On the application of MCSCF models for the calculation of spectroscopic constants for several low lying states of \( \text{O}_2^+ \)\(^a\)

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The behavior of multiconfiguration self-consistent field (MCSCF) and restricted configuration interaction (CI) wave functions are investigated for the case of a homonuclear positive diatomic, i.e., \( \text{O}_2^+ \). Both molecular orbital (MO) and orthogonalized valence bond (VB) models are used. In the MO model the normal symmetry restrictions \( D_{\infty h} \) are imposed on the orbital while these are lifted in the VB model, thus permitting a more correct behavior on dissociation. Using \( \text{He}^+ \) as a prototype system, the customary partitioning of the MO configuration set into subsets corresponding to proper dissociation, molecular extra correlation, and atomic correlation is examined. It is shown that when the orbitals are optimized this partitioning is no longer valid, i.e., atomic correlation cannot be excluded. For \( \text{O}_2^+ \) the proper dissociation function in the MO model is rather unwieldy. This arises because allowance must be made for the difference between the atomic orbitals of \( \text{O} \) and \( \text{O}^- \). We therefore use, as our starting point in the configuration selection procedure, the much simpler base wave function which corresponds to a correct dissociation limit in a minimal basis set. The VB model does not suffer from these difficulties. However, due to the absence of symmetry restrictions, there is a symmetry breakdown in the VB calculation in the range \( 1.5 < R < 2.5 \) \( \text{Å} \) caused by a transition from \( D_{\infty h} \) symmetry in the equilibrium conformation to effective \( C_{\infty v} \) symmetry for \( R = \infty \). Using a double zeta + polarization basis, satisfactory results were obtained for the spectroscopic constants of four of the five lowest lying states, viz., \( ^1\Pi_u \), \( ^3\Pi_u \), \( ^3\Pi_u \), and \( ^3\Phi_u \), via MO–MCSCF calculations using the base wave function augmented by all valence shell \( 2p \) configurations of the correct symmetry. For the \( ^1\Pi_u \) and for the \( ^3\Sigma_u^+ \) state (which poor results were obtained in the MO model) VB–CI calculations were also performed. In these calculations all single excitations from a reference state consisting of the proper dissociation function and all valence shell \( 2p \) \( C_{\infty v} \) configurations were included, leading to satisfactory agreement with experimental data.

I. INTRODUCTION

In the past few years the multiconfiguration self-consistent field method has successfully been used for the calculation of potential energy curves for various diatomic molecules.\(^{1-4}\) From these calculations it appears that the MCSCF method is capable of yielding accurate spectroscopic constants with a relatively compact wave function. Usually symmetry adapted molecular orbitals (MO's) are used throughout and the configuration set is chosen such that in the dissociation limit the MCSCF function corresponds to Hartree–Fock descriptions of the separate atoms, i.e., it is assumed that atomic correlation is not important for the shape of the potential energy curve.

It is the purpose of this paper to investigate the behavior of various MCSCF functions including only internal correlation,\(^{5,6}\) as well as limited CI based upon these functions for a wide range of internuclear separations for a homonuclear ion. Two orbital models may be distinguished when using an orthonormal basis, viz.

1. The molecular orbital (MO) model; The orbitals are delocalized and satisfy the full symmetry of the system \( D_{\infty h} \).

2. The orthogonalized valence bond (VB) model. The orbitals are more or less localized on the atoms (orthogonalized atomic orbitals) and satisfy only \( C_{\infty v} \) symmetry.

As will be shown below, both models suffer from serious drawbacks, when applied to a homonuclear positive ion.

The practical usefulness of some MCSCF wave functions using either orbital model is investigated for the \( \text{O}_2^+ \) ion. This molecular ion has been chosen for the following reasons:

1. Experimental data are available for various low lying states.\(^7-9\)

2. \( \text{O}_2^+ \) takes part in a number of gas phase reactions which are of interest in connection with processes in the upper atmosphere. Some of these reactions have been the subject of laboratory experiments\(^10\) and theoretical investigations.\(^11\)

3. Although some theoretical results are available for \( \text{O}_2^+ \),\(^11,12\) no calculations have been performed so far using multiconfiguration wave functions with an extended orbital basis.

In Secs. II and III, the behavior of the MO and VB type wave functions at the dissociation limit are analyzed, using \( \text{He}^+ \) as an example. The configuration selection procedure for \( \text{O}_2^+ \) is discussed in Sec. IV and the orbital basis set used is described in Sec. V. In Secs. VI–VIII the results of our calculations for \( \text{O}_2^+ \) are presented and discussed. The models and wave functions used are briefly described in Table I for future reference.

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\(^a\)Used as part of a Ph.D. Thesis by one of the authors (J. H. van Lenthe).
TABLE I. Table of wave functions.

