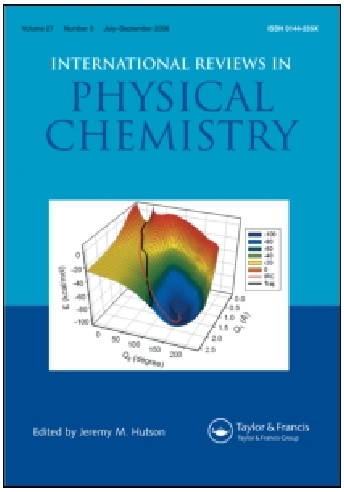

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

The equilibrium geometry of F_2^+ in its ground electronic state. A simple example of the effects of symmetry breaking on an observable molecular property

Robert Murphy[a]; Henry F. Schaefer III[a]; Ross H. Nobes[b]; Leo Radom[b]; Russell M. Pitzer[c]
[a] Department of Chemistry, University of California, Berkeley, California, USA [b] Research School of Chemistry, Australian National University, Canberra, A.C.T., Australia [c] Department of Chemistry, Ohio State University, Columbus, Ohio, USA

To cite this Article Murphy, Robert , Schaefer III, Henry F. , Nobes, Ross H. , Radom, Leo and Pitzer, Russell M.(1986) 'The equilibrium geometry of F_2^+ in its ground electronic state. A simple example of the effects of symmetry breaking on an observable molecular property', International Reviews in Physical Chemistry, 5: 2, 229 — 237

To link to this Article: DOI: 10.1080/01442358609353387

URL: http://dx.doi.org/10.1080/01442358609353387

International Reviews in Physical Chemistry, 1986, Vol. 5, Nos. 2 & 3, 229–237

The equilibrium geometry of F_2^+ in its ground electronic state. A simple example of the effects of symmetry breaking on an observable molecular property

by ROBERT MURPHY and HENRY F. SCHAEFER III
Department of Chemistry, University of California,
Berkeley, California 94720, U.S.A.

ROSS H. NOBES and LEO RADOM
Research School of Chemistry, Australian National University,
Canberra, A.C.T. 2601, Australia

and

RUSSELL M. PITZER
Department of Chemistry, Ohio State University,
Columbus, Ohio 43210, U.S.A.

A wide variety of theoretical methods have been applied to a very simple but notoriously difficult problem, the calculation of the bond distance in F_2^+. All theoretical methods used the same basis set, the standard Huzinaga–Dunning double-zeta plus polarization (DZ+P) set, designated F (9s 5p 1d/4s 2p 1d). All methods which enforce inversion symmetry and go beyond second-order perturbation theory are qualitatively successful, giving bond distances within 0·05 Å of experiment. Methods not enforcing inversion symmetry are successful to within 0·03 Å if based on a restricted Hartree–Fock (RHF) starting point. When the wavefunction is not constrained to have inversion symmetry, methods based on an unrestricted Hartree–Fock (UHF) starting point are less satisfactory, yielding errors in the F_2^+ bond distance ranging from 0·092 Å (full fourth-order perturbation theory, UMP4) to 0·850 Å (single-determinant UHF).

1. Introduction

A recent theoretical study by Farnell *et al.* (1983) examined structural predictions for open-shell systems at various levels of theory. Both the restricted Hartree–Fock (RHF) (Roothaan 1960) and unrestricted Hartree–Fock (UHF) (Pople and Nesbet 1954) methods were considered, while electron correlation effects were examined by appending second- and third-order Møller–Plesset perturbation theory (Møller and Plesset 1934, Pople *et al.* 1976) to the latter. In general, predicted geometries were in good agreement with experiment, typical deviations being 0·01 Å in bond distances and 2° in bond angles. However, one very simple molecule, F_2^+, proved to be particularly troublesome. The purpose of the present theoretical study described in this article is to examine the F_2^+ ground-state bond distance in considerably greater depth than was possible in a broad-ranging study such as that of Farnell *et al.* (1983).

