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Analytic evaluation of infrared intensities and polarizabilities by two-configuration self-consistent field wave functions

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For more than a few molecular electronic states, the simplest qualitatively correct picture of the electronic structure is provided by the two-configuration self-consistent-field (TCSCF) method. Here, analytic methods are reported for the evaluation of TCSCF infrared intensities and polarizabilities. These new methods have been implemented and applied to the molecules $CH_2(^1A_1)$, CF_2, CH_3^-, NH_3, HF and O_3. Nine different basis sets, ranging from 3-21G to triple zeta plus double polarization ($TZ+2P$), have been used. In several cases one finds qualitative differences between the analogous SCF and TCSCF predictions.

Key words: TCSCF-IR intensities — Polarizabilities

Introduction

In their landmark paper of 1966 Das and Wahl [1] were the first to apply the multiconfiguration self-consistent-field (MCSCF) [2] method to molecular systems. In particular they noted that the proper dissociation of diatomic molecules composed of two monovalent atoms required within the molecular orbital framework a two-configuration (TC)SCF wavefunction. They reported such TCSCF wavefunctions for the H_2, Li_2, and F_2 molecules.

The TCSCF method introduced by Das and Wahl [1, 2] has also proved tremendously helpful in describing the electronic structure of singlet diradical states of more complicated molecules. The most frequently cited examples include singlet

($^1A_1$) methylene [3], the singlet ground state of ozone [4], and the trimethylene diradical $CH_2CH_2CH_2$ [5]. In addition the TCSCF wavefunction is the simplest member of a more complete set of MCSCF wavefunctions, the generalized valence bond (GVB) series [6]. Often it has been found that the TCSCF treatment of diradical singlet states provides a level of theory analogous to that given by the single-configuration SCF description of the lowest triplet state. Such a combined SCF (triplet)/TCSCF (singlet) approach has been found to yield quite reliable values of the singlet-triplet energy separations for carbenes, for example [7].

The recently-developed ability of *ab initio* methods to provide reliable estimates [8, 9] of vibrational frequencies has led to concurrent interest in the theoretical prediction of infrared [10] and Raman [11] intensities. The development of analytic methods for the evaluation of such intensities should prove to be quite helpful in the assignment of experimental spectra [12]. To date analytic IR and Raman intensity methods have been restricted to single-configuration SCF methods [13–16].

As suggested above, the TCSCF method for singlet diradicals may reasonably be taken as a zeroth-order starting point for theoretical studies of the electronic structures of such systems. With this in mind we present here a theoretical treatment of analytic IR intensities and polarizabilities for TCSCF wavefunctions.

Theory

A. Electronic energy expression

Let us consider a two-configuration self-consistent-field (TCSCF) wavefunction Ψ

$$\Psi = C_1\Phi_1 + C_2\Phi_2 \tag{1}$$

which consists of two configurations

$$\Phi_1 = |\cdots m\bar{m}| \tag{2}$$

$$\Phi_2 = |\cdots n\bar{n}|. \tag{3}$$

The electronic energy of this TCSCF wavefunction can be expressed as

$$E_{\text{TCSCF}} = \sum_{IJ} C_I C_J H_{IJ} \tag{4}$$

where H_{IJ} are the matrix elements between configurations I and J and can be explicitly given as,

$$H_{11} = 2\sum_{i}^{\text{d.o.}} h_{ii} + \sum_{ij}^{\text{d.o.}} \{2(ii|jj) - (ij|ij)\}$$
$$+ 2h_{mm} + 2\sum_{i}^{\text{d.o.}} \{2(mm|ii) - (mi|mi)\} + (mm|mm) \tag{5}$$

$$H_{22} = 2\sum_{i}^{\text{d.o.}} h_{ii} + \sum_{ij}^{\text{d.o.}} \{2(ii|jj) - (ij|ij)\}$$
$$+ 2h_{nn} + 2\sum_{i}^{\text{d.o.}} \{2(nn|ii) - (ni|ni)\} + (nn|nn) \tag{6}$$

$$H_{12} = (mn\,|\,mn). \tag{7}$$

In the equations above the h_{ij} are one electron and the $(ij\,|\,kl)$ are two electron MO integrals. Alternatively, the electronic energy of Eq. (1) can be given by [5]

$$E_{\text{TCSCF}} = 2 \sum_{i}^{\text{occ}} f_i h_{ii} + \sum_{ij}^{\text{occ}} \{\alpha_{ij}(ii\,|\,jj) + \beta_{ij}(ij\,|\,ij)\} \tag{8}$$

where f_i is a one electron coupling constant, and α_{ij} and β_{ij} are Coulomb and exchange coupling constants.

