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# One-electron property from MCHF wavefunction: the dipole moment of ozone

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A systematic study of electron correlation contributions to the dipole moment of ozone is presented. GVB and MCHF wavefunctions have been designed and calculated which point to the key role played by a charge transfer configuration in providing an accurate description of the charge separation in ozone. It is expected that the approach followed here could also be useful for other molecules.

**Key words:** Dipole moment — Ozone — *Ab initio* computation

## 1. Introduction

Multiconfiguration Hartree-Fock (MCVHF) wavefunction enjoy wide popularity. Indeed, for several years now, the methodology for the calculation of MCHF wavefunctions has been the subject of intensive research [1]. It is fair to say that the MCHF method has been mainly used for two types of problems. Early in its development [2, 3] the MCHF method proved to be an efficient means to describe the correlation arising solely from "internal" correlation, i.e., the correlation arising from the valence electrons, a key factor for the accurate determination of excitation energies [4, 5]. The MCHF method has been applied extensively also to the description of bond-breaking and bond-formation processes [6, 7]. By mixing appropriate electronic configurations it is possible to determine a

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** Also, Department of Chemistry, University of California, Berkeley, CA 94720, USA qualitatively accurate potential energy surface for systems whose Hartree-Fock (HF) wavefunction does not "dissociate properly".

In contrast the MCHF method is rarely used to obtain one-electron properties including electron-correlation effects for polyatomic systems, although many such calculations have been reported for diatomic molecules [8]. One of us (MD) presented a systematic study [9] of the dipole moment and its derivatives for some simple hydrocarbons using a generalized valence bond (GVB) model [10]. It turned out that GVB wavefunctions in the perfect pairing approximation do not yield satisfactory agreement with experiment for those properties.

The ozone molecule has spectral properties of great importance [12, 13]. For many years the theoretical treatment of these properties met with questionable success [13], even though the electronic structure of ozone in its ground state and excited states was well understood [14]. Recently Alder-Golden et al. [15], reported vibrational infrared intensities based on MCHF calculations in remarkably excellent agreement with experiment.

An interesting aspect of that study [15], in line with earlier work [16], is the high quality of the MCHF results, in particular, for the dipole moment while results obtained with all other wavefunctions are not nearly so consistently good even when these wavefunctions describe dynamical electron correlation effects. For example, the results from an extended configuration interaction (CI) wavefunction including all single and double excitations from two references (the two configurations needed to describe the diradical character of $O_3$) are very sensitive to the choice of molecular orbitals [15]. We wish to analyze the success of the MCHF method in contrast to the extended CI method in the present case, with the expectation that our findings will be extendable to other systems.

We report here a study which firmly establishes the key ingredient needed for an accurate description of the ozone dipole moment. We show that the success of the MCHF method for this system is due to the ability to account for a certain charge-transfer configuration. This is not an exclusive capability of the MCHF method; carefully constructed wavefunctions following other methods, e.g. SOGI [16] also have the capability. Although this charge-transfer configuration is a primary determiner of the dipole moment, its contribution to the structure determination is minor. The effect of this configuration on the dipole moment determination could be recovered with a very extended CI expansion, but the results of Alder-Golden et al. [15] show that this is difficult to achieve in a consistent manner.

It should be noted that the choice of MCSCF configurations adopted in this study were first proposed, developed, and applied by K. Ruedenberg and coworkers who called the approach Full Optimized Reaction Space (FORS) [6].

## 2. Computational details

Calculations were carried out for the ozone molecule using HF, GVB, and MCHF wavefunctions using a standard double-zeta plus polarization (DZP) quality basis set [17] of the form (9S5P1D)/[3S2P1D]. The exponent for the *d*-type polarization function was 0.85. Some of the calculations employed two sets of polarization functions with exponents 0.85 and 0.2. This set is denoted DZPP. For all the wavefunctions considered the molecular geometry was optimized using analytically calculated gradients. All calculations were carried out with the HONDO program [18].

## 3. Valence configurations of ozone: GVB representation

The electronic structure of ground-state ozone is well understood. It resembles a diradical with two unpaired $\pi$ electrons on the end oxygen atoms as schematically represented in Fig. 1. These two electrons are loosely coupled in a singlet state (structure I of Fig. 1) because of the weak overlap of the $p\pi$ atomic orbitals. The HF model does not describe weakly overlapping situations well. The analysis of Hay and Dunning [14] showed that a molecular orbital representation of this structure involves two configurations denoted $n^2$ and $\pi^{*2}$, i.e.

$$\begin{aligned}&\text{core} \times 5a_1^2 3b_2^2 6a_1^2 4b_2^2 1b_1^2 1a_2^2 2b_1^0 (n^2)\\&\text{core} \times 5a_1^2 3b_2^2 6a_1^2 4b_2^2 1b_1^2 1a_2^0 2b_1^2 (\pi^{*2})\end{aligned} \tag{1}$$