<table>
<thead>
<tr>
<th>Wave Function</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi_B$</td>
<td>Base wave function = proper dissociation wave function for a minimal basis [cf. Eq. (1)].</td>
</tr>
<tr>
<td>$\Psi_D$</td>
<td>Proper dissociation function in an extended basis [Eq. (9)].</td>
</tr>
<tr>
<td>$\Psi_{HF}$</td>
<td>Antisymmetrized product of Hartree–Fock functions for atom and ion. ($C_{\infty v}$ symmetry) [Eq. (3)].</td>
</tr>
<tr>
<td>$\Psi_{RVB}$</td>
<td>$D_{\infty h}$ symmetry restricted valence bond wave function with the same orbitals for atom and ion [Eq. (6)].</td>
</tr>
<tr>
<td>MECE CSF’s</td>
<td>Molecular extra correlation energy configuration state functions, i.e., CSF’s which are in the first order interacting space but do not contribute in the dissociation limit.</td>
</tr>
<tr>
<td>AC CSF’s</td>
<td>Atomic correlation CSF’s, i.e., CSF’s which do contribute to the correlation energy in the dissociation limit.</td>
</tr>
<tr>
<td>$\Psi_{A-B}$</td>
<td>Brillouin state, i.e., the state obtained from the function being optimized by replacing orbital $A$ by orbital $B$.</td>
</tr>
<tr>
<td>MO model</td>
<td>$D_{\infty h}$ symmetry adapted delocalized ortho-normal orbitals.</td>
</tr>
<tr>
<td>VB model</td>
<td>$C_{\infty v}$ symmetry adapted localized orthonormal orbitals.</td>
</tr>
<tr>
<td>Function models</td>
<td>Compact multiconfiguration wave function with fully optimized orbitals.</td>
</tr>
<tr>
<td>CI model</td>
<td>Configuration interaction function containing the MCSCF configuration set and all single excitations from this set.</td>
</tr>
</tbody>
</table>

II. ANALYSIS OF MO–MCSCF FUNCTION AT THE DISSOCIATION LIMIT, USING $He_2^+$ AS AN EXAMPLE

The two most important functions in a MCSCF description of the dissociation of a molecule are the base wave function, which describes the (near-)degeneracy effects at infinite internuclear distances for a minimal basis, and the proper dissociation function, which allows for dissociation into Hartree–Fock subsystems for an extended basis. We will now discuss the behavior of these functions and some of their extensions in the MO model for the $He_2^+$ molecular ion.

A. The base wave function

For the $He_2^+$ groundstate the base wave function $\Psi_B$ happens to be identical to the restricted Hartree–Fock function (cf. Ref. 14)

$$\Psi_B = \Psi_{HF} = |\phi_A \Phi_A \phi_B \Phi_B|.$$  \hspace{1cm} (1)

At the internuclear distance $R = \infty$, this function can be expressed in functions localized on the nuclei $A$ and $B$ as follows: \hspace{1cm} 

$$\Psi_{RVB} = 2^{-1/2}(1 - \delta) |\phi_A \Phi_A \phi_B \Phi_B| ,$$  \hspace{1cm} (2)

where $\delta$ is the inversion operator, which interchanges $\phi_A$ and $\phi_B$. The base wave function in a \textit{minimal} basis is identical to the restricted valence bond function ($\Psi_{RVB}$), which is the valence bond function for which the orbitals for atom and ion are restricted to be the same. This function corresponds to the $D_{\infty h}$ antisymmetrized product of Hartree–Fock functions of atom and ion, using the same orbitals for both. (The exponential parameters are kept fixed over the whole range of $R$.) The energy difference between the RVB function at $R = \infty$ and the separated HF systems as described by $\Psi_{HF}$:

$$\Psi_{HF} = |s_A \Phi_A s_B \Phi_B| ,$$  \hspace{1cm} (3)

where $s$ and $s'$ are the He and He' orbitals respectively, (note that $\Psi_{HF}$ is only $C_{\infty v}$ symmetry adapted) will be called the \textit{reorganization energy}, since it corresponds to the reorganization of the equivalent orbitals to the optimal orbitals for atom and ion, respectively. Whether this energy contribution should be considered to be part of the correlation energy depends on the kind of (HF) wave function chosen as reference. Following Shavitt, \hspace{1cm} we feel that the antisymmetrized product of atom and ion HF wave functions ($\Psi_{HF}$) is the more natural choice. Therefore we consider the reorganization energy to be a separate effect.

In order to analyze the behavior of the base wave function in an extended basis we assume a double zeta basis and express the MO’s in localized orbitals:

$$\sigma_a = 2^{-1/2}(\phi_A + \phi_B) , \quad \sigma_a = 2^{-1/2}(\phi_A' - \phi_B') ,$$  \hspace{1cm} (4)

where $\phi_{A,B}$ and $\phi_{A,B}'$ are not orthogonal to each other.

