Theoret. Chim. Acta (Berl.) 36, 125—134 (1974)

A Comparison of Different Methods in Determining Energies and Geometries of Open-Shell Systems*

Norman Colin Baird and Robert Francis Barr**

Photochemistry Unit, Department of Chemistry, University of Western Ontario, London, Canada

Received April 9, 1974/July 11, 1974

Three methods of obtaining eigenvectors for open-shell systems, namely the Roothaan restricted open-shell method, the "half-electron" method, and the use of ground state orbitals, are compared with each other both on a formal basis, and by contrasting the *ab initio* energies predicted by these schemes for a series of radicals and triplets. The r.m.s. improvement in the energy of eight radicals by use of the Roothaan method rather than the half-electron approximation amounts to 4.8 kcal mole^{-1}, whereas the r.m.s. improvement for nineteen triplet states is 8.2 kcal mole^{-1}. Optimum geometries predicted by these two methods do not differ appreciably. The use of closed-shell eigenvectors rather than those of the half-electron method leads to very large errors for triplet states whose electron density distributions differ appreciably from those of the ground state.

Key words: Open-shell methods, comparison of ~ – Roothaan open-shell method – Half-electron method

1. Introduction

Although the overwhelming majority of modern molecular orbital calculations for closed-shell systems employ the Hartree-Fock-Roothaan method [1], the corresponding calculations for open-shell systems are currently executed using a variety of methods. Most *ab initio* calculations on radicals and triplet states employ either the Roothaan restricted open-shell technique [2] or the "unrestricted" method proposed by Pople and Nesbet [3]. On the other hand, many semi-empirical MO calculations for open-shell configurations use the simpler "half-electron" method [4]. Given the difficulties in convergence and computational expense associated with the Roothaan technique, it seems desirable to explore the use of the half-electron method in the context of *ab initio* calculations. In particular, we are interested here in comparing the energies of open-shell systems as calculated at three levels of sophistication – the Roothaan open-shell method, the half-electron method, and in the case of triplets the simple use of optimum ground state eigenvectors for the excited state.

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* Publication No. 106 of the Photochemistry Unit. Research supported by the National Research Council of Canada. Abstracted, in part, from the thesis submitted by R. F. Barr in partial fulfillment for the Ph. D. degree, University of Western Ontario, 1974.

** Holder of National Research Council of Canada Scholarships 1970–74.

The half-electron method for radicals and triplets [4] retains the computational simplicity and speed of a closed-shell, single determinant calculation[1], while employing the correct populations (0, 1, or 2 electrons) for the molecular orbitals in the open-shell problem. The "error" in the half-electron method occurs because the quantity that is minimized in determining the MO coefficients does *not* correspond exactly to the energy of the radical or triplet. The method does account properly for the total one-electron energy and for most of the two-electron terms; in particular, the Coulomb and exchange repulsion between the paired electrons with each other and with the unpaired electron(s) and the Coulomb repulsion between unpaired electrons in different MOs are all correctly included. For radicals, the only error in the quantity minimized is a spurious Coulomb repulsion between the two "half-electrons". For triplets, this error appears twice (once for each singly-occupied MO) and in addition the exchange repulsion term between the two unpaired electrons is underestimated by one-half. Thus the quality of the half-electron method wavefunction is affected by the extent to which the wavefunction is altered by minimizing not the true energy but the true energy plus the errors. For minimal basis set calculations in which the MOs of the unpaired electrons are completely determined by symmetry, use of the method entails no error since the spurious terms enter the energy expression as additive constants.

In contrast to the determination of wavefunctions by the half-electron method, use of closed-shell eigenvectors for radicals and triplets involves much larger errors since the MO populations for the latter differ from those for the closed-shell problem. Thus the quantity minimized here differs from the true open-shell energy by 100% of the one-electron energy for one of the unpaired electrons as well as by a 100% error in the total repulsion energy (Coulomb plus exchange) between this electron and all other electrons present. For this reason, use of half-electron method wavefunctions is expected to yield an energy superior to that calculated from the closed-shell eigenvectors in most cases.

Our intention in this research is to make a thorough and quantitative comparison between the three techniques mentioned above in the context of minimal basis set *ab initio* calculations of the total energy and predicted geometries for polyatomic radicals and triplets. To this end, the half-electron and Roothaan open-shell procedures are compared on a formal basis in the next section, and the performance of the three methods is compared for 8 different radicals and 19 different triplets in the final section.