It should be noted that the following relationships between the constants in Eqs. (4) and (8) exist:

$$\begin{aligned} f_m &= \alpha_{mm} = C_1^2 \\ f_n &= \alpha_{nn} = C_2^2 \\ \alpha_{mn} &= \beta_{mm} = \beta_{nn} = 0 \\ \beta_{mn} &= C_1 C_2. \end{aligned} \tag{9}$$

B. First derivatives of the TCSCF *electronic energy* [17]

The first derivative of the electronic energy, Eq. (8), with respect to a nuclear coordinate "a" is simply written as

$$E^a_{\text{TCSCF}} = 2 \sum_{i}^{\text{occ}} f_i h^a_{ii} + \sum_{ij}^{\text{occ}} \{\alpha_{ij}(ii\,|\,jj)^a + \beta_{ij}(ij\,|\,ij)^a\} - 2 \sum_{ij}^{\text{occ}} \varepsilon_{ij} S^a_{ij}. \tag{10}$$

In Eq. (10),

$$h^a_{ij} = \sum_{\mu\nu}^{AO} C^i_\mu C^j_\nu \frac{\partial h_{\mu\nu}}{\partial a} \tag{11}$$

$$(ij\,|\,kl)^a = \sum_{\mu\nu\rho\sigma}^{AO} C^i_\mu C^j_\nu C^k_\rho C^l_\sigma \frac{\partial(\mu\nu\,|\,\rho\sigma)}{\partial a} \tag{12}$$

$$S^a_{ij} = \sum_{\mu\nu}^{AO} C^i_\mu C^j_\nu \frac{\partial S_{\mu\nu}}{\partial a} \tag{13}$$

and the Lagrangian matrix ε is defined as

$$\varepsilon_{ij} = f_i h_{ij} + \sum_{k}^{\text{occ}} \{\alpha_{ik}(ij\,|\,kk) + \beta_{ik}(ik\,|\,jk)\}. \tag{14}$$

The first derivative of the electronic energy with respect to an electric field "f" is given in a simpler form,

$$E^f_{\text{TCSCF}} = 2 \sum_{i}^{\text{occ}} f_i h^f_{ii} \tag{15}$$

where

$$\begin{aligned} h^f_{ij} &= \sum_{\mu\nu}^{AO} C^i_\mu C^j_\nu \frac{\partial h_{\mu\nu}}{\partial f} \\ &= -e \sum_{\mu\nu}^{AO} C^i_\mu C^j_\nu \langle \mu | f | \nu \rangle. \end{aligned} \tag{16}$$

As can be seen from Eqs. (15) and (16), the evaluation of the derivative of the TCSCF energy with respect to an electric field at the point where the magnitude of the electric field is zero is equivalent to the expectation value of the dipole moment operator. In other words, the Hellmann-Feynman theorem holds for the TCSCF energy and wavefunctions when the perturbation is due to an electric-field [18], and the basis set is electric field independent.

C. Coupled perturbed Hartree-Fock (CPHF) *equations*

In order to calculate second-order properties, it is known to be necessary to evaluate the first-order change matrices of MO coefficients, U^a and U^f, and the derivatives of the CI coefficients, $\partial C_I/\partial a$ and $\partial C_I/\partial f$.

These quantities can be obtained by solving the following coupled perturbed multiconfiguration Hartree-Fock (CPMCHF) equations [5b, 19, 20]:

$$\begin{bmatrix} A^{11} & A^{21+} \\ A^{21} & A^{22} \end{bmatrix} \begin{bmatrix} U^a & \vdots & U^f \\ \dfrac{\partial C_I}{\partial a} & \vdots & \dfrac{\partial C_I}{\partial f} \end{bmatrix} = \begin{bmatrix} B^{a^1} & \vdots & B^{f^1} \\ B^{a^2} & \vdots & B^{f^2} \end{bmatrix}. \tag{17}$$

The A matrix elements of Eq. (17) for the TCSCF wavefunction have previously been determined to be:

$$\begin{aligned} A^{11}_{ij,kl} = {} & 2(\alpha_{ik} - \alpha_{jk} - \alpha_{il} + \alpha_{jl})(ij|kl) \\ & + (\beta_{ik} - \beta_{jk} - \beta_{il} + \beta_{jl})\{(ik|jl) + (il|jk)\} \\ & + \delta_{jk}(\varepsilon_{il} - \zeta^j_{il}) - \delta_{ik}(\varepsilon_{jl} - \zeta^i_{jl}) \\ & - \delta_{jl}(\varepsilon_{ik} - \zeta^j_{ik}) + \delta_{il}(\varepsilon_{jk} - \zeta^i_{jk}), \end{aligned} \tag{18}$$

$$A^{21}_{I,ij} = 2 \sum_J C_J (\varepsilon^{IJ}_{ij} - \varepsilon^{IJ}_{ji}), \tag{19}$$

and

$$A^{22}_{I,J} = \tfrac{1}{2}\{H_{IJ} - \delta_{IJ} E + C_I C_J\}. \tag{20}$$

The generalized Lagrangian matrix ζ appearing in Eq. (18) is defined as follows,

$$\zeta^l_{ij} = f_l h_{ij} + \sum_k^{\text{occ}} \{\alpha_{lk}(ij|kk) + \beta_{lk}(ik|jk)\}. \tag{21}$$