The value of the bond distance for the X $^2\Pi_g$ ground state of the F_2^+ molecular ion is known from recent experiments (Tuckett *et al.* 1983) to be $r_e = 1{\cdot}305 \pm 0{\cdot}007$ Å. Farnell *et al.* (1983) reported two sets of calculated bond distances in F_2^+. In the first set, in which neither spin nor spatial symmetry was enforced, UHF equilibrium bond distances were obtained using three basis sets of increasing flexibility: a minimum basis set (STO-3G) (Hehre *et al.* 1969), a small split-valence basis set (3-21G) (Binkley *et al.* 1980), and a larger split-valence basis set augmented by d functions (6-31G*) (Hariharan and Pople 1973). The three predicted structures were $r_e = 1{\cdot}407$ Å (STO-3G), 1·731 Å (3-21G), and ∞ (6-31G*), the latter implying that F_2^+ is unbound (dissociative to $F + F^+$) at this level of theory except for a small long-range attraction of a non-chemical nature. With the 6-31G* basis set, second and third-order perturbation theories (designated UMP2 and UMP3) gave predictions of 1·184 and 1·185 Å, respectively. All five theoretical predictions are in poor agreement with the experimental bond distance.

Farnell *et al.* (1983) found in a second set of calculations that better agreement with the experimental bond distance was obtained when inversion symmetry was enforced on the wavefunctions. These calculations yielded bond lengths at the Hartree–Fock level of 1·226 (STO-3G), 1·327 (3-21G) and 1·232 Å (6-31G*), and UMP2 and UMP3 lengths of 1·411 and 1·320 Å with the 6-31G* basis set. Nevertheless, Farnell *et al.* (1983) expressed hesitation concerning the general use of such symmetry-constrained procedures, stating that 'this approach is rather unsatisfactory because the solutions obtained are not true minima in the full UHF space. Furthermore, the processes leading to an asymmetrical answer are presumably also acting in heteronuclear diatomics where symmetry *cannot* be enforced'. We believe the point raised to be of inherent interest and have therefore considered in the present research all possible subgroups of the homonuclear diatomic point group $D_{\infty h}$.

The observation of Farnell *et al.* (1983) concerning inversion symmetry in F_2^+ is an interesting and very simple example of a theoretical problem known as the 'symmetry dilemma', or 'symmetry breaking'.† Symmetry breaking occurs when an approximate wavefunction fails to display the full symmetry of the molecule. The most widely discussed (McKelvey and Hehre 1973, McKelvey and Berthier 1976, Paldus and Veillard 1978, Baird *et al.* 1979, Voter and Goddard 1981 a, b, Feller *et al.* 1983) example of symmetry breaking is the allyl radical,‡ which RHF theory incorrectly predicts to have an asymmetrical equilibrium geometry. Closer to the F_2^+ problem is the X $^2\Sigma_g^+$ ground state of N_2^+, where symmetry breaking with respect to inversion has been demonstrated by de Castro *et al.* (1981). Such symmetry breaking in N_2^+ leads to a charge distribution which is skewed relative to the two atoms.

2. Basis set

There are several possible strategies with which to approach the molecular structure of F_2^+. One approach is to take a given method, perhaps second-order perturbation theory, and explore the problem with progressively larger basis sets, hoping eventually to approach the basis set limit. A good start in this direction has already been made for the UHF, UMP2, and UMP3 methods by Farnell *et al.* (1983).

---

† For a discussion of symmetry breaking, see Dixon (1971), Walker (1971), Manne (1972), Bagus and Schaefer (1972), McKelvey and Hehre (1973), Yarkony and Schaefer (1974), Wadt and Goddard (1975), McKelvey and Berthier (1976), Davidson and Borden (1976, 1977), Jackels and Davidson (1976), Borden (1976), Poppinger *et al.* (1977), Seeger and Pople (1977), Paldus and Veillard (1978), Chambaud *et al.* (1978), Müller *et al.* (1979), Benard (1979), Baird *et al.* (1979), Benard and Paldus (1980), Borden *et al.* (1980, 1982), Voter and Goddard (1981 a, b), de Castro *et al.* (1981), Engelbrecht and Liu (1983), Feller *et al.* (1983) and Hoffmann *et al.* (1984).

‡ Further theoretical studies of the allyl radical include Levin and Goddard (1975 a, b).