2. Theory

The expectation value for the energy of an open-shell electron configuration is given in Roothaan's formulation [3] by Eq. (1), in which f, a, and b are

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[1] The only changes in a closed-shell MO computer program which are required to execute half-electron method calculations are a) calculation of the bond order matrix P by the equation $P_{uv} = \Sigma_i N_i C_{iu} C_{iv}$ where the MO occupation numbers $N_i = 0$, 1, or 2 rather than just 0 or 2; and b) correction of the electronic energy by $\frac{1}{4}\Sigma_m \Sigma_n K_{mn}$ if it is calculated using the expression $\frac{1}{2}\Sigma_i N_i(\varepsilon_i + I_i)$ or the expression $\frac{1}{2}\Sigma_i N_i \varepsilon_i + \frac{1}{2}\Sigma_u \Sigma_v P_{uv} H_{uv}$ rather than by Eq. (4) directly.

numerical constants:

$$E=2\sum_k I_k+\sum_k\sum_l(2J_{kl}-K_{kl})$$
$$+f\left[2\sum_m I_m+f\sum_m\sum_n(2aJ_{mn}-bK_{mn})+2\sum_k\sum_m(2J_{km}-K_{km})\right]. \quad (1)$$

Note that indices k, l are used for individual doubly-occupied orbitals, m and n are used for singly-occupied orbitals, and we reserve the indices i, j for orbitals of either type. The radicals and triplet states of concern herein all have "half-filled shells" (i.e. they possess the same number of open-shell electrons as occupied open-shell orbitals, with all spins parallel for the singly-occupied orbitals) in which case f, a, and b have the fixed values of $\frac{1}{2}$, 1, and 2 respectively [3]. For such cases Eq. (1) simplifies to the form

$$E=2\sum_k I_k+\sum_k\sum_l(2J_{kl}-K_{kl})+\sum_m I_m+\tfrac{1}{2}\sum_m\sum_n(J_{mn}-K_{mn})+\sum_k\sum_m(2J_{km}-K_{km}). \quad (2)$$

In the half-electron method, the quantity E' minimized in the SCF process is given by a modification of the usual closed-term expression:

$$E'=\sum_i N_iI_i+\tfrac{1}{4}\sum_i\sum_j N_iN_j(2J_{ij}-K_{ij}). \quad (3)$$

Here N_i represents the occupation number of MO number i. For the half-filled shell, Eq. (3) becomes

$$E'=2\sum_k I_k+\sum_k\sum_l(2J_{kl}-K_{kl})+\sum_m I_m+\tfrac{1}{4}\sum_m\sum_n(2J_{mn}-K_{mn})+\sum_k\sum_m(2J_{km}-K_{km}). \quad (4)$$

Thus the only difference between the true energy E of Eq. (2) and the quantity E' of Eq. (4) minimized in the half-electron method is a term associated with the singly-occupied orbitals:

$$E-E'=-\tfrac{1}{4}\sum_m\sum_n K_{mn}. \quad (5)$$

The extent to which the wavefunctions of the two methods differ due to inclusion of this spurious term can be examined easily for the diatomic radical HeH. In the LCAO-MO formulation of this problem using a minimal basis set, the MOs can be written as

$$\psi_1=C_{11}\phi_{\mathrm{H}}+C_{12}\phi_{\mathrm{He}}, \quad (6)$$

$$\psi_2=C_{21}\phi_{\mathrm{H}}+C_{22}\phi_{\mathrm{He}}. \quad (7)$$

Here ψ_1 is the doubly-occupied, bonding MO and ψ_2 is the singly-occupied, antibonding MO. Given any arbitrary value for one of the four coefficients (say C_{11}) and a value for the overlap integral S_{12}, the other three coefficients can be determined easily using orthogonality and normalization conditions. Thus both E and E' can be calculated as a function of C_{11} for this system. The Roothaan energy E and the quantity E' are plotted against C_{11} for the range of interest in Fig. 1. (These calculations refer to a He—H separation of 3.0 a.u. using an STO-4G basis (5) with 1s exponents for He and H of 1.69 and 1.24 respectively.) The minimum for the E function occurs at $C_{11}=0.033$ whereas that for E' occurs at $C_{11}=0.059$; complete wavefunctions for these