The elements of the "bare" Lagrangian matrices, ε^{IJ}, appearing in Eq. (19) are defined by,

$$\varepsilon^{11}_{ik} = h_{ik} + \sum_j^{\text{d.o.}} \{2(ik|jj) - (ij|kj)\} + 2(ik|mm) - (im|km) \tag{22}$$

for $k =$ d.o. and m,

$$\varepsilon^{22}_{ik} = h_{ik} + \sum_j^{\text{d.o.}} \{2(ik|jj) - (ij|kj)\} + 2(ik|nn) - (in|kn) \tag{23}$$

for $k = \text{d.o.}$ and n,

$$\varepsilon_{im}^{12} = \varepsilon_{im}^{21} = \tfrac{1}{2}(in\,|\,mn) \tag{24}$$

$$\varepsilon_{in}^{12} = \varepsilon_{in}^{21} = \tfrac{1}{2}(im\,|\,nm). \tag{25}$$

In Eqs. (22)-(25) the index i includes all molecular orbitals, k includes only the doubly occupied MO's and m or n refer to the two molecular orbitals with variable occupation numbers. The elements not included in the range of these indices are equal to zero. Using these relationships, the Lagrangian matrix in Eq. (14) is alternatively defined as,

$$\varepsilon_{ij} = \sum_{IJ} C_I C_J \varepsilon_{ij}^{IJ}. \tag{26}$$

The B matrix elements for a nuclear perturbation are found to be

$$\begin{aligned} B_{ij}^{a^1} = {} & \varepsilon_{ij}^{a} - \varepsilon_{ji}^{a} + \sum_{k>}^{\text{all}} \sum_{l}^{\text{occ}} S_{kl}^{a}[2(\alpha_{jk} - \alpha_{ik})(ij\,|\,kl) \\ & + (\beta_{jk} - \beta_{ik})\{(ik\,|\,jl) + (il\,|\,jk)\} - \delta_{kj}(\varepsilon_{il} - \zeta_{il}^{j}) + \delta_{ki}(\varepsilon_{jl} - \zeta_{jl}^{i})] \\ & + \sum_{k}^{\text{occ}} S_{kk}^{a}[(\alpha_{jk} - \alpha_{ik})(ij\,|\,kk) + (\beta_{jk} - \beta_{ik})(ik\,|\,jk)] \end{aligned} \tag{27}$$

$$B_{I}^{a^2} = -\tfrac{1}{2} \sum_{J} \mathrm{C}_J \mathrm{H}_{IJ}^{a} + \tfrac{1}{2} \mathrm{C}_I \mathrm{E}^{a} + \sum_{J} \mathrm{C}_J \left\{ 2 \sum_{i>j}^{\text{occ}} S_{ij}^{a} \varepsilon_{ji}^{IJ} + \sum_{i}^{\text{occ}} S_{ii}^{a} \varepsilon_{ii}^{IJ} \right\}. \tag{28}$$

The (skeleton) derivative Lagrangian matrix ε^{a} and the (skeleton) derivative CI matrix H_{IJ}^{a} used in the equations above have the following definitions:

$$\varepsilon_{ij}^{a} = f_i h_{ij}^{a} + \sum_{k}^{\text{occ}} \{\alpha_{ik}(ij\,|\,kk)^{a} + \beta_{ik}(ik\,|\,jk)^{a}\} \tag{29}$$

$$\begin{aligned} \mathrm{H}_{11}^{a} = {} & 2 \sum_{i}^{\text{d.o.}} h_{ii}^{a} + \sum_{ij}^{\text{d.o.}} \{2(ii\,|\,jj)^{a} - (ij\,|\,ij)^{a}\} \\ & + 2h_{mm}^{a} + 2 \sum_{i}^{\text{d.o.}} \{2(mm\,|\,ii)^{a} - (mi\,|\,mi)^{a}\} + (mm\,|\,mm)^{a} \end{aligned} \tag{30}$$

$$\begin{aligned} \mathrm{H}_{22}^{a} = {} & 2 \sum_{i}^{\text{d.o.}} h_{ii}^{a} + \sum_{ij}^{\text{d.o.}} \{2(ii\,|\,jj)^{a} - (ij\,|\,ij)^{a}\} \\ & + 2h_{nn}^{a} + 2 \sum_{i}^{\text{d.o.}} \{2(nn\,|\,ii)^{a} - (ni\,|\,ni)^{a}\} + (nn\,|\,nn)^{a} \end{aligned} \tag{31}$$

$$\mathrm{H}_{12}^{a} = (mn\,|\,mn)^{a} \tag{32}$$

The B matrix elements for an electric field perturbation can be shown to be

$$B_{ij}^{f^1} = \varepsilon_{ij}^{f} - \varepsilon_{ji}^{f} \tag{33}$$

$$B_{I}^{f^2} = -\tfrac{1}{2} \sum_{J} \mathrm{C}_J \mathrm{H}_{IJ}^{f} + \tfrac{1}{2} \mathrm{C}_I \mathrm{E}^{f}. \tag{34}$$

In the above equations, ε^f_{ij} and H^f_{IJ} are

$$\varepsilon^f_{ij} = f_i h^f_{ij} \tag{35}$$

$$\mathrm{H}^f_{11} = 2 \sum_i^{\text{d.o.}} h^f_{ii} + 2h^f_{mm} \tag{36}$$

$$\mathrm{H}^f_{22} = 2 \sum_i^{\text{d.o.}} h^f_{ii} + 2h^f_{nn} \tag{37}$$

$$\mathrm{H}^f_{12} = 0. \tag{38}$$

D. Derivatives of dipole moment

An analytical expression for derivatives of the dipole moment may be obtained by differentiating Eqs. (4) or (8) with respect to a nuclear coordinate (a) and an electric field (f).