However, since the present study is more methodological in nature, we have taken the alternative approach of choosing a single, good quality, relatively standard basis set and using this consistently with a comprehensive range of theoretical methods. The basis set chosen was the Huzinaga–Dunning contracted gaussian double-zeta plus polarization (DZ+P) set. This basis set, seen in table 1, may be designated F (9s 5p 1d/4s 2p 1d), and is sufficiently small so as to be useful for much larger molecules.

3. Methods based on spin-restricted Hartree–Fock orbitals

A number of theoretical predictions based on the restricted Hartree–Fock method are shown in table 2. Among the single-configuration wavefunctions, we have identified three distinct levels of symmetry breaking. The first entry in table 2 is labelled $D_{\infty h}$ and is the completely proper Roothaan RHF wavefunction (Roothaan 1960). That is, the molecular orbitals transform according to the irreducible representations of the $D_{\infty h}$ point group. In particular, this requires that the degenerate orbitals in the F_2^+ electron configuration

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^3 \quad X\,^2\Pi_g \tag{1}$$

be equivalent. Specifically,

$$1\pi_{ux}/1\pi_{uy} = 1\pi_{gx}/1\pi_{gy} = x/y$$

When the (π_x, π_y) equivalence is removed, the point group symmetry of F_2^+ is reduced from $D_{\infty h}$ to D_{2h}. Table 2 shows that there is a $D_{\infty h} \rightarrow D_{2h}$ symmetry breaking, with the total energy being lowered by 0·00187 hartrees. This symmetry breaking is accompanied by a very small increase (0·0003 Å) in the equilibrium bond distance, from 1·2207 ($D_{\infty h}$) to 1·2210 Å (D_{2h}). Both the $D_{\infty h}$ and D_{2h} bond distances are in much poorer agreement with the experimental r_e of 1·305 Å (Tuckett *et al.* 1983) than is normally expected (Schaefer 1974) for the DZ+P SCF level of theory.

Table 1. Standard contracted gaussian basis set for the study of symmetry breaking in the F_2^+ ground electronic state.

Type	Orbital exponent	Contraction coefficient
s	9994·7900	0·002017
s	1506·0300	0·015295
s	350·2690	0·073110
s	104·0530	0·246420
s	34·8432	0·612593
s	4·3688	0·242489
s	12·2164	1·0
s	1·2078	1·0
s	0·3634	1·0
p	44·3555	0·020868
p	10·0820	0·130092
p	2·9959	0·396219
p	0·9383	0·620368
p	0·2733	1·0
d	0·9	1·0

Table 2. Theoretical predictions for the X $^2\Pi_g$ ground state of F_2^+ based on spin-restricted Hartree–Fock (RHF) wavefunctions constrained to different spatial symmetries.

Point group	Wavefunction	Bond distance, r_e (Å)	Total energy (hartrees)
$D_{\infty h}$	RHF	1·221	−198·16343
$D_{\infty h}$	TCSCF	1·278	−198·21479
D_{2h}	RHF	1·221	−198·16530
D_{2h}	TCSCF	1·288	−198·22003
D_{2h}	CISD	1·296	−198·50422
D_{2h}	Davidson-corrected CISD	1·332	−198·53675‡
$C_{\infty v}$	RHF	1·332	−198·17668
C_{2v}	RHF	1·329	−198·17776
C_{2v}	CISD	1·284	−198·49232
C_{2v}	Davidson-corrected CISD	1·307	−198·53359‡
Experiment†		1·305 ± 0·007	

† Tuckett *et al.* (1983).
‡ Non-variational energy (see text).

A symmetry breaking of larger extent occurs with respect to $D_{\infty h}$ when the centre of inversion is no longer enforced. Moreover, a significant change in the predicted equilibrium internuclear separation accompanies the lowering from $D_{\infty h}$ to $C_{\infty v}$ symmetry. The lowering in the total energy is 0·01325 hartrees, or 8·3 kcal mol^{-1}, a significant amount in chemical terms. The increase in bond distance is 0·111 Å, from 1·221 ($D_{\infty h}$) to 1·332 Å ($C_{\infty v}$). Perhaps more importantly, this $C_{\infty v}$ bond distance is now only 0·02 Å longer than experiment, and represents a nearly acceptable level of agreement with the true structure.