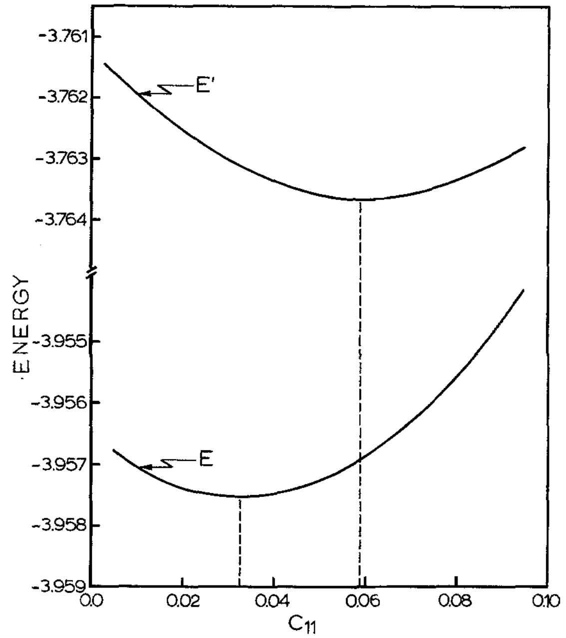

Fig. 1. Roothaan energy E, and the quantity E' (both in a.u.), versus c_{11}

Table 1. *Ab initio* wavefunctions for HeH

AO MO	Coefficients in Roothaan's method		Coefficients in the half-electron method	
	ϕ_{H}	ϕ_{He}	ϕ_{H}	ϕ_{He}
ψ_1	0.0328	0.9946	0.0593	0.9894
ψ_2	1.0108	−0.1832	1.0096	−0.2093

points are listed in Table 1. The fact that the electron in the singly-occupied MO is more delocalized in the half-electron wavefunction than in the open-shell is consistent with the attempt of the former method to reduce a spurious repulsion between the half-electrons. In general, this type of effect will always be present for radicals since, from Eq. (5), for a radical

$$E' = E + K_{22}/4 = E + J_{22}/4 . \tag{8}$$

Although the difference in the energy calculated properly from both wavefunctions amounts to only 0.0006 a.u. in this case[2], the difference is generally expected to be larger for triplet states since E' contains three, rather than just one, spurious terms:

$$E' = E + J_{mm}/4 + J_{nn}/4 + K_{mn}/2 . \tag{9}$$

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[2] The terms E and E' in Fig. 1 differ by ~0.2 a.u. *before* E' is corrected by $J_{22}/4$. The value of 0.0006 a.u. refers to the difference *after* the correction has been made.

Carsky and Zahradnik have discussed several instances for semiempirical calculations in which the Roothaan and half-electron methods yield identical energies and wavefunctions [6]. This will always occur in minimal basis set calculations in which the singly-occupied MOs are completely determined by symmetry, since the spurious terms in E' involve only the singly-occupied MOs and are constants in such cases. In general, the Fock operators in the Roothaan and half-electron methods differ for both the open and closed shells:

$$\hat{F}_c = \hat{F}_{\frac{1}{2}} + \sum_m \hat{M}_m \qquad \text{for doubly-occupied MOs } k\,, \tag{10}$$

$$\hat{F}_0 = \hat{F}_{\frac{1}{2}} - \tfrac{1}{2}\sum_m \hat{K}_m + \sum_k \hat{M}_k \qquad \text{for singly-occupied MOs } m\,. \tag{11}$$

The effect of the closed shell operators on an arbitrary function however, is the same:

$$\hat{F}_c \phi_k = \hat{F}_{\frac{1}{2}} \phi_k\,. \tag{12}$$

For the singly-occupied orbitals, even in symmetry-determined cases the eigenvalues determined by the Roothaan and half-electron methods differ, though the total energies are identical. If the Roothaan method is formulated in terms of a single Fock operator $\hat{F}$, then the eigenvalues of the singly-occupied MOs become identical, but those for the doubly-occupied MOs now differ:

$$\hat{F}\phi_k = \hat{F}_{\frac{1}{2}}\, \phi_k + \sum_m K_{km} \phi_k\,, \tag{13}$$