Substituting Eqs. (4) in the MO expression for $\Psi_B$ (1) yields

$$\Psi_B = 2^{-1/2}(1 - \delta) |\phi_A \Phi_A \phi_B \Phi_B|$$

$$+ |\phi_A' \Phi_A' \phi_B \Phi_B'| + |\phi_A' \Phi_A \phi_B \Phi_B'| / 2 .$$  \hspace{1cm} (5)

For a minimal basis $\phi_A$ equals $\phi_A'$ and Eq. (5) is identical to Eq. (2). If we start with this and allow the orbitals to be optimized in the DZ basis, the energy is lowered initially due to the first term in Eq. (5). Soon, however, this is counteracted by the other terms, in particular by the increasing contribution of the energetically unfavorable ionic terms $|\phi_A \Phi_A \phi_B \Phi_B'|$. As a result the base wave function turns out to be little different from the RVB function.

We have calculated the energies for $\Psi_B$, $\Psi_{RVB}$, and $\Psi_{HF}$ using a DZ (5)–[2] contracted Gaussian basis (Table II). The exponents and contraction coefficients were taken from van Duijnneveldt. \hspace{1cm} Since the reorganization energy $E_{RVB} - E_{HF} = 1.01$ eV appears to be rather large compared to the dissociation energy of 2.47 eV, \hspace{1cm} it is a non-negligible energy contribution in the calculation of potential energy curves. The deviation of $\Psi_B$ from $\Psi_{RVB}$ is only 0.06 eV, so the distortion due to the orbital optimization is very small and a large portion of the reorganization energy is unaccounted for in $\Psi_B$. (Note that since the energies of $\Psi_B$ and $\Psi_{RVB}$ are higher than the energy of the $C_{\infty v}$ symmetry HF function, both functions are unstable with respect to symmetry lowering.)

B. The proper dissociation function

The proper dissociation function (in an extended basis) $\psi_D$, which allows for the reorganization effect, is given by the projection to $D_{ab}$ symmetry of the antisymmetrized product of the HF functions for He and He$^+$:

$$\psi_D = 2^{-1/2} \left( 1 - \hat{\tau} \right) \psi_{HF} = 2^{-1/2} \left( 1 - \hat{\tau} \right) |s_A s_B \rangle.$$  \hfill (6)

We obtain the proper dissociation function in terms of (orthonormal) $D_{ab}$ symmetry adapted MO's by transforming the HF atomic orbitals $s$ and $s'$ to (Schmidt orthogonalized) MO's according to

$$s_{A,B} = 2^{1/2} (\sigma_2 \pm \sigma_0),$$

$$s'^{\prime}_{A,B} = 2^{-1/2} (\cos(\phi_2 + \phi_0) + \sin(\phi_2 + \phi_0)), \quad \text{where} \cos \phi = \text{overlap between atomic and}$$

$$\text{the ionic orbital:} \quad \cos \phi = \langle s_A | s'_B \rangle = \langle s_B | s'_A \rangle.$$ \hfill (7a)

This yields

$$\psi_D = \cos \phi \left| \sigma_2 \sigma_2 \right| + \sin \phi \left| \sigma_0 \sigma_0 \right|$$

$$+ \left| \sigma_2 \sigma_2 \right| - \left| \sigma_0 \sigma_0 \right|/2.$$ \hfill (8)

The MO representation of $\psi_D$ thus includes all configuration state functions (CSF's) with one electron in the external MO's $\sigma_2$ or $\sigma_0$, in a fixed contraction. Since these terms vanish if $s$ and $s'$ are identical (i.e., $\sin \phi = 0$), they are reorganization terms, i.e., they are responsible for the reorganization energy.

In order to analyze the behavior of $\psi_D$ under orbital optimization, we consider its AO representation (6). In the $D_{ab}$ basis the orbital set encountered on each atom consists of the HF AO's $s$ and $s'$ and their orthogonal complements $s''$ and $s'''$, respectively [cf. Eq. (7)].

(Note that the function $s$ is only orthogonal to $s''$ and not to $s'$ and $s'''$. Likewise $s'$ is only orthogonal to $s'''$. These four functions span a two-function space, i.e., they are linearly dependent.)

The $D_{ab}$ adapted CSF space may be partitioned into the subspace spanned by $\psi_D$ as defined by Eq. (6), the MECE (molecular extra correlation energy) subspace spanned by all CSF's in the first-order interacting space which do not interact with $\psi_D$ at $R = \infty$, the AC (Atomics correlation) subspace, here consisting of only one term, viz.,

$$\psi_{AC} = 2^{1/2} \left( 1 - \hat{\tau} \right) |s_A \rangle |s_B \rangle.$$ \hfill (9)

and the AC/MECE coupling terms (higher-order interacting spaces). Now we optimize $\psi_D$ as given by Eq. (6) using the MCGBT method,18,19 $D_{ab}$ symmetry adapted Brillouin state28,29 corresponding to the decoupling of the AO's for He, i.e., to mixing $s_A$ and $s_B$ with $s''_A$ and $s'''_B$, respectively, is given by (cf. Table I)

$$\psi_{A-B'} = 2^{1/2} \left( 1 - \hat{\tau} \right) |s_A \rangle |s_B \rangle$$

$$- 2^{1/2} \left( 1 - \hat{\tau} \right) |s_B \rangle |s_A \rangle.$$ \hfill (10)