$$\begin{aligned}\frac{\partial^2 E_{\text{TCSCF}}}{\partial a\, \partial f} = {} & 2 \sum_i^{\text{occ}} f_i h^{af}_{ii} - 2 \sum_{ij}^{\text{occ}} S^a_{ij} \varepsilon^f_{ij} + 2 \sum_i^{\text{all}} \sum_j^{\text{occ}} W^a_{ij} U^f_{ij} \\ & + 2 \sum_{IJ} \left(\frac{\partial C_I}{\partial f}\right) \mathrm{C}_J \{\mathrm{H}^a_{IJ} - 2 \sum_{ij}^{\text{occ}} S^a_{ij} \varepsilon^{IJ}_{ij}\}\end{aligned} \tag{39}$$

where

$$h^{af}_{ij} = \sum_{\mu\nu}^{AO} \mathrm{C}^i_\mu \mathrm{C}^j_\nu \frac{\partial^2 h_{\mu\nu}}{\partial a\, \partial f} \tag{40}$$

$$\begin{aligned}W^a_{ij} = {} & 2\varepsilon^a_{ji} - \sum_k^{\text{occ}} \{(\varepsilon_{ik} + \zeta^j_{ik}) S^a_{jk} + 2\varepsilon_{jk} S^a_{ik}\} \\ & - \sum_{kl}^{\text{occ}} S^a_{kl} \{2\alpha_{jl}(ij\,|\,kl) + \beta_{jl}[(ik\,|\,jl) + (il\,|\,jk)]\}.\end{aligned} \tag{41}$$

An alternative equation is obtained by taking derivatives of Eq. (4) or (8) in the reverse order,

$$\frac{\partial^2 E_{\text{TCSCF}}}{\partial f\, \partial a} = 2 \sum_i^{\text{occ}} f_i h^{fa}_{ii} + 4 \sum_i^{\text{all}} \sum_j^{\text{occ}} \varepsilon^f_{ji} U^a_{ij} + 2 \sum_{IJ} \left(\frac{\partial C_I}{\partial a}\right) \mathrm{C}_J \mathrm{H}^f_{IJ}. \tag{42}$$

It should be noted that in Eqs. (39) and (42), the last terms require the derivatives of the CI coefficients $\partial C_I / \partial f$ and $\partial C_I / \partial a$. Although Eqs. (39) and (42) look quite different, they are mathematically equivalent.

E. Polarizabilities

The second derivative of the electronic energy with respect to an electric field is referred to as the electric polarizability and for a TCSCF wavefunction is expressed as

$$\frac{\partial^2 E_{\text{TCSCF}}}{\partial f\, \partial g} = 4 \sum_i^{\text{all}} \sum_j^{\text{occ}} U^f_{ij} \varepsilon^g_{ji} + 2 \sum_{IJ} \left(\frac{\partial C_I}{\partial f}\right) \mathrm{C}_J \mathrm{H}^g_{IJ} \tag{43}$$

where the ε^g_{ji} and H^g_{IJ} matrices are given by Eqs. (35) through (38) and the U^f_{ij} and $\partial C_I/\partial f$ are determined from the set of linear equations (17). The most striking aspect to be noted is the great reduction in computational effort due to the electric-field independence of the basis sets commonly used in quantum chemical applications.

Applications

The theoretical methods described above have been implemented (on the IBM 4381-2 computer at Berkeley) and testing was carried out by comparison with finite difference procedures. Subsequently the method was applied to CH_2, CF_2, CH_3^-, NH_3, HF and O_3 using a range of contracted gaussian basis sets. These computations parallel those completed earlier [14] using single configuration SCF wavefunctions, and the basis sets chosen are described in Table 1.

A. Singlet methylene

The TCSCF wavefunction for $^1A_1CH_2$ is

$$\Psi = C_1 1a_1^2 2a_1^2 1b_2^2 3a_1^2 + C_2 1a_1^2 2a_1^2 1b_2^2 1b_1^2. \tag{44}$$

Table 2 gives TCSCF predictions with nine different basis sets for the geometry, harmonic vibrational frequencies, dipole moments, infrared intensities, and polarizabilities. With the largest basis set, triple zeta plus double polarization ($TZ+2P$) [21], the energy difference between the SCF and TCSCF energies is $(-38.91133 - -38.88927) = 0.02206$ hartrees. The SCF and TCSCF intensities in $(D/\text{Å})^2/\text{amu}$ are 1.54 and 1.83 (asymmetric CH stretch); 1.29 and 1.38 (symmetric CH stretch); 0.12 and 0.13 (bending). The change of nearly 30% for I_1 suggests that correlation effects may be rather important for such diradical singlet states. The predicted dipole moments are 1.87 (SCF) and 1.66 (TCSCF) debyes. Again with the $TZ+2P$ basis set the predicted polarizabiliites are 2.12 (SCF) and 2.10 (TCSCF) Å^3.