$$\hat{F}\, \phi_m = \hat{F}_{\frac{1}{2}} \phi_m\,. \tag{14}$$

Note that the eigenvectors of $\hat{F}_c$ and $\hat{F}_0$ must be identical to those deduced from $\hat{F}_{\frac{1}{2}}$ whenever the singly-occupied MOs are symmetry-determined. Thus our arguments are more generally applicable than those given by Carsky and Zahradnik who arrive at this conclusion only for special cases in which certain exchange integrals are zero. Our conclusions have been tested by calculations on several symmetry-determined systems (planar CH_3, NH_2, planar $C_2H_4^+$, planar $C_2H_4^-$, and the planar $^3(\pi, \pi^*)$ state of C_2H_4); in all cases the total energy deduced by the Roothaan scheme and the half-electron method agreed exactly, whereas the doubly occupied MO eigenvalues of $\hat{F}$ and of $\hat{F}_{\frac{1}{2}}$ differed since the exchange integrals were nonzero.

3. Results and Discussion

In order to compare quantitatively the performance of the three methods (i.e. the Roothaan restricted open-shell procedure, the half-electron method, and the use of closed shell orbitals), *ab initio* calculations using Pople's STO-3G expansions and standard molecular exponents [5] have been performed for a number of radicals and triplets.

The total energies for the ground states of eight small free radicals calculated by the Roothaan open-shell method are compared with those

Table 2. Energies (in a.u.) for ground states of free radicals

Radical	State designation	Roothaan energy	Roothaan method energy improvement over half-electron method
BH_2[a]	$^2A_1$	− 25.40817	0.00234
H_2CN[b]	$^2A'$	− 92.23328	0.00985
H_2NO[c]	$^2A'$	−128.67874	0.01447
HCO[a]	$^2A'$	−111.72751	0.00129
C_2H_3[d]	$^2A'$	− 76.41135	0.00796
C_2H_5[d]	$^2A'$	− 77.65919	0.00458
NO_2[a]	$^2A_1$	−201.26761	0.00060
NF_2[a]	$^2B_1$	−249.74005	0.00810

[a] Calculated using experimental geometry listed in Herzberg, G.: Molecular spectra and molecular structure, Vol. III. Princeton, N. J.: Van Nostrand, 1967.

[b] Geometry assumed: $R(CN) = 1.273$ Å, $R(CH) = 1.088$ Å, angle (HCN) = 121.5°. Baird, N.C.: unpublished STO-3G calculations.

[c] Calculated using geometry calculated in Salotte, A. W., Burnelle, L.: J. Chem. Phys. **53**, 333 (1970).

[d] Calculated using geometry listed in Lathan, W. A., Hehre, W. J., Pople, J. A.: J. Am. Chem. Soc. **93**, 808 (1971).

Table 3. Predicted and experimental geometries of HCO, NO_2, and NF_2

Radical	State	Parameter[a]	Method		Experimental[b]
			Half-electron	Roothaan	
HCO	$^2A'$	R(CO)	1.19_5	1.19_4	1.198
		R(CH)	1.11_1	1.11_4	1.08
		angle (CHO)	125.8	126.6	119.5
		total energy	−111.72665	−111.72927	
NO_2	$^2A_1$	R(NO)	1.23_6	1.23_6	1.1934
		angle (ONO)	134.2	134.6	134.1
		total energy	−201.27620	−201.27679	
NF_2	$^2B_1$	R(NF)	1.35_5	1.36_1	1.37
		angle (FNF)	101.9	101.9	104.2
		total energy	−249.7326	−249.7404	

[a] Bond lengths are in Å, angles in degrees, and energies in a.u.

