZ) calculations of Chambaud and co-workers [9] and Brucena et al [10]. The former authors have also shown that the RHF solution for F_2 at its "equilibrium" bond length ($R_e = 1.418$ Å) is unstable with respect to a UHF description. Brucena et al calculated the RHF and UHF energies at 2.65, 4.23, 4.76, and 5.29 Å, as well as at R_e. The RHF solutions were found to be unstable with respect to UHF at all of these points, but the UHF curve appears to be dissociative although no points within 1 Å of R_e were investigated.

Since the UHF method is widely employed for practical calculations on potential energy surfaces of open shell systems, both in its own right and as a reference for Møller-Plesset perturbation theory [11], there is increased interest in the character of the potential curves it predicts for simple systems. For this reason we have investigated the RHF and UHF potential energy curves for F_2 with a much larger number of points and with larger basis sets than previously used, in an attempt to determine whether the PEC corresponding to the best single determinant description of this molecule is purely dissociative in the internuclear distance range between $R = R_e$ and infinity.

2. Computational methods

Three basis sets have been used in this work. Preliminary calculations of the RHF and UHF PEC's have been carried out with the 6-31G(d) basis set [12], and the RHF R_e has also been obtained with the 6-311+G(3d) basis [13]. Finally, the RHF and UHF PEC's were also obtained with the 6-311+G(3df) basis set [13]. Locally modified versions of both GAUSSIAN82 [14] and GAMESS [15] have been used in this study, and all calculations have been performed on the IBM 3081/D computer at North Dakota State University.

An important aspect of the results is whether or not, for each internuclear distance R, a UHF calculation converges to a solution for which the orbitals are doubly occupied. In such cases, $E(\mathrm{UHF}) = E(\mathrm{RHF})$, and the RHF solution is stable. In other cases $E(\mathrm{UHF}) < (\mathrm{RHF})$, and the solution is unstable. In all cases a stability analysis [14, 16] of the RHF wave function itself confirmed our conclusions based on the UHF calculation.

3. Results and discussion

With the smallest basis set, 6-31G(d), the RHF equilibrium bond length is predicted to be 1.34 Å, as compared with the experimental value [17] of 1.412 Å. However, the RHF solution is found to be unstable with respect to relaxation to an unrestricted description at bond lengths equal to and longer than this value. Table 1 gives the RHF energy as a function of R, as well as the UHF values of the energy and $\langle S^2 \rangle$, where S is the total electron spin angular momentum. As shown in the table, the UHF energy is slightly below the RHF value at the RHF R_e, and the gap widens as the internuclear distance increases. As one would expect, the triplet contamination of the singlet increases as the molecule dissociates, since the two states become degenerate at infinite separation. Thus, $\langle S^2 \rangle$ approches 1.0 as the molecule dissociates. Note that at the UHF level, F_2 dissociates smoothly to two fluorine atoms with no minimum on the PEC at finite R. This consistent with the calculations of Brucena and co-workers [10].

The nature of the molecular orbitals is of interest as well. At large distances, the left-right $(g-u)$ symmetry of individual orbitals is lost in the UHF wave function, with the highest alpha (beta) orbital being highly localized on the left (right) fluorine. The symmetry of the total wavefunction is retained, as is evidenced by the fact that the alpha and beta orbital coefficients are similar on symmetrically related atomic orbitals. The sigma vs pi symmetry is retained throughout, and the alpha and beta orbital energies remain identical to each other. At smaller R values, where the RHF description is stable, the left-right symmetry of individual orbitals is regained.

To determine the effect of improving the basis set, the RHF geometry was re-optimized with the 6-311+G(3d) basis set. The RHF bond length at this level is 1.329 Å, and at this bond length, the RHF solution is stable. As a consequence

Table 1. 6-311G(d) Potential energy curve for ground state F_2 (hartrees)

R (Å)	E(UHF)	$\langle S^2 \rangle$	$E(RHF)$
1.3	−198.67556	0.000	−198.67556
1.344	−198.67781	0.031	−198.67776
1.4	−198.68128	0.294	−198.67504
1.5	−198.69234	0.584	−198.65988
1.6	−198.70330	0.747	−198.63720
1.8	−198.71815	0.902	−198.58472
2.0	−198.72514	0.962	−198.53432
2.5	−198.72945	1.000	−198.43862
3.0	−198.72975	1.005	−198.38204
4.0	−198.72982	1.005	−198.33827
5.0	−198.72988	1.005	−198.32334

of this stability, the RHF and UHF solutions are locally equivalent, and the UHF PEC also has a local minimum at $R=1.329$ Å. Thus, the improvement of the basis set has introduced a barrier to dissociation on the UHF PEC.

To investigate this effect further, the RHF and UHF PEC's were reinvestigated with the 6-311+G(3df) basis set. The results of these calculations are summarized in Table 2. Here also, the RHF solution is stable at R_e and at bond lengths slightly longer than R_e. This gives rise to a very small dissociation barrier of about 0.1 kcal/mol. In particular, interpolation of the UHF results in Table 2 yields a local maximum of $E=-198.74893$ hartrees at $R=1.344$ Å and a local minimum of $E=-198.74910$ hartrees at $R=1.324$ Å. Thus, the local maximum in the UHF potential is at $R_e+0.02$ Å and the local barrier height is 0.11 kcal/mol. Thus, while the RHF solution does indeed appear to be stable for very large basis sets, the single determinant potential energy curve remains effectively dissociative for F_2 except for a small feature on the order of 0.1 kcal/mol. The fact that the best single determinant wavefunction for F_2 predicts such a small barrier to dissociation should make one very cautious about simple interpretations of bonding.

These results raise a similarly interesting question with regard to the potential energy curves for other systems for which the RHF wave functions are unstable at $R=R_e$ and the RHF dissociation energy (with respect to RHF atoms) is negative; for example [9], MgO. The dissociation of hydrogen peroxide into two OH radicals is isoelectronic to the $F_2 \rightarrow 2F$ process considered above. Recent calculations [18] with a triple zeta plus polarization basis set finds this dissociation

Table 2. 6-311+G(3df) Potential energy curve for ground state F_2 (hartrees)

R (Å)	E(UHF)	$\langle S^2 \rangle$	E(RHF)
1.30	−198.74844	0.0	−198.74844
1.31	−198.74888	0.0	−198.74888
1.32	−198.74908	0.0	−198.74908
1.325	−198.74910	0.0	−198.74910
1.33	−198.74907	0.001	−198.74907
1.335	−198.74899	0.004	−198.74899
1.34	−198.74894	0.034	−198.74887
1.35	−198.74897	0.090	−198.74847
1.36	−198.74920	0.141	−198.74790
1.37	−198.74958	0.190	−198.74717
1.4	−198.75150	0.317	−198.74409
1.5	−198.76204	0.603	−198.72678
1.6	−198.77325	0.761	−198.70331
1.8	−198.78919	0.910	−198.65154
2.0	−198.79710	0.967	−198.60315
2.5	−198.80249	1.003	−198.51480
3.0	−198.80337	1.007	−198.46515
4.0	−198.80457	1.008	
5.0	−198.80358	1.008	

to be very slightly (<1.0 kcal/mol) exothermic using a UHF wavefunction for OH and an RHF wavefunction for H_2O_2. It would be interesting to do further calculations on this system to study the shape of the PEC for dissociation to see if it is nearly flat or has a large barrier.

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