Both the *IR* intensities and polarizability show a considerable dependence on the basis set. For example, the popular 6-31G(d) basis yields a value for I_1 nearly

Table 1. Basis sets

Name	Contraction (first row atoms)	Contraction (hydrogen)
1. 3-21G	(6s3p/3s2p)	(3s/2s)
2. *DZ*	(9s5p/4s2p)	(4s/2s)
3. *TZ*	(9s5p/5s3p)	(5s/3s)
4. 6-31G(d)	(10s4p1d/3s2p1d)	(4s/2s)
5. *DZ*+Pol	(9s5p1d/4s2p1d)	(4s1p/2s1p)
6. 6-31+G(d)	(11s5p1d/4s3p1d)	(4s/2s)
7. *TZ*+Pol	(9s5p1d/5s3p1d)	(5s1p/3s1p)
8. 6-311++G(d, p)	(11s6p1d/5s4p1d)	(6s1p/4s1p)
9. *TZ*+Double Pol	(9s5p2d/5s3p2d)	(5s2p/3s2p)

Table 2. Theoretical structures, vibrational frequencies, IR intensities, dipole moments and polarizabilities of CH_2 ($^1A_1$)

	3-21G	*DZ*	*TZ*	6-31G(*d*)	*DZ* + *P*	6-31 + G(*d*)	*TZ* + *P*	6-311++G(*d*, *p*)	*TZ* + 2*P*
Energy (Hartrees)	−38.66746	−38.87702	−38.87872	−38.89345	−38.90600	−38.89680	−38.90756	−38.91000	−38.91133
C_1	0.984	0.986	0.986	0.979	0.981	0.980	0.981	0.981	0.978
C_2	−0.179	−0.165	−0.164	−0.202	−0.195	−0.197	−0.195	−0.197	−0.207
r_{CH}(Å)	1.106	1.108	1.106	1.100	1.104	1.098	1.101	1.101	1.100
< HCH degrees	103.3	104.9	104.6	102.3	102.7	103.0	102.7	102.6	102.8
$\nu_1(B_2)$(cm^{-1})	3046	3124	3052	3161	3158	3176	3132	3130	3137
$\nu_2(A_1)$	2996	3044	2995	3107	3094	3120	3074	3075	3079
$\nu_3(A_1)$	1582	1511	1525	1581	1512	1559	1509	1512	1521
I_1 [(D/Å)^2/amu]	3.103	3.450	2.227	3.238	2.651	2.527	1.987	2.298	1.831
I_2	1.233	2.566	1.756	1.545	1.606	2.001	1.202	1.859	1.382
I_3	0.022	0.022	0.035	0.001	0.009	0.000	0.001	0.003	0.128
μ(D)	1.976	2.198	2.170	1.771	1.858	1.977	1.824	1.886	1.664
$\bar{\alpha}$(Å^3)	1.546	1.597	1.629	1.528	1.580	1.745	1.617	1.838	2.099

twice as large as that predicted with the much more complete $TZ+2P$ basis. Similarly $\bar{\alpha}$ with the 6-31G(d) basis is 1.53 Å^3, but 2.10 with the more satisfactory $TZ+2P$ basis. Examination of Table 2 shows that the 6-31G(d) basis requires extension both with respect to the (sp) set and the polarization functions for precise predictions of I and $\bar{\alpha}$.

B. *Ground state* CF_2

The $^1A_1$ ground state of CF_2 is described by the TCSCF wavefunction

$$\begin{aligned}\Psi &= C_1 1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 3b_2^2 5a_1^2 1b_1^2 1a_2^2 4b_2^2 6a_1^2 \\ &\quad + C_2 1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 3b_2^2 5a_1^2 1b_1^2 1a_2^2 4b_2^2 2b_1^2. \qquad (45)\end{aligned}$$

CF_2 is in a general sense valence isoelectronic with CH_2, the prototype carbene, and this is seen in the comparison between (44) and (45). For CH_2 $3a_1$ is the carbene lone pair orbital, while the analogous orbital of CF_2 is $6a_1$. Similarly the $1b_1(CH_2)$ and $2b_1(CF_2)$ orbitals are the vacant (in the single configuration picture) $2p$ orbitals perpendicular to the plane of the molecule.

TCSCF predictions for CF_2 are seen in Table 3, and the intensities are quite different from those of the prototype carbene CH_2. For the symmetric C-X stretch, with the $TZ+2P$ basis set, the CF_2 intensity value (3.72 (D/Å)^2/amu) is more than twice the analogous CH_2 prediction, 1.38. The asymmetric C-X stretching intensities show an even bigger difference, 10.31 (CF_2) and only 1.83 for CH_2. Both bending modes, however, show weak intensities, 0.12 (CF_2) and 0.13 (CH_2). CF_2 has a small dipole moment (0.20 debye, C^-F^+ polarity as discussed elsewhere [22]), while for the parent methylene μ is a substantial 1.66 debye. The $TZ+2P$ TCSCF polarizabilities of CH_2 (2.10 Å^3) and CF_2 (2.04) are surprisingly similar.