The only additional energy lowering observed for F_2^+ in decreasing the symmetry from $C_{\infty v}$ occurs when the (π_x, π_y) equivalence is removed, lowering the symmetry imposed to C_{2v}. An energy lowering of 0·00108 hartrees is seen in table 2, and the bond distance is decreased by 0·003 Å, from 1·332 ($C_{\infty v}$) to 1·329 Å (C_{2v}). Further reductions in point-group symmetry to C_s and C_1 (no elements of symmetry in the latter case other than the identity) yield total energies identical to the C_{2v} energy reported in table 2. The entire energy lowering from $D_{\infty h}$ to C_{2v} is 0·01433 hartrees, or 9·0 kcal mol^{-1}.

The simplest interpretation of the large energy lowering due to symmetry breaking is that the RHF wavefunction for the X $^2\Pi_g$ ground state of F_2^+ is a poor approximation to the true wavefunction. Therefore, configuration interaction (CI) wavefunctions have been used to address the problem. The CI treatment included all single and double excitations relative to the appropriate RHF reference configuration. The core molecular orbitals ($1\sigma_g$ and $1\sigma_u$ in $D_{\infty h}$ point group) were held doubly occupied in all configurations. This leads to 1918 configurations for point group D_{2h} and 3767 configurations for point group C_{2v}.

The CI results for F_2^+ are summarized in table 2. One of the most interesting results is that the D_{2h} orbitals provide a lower CI energy (by 0·01190 hartrees) than do the C_{2v} orbitals. Given that the single-configuration D_{2h} energy was 0·01246 hartrees above the analogous C_{2v} energy, this represents a significant reversal. It may be concluded that, while the removal of the constraint of inversion symmetry lowers the single-configuration RHF energy considerably, the D_{2h} orbitals nevertheless provide the better orbitals for a CI expansion. The CI using D_{2h} orbitals yields a bond distance r_e of 1·296 Å, just 0·002 Å outside the experimental error bars (Tuckett *et al.* 1983). The CI based on C_{2v} orbitals yields $r_e = 1{\cdot}284$ Å, or 0·021 Å less than experiment.

A simple correction for the effect of unlinked clusters, specifically quadruple excitations, is that due to Davidson (1974), namely

$$\Delta E_Q = (1 - c_0^2)\Delta E_{SD} \qquad (2)$$

where c_0 is the coefficient of the SCF wavefunction in the CISD wavefunction and ΔE_{SD} is the correlation energy due to single and double excitations, namely $E_{CISD} - E_{SCF}$. Since this simple correction has widely been found to be helpful, we have included in table 2 bond distance predictions made in this manner. Using D_{2h} orbitals, the Davidson-corrected bond distance is 1·332 Å, some 0·027 Å longer than experiment. It should be noted that a further extension of the basis set will almost certainly reduce the predicted bond distance (Schaefer 1974). On the other hand, the effect of inclusion of triple substitutions may lead to a lengthening of the F–F bond (see below). Using C_{2v} orbitals, the Davidson-corrected bond distance for F_2^+ is 1·307 Å, in good agreement with experiment. This latter result would also be obtained by ignoring symmetry entirely, since we have earlier observed that there is no symmetry breaking below point group C_{2v}. In this sense, all the C_{2v} results reported here (SCF, CI, Davidson-corrected CI) avoid the symmetry bias described as 'rather unsatisfactory' by Farnell *et al.* (1983).

Before concluding this section, it is reasonable to ask if there is some RHF-based method (of correct symmetry) simpler than CISD which renders the F_2^+ bond distance qualitatively correct. An obvious choice is the two-configuration (TC) SCF model, which for F_2^+ includes the second configuration