Since

$$\langle \psi_{A-B'} | \psi_{AC} \rangle = \langle s_A | s_B \rangle \langle s_B | s_A \rangle \neq 0,$$ \hfill (11)

this Brillouin state does not lie entirely in the MECE subspace and interacts with $\psi_D$ via $\psi_{AC}$:

$$\langle \psi_{A-B'} | H | \psi_D \rangle = \langle \psi_{A-B'} | \psi_{AC} \rangle H | \psi_D \rangle = 0.$$ \hfill (12)

Thus $\psi_D$ does not satisfy the generalized Brillouin theorem,34 in spite of the fact that $\psi_D$ corresponds to HF subsystems, and an energy lowering can be obtained by decoupling the AO's. Since the optimized $\psi_D$ does not correspond to Hartree–Fock subsystems but includes some atomic correlation instead, the division between the $\psi_D$ space, AC space and MECE space is not valid for this system. For the MO representation of $\psi_D$ (8), this effect is produced by a distortion of the AO's in the $\sigma_2$ orbital with respect to those in the $\sigma_0$ MO, analogous to what happens for the base wave function (Sec. II A).

We conclude that it is not possible to reproduce the Hartree–Fock dissociation limit exactly using a $D_{ab}$ symmetry adapted CSF set with fully optimized MO's. Note that this problem does not exist for a $C_{ab}$ symmetry function like $\psi_{HF}$ [Eq. (3)].

We will now discuss some numerical results (Table II). From the fact that the contracted $\psi_D$, for which only $\alpha$ and the orbitals in Eq. (8) are optimized, gives an energy lowering with respect to $\psi_{HF}$ of only 0.01 eV, it appears that the contraction gives sufficient protection against significant atomic correlation contributions at $R = \infty$. This is still true if the contraction is released after orbital optimization. The energy of the unrestricted $\psi_D$, however, is 0.11 eV lower than the energy of $\psi_{HF}$, which is a rather large part of the atomic correlation energy $E_{\text{corr}} - E_{\text{HF}} = 0.37$ eV.

If MECE terms are added to $\psi_D$, the situation is even worse. The same procedure as was used to obtain Eq. (8) yields a number of fixed contractions over all CSF's having at most two electrons in the external MO's $\sigma_2$ and $\sigma_0$. If the orbitals are optimized for this contracted set, the calculation converges very slowly (2000 iterations) to the full CI result, thus including all atomic correlation obtainable in our basis. Therefore in this case the MECE terms can only be defined with respect to a particular fixed orbital basis.

If the orbitals are optimized for the contracted $\psi_D$ and then used in the $\psi_D$ + MECE calculation the contraction of the MECE CSF's appears to be vital to exclude a sig-
significant amount of atomic correlation (0.01 eV for the contracted CSF’s vs 0.35 eV for the uncontracted set).

We conclude that the partitioning of the CSF set into subsets corresponding to proper dissociation, MECE, AC, etc., terms is not suitable with respect to orbital optimization if the full symmetry of the system is imposed. Consequently, if dissociation into HF subsystems is sought, some orbitals have to be frozen at an intermediate level. This approach was used by Das and Wahl and co-workers in their paper on O$_{2}^{+}$.

Since the main attractive feature of the MCSCF method, viz. the compactness, is nevertheless lost in this case, we decided instead to use the base wave function as a reference function in defining the MECE terms, i.e., they are those CSF’s which do not interact with $\Psi_{HF}$ at infinite internuclear distance. This amounts to excluding all CSF’s corresponding to semi-internal correlation from the wave function. In using this approach we therefore assume that the reorganization effects at infinite internuclear distance and the semi-internal correlation at equilibrium cancel.

III. THE VB MODEL

The alternative solution to the problems at $R = \infty$, which were discussed in the preceding section, is to use localized orbitals and a $C_{\infty v}$ symmetry adapted wave function. The proper dissociation function in this model is the antisymmetrized product of atom and ion HF functions $\Psi_{HF}$ [Eq. (3)]. The reorganization effect is fully accounted for in this function.

Clearly, this model is well suited to calculations at large $R$. For small $R$ the configuration set needed may be very large due to the importance of ionic terms, which are MECE terms in this model. Although any proper function for a homonuclear diatomic ion has $D_{\infty v}$ symmetry we have not attempted to use a function which is projected to this symmetry because of the large number of CSF’s needed in an orthogonal basis.

The VB MCSCF function discussed above corresponds to including all of the reorganization energy in a semi-internal correlation. The single excitation CI CSF set, corresponding to this VB MCSCF function, contains a reasonably large number of semi-internal correlation terms for small $R$, and it still corresponds to HF subsystems in the dissociation limit. This VB CI function may therefore be useful to check the hypothesis underlying our MO MCSCF model, viz. that this semi-internal correlation at the equilibrium distance and the reorganization effect at infinity are of the same magnitude, if $R \approx R_{e}$.