The core contains the twelve oxygen $1s$ and $2s$ electrons. In Eq. (1) $5a_1$ and $3b_2$ label the bonding orbitals for the symmetric and antisymmetric combinations of the oxygen-oxygen $\sigma$ bonds; $6a_1$ and $4b_2$ label the orbitals for the symmetric and antisymmetric combinations of the terminal oxygen in-plane lone-pairs, $1b_1$ is the nodeless $\pi$ orbital mainly localized on the central oxygen atom, $1a_2$ is the non-bonding out-of-plane orbital $n$ with a node at the center oxygen atom and localized on the terminal oxygens; $2b_1$ is the antibonding $\pi^*$ orbital mainly localized on the terminal oxygen atoms. The $n^2$ configuration constitutes the HF configuration, while the configurations $n^2$ and $\pi^{*2}$ together form a GVB pair of configurations in the perfect pairing approximation, here denoted GVB-1.

Using the GVB model we can account for some other important correlation effects. Left-right correlation in the oxygen-oxygen $\sigma$ bonds can be represented by two GVB pairs involving the bonding and antibonding orbitals for these bonds. We can combine these two bond pairs with the GVB pair which describes the biradical character to form a three-pair wavefunction which we denote GVB-3.

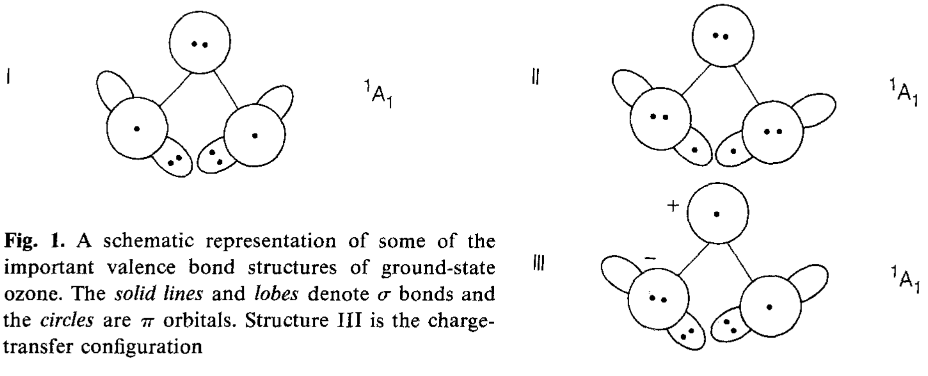

**Fig. 1.** A schematic representation of some of the important valence bond structures of ground-state ozone. The *solid lines* and *lobes* denote $\sigma$ bonds and the *circles* are $\pi$ orbitals. Structure III is the charge-transfer configuration

**Table 1.** Correlation effects in GVB wavefunctions

| Wavefunction | Correlation effects |
|---|---|
| HF | — |
| GVB-1 | $n^2 \rightarrow \pi^{*2}$ diradical character |
| GVB-3 | GVB-1 + $\sigma$ left-right correlation |
| GVB-6 | GVB-3 + *lp* in-out correlation |
| GVB-9 | GVB-6 + 2*s* in-out correlation |

In-out correlation effects for the oxygen $2p$ lone-pairs $6a_1$, $4b_2$, and $1b_1$ can be accounted for by forming three new GVB pairs from these three orbitals and a set of correlating orbitals. Together with the previous three pairs, they form the wavefunction which we denote GVB-6. We can also include additional in-out correlation effects in the oxygen $2s$ electron pairs. These effects can be accounted for via three additional GVB pairs which are included in the wavefunction denoted GVB-9. A summary of the correlation effects in the various GVB wavefunctions is given in Table 1.

In Table 2 we summarize the results for the optimized structures, and list the corresponding dipole moments. The sign convention for the dipole moment corresponds to a positive charge near the central oxygen atom with a negative charge in the neighborhood of the terminal atoms. It appears that the GVB description, although providing a qualitatively correct picture of the electronic structure, fails to provide good agreement for the geometrical parameters. The GVB-1 description certainly leads to an improved structure relative to the HF values. However, the improvement disappears with the more correlated GVB-3, GVB-6, and GVB-9 wavefunctions. In the latter cases the calculated bond length is ≈0.045 Å too long, while the bond angle is too small by ≈4°. In addition, our