[b] Experimental geometries from Herzberg, G.: Molecular spectra and molecular structure, Vol. III. Princeton, N. J.: Van Nostrand 1967.

calculated for the same geometries by the half-electron procedure in Table 2. (Calculations for CH_3, NH_2, $C_2H_4^+$, and $C_2H_4^-$ have been omitted since the unpaired electron MOs are determined by symmetry in the STO-3G approximation, with the result that the energies calculated by the two methods are identical.) The root mean square improvement using the Roothaan wavefunctions is 0.0076 a.u., or 4.8 kcal mole^{-1}. Given this difference, one might expect that the geometries predicted by the two methods for such radicals would differ significantly. However, complete optimization of the geometrical structures

Table 4. Calculated energies (in a.u.) for triplet states

Molecule	Geometry	State Designation	Roothaan Energy	Roothaan method energy improvement over	
				Half-electron method	Closed-shell orbitals
CH_2	[a]	$^3B_1$	-38.42916	0.00617	0.00316
NH_2^+	[b]	$^3B_1$	-54.54242	0.00418	0.00122
C_2H_2	[c]	$^3B_2$	-75.74540	0.01074	0.01523
C_2H_4	[d]	$^3A_2$	-77.01162	0.00855	0.00887
C_4H_6	[e]	^3B_u	-152.90442	0.01533	0.03195
HCF	[f]	$^3A''$	-135.89433	0.01168	0.01125
CF_2	[g]	$^3B_1$	-233.36019	0.01190	0.01409
CH_3CH	[a,h]	$^3A''$	-77.01453	0.01523	0.02156
HCN	[f]	$^3A''$	-91.54580	0.01587	0.02753
HCP	[f]	$^3A''$	-374.68753	0.00731	0.00676
HNO	[f]	$^3A''$	-126.07196	0.01331	0.01827
HNNH	[i]	^3B	-108.51529	0.01732	0.02250
H_2BNH_2	[j]	$^3A_2$	-80.28197	0.02033	0.05941
H_2CNH	[k]	$^3A''$	-92.77203	0.01147	0.10944
H_2NN	[l]	$^3A''$	-108.58886	0.01711	0.01907
H_2CO	[f]	$^3A''$	-112.31850	0.01824	0.07535
H_2CS	[m]	$^3A_2$	-431.65805	0.01117	0.06080
NCN	[f]	$^3\Sigma_g^-$	-144.75811	0.00000	0.02061
O_3	[n]	$^3B_2$	-221.42485	0.01640	0.06035

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for HCO, NO_2, and NF_2 produce r.m.s. differences of only ± 0.003 Å in the bond lengths and $\pm 0.5°$ in the bond angles (see Table 3). Thus the energetic inferiority of the half-electron method wavefunction is appreciable but is almost independent of geometry for these free radicals.

As anticipated above, the inferiority of the half-electron wavefunction is greater for triplet states than for free radicals according to the results for the nineteen molecules listed in Table 4. The r.m.s. energy improvement using the Roothaan open-shell wavefunction relative to that of the half-electron procedure is 0.013 a.u., or 8.2 kcal mole^{-1}. The differences in the optimum geometrical structures for the six triplet states documented in Table 5 are also more appreciable than for the free radicals; the r.m.s. deviation in the distances is ±0.007 Å and in the bond angles is ±2.4°.

In fifteen of the nineteen triplets listed in Table 4, the half-electron method yields an energy superior to that obtained using MOs of lowest closed-shell singlet state. On the average the energy obtained using the closed-shell eigenvectors is much farther from the Roothaan open-shell result (r.m.s. deviation of 0.042 a.u. or 26 kcal mole^{-1}) than is the half-electron energy (r.m.s. deviation of 0.013 a.u. or 8.2 kcal mole^{-1}). In addition, the magnitude of the energy improvement from the closed-shell result is much less predictable than is that from the half-electron results, since the standard deviation from the mean deviation of the former is five times that of the latter.