The problems for the VB MCSCF function arise at small $R$. As will be shown in the calculations for O$_{2}^{+}$, the MCSCF optimization of the $C_{\infty v}$ VB MCSCF function yields a $D_{\infty v}$ symmetry adapted function for the equilibrium distance of O$_{2}^{+}$. This leads to a symmetry dilemma and consequently to a continuity dilemma for some range of $R > R_{e}$. Since for the VB CI function the final orbitals from the VB MCSCF calculation are used, the same problems occur for that function.

IV. CONFIGURATION SELECTION PROCEDURE FOR O$_{2}^{+}$

We will assume the 1s and 2s AO’s to be doubly occupied in all MCSCF CSF’s in the following.

Considering as an example the O$_{2}^{+}$ II states, which correlate with the atomic ground states O$_{2}^{+}$($P$) and O($^{1}S$), the results for He$_{2}^{+}$ may be generalized to O$_{2}^{+}$ as follows. The $C_{\infty v}$ single configuration function on AO basis is

$$\Psi_{HF}(R_{a}, R_{b}) = \Pi_{j=1}^{\infty} (p_{ij}^{a} p_{ij}^{b} p_{ij}^{a} p_{ij}^{b} p_{ij}^{a} p_{ij}^{b} p_{ij}^{a} p_{ij}^{b}) \phi_{j},$$

where the $\rho$-AO’s are the (complex) eigenfunctions of $L_{\rho}$ and $\phi$ is the spin function. (The 1s and 2s orbitals are deleted for simplicity.) In our case we have $S = \frac{1}{2}, \frac{3}{2},$ or $\frac{5}{2}$. From this function we will derive the CSF sets used in the MO and VB calculations.

A. MO model

The spatial orbital part of $\Psi_{HF}$ may be expanded in terms of MO’s using procedures analogous to those used to obtain Eq. (8). The resulting MO configuration set includes configurations with up to three electrons in the external MO’s. The dimension of this set depends on $S$. For the doublet states the dimensions of the sets for $\Psi_{HF}$ and $\Psi_{p}$ are given by

$$N_{p} = \frac{1}{2}n_{p}m_{p},$$

$$N_{p} = \frac{1}{2}(n_{p} + m_{p})^{2} + n_{p}(n_{p} + m_{p}) + m_{p}(n_{p} + m_{p}),$$

where $n_{p}$ and $m_{p}$ ($i = 1, 0, -1$) are the numbers of valence shell terms [i.e., terms like the first in Eq. (8)] and reorganization terms, respectively, for the $i$th subshell [cf. Eq. (8)]. [Note that the transformations in the three subshells ($\pi_{z}, \sigma$, and $\pi_{x}$) are independent.] For $\Psi_{HF}$ as given by Eq. (13) we have $n_{p} = 2, m_{p} = 6, n_{p} = n_{p} = 3$, and $m_{p} = m_{p} = 4$, so $N_{p}(\Pi_{l}) = 9$ and $N_{p}(\Pi_{l}) = 196$. The proper dissociation function thus contains 106 configurations, including a number of quadrupole excitations with respect to $\Psi_{HF}$. (The proper dissociation configuration set is much larger than the proper dissociation OVC configuration set for the isoelectronic molecule NO.) This is due to the projection to $D_{\infty v}$ symmetry in O$_{2}^{+}$ needed in the dissociation limit, where the effective symmetry is $C_{\infty v}$. No such projection is needed for the NO molecule since the symmetry of this molecule is $C_{\infty v}$ over the whole potential surface.) This corresponds to several hundreds of CSF’s, the exact number depends on the representation. The base wave function, on the other hand, contains only 9 configurations (12 CSF’s for a branching diagram representation if the order of the orbitals may be chosen freely). For the $\Pi_{l}$ state, $N_{p}$ and $N_{p}$ are somewhat smaller, because in this case no configurations with less than three open shells occur. We then find $N_{p}(\Pi_{l}) = 5$ and $N_{p}(\Pi_{l}) = 184$.

Since the proper dissociation function is unwieldy (cf. Sec. II B), we use the base wave function as a reference. In order to obtain a MCSCF function which includes the main molecular correlation effects, $\Psi_{HF}$ is augmented with all valence shell CSF’s (i.e., CSF’s with variable occupations in the $3\pi_{y}, 1\sigma_{x}, 1\pi_{z}$, and $3\pi_{y}$ shells) of the correct symmetry. Since these CSF’s do not contain external orbitals, they cannot account for
TABLE III. Numera of CSFs’s used in the MO MCSCF calculations for various states of O₂.