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_u^2 1\pi_g^3 \qquad (3)$$

in addition to (1). Such a TCSCF treatment is analogous to that used to describe the proper dissociation of F_2 to two F atoms (Das and Wahl 1966). Moreover, since the predicted $D_{\infty h}$ and D_{2h} RHF bond distances are much too short, the idea of adding some antibonding character, in the form of the double excitation $3\sigma_g^2 \rightarrow 3\sigma_u^2$, obviously recommends itself. The resulting $D_{\infty h}$ and D_{2h} TCSCF optimized geometries are included in table 2. The importance of the second configuration (3) is apparent from the total energies, not to mention the predicted bond distances. For a $D_{\infty h}$ symmetry constraint, the energy difference between the one and two-configuration SCF wavefunctions is 0·05136 hartrees. This difference clearly corresponds to an important near-degeneracy correlation effect (Clementi and Veillard 1966), since the *entire* correlation energy associated with a normal electron pair is only about 0·04 hartrees (Nesbet 1967). The importance of the second configuration is also seen in its large coefficient, 0·255, corresponding to 6·5 per cent of the wavefunction. The predicted $D_{\infty h}$ TCSCF bond distance is 1·278 Å, still 0·027 Å less than experiment, but an improvement of 0·057 Å over the analogous one-configuration SCF result. The D_{2h} TCSCF bond distance is 1·288 Å, and thus only 0·017 Å less than the experimental equilibrium internuclear separation.

4. Methods based on spin-unrestricted Hartree–Fock orbitals

The spin-unrestricted Hartree–Fock (UHF) method provides an alternative path to the description of the electronic structure of open-shell molecules such as F_2^+. Theoretical predictions based on UHF orbitals are seen in table 3. Given the previously described experience with the RHF method, the UHF investigations were restricted to

Table 3. Theoretical predictions for the X $^2\Pi_g$ ground state of F_2^+ based on spin-unrestricted Hartree–Fock (UHF) wavefunctions constrained to different spatial symmetries.

Point group	Theoretical method†	Bond distance, r_e (Å)	Total energy (hartrees)
D_{2h}	UHF	1·223	−198·17602
D_{2h}	UMP2	1·392	−198·53762
D_{2h}	UMP3	1·310	−198·52167
D_{2h}	UMP4DQ	1·308	−198·52403
D_{2h}	UMP4SDQ	1·322	−198·53260
D_{2h}	UMP4SDTQ	1·352	−198·54743
C_{2v}	UHF	2·155	−198·22795
C_{2v}	UMP2	1·180	−198·50262
C_{2v}	UMP3	1·180	−198·50031
C_{2v}	UMP4DQ	1·180	−198·50269
C_{2v}	UMP4SDQ	1·212	−198·50971
C_{2v}	UMP4SDTQ	1·213	−198·51924
Experiment‡		1·305 ± 0·007	

† The abbreviation UMP4SDTQ implies the use of fourth-order Møller–Plesset perturbation theory including single, double, triple and quadruple excitations.

‡ Tuckett *et al.* (1983).

point groups D_{2h} and C_{2v}. Here we discuss first the D_{2h} results (in which inversion symmetry was enforced on the UHF orbitals) and then the C_{2v} predictions (where inversion symmetry was ignored).

4.1. D_{2h} *symmetry results*

Perhaps the first observation to be made concerning table 3 is that the UHF and RHF bond distances are very similar in point group D_{2h}. Specifically, the RHF bond distance of 1·221 Å is increased to 1·223 Å when UHF theory is used. The energy difference ($E_{UHF} - E_{RHF}$) is however significant, −0·01072 hartrees. For the RHF wavefunction, the expectation value $\langle S^2 \rangle$ is precisely $S(S+1) = 3/4$, while for the UHF wavefunction $\langle S^2 \rangle$ is marginally higher at 0·766. One concludes that the D_{2h} RHF and UHF wavefunctions share the same problem leading to an unrealistically short bond distance for F_2^+.

Continuing in D_{2h} symmetry, second-order perturbation theory (UMP2) overcompensates for the deficiencies of UHF theory. From a bond distance prediction 0·082 Å too short (UHF), UMP2 proceeds to a prediction ($r_e = 1·392$ Å) that is 0·087 Å too long with respect to experiment. This tendency to overestimate the importance of double excitations (Slater determinants differing by two spin orbitals from the Hartree–Fock reference function) is a general finding and is by no means restricted to the F_2^+ bond distance (Krishnan *et al.* 1980 a). Table 3 shows that third-order perturbation theory (UMP3) predicts an r_e value of 1·310 Å, which lies within the experimental error bars. Again, this is not a surprising result, since UMP3 is known to provide a fairly realistic estimate of the importance of double excitations (Frisch *et al.* 1980).