C. *The methyl anion* CH_3^-

CH_3^- was chosen as a potentially interesting case because the single configuration SCF wavefunction

$$1a_1^2 2a_1^2 1e^4 3a_1^2 \qquad (46)$$

forces the outermost two electrons to occupy the same spatial orbital, namely $3a_1$. Intuitively, of course, one expects the outermost electron to correspond to a more diffuse electron distribution. One of the simplest ways to accomplish this is via the TCSCF wavefunction

$$\Psi = C_1 1a_1^2 2a_1^2 1e^4 3a_1^2 + C_2 1a_1^2 2a_1^2 1e^4 4a_1^2. \qquad (47)$$

Table 4 gives the present TCSCF predictions for the methyl anion. Due to its diffuse charge distribution, CH_3^- is the only molecule of the sample set where the 6-311++G(d, p) basis [23] yields a significantly lower energy than the $TZ+2P$ set. This is because the former basis set specifically includes functions with smaller orbital exponents than those required for the neutral carbon atom [23]. With the 6-311++G(d, p) basis the SCF and TCSCF total energies are −39.51822 and −39.53811 hartrees, the difference being 0.01989 hartrees. Note also in Table 4

Table 3. Theoretical structures, vibrational frequencies, IR intensities, dipole moments and polarizabilities of the $6a_1^2 \rightarrow 2b_1^2$ TCSCF description of CF_2

	3-21G	*DZ*	*TZ*	6-31G(*d*)	*DZ*+*P*	6-31+G(*d*)	*TZ*+*P*	6-311++G(*d*, *p*)	*TZ*+2*P*
Energy (Hartrees)	−235.38855	−236.64663	−236.66039	−236.68083	−236.74675	−236.69195	−236.75558	−236.75182	−236.75937
C_1	0.988	0.986	0.986	0.985	0.985	0.985	0.985	0.985	0.984
C_2	−0.154	−0.165	−0.164	−0.171	−0.173	−0.173	−0.173	−0.175	−0.176
r_{CF}(Å)	1.325	1.347	1.327	1.287	1.286	1.288	1.282	1.281	1.283
<FCF degrees	104.2	103.6	104.1	104.7	104.9	104.8	105.0	105.1	105.1
$\nu_1(A_1)$(cm^{-1})	1308	1172	1192	1378	1371	1351	1371	1350	1361
$\nu_2(B_2)$	1270	1107	1101	1286	1282	1254	1270	1251	1265
$\nu_3(A_1)$	663	634	663	715	721	712	726	726	723
I_1[(D/Å)^2/amu]	3.662	5.058	4.700	3.610	4.125	4.137	3.954	4.371	3.722
I_2	7.316	10.340	9.327	9.633	11.230	10.965	10.461	11.367	10.310
I_3	0.302	0.195	0.200	0.122	0.134	0.128	0.137	0.148	0.116
μ(D)	−0.192	−0.514	−0.423	0.155	0.170	0.091	0.177	0.142	0.201
$\bar{\alpha}$(Å^3)	1.314	1.617	1.650	1.571	1.653	1.921	1.715	1.849	2.040

Table 4. Theoretical structures, vibrational frequencies, IR intensities, dipole moments and polarizabilities of CH_3^-

	3-21G	*DZ*	*TZ*	6-31G(*d*)	*DZ*+*P*	6-31+G(*d*)	*TZ*+*P*	6-311++G(*d*, *p*)	*TZ*+2*P*
Energy (Hartrees)	−39.24813	−39.48833	−39.49191	−39.47746	−39.51040	−39.52435	−39.51555	−39.53811	−39.52148
C_1	0.998	0.994	0.994	0.997	0.994	0.982	0.994	0.983	0.993
C_2	−0.065	−0.110	−0.111	−0.079	−0.108	−0.187	−0.110	−0.182	−0.114
r_{CH}(Å)	1.120	1.104	1.102	1.118	1.107	1.092	1.103	1.093	1.108
< HCH degrees	103.5	108.5	108.2	102.0	105.2	110.9	105.6	110.6	104.7
$\nu_1(E)(\mathrm{cm}^{-1})$	2823	3077	3018	2854	3028	3178	3016	3132	2948
$\nu_2(A_1)$	2822	2994	2960	2863	2980	3101	2975	3042	2933
$\nu_3(E)$	1664	1602	1611	1629	1589	1573	1576	1538	1554
$\nu_4(A_1)$	1146	959	979	1224	1074	889	1059	871	1108
$I_1[(\mathrm{D}/\text{Å})^2/\mathrm{amu}]$	28.105	18.159	14.263	29.755	16.689	8.235	13.197	9.011	17.186
I_2	2.820	1.120	0.862	3.615	1.540	5.976	1.080	20.516	3.552
I_3	1.281	0.022	0.010	0.808	0.011	0.003	0.000	0.068	0.166
I_4	0.020	4.783	4.279	0.021	2.697	8.740	2.348	5.107	0.951
μ(D)	1.691	2.072	2.050	1.552	1.927	2.244	1.848	2.297	1.443
$\bar{\alpha}(\text{Å}^3)$	1.920	1.974	2.075	2.205	2.210	7.538	2.294	10.862	4.170

Table 5. Theoretical structures, vibrational frequencies, *IR* intensities, dipole moments and polarizabilities of NH_3