<table>
<thead>
<tr>
<th>State</th>
<th>5Π₂</th>
<th>4Π₄</th>
<th>3Π₄</th>
<th>2Σ⁺</th>
<th>2Σ⁻</th>
<th>2Δ₁</th>
<th>2Σ⁺ *</th>
</tr>
</thead>
<tbody>
<tr>
<td>n (CSF)</td>
<td>22</td>
<td>9</td>
<td>22</td>
<td>7</td>
<td>5</td>
<td>12</td>
<td>11</td>
</tr>
</tbody>
</table>

atomic correlation effects, i.e., they are MECE terms with respect to Ψ₀ (valence shell MECE terms). The number of CSFs’s included in the MCSCF functions for each state is shown in Table III.

We have also carried out CI calculations, involving all single excitations from the MO MCSCF CSF set, i.e., a MO CI calculation (cf. Table I). The additional CSFs’s take care of a part of the reorganization energy at R = ∞ and therefore lead to an energy lowering for all R.

B. VB model

Using the VB model the proper dissociation function has the simple form (13) in C₂ᵥ symmetry. We have augmented Eq. (13) with all (Cᵥ) valence shell CSF’s analogous to the treatment above. In this case all CSFs’s added in the MCSCF and (single excitation) CI calculations correspond to MECE terms, i.e., both calculations should lead to the HF dissociation limit. [In practice this does not hold rigorously in the CI calculations because the equivalence restrictions on the π subshells as used in the MCSCF calculations cannot be applied to the CI in our programs. This leads to a small distortion of the ρ, AO with respect to the ρ, AO on the O atom, caused by the difference in occupancy in the O(3P) state. The corresponding energy lowering is, however, small (−0.03 eV).] For Rₚ, the CI calculation may be expected to yield an appreciable energy lowering with respect to the MCSCF result and so we expect the VB CI calculation to yield substantially larger Dp values than the VB MCSCF calculation. Since the VB CI calculations involve a rather large number of CSF’s (~1000) the orbital optimization would not really be needed if nonorthogonal orbitals could be used. As it is, however, the orbital optimization is necessary in order to obtain results which are independent of the orthogonalization procedure used.

V. BASIS SET AND MCSCF OPTIMIZATION METHOD

A. Basis

A Gaussian (9, 5, 1)−[4, 2, 1] contracted double zeta + polarization (DZP) basis was chosen. The s and p exponents and contraction coefficients were taken from (Ref. 16) (without scaling). The partitionings of the primitive set were s (5211) and p (41). Using this contraction, the single configuration energy obtained for O(3P) (for which the set is optimized) is −74,800 403 hartree. The single configuration energy for O(5S) in this basis is −74,362 309 hartree. The exponent for the d-polarization function was energy optimized at the equilibrium distance for the two lowest lying O₂ states, viz., 5Π₂ and 4Π₄, using the corresponding base wave functions. Since these optimizations yielded nearly the same result an average value of αd = 0.75 was adopted for all calculations. The spherically symmetric component d₁ + d₂ + d₃ of the primitive 3d-GTO set was projected out.

The 1s inner shells were frozen in all calculations, as test calculations showed that optimization of these orbitals is of minor importance for the form of the potential energy curves. The contraction coefficients were determined in a MO calculation for the 5Π₂ state at R = 50a₀ using the base wave function. Since it was considered desirable to have spherically symmetrical inner shells, the 3d components in the inner shells were projected out afterwards. The resulting energy was −149,113 854 hartree. The inner shells obtained in this way may be regarded as a reasonable compromise between the O(3P) and O(5S) inner shells.

Basis sets of this size may be considered large enough for an adequate description of the valence states of O₂. The quality of the basis may also be judged by comparing the RHF results for the 5Π₂ and 4Π₄ states with those obtained in a large STO basis (Table IV). Except for the energy difference Tₑ between these states the agreement is good.

B. MCSCF optimization method

In the MCSCF method a multiconfiguration function is optimized with respect to the orbital and configuration coefficients simultaneously. We have used the generalized Brillouin theorem optimization method (MCGBT) as described by several authors and therefore we will not comment upon the theory in detail. For each symmetry the lowest state may be optimized separately. Symmetry-adapted CSFs’s may be constructed by contracting a number of spin-adapted N-electron functions with fixed coefficients. Equivalence restrictions, which are frequently necessary in order to prevent a symmetry breakdown, are implemented via a contraction of the Brillouin states by a method described by Yarkony et al. These two features have, however, not been implemented for the single excitation CI calculations.

<table>
<thead>
<tr>
<th>Tₑ (eV)*</th>
<th>Rₑ (Å)</th>
<th>ωₑ (cm⁻¹)</th>
<th>Eₜₑ (Rₑ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTO</td>
<td>STO</td>
<td>GTO</td>
<td>STO</td>
</tr>
<tr>
<td>5Π₂</td>
<td>0</td>
<td>0</td>
<td>1.03</td>
</tr>
<tr>
<td>4Π₄</td>
<td>1.98</td>
<td>2.40</td>
<td>1.29</td>
</tr>
</tbody>
</table>

aTₑ is the adiabatic excitation energy relative to the ground state.
TABLE V. MCSCF and CI results for the $^1\Pi_u$ state.