**Table 2.** Structure and dipole moment of ozone

| Wavefunction | $E$ (a.u.) | $R_e$ (Å) | $\theta_e$ (Deg.) | $\mu(D)$ |
|---|---|---|---|---|
| HF | −224.323526 | 1.207 | 117.0 | −0.87 |
| GVB-1 | −224.405889 | 1.257 | 115.1 | −0.22 |
| GVB-3 | −224.468472 | 1.319 | 112.3 | −0.08 |
| GVB-6 | −224.490782 | 1.325 | 111.8 | −0.03 |
| GVB-9 | −224.507664 | 1.316 | 112.5 | −0.08 |
| MC(6 el, 6 orb) | −224.487548 | 1.298 | 114.2 | −0.225 |
| MC(8 el, 7 orb) | −224.529399 | 1.296 | 114.8 | −0.544 |
| MC(12 el, 9 orb) | −224.542825 | 1.296 | 116.4 | −0.528 |
| MC(12 el, 9 orb)[a] | −224.547909 | 1.295 | 116.5 | −0.507 |
| POL-CI[b] | — | 1.299 | 116.0 | −0.536 |
| Experiment[c] | — | 1.271 | 116.8 | −0.532 |

[a] DZPP basis set
[b] [14]
[c] [18]

results clearly show the inability of these GVB wavefunctions to describe the dipole moment accurately. As expected the HF wavefunction overestimates the charge separation, while the inclusion of the $\pi^{*2}$ configuration leads to a decrease in the dipole moment. As discussed by Curtis et al. [13] the nodal shape of the $2b_1$ orbital is responsible for this decrease. Correlation in additional pairs fails to improve the dipole moment and further lessens agreement with experiment.

Similar findings were obtained in GVB studies of infrared intensities for small hydrocarbons [9]. There too it was found that GVB wavefunctions in the perfect-pairing approximation overemphasize left-right and in-out correlation, and lack flexibility to describe charge-transfer phenomena which are the key to accurate determination of dipole moments. To remedy this problem one must use more flexible MCHF wavefunctions, as described in Sect. 4.

Our findings can be compared to some of the results presented by Alder-Golden et al. [15]. Their HF and GVB-1 dipole moments calculated with a similar basis set differ slightly from ours. The difference may be due to our structure optimization for each wavefunction. In addition, they report results obtained from other GVB wavefunctions which presumably are intended to describe similar correlation effects as the present. The corresponding numerical values are, however, dissimilar. It is likely that the correlating orbitals used by those researchers are different in character than the ones used here.

## 4. Valence configuration ozone: MCHF representation

Hay and Dunning [14] showed that structures (II) and (III) of Fig. 1 represent two additional valence-bond structures with the same ${}^1A_1$ symmetry as the ground state. In structure (II) the terminal oxygen atoms have out-of-plane lone pairs, while in structure (III) an electron from the central oxygen atom lone pair is transferred to one of the terminal oxygen atoms. Both of these structures have higher energy and play a lesser role in the structure determination. The most important feature of structure III, however, resides in its high polarity, and thus the inclusion of this configuration ought to have a significant effect on properties such as the dipole moment and its derivatives. Clearly, the GVB wavefunctions used earlier do not include configurations which can describe this charge transfer.

With this notion in mind we constructed MCHF wavefunctions, denoted MC ($m$ el, $n$ orb) which included all configurations obtained by distributing $m$ electrons among $n$ orbitals in all possible ways consistent with ${}^1A_1$ symmetry. By analogy to the GVB-3 wavefunction we constructed the MC (6 el, 6 orb) wavefunction, which includes the orbitals needed to describe the biradical character of ozone, and the left-right correlation effects in the $\sigma$ bonds. In order to incorporate the charge-transfer effects of the additional valence structures (II) and (III), the valence space must include the two electrons from the ${}^1b_1$ orbital (the lone pair on the central oxygen). We denote this wavefunction MC (8 el, 7 orb). A more complete treatment of electron correlation includes the $6a_1$ and $4b_2$ orbitals that correspond to the in-plane lone pairs on the terminal oxygen atoms. This wavefunction is designated MC(12 el, 9 orb). The remaining 12 electrons of the ozone molecule occupy the 1*s* and 2*s* oxygen orbitals and are assigned to the core. A summary of correlation effects included in the various MC wavefunctions is given in Table 3. We note that the MC (12 el, 9 orb) wavefunction is identical to the CASSCF wavefunction of Alder-Golden et al. [15].

The added flexibility of the MC (6 el, 6 orb) wavefunction compared to GVB-3 constitutes a more extended treatment of electron correlation in the $\sigma$ bonds. It leads to significantly improved agreement between calculated and experimental structures. Calculated bond lengths are now ≈0.025 Å longer than the experimental value, but the bond angle is in excellent agreement with experiment. These results are very similar to the POLCI results of Hay and Dunning. Although the MC description provides a much improved structure, the difference between experimental and calculated bond lengths is inherent in the type of MC wavefunction used which overemphasizes left-right correlation [9]. The MCHF method does not account for semi-internal and external correlation effects which can only be included by a description which extends beyond the valence space.