	3-21G	*DZ*	*TZ*	6-31G(*d*)	*DZ*+*P*	6-31+G(*d*)	*TZ*+*P*	6-311++G(*d*, *p*)	*TZ*+2*P*
Energy (Hartrees)	−55.88163	−56.19201	−56.19407	−56.19583	−56.22091	−56.20238	−56.22255	−56.22801	−56.22479
C_1	0.998	0.997	0.997	0.997	0.997	0.997	0.997	0.996	0.997
C_2	−0.057	−0.084	−0.081	−0.072	−0.079	−0.083	−0.079	−0.085	−0.081
r_{NH}(Å)	1.002	0.994	0.996	1.002	1.002	1.001	1.002	1.000	1.003
<HNH degrees	112.6	116.4	115.1	107.5	108.1	108.6	108.2	108.9	107.7
$\nu_1(E)(\mathrm{cm}^{-1})$	3806	3993	3904	3831	3864	3848	3820	3837	3807
$\nu_2(A_1)$	3650	3780	3703	3697	3723	3709	3685	3705	3676
$\nu_3(E)$	1856	1799	1800	1848	1796	1843	1795	1789	1786
$\nu_4(A_1)$	841	600	693	1190	1108	1141	1109	1071	1126
$I_1[(\mathrm{D}/\text{Å})^2/\mathrm{amu}]$	0.058	0.967	0.581	0.038	0.208	0.343	0.198	0.373	0.295
I_2	0.008	0.009	0.013	0.010	0.011	0.000	0.012	0.005	0.028
I_3	1.096	2.637	2.429	1.032	1.105	1.551	1.085	1.372	0.854
I_4	9.312	16.177	13.569	5.295	5.310	6.521	5.260	5.703	4.055
μ(D)	1.731	1.374	1.532	1.927	1.798	1.882	1.783	1.744	1.599
$\bar{\alpha}$(Å^3)	0.898	1.023	1.075	1.146	1.296	1.452	1.308	1.610	

that the magnitude of the coefficient C_2 in (47) increases significantly when diffuse functions are added to the basis set. For example, C_2 is -0.079 for the 6-31G(d) basis set but -0.187 for the 6-31+G(d) basis.

Again with the 6-311++G(d, p) basis set, the SCF and TCSCF dipole moments are 1.85 and 2.30 debyes, respectively. The *IR* intensities labeled according to Table 4 are $I_1 = 14.20$ (SCF) and 9.01 (TCSCF); $I_2 = 9.76$ (SCF) and 20.52 (TCSCF); $I_3 = 0.02$ (SCF) and 0.07 (TCSCF); $I_4 = 3.80$ (SCF) and 5.11 (TCSCF). The relative I_1 and I_2 values exhibit the need for at least a TCSCF description in order to correctly predict the most intense mode. The results presented here for CH_3^- using the 6-311++G(d, p) basis, though, may change with further basis set enhancements as was shown at the single configuration SCF level of theory [24].

D. Ammonia

The NH_3 molecule was studied to provide a neutral comparison with the isoelectronic anion CH_3^-. The SCF and TCSCF energies with the 6-311++G(d, p) basis were -56.21475 and -56.22801 hartrees, respectively. The SCF/TCSCF energy difference is thus 0.01326, about two-thirds the analogous difference for CH_3^-. Similarly the coefficient C_2 of the second configuration is -0.085, much less in absolute magnitude than the CH_3^- value of -0.182. It is clear that the second configuration is notably more important for CH_3^- than for NH_3.

The largest percentage difference between SCF and TCSCF intensities of ammonia occurs for the asymmetric N-H stretch, where $I_1 = 0.257$ (SCF) and 0.373 (TCSCF) $(D/Å)^2$/amu. The dipole moments themselves are rather similar, 1.719 debye (SCF) and 1.744 debye (TCSCF). The 6-311++G(d, p) polarizabilities $\bar{\alpha}$ are 1.54 (SCF) and 1.61 $Å^3$ (TCSCF).

E. The HF *Molecule*

The TCSCF wavefunction for HF has the general form

$$\Psi = C_1 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 + C_2 1\sigma^2 2\sigma^2 1\pi^4 4\sigma^2. \tag{48}$$

TCSCF is the simplest wavefunction that dissociates to Hartree–Fock wavefunctions for the atoms H and F.

With the *TZ*+2*P* basis set the intensities in $(D/Å)^2$/amu are 3.90 (SCF) and 1.69 (TCSCF). In fractional terms, this is one of the largest SCF/TCSCF differences found in the present research. The dipole moment at the SCF/TCSCF levels of theory is predicted to be 1.91 (SCF) and 1.82 debyes (TCSCF). The predicted polarizabilities are 0.674 (SCF) and 0.700 (TCSCF) $Å^3$, in close agreement.