<table>
<thead>
<tr>
<th>Model</th>
<th>$\pi$ (CSF)</th>
<th>$R_e$ (Å)</th>
<th>$D_e$ (eV)</th>
<th>$\omega_x$ (cm$^{-1}$)</th>
<th>$\omega_x \Delta \pi_x$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO MCSCF</td>
<td>9</td>
<td>1.41</td>
<td>2.57</td>
<td>1007</td>
<td>9.4</td>
</tr>
<tr>
<td>MO CI</td>
<td>250 (225)$^b$</td>
<td>1.42</td>
<td>2.34</td>
<td>948</td>
<td>10.5</td>
</tr>
<tr>
<td>VB MCSCF</td>
<td>18</td>
<td>1.41</td>
<td>1.23</td>
<td>997</td>
<td>4.6</td>
</tr>
<tr>
<td>VB CI</td>
<td>888 (830)$^c$</td>
<td>1.40</td>
<td>2.60</td>
<td>1013</td>
<td>12.6</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.38</td>
<td>2.69</td>
<td>1035</td>
<td>16.4</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $D_e$ was calculated as $E(R=50$ a. u.) $- E(R=R_e)$.
$^b$ These results were obtained by using a 5th degree polynomial fit to 11 energy points corresponding to $R=2.3$ (0.1) 3.3 a. u. This fit was used to calculate the energies of the six lowest vibrational levels, which in turn were fitted by a 3rd degree polynomial yielding $\omega_x$ and $\omega_x \Delta \pi_x$ (see text for details).
$^c$ Since real $\pi$-MO's are used, CSF's of $^1\Pi_u$ symmetry are mixed in slightly in the CI calculations. These CSF's are included in $\pi$ (CSF). The numbers of CSF's with $^1\Pi_u$ symmetry are in parentheses.

VI. ANALYSIS OF THE VB AND MO MODEL RESULTS FOR THE $^1\Pi_u$ STATE

Since the $^1\Pi_u$ ground state of O$_2^+$ leads to rather large configuration sets it was not considered appropriate for test calculations. Instead we have chosen the first excited metastable $^1\Sigma_u^+$ state which is experimentally well known. In the VB model ($C_{\infty v}$) we then have 18 valence shell CSF's. In the MO model we use the restriction of this set to $D_{\infty h}$ symmetry (9 CSF's).

The results of the MCSCF and CI calculations using these sets are given in Table V and Fig. 1. In addition, we find for the energy difference between these models at the MCSCF level for $R=\infty E_{\pi} - E_{\Pi} = 1.25$ eV, which approximately equals the reorganization energy $E_{\pi} - E_{\Pi} = 1.35$ eV, where $\Psi_{\pi \Pi}$ is defined analogous to Eq. (2). (Note $E_{\Pi} = E_{\pi \Pi}$.) Clearly the reorganization effect is quite large for this system, in contrast to the result obtained for Mg$^+$ by Stevens and Krauss. At the calculated $R_e$ (1.41 Å) both models lead to the same wave function, implying that for this distance the $D_{\pi \pi}$ function is stable with respect to symmetry lowering within the VB function space.

A. The VB model

The behavior of the VB MCSCF and CI functions was analyzed in two ways, viz. by constructing the natural orbitals (NO's) of these functions and by calculating the dipole moment function. The results (Fig. 2) are as follows.

For $R < 1.65$ Å the NO's are $D_{\pi \pi}$ symmetry-adapted and the dipole moment is accordingly small ($|\mu| < 10^{-5}$ a. u., for $\delta = 10^{-8}$ with the origin at the center of mass of the system). (This is the convergence criterion for the orbital coefficients.) For $R > 1.65$ Å, however, the NO's start to be localized on either one of the atoms, accompanied by a sudden increase in $|\mu|$. For the CI function $|\mu|$ initially is much smaller than for the MCSCF function, but for large $R$, both functions approximately yield the asymptotic value of $\frac{1}{2} R$. This corresponds to $C_{\infty v}$ functions with a hole localized on one of the atoms.

From these considerations we conclude that the VB functions lead to discontinuities in the derivatives of the corresponding potential energy curves at the transition point ($R_t = 1.65$ Å).

Although in principle, no conclusive evidence can be obtained from numerical results with respect to the order of the transition point, our dipole moment curves strongly suggest a first-order transition. Since the standard deviations in various polynomial fits to the calculated energy values appear to be small, the discontinuities in the first derivative of the potential energy curves will be small. The effect of these discontinuities on $\omega_x$ and $\omega_x \Delta \pi_x$ was further investigated in the following way. Various polynomial fits were obtained from

![FIG. 1. Potential energy curves for the $^1\Pi_u$ state of O$_2^+$. a. MO MCSCF; b. MO CI ($\omega_{\pi \pi}$); c. VB MCSCF; d. VB CI ($C_{\infty v}$); $R_t$ is the transition point for the VB curves.]