Table 3 gives three separate entries associated with fourth-order perturbation theory (UMP4). The first of these, labelled UMP4DQ, incorporates only the contributions in fourth order from double and quadruple excitations (Krishnan and Pople 1978). Alternatively, this form of fourth-order perturbation theory adds to the UMP3 energy expression the fourth-order doubles contribution and, for the first time, a contribution from quadruples. The predicted bond distance is $r_e = 1{\cdot}308$ Å, in close agreement with experiment. Adding the fourth-order contribution of single excitations (UMP4SDQ) leads to a slight extension of the bond distance to $r_e = 1{\cdot}322$ Å. However, when the fourth-order contribution of triple excitations is appended (giving UMP4SDTQ, the complete fourth-order treatment) (Krishnan *et al.* 1980 b), the bond distance again increases, this time to 1·352 Å. At this level, the F_2^+ bond distance is 0·047 ± 0·007 Å longer than experiment.

To this discussion of the results of table 3, some comments must be added concerning the adequacy of the standard DZ + P basis set used in this research. It seems likely (Schaefer 1974) that *all* the bond distances in tables 2 and 3 will be shortened when significantly more complete basis sets are applied to the F_2^+ problem. As a simple example, the DZ + P SCF method yields a bond distance of 1·082 Å for the N_2 molecule (de Castro *et al.* 1981), while the Hartree–Fock limit has been known for some time (Cade *et al.* 1966) to be 1·066 Å, some 0·016 Å shorter. Such a basis set effect would bring the UMP4SDTQ bond length mentioned above into better agreement with experiment.

4.2. C_{2v} *symmetry results*

The UHF equations also have solutions without inversion symmetry. At the single-determinant UHF level, such symmetry breaking leads to a lowering of the energy. However, examination of table 3 indicates that, analogous to the RHF + CI results discussed above, the Møller–Plesset calculations based on D_{2h} orbitals lead to a lower energy than those based on C_{2v} orbitals.

As anticipated from the UHF/6-31G* SCF results of Farnell *et al.* (1983), there is no minimum near 1·3 Å for the ground state of F_2^+ when inversion symmetry is not enforced. At r(F–F) = 1·3 Å, the C_{2v} UHF total energy is −198·18488 hartrees, some 0·01695 hartrees below the analogous D_{2h} UHF energy. The expectation value $\langle S^2 \rangle$ for $r = 1{\cdot}3$ Å is 0·815, compared with 0·767 for the D_{2h} UHF wavefunction at the same bond distance. Thus, the lowering of the spatial symmetry from D_{2h} to C_{2v} is accompanied by a shift in the expectation value $\langle S^2 \rangle$ away from the correct value 0·75.

Farnell *et al.* (1983) noted that, when inversion symmetry is removed, the UHF method does not predict a normal equilibrium bond distance for F_2^+. This observation has been pursued in the present research to the extent of locating the precise minimum in the C_{2v} UHF potential curve. This minimum occurs at 2·155 Å, as seen in table 3. Given that this bond distance is nearly twice the experimental value, we must concur with Farnell *et al.* (1983) that the truly unrestricted HF method does not describe the F_2^+ molecular ion in a satisfactory manner.

Although the five different C_{2v} perturbation theory approaches summarized in table 3 improve upon the UHF result, they all yield bond distances considerably shorter than experiment. The most complete level of theory, the full fourth-order method (UMP4SDTQ), predicts $r_e(F_2^+) = 1{\cdot}213$ Å, nearly 0·1 Å less than the experimental value of 1·305 ± 0·007 Å. It may be reasonably concluded that fourth-order perturbation theory based on a UHF starting point without inversion symmetry does not give a satisfactory description of the structure of F_2^+. This is one example for which an RHF starting point (C_{2v} entries in table 2) is evidently preferable.

5. Concluding remarks

The F_2^+ ion is clearly one of the more difficult cases for quantum electronic structure theory, but it is also clear that accurate results can be obtained when sufficient effort is put into the calculation. It is apparent that the effort required depends appreciably on the type of molecular orbitals used.

Ordinarily, one would expect that the lowest-energy orbitals—those computed with the fewest restrictions on their form—would be the best basis on which to build configuration-interaction or perturbation-theory refinements. A growing number of examples, now including F_2^+, show this expectation to be invalid.