The contrast between the GVB model and the MCHF model can be seen, however, very dramatically in the dipole moment results. In the case where only six valence electrons are correlated the MC description improves the calculated dipole moment by a factor of ≈3. This is because the space available for electron correlation favors charge transfer toward the terminal oxygens. The charge-transfer configuration represented by structure (III) and included in the other MC wavefunctions is responsible for the near quantitative agreement between theory and experiment.

In Table 2 we also included the results from a MC (12 el, 9 orb) wavefunction calculation using the DZPP basis set. The DZPP dipole moment is not as close to the experimental value as the DZP value, which indicates, not surprisingly, that we are not close to the basis set limit. Nevertheless, this wavefunction includes the key ingredients for a correct dipole moment description and the results are consistently in near quantitative agreement with experiment and with the findings of Alder-Golden et al. [15].

The MC (12 el, 9 orb) wavefunction is analyzed in more detail in Table 4 which contains the occupation numbers and configuration coefficients in the natural orbital representation. There are 14 coefficients greater than 0.05. Other than the

**Table 3.** Correlation effects in MC wavefunctions of ozone

| Wavefunction | Correlation effects |
|---|---|
| HF | — |
| GVB-1 | $n^2 \rightarrow \pi^{*2}$ diradical character |
| MC(6 el, 6 orb) | GVB-1 + $\sigma$ left-right correlation |
| MC(8 el, 7 orb) | MC(6 el, 6 orb) + charge transfer |
| MC(12 el, 9 orb) | MC(8 el, 7 orb) + *lp* correlation |

**Table 4.** Occupation numbers and CI coefficients of the MC(12 el, 9 orb) wavefunction

| Orbital | *lp* | *lp* | $\sigma$ | $\sigma$ | $\sigma^*$ | $\sigma^*$ | $\pi$ | $n$ | $\pi^*$ |
|---|---|---|---|---|---|---|---|---|---|
| Symmetry | $b_2$ | $a_1$ | $a_1$ | $b_2$ | $a_1$ | $b_2$ | $b_1$ | $a_2$ | $b_1$ |
| Occupation | 1.991 | 1.990 | 1.952 | 1.943 | 0.067 | 0.056 | 1.961 | 1.763 | 0.276 |
| CI | | | | | | | | | |
| −0.902 | 2 | 2 | 2 | 2 | 0 | 0 | 2 | 2 | 0 |
| 0.309 | 2 | 2 | 2 | 2 | 0 | 0 | 2 | 0 | 2 |
| −0.089 | 2 | 2 | 1 | 1 | 1 | 1 | 2 | 2 | 0 |
| 0.075* | 2 | 2 | 2 | 2 | 0 | 0 | 0 | 2 | 2 |
| −0.083 | 2 | 2 | 2 | 1 | 1 | 2 | 2 | 1 | 1 |
| −0.074 | 2 | 2 | 2 | 1 | 1 | 0 | 2 | 1 | 1 |
| 0.068* | 2 | 2 | 2 | 1 | 0 | 1 | 1 | 2 | 1 |
| 0.067* | 2 | 2 | 2 | 1 | 0 | 1 | 1 | 2 | 1 |
| 0.067 | 2 | 2 | 0 | 2 | 2 | 0 | 2 | 2 | 0 |
| 0.062 | 2 | 2 | 2 | 0 | 0 | 2 | 2 | 2 | 0 |
| −0.065* | 2 | 2 | 1 | 2 | 1 | 0 | 1 | 2 | 1 |
| −0.061* | 2 | 2 | 1 | 2 | 1 | 0 | 1 | 2 | 1 |
| 0.065 | 2 | 2 | 1 | 2 | 0 | 1 | 2 | 1 | 1 |
| 0.055 | 2 | 2 | 1 | 2 | 0 | 1 | 2 | 1 | 1 |

HF configuration, the $n^2 \rightarrow \pi^{*2}$ configuration required to properly describe the biradical character is the most important one. The remaining configurations describe left–right correlation in the $\sigma$ bonds, as well as the charge-transfer phenomenon. These latter configurations are labeled with an asterisk in the table. Their contributions are no less important than those configurations which correlated the $\sigma$ bonds.

We note that the total occupation of the $\sigma$ and $\sigma^*$ orbitals is 4.02 electrons. Most importantly only 0.04 electron has been transferred from the central atom lone pair (${}^1b_1$ orbital) to the terminal atoms. This small charge transfer is, however, responsible for the near quantitative description of the charge separation in ozone.

## 5. Conclusion

Through a carefully designed series of wavefunctions we have been able to identify the key ingredient for an accurate description of the dipole moment of ozone. One expects that a wavefunction of the quality of the MC (12 el, 9 orb) described above would also provide very accurate derivatives of the dipole moment function, i.e., infrared intensities. The results of Alder-Golden et al. [15] confirm this expectation. Finally, we note that a similar analysis should also apply to other molecules.

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