F. Ozone

The TCSCF description of O_3 is given by the following

$$\begin{aligned} \psi = {} & C_1 1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 4b_2^2 6a_1^2 1a_2^2 \\ & + C_2 1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 4b_2^2 6a_1^2 2b_1^2 \end{aligned} \tag{49}$$

Table 6. Theoretical structures, vibrational frequencies, *IR* intensities, dipole moments and polarizabilities of HF

	3-21G	*DZ*	*TZ*	6-31G(*d*)	*DZ* + *P*	6-31+G(*d*)	*TZ* + *P*	6-311++G(*d*, *p*)	*TZ* + 2*P*
Energy (Hartrees)	−99.48641	−100.04759	−100.05134	−100.02720	−100.07076	−100.03905	−100.07307	−100.07636	−100.07610
C_1	0.993	0.994	0.994	0.994	0.995	0.994	0.995	0.995	0.995
C_2	−0.116	−0.114	−0.113	−0.106	−0.101	−0.106	−0.102	−0.100	−0.101
r_{HF}(Å)	0.963	0.944	0.942	0.931	0.922	0.933	0.922	0.916	0.922
ν(cm^{-1})	3613	3806	3809	3987	4132	3963	4098	4134	4110
I[(D/Å)^2/amu]	0.012	0.280	0.216	1.180	1.726	1.667	1.498	2.044	1.687
μ(D)	2.023	2.230	2.204	1.874	1.903	1.972	1.891	1.938	1.816
$\bar{\alpha}$(Å^3)	0.260	0.300	0.315	0.412	0.422	0.513	0.444	0.469	0.700

Table 7. Theoretical structures, vibrational frequencies, *IR* intensities, dipole moments and polarizabilities of O_3. ($C_1(1a_2)^2+C_2(2b_1)^2$)

	3-21G	*DZ*	*TZ*	6-31G(*d*)	*DZ* + *P*	6-31 + *G*(*d*)	*TZ* + *P*	6-311++G(*d*, *p*)	*TZ* + 2*P*
Energy (Hartrees)	−223.11747	−224.31652	−224.33040	−224.34295	−224.40637	−224.34925	−224.41209	−224.41208	−224.41655
C_1	0.801	0.840	0.842	0.895	0.894	0.897	0.893	0.897	0.894
C_2	−0.599	−0.543	−0.539	−0.446	−0.448	−0.442	−0.451	−0.442	−0.448
r_{OO}(Å)	1.407	1.336	1.330	1.256	1.257	1.254	1.260	1.245	1.257
< 000 degrees	109.3	113.7	113.8	115.1	115.1	115.4	115.0	115.7	115.2
$\nu_1(B_2)$(cm^{-1})	1159	1202	1261	1486	1504	1491	1486	1495	1495
$\nu_2(A_1)$	976	958	995	1171	1190	1177	1174	1188	1180
$\nu_3(A_1)$	562	649	657	780	777	781	773	798	778
I_1[(D/Å)^2/amu]	0.277	0.395	0.381	0.071	0.055	0.022	0.063	0.028	0.044
I_2	0.029	0.169	0.159	0.355	0.382	0.404	0.378	0.419	0.343
I_3	0.055	0.115	0.117	0.121	0.127	0.105	0.125	0.154	0.100
μ(D)	0.349	0.251	0.225	0.199	0.219	0.249	0.219	0.238	0.232
$\bar{\alpha}$(Å^3)	1.452	1.628	1.616	1.755	1.824	2.101	1.825	2.021	2.286

It is well known [25] that an SCF description of O_3 is not adequate. The simplest wavefunction which may provide a good zeroth-order characterization of O_3 then is the above TCSCF wavefunction. The present theoretical predictions for ozone are summarized in Table 7. The better agreement one obtains for the structure with a TCSCF description supports this assessment. For example, using the $DZ+P$ basis, the SCF method gives an equilibrium structure of $\theta_e = 119.0°$ and $r_e = 1.207$ Å whereas TCSCF gives $\theta_e = 115.1°$ and 1.257 Å. Comparing these values to the experimentally determined quantities ($\theta_e = 116.8°$ and $r_e = 1.272$ Å[26]) one sees a significant improvement in the bond length. The bond angle is only slightly improved, going from 2.2° too high to 1.7° too low. This confirms the understanding that the TCSCF method does give a better zeroth-order description of O_3 than does SCF. However, the TCSCF description of O_3 reverses the symmetric and antisymmetric harmonic frequencies. This result is in direct conflict with experiment [$\nu(a_1) = 1103$, $\nu(b_2) = 1042$, and $\nu(a_1) = 701$ cm^{-1}] and complete active space SCF (CASSCF) calculations [27]. Note also that the infrared intensities of these two modes are switched [26, 27]. The TCSCF results are also reversed from those obtained at the SCF level of theory where $\nu_1(b_2) = 1446$ cm^{-1} (21.3), $\nu_2(a_1) = 1545$ cm^{-1} (0.0) and $\nu_3(a_1) = 843$ cm^{-1} (0.3) are predicted with the $DZ+P$ basis. The values in parentheses are the IR intensities in $(D/Å)^2/amu$. Thus, we concur with [27] in that a TCSCF description of O_3 is lacking other important configurations.

Concluding remarks

Diradical singlet states often require a two-configuration SCF wavefunction as a zeroth-order starting point. Analytic methods have been developed for the evaluation of TCSCF infrared intensities and polarizabiliites. For several of the molecules considered, the TCSCF method yields qualitatively different predictions from those obtained with the single configuration SCF method. Specifically, the *IR* intensities of CH_3^- and HF change considerably in progressing from SCF to TCSCF wave functions. The infrared intensities of difluorocarbene, :CF_2, are very different from those of the prototype singlet methylene, :CH_2. Caution must be exercised in using the TCSCF method, though, as evidenced by O_3.

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