Relaxing the rotational symmetry restriction on F_2^+ ($D_{\infty h} \rightarrow D_{2h}$, $C_{\infty v} \rightarrow C_{2v}$) allows the π_x and π_y orbitals to take different shapes when they are occupied by different numbers of electrons. The effects are comparatively small: a maximum of 0·005 hartrees in energy and 0·01 Å in bond distance.

Relaxing the inversion symmetry ($D_{\infty h} \rightarrow C_{\infty v}$, $D_{2h} \rightarrow C_{2v}$) allows orbitals, and therefore the positive charge, to concentrate more at one end of the molecule than the other. This change, when applied to RHF wavefunctions, is somewhat larger: 0·01 hartrees in energy and 0·1 Å in bond distance.

Relaxing the spin eigenfunction requirement (RHF→UHF) has only a modest effect unless coupled with relaxation of the inversion symmetry restriction: 0·01 hartrees in energy and 0·002 Å in bond distance for the D_{2h} case vs 0·05 hartrees in energy and 0·8 Å in bond distance for the C_{2v} case.

Nevertheless, at the singles-and-doubles configuration interaction and second-order perturbation theory levels, and at all higher levels of correlation, the calculations based on the more restricted wavefunctions gave lower energies and generally better bond distances. This phenomenon has been noted in a number of other cases, including N_2 over a considerable range of bond distance (Bartlett 1981), ONCN for a large range of geometries (Bell 1981), and CO_2H^+, also for several geometries (Frisch *et al.* 1985).

The possible conclusion to be drawn is that when moderate bond distances are involved, correlated calculations are best based on self-consistent-field wavefunctions which have been constrained to have the same spin and spatial symmetry properties that the exact solution possesses. In extreme cases, such as diatomic molecules at large internuclear distance, where the RHF wavefunctions are grossly inadequate, this conclusion clearly does not apply. Another type of exception may be illustrated by the excited singlet states of trimethylenemethane at the ground-state D_{3h} geometry (Yarkony and Schaefer 1974), where the D_{3h}-constrained singlet wavefunctions are also seriously in error.

The need for a general solution to the problem of obtaining orbitals for correlated wavefunctions is a prime reason for the wide current interest in MCSCF wavefunctions, of which the two-configuration wavefunctions used here are the simplest type. The difficulties in treating F_2^+ by simple conventional methods provide another indication of the need for further development of the techniques for obtaining electronic wavefunctions.

Acknowledgments

RM and HFS were supported by the U.S. National Science Foundation, Grant CHE-8218785, and RMP by Grant CHE-8312286. Part of the computer time was supplied by NASA-Lewis Laboratory.

References

Bagus, P. S., and Schaefer, H. F., 1972, *J. chem. Phys.*, **56,** 224.
Baird, N. C., Gupta, R. R., and Taylor, K. F., 1979, *J. Am. chem. Soc.*, **101,** 4531.
Bartlett, R. J., 1981, *A. Rev. phys. Chem.*, **32,** 359.

Bell, S., 1981, *J. chem. Soc. Faraday Trans.* II, **77,** 321.

Benard, M., 1979, *J. chem. Phys.*, **71,** 2546.

Benard, M., and Paldus, J., 1980, *J. chem. Phys.*, **72,** 6546.

Binkley, J. S., Pople, J. A., and Hehre, W. J., 1980, *J. Am. chem. Soc.*, **102,** 939.

Borden, W. T., 1976, *J. Am. chem. Soc.*, **98,** 2695.

Borden, W. T., Davidson, E. R., and Feller, D., 1980, *J. Am. chem. Soc.*, **102,** 5302.

Borden, W. T., Davidson, E. R., and Feller, D., 1982, *Tetrahedron*, **38,** 737.

Cade, P. E., Sales, K. D., and Wahl, A. C., 1966, *J. chem. Phys.*, **44,** 1973.

Chambaud, G., Levy, B., and Millie, P., 1978, *Theor. chim. Acta*, **48,** 103.

Clementi, E., and Veillard, A., 1966, *J. chem. Phys.*, **44,** 3050.

Das, G., and Wahl, A. C., 1966, *J. chem. Phys.*, **44,** 87.

Davidson, E. R., 1974, *The World of Quantum Chemistry*, edited by R. Daudel and B. Pullman (Dordrecht: Reidel), pp. 17–30.

Davidson, E. R., and Borden, W. T., 1976, *J. chem. Phys.*, **64,** 663.