It is instructive to consider more closely the five triplets (those of H_2CO, H_2CS, H_2CNH, O_3, and H_2BNH_2) for which the energy computed from closed-shell eigenvectors is particularly bad (open-shell improvement >0.05 a.u.). In all five cases, the electronic charge distribution in the triplet state is appreciably different from that in the ground state since the excitation involves moving an electron from a highly localized orbital on the most electronegative atom to a π^* orbital which has its greatest amplitude on the heavy atom(s) of lesser electronegativity. Evidently the charge reorganization accompanying such an excitation is handled rather well by the half-electron method, since the half-electron to Roothaan energy improvement for these five cases averages one-quarter the closed-shell to Roothaan energy difference. This conclusion regarding electron redistribution is supported by an analysis of the unpaired electron MO coefficients used in the three methods. For example, the optimum π and π^* MOs for the ground state of formaldehyde are polarized *slightly* toward the oxygen and carbon atoms respectively. Thus excitation from the oxygen lone-pair (n) orbital into the π^* MO leads to an electron distribution with a net negatively charged carbon and positively charged oxygen if ground state MOs are employed. In contrast, both the half-electron and Roothaan open-shell methods predict a substantial reorganization of the π and π^* MOs for this state such that the former is localized essentially on the oxygen and the latter on the carbon. Thus both methods predict that both the carbon and the oxygen net charges are slightly negative in the lowest triplet state. Note also that the reorganization of the electron distribution in the half-electron and Roothaan methods leads to an optimum geometry for the $^3(n,\pi^*)$ state which is significantly different from that predicted using closed shell MOs. In particular, the carbon-oxygen bond length elongation (compared to the ground state) is predicted to be ~0.2 Å according to the first two methods, compared to ~0.1 Å according to the latter (Table 5). In addition, use of the closed shell wavefunctions yields a planar, rather than a pyramidal "flapped" geometry for the $^3(n,\pi^*)$ state. For the other molecules and states listed in Table 5, the excitation does not lead to much charge reorganization and the agreement between the closed-shell and open-shell wavefunction geometries is rather good.

In summary, it can be concluded that the use of the half-electron method to generate wavefunctions for open-shell systems is generally superior to the use

Table 5. Predicted geometries for six triplet states

Molecule	State	Parameter[a]	Method		
			Roothaan	Half-electron	Closed-shell orbitals
CH_2	$^3B_1$	R(CH)	1.082	1.078	1.079
		angle (HCH)	124.0	125.0	124.0
		total energy	− 38.43174	− 38.42504	− 38.42860
CO	$^3\Pi$	R(CO)	1.220	1.222	1.227
		total energy	−111.03651	−111.02353	−111.02524
NCN	$^3\Sigma_g^-$	R(CN)	1.238	1.239	1.231
		angle (NCN)	180.0	180.0	180.0
		total energy	−144.75825	−144.75830	−144.73750
H_2CO	$^3A''$	R(CO)	1.395	1.411	1.318
	$^3(n\pi^*)$	R(CH)	1.088	1.077	1.062
		angle (HCH)	117.0	121.0	125.0
		β[b]	37.0	36.0	0.0
		total energy	−112.32588	−112.31043	−112.24651
H_2CO	$^3A'$	R(CO)	1.472	1.470	1.456
	$^3(\pi\pi^*)$	R(CH)	1.092	1.087	1.081
		angle (HCH)	115.5	118.8	121.6
		β[b]	36.0	23.0	23.0
		total energy	−112.29489	−112.29118	−112.28875
C_2H_2	$^3B_2$	R(CO)	1.314	1.313	1.316
		R(CH)	1.091	1.085	1.084
		angle (HCC)	126.0 (*cis*)	127.0 (*cis*)	126.0 (*cis*)
		total energy	− 75.74567	− 75.73479	− 75.73046

[a] Bond lengths are in Å, angles in degrees, energies in a.u. Angles are optimized to ± 0.5°.

[b] β is the angle between the HCH plane and CO bond.

of eigenvectors deduced for the lowest closed-shell singlet state, particularly when the electronic charge distributions of the states differ appreciably. The r.m.s. deviations between the half-electron and Roothaan open-shell energies of ~5 and ~8 kcal mole^{-1} for radicals and triplet states respectively are probably too great for the former method to be used instead of the latter in applications where total energies (rather than geometries) are of prime importance. It should be pointed out, however, that use of SCF half-electron method eigenvectors as the "initial guess" for Roothaan open-shell calculations often decreases the number of iterations (and thus the computational cost) required to reach an SCF solution, although the saving in time varies from case to case. In some cases, use of the half-electron method eigenvectors can overcome the tendency of the Roothaan open-shell method either to diverge, oscillate, or to converge to a higher excited state. For example, calculations by our program for formaldehyde with a long carbon-oxygen bond (1.40 Å) leads to oscillation if the Roothaan open-shell method alone is used, and results in convergence to the $^3\pi\pi^*$ state if ground-state eigenvectors are used initially. The correct convergence to the lowest triplet state ($^3n\pi^*$ in character) is achieved if half-electron eigenvectors are used as the initial guess.

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Prof. Dr. N. C. Baird
Photochemistry Unit
University of Western Ontario
London, Ont., Canada