Davidson, E. R., and Borden, W. T., 1977, *J. chem. Phys.*, **67,** 2191.

De Castro, S. C., Schaefer, H. F., and Pitzer, R. M., 1981, *J. chem. Phys.*, **74,** 550.

Dixon, R. N., 1971, *Molec. Phys.*, **20,** 113.

Engelbrecht, L., and Liu, B., 1983, *J. chem. Phys.*, **78,** 3097.

Farnell, L., Pople, J. A., and Radom, L., 1983, *J. phys. Chem.*, **87,** 79.

Feller, D., Davidson, E. R., and Borden, W. T., 1983, *J. Am. chem. Soc.*, **105,** 3347.

Frisch, M. J., Krishnan, R., and Pople, J. A., 1980, *Chem. Phys. Lett.*, **75,** 66.

Frisch, M. J., Schaefer, H. F., and Binkley, J. S., 1985, *J. phys. Chem.*, **89,** 2192.

Hariharan, P. C., and Pople, J. A., 1973, *Theor. chim. Acta*, **28,** 213.

Hehre, W. J., Stewart, R. F., and Pople, J. A., 1969, *J. chem. Phys.*, **51,** 2657.

Hoffmann, M. R., Laidig, W. D., Kim, K. S., Fox, D. J., and Schaefer, H. F., 1984, *J. chem. Phys.*, **80,** 338.

Jackels, C. F., and Davidson, E. R., 1976, *J. chem. Phys.*, **64,** 2908.

Krishnan, R., and Pople, J. A., 1978, *Int. J. quantum Chem.*, **14,** 91.

Krishnan, R., Binkley, J. S., Seeger, R., and Pople, J. A., 1980 a, *J. chem. Phys.*, **72,** 650.

Krishnan, R., Frisch, M. J., and Pople, J. A., 1980 b, *J. chem. Phys.*, **72,** 4244.

Levin, G., and Goddard, W. A., 1975 a, *J. Am. chem. Soc.*, **97,** 1649.

Levin, G., and Goddard, W. A., 1975 b, *Theor. chim. Acta*, **37,** 253.

Manne, R., 1972, *Molec. Phys.*, **24,** 935.

McKelvey, J., and Hehre, W. J., 1973, *Molec. Phys.*, **25,** 983.

McKelvey, J. M., and Berthier, G., 1976, *Chem. Phys. Lett.*, **41,** 476.

Møller, C., and Plesset, M. S., 1934, *Phys. Rev.*, **46,** 618.

Müller, J., Agren, H., and Goscinski, O., 1979, *Chem. Phys.*, **38,** 349.

Nesbet, R. K., 1967, *Phys. Rev.*, **155,** 51.

Paldus, J., and Veillard, A., 1978, *Molec. Phys.*, **35,** 445.

Pople, J. A., and Nesbet, R. K., 1954, *J. chem. Phys.*, **22,** 571.

Pople, J. A., Binkley, J. S., and Seeger, R., 1976, *Int. J. quantum Chem. Symp.*, **10,** 1.

Poppinger, D., Radom, L., and Vincent, M. A., 1977, *Chem. Phys.*, **23,** 437.

Roothaan, C. C. J., 1960, *Rev. mod. Phys.*, **32,** 179.

Schaefer, H. F., 1974, in *Critical Evaluation of Chemical and Physical Structural Information* (Washington, D.C.: National Academy of Sciences).

Seeger, R., and Pople, J. A., 1977, *J. chem. Phys.*, **66,** 3045.

Tuckett, R. P., Dale, A. R., Jaffey, D. M., Jarrett, P. S., and Kelly, T., 1983, *Molec. Phys.*, **49,** 475.

Voter, A. F., and Goddard, W. A., 1981 a, *Chem. Phys.*, **57,** 253.

Voter, A. F., and Goddard, W. A., 1981 b, *J. chem. Phys.*, **75,** 3638.

Wadt, W. R., and Goddard, W. A., 1975, *J. Am. chem. Soc.*, **97,** 2034.

Walker, T. E. H., 1971, *Chem. Phys. Lett.*, **9,** 174.

Yarkony, D. R., and Schaefer, H. F., 1974, *J. Am. chem. Soc.*, **96,** 3754.