![FIG. 2. Dipole moment curves for the $C_{\infty v}$ VB-models ($^1\Pi_u$). a. VB MCSCF; b. VB CI; c. O+O$^*$ ($\mu = \frac{1}{2} R$); $R_t$ is the transition point.]
TABLE VI. Spectroscopic constants for various states of $O_2^+$ calculated with the MO MCSCF model (experimental data are given in parentheses).

<table>
<thead>
<tr>
<th>State</th>
<th>Dissociation limit</th>
<th>$T_a$ (eV)</th>
<th>$R_e$ (Å)</th>
<th>$D_e$ (eV)</th>
<th>$\omega_a$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3^\Pi_u$</td>
<td>$3^P + ^1S$</td>
<td>0</td>
<td>1.15(1.11)</td>
<td>6.35(6.78)</td>
<td>1856(1904)</td>
</tr>
<tr>
<td>$^3^\Pi_g$</td>
<td>$3^P + ^1P$</td>
<td>3.77(4.03)</td>
<td>1.41(1.38)</td>
<td>2.57(2.69)</td>
<td>1050(1036)</td>
</tr>
<tr>
<td>$^1^\Pi_u$</td>
<td>$3^P + ^1S$</td>
<td>4.75(4.98)</td>
<td>1.45(1.40)</td>
<td>1.60(1.76)</td>
<td>847(896)</td>
</tr>
<tr>
<td>$^3^\Sigma^-$</td>
<td>$1^D + ^1S$</td>
<td>6.98(6.12)</td>
<td>1.39(1.28)</td>
<td>1.62(2.60)</td>
<td>821(1197)</td>
</tr>
<tr>
<td>$^3^\Sigma^+$</td>
<td>$2^P + ^1D$</td>
<td>6.33(6.60)</td>
<td>1.40(1.4)</td>
<td>3.50(3.5)</td>
<td>1030(900)</td>
</tr>
<tr>
<td>$^3^\Delta^-$</td>
<td>$2^P + ^3D$</td>
<td>8.50(7.87)</td>
<td>1.47(1.33)</td>
<td>1.30(2.44)</td>
<td>655(930)</td>
</tr>
<tr>
<td>$^3^\Delta^+$</td>
<td>$2^P + ^5D$</td>
<td>7.79(8.36)</td>
<td>1.49</td>
<td>2.67</td>
<td>720</td>
</tr>
<tr>
<td>$^3^\Pi_u$</td>
<td>$3^P + ^1D$</td>
<td>9.42(8.30)</td>
<td>1.47(1.30)</td>
<td>0.48(1.83)</td>
<td>648(1156)</td>
</tr>
</tbody>
</table>

$^a$ $\omega_a$ was calculated from the second derivative of $E(R)$ at the interpolated equilibrium distance.

The energies for the second $^3\Pi_u$ state were obtained using the MCSCF orbitals for the first $^3\Pi_u$ state. Experimental data are not available for the $2^3\Pi_u$ state. The $T_a$ value given was obtained by Raftery and Richards$^b$ from a HF calculation with semiempirical correlation corrections.

energy values corresponding to equidistant values of R($\Delta R = 0.1$ a.u.). From these fits the vibrational energy levels were calculated and all levels with classical turning points within the $R$ values used for the polynomial fits were then used to calculate $\omega_e$ and $\omega_e x_e$. This was done by fitting a 3 rd degree polynomial in $(v + \frac{1}{2})$ to the vibrational energy levels ($v$ is the vibrational quantum number). The coefficients of these fits were then interpreted as $G(0)$ (i.e., the zero-point energy), $\omega_e$, $\omega_e x_e$, and $\omega_e y_e$.

For all calculations, the $\omega_e x_e$ values turned out to be small ($|\omega_e x_e| < 1$ cm$^{-1}$). The VB MCSCF results for $\omega_e$ and $\omega_e x_e$ appear to depend rather strongly on the range of energy points used if values of $R > R_e$ (see Fig. 1) are used in the fitting procedure. Consequently different $\omega_e$ values are obtained for the MO MCSCF and VB MCSCF calculations, even though the corresponding potential energy curves are identical in the neighborhood of the equilibrium conformation.

From our results the following conclusions may be drawn. Since the $D_e$ derived from the VB MCSCF curve is small (1.23 eV) and since the VB MCSCF function contains a number of redundant parameters at $R_e$, we conclude that this function is not suitable for the calculation of potential energy curves.

The VB CI method yields much smaller inaccuracies in the calculated $\omega_e$ and $\omega_e x_e$ values. The results are good for all spectroscopic constants given in Table IV, so that this method yields a potential energy curve which is useful for practical purposes, e.g., the calculation of vibrational energy levels, even though there is an inherent inaccuracy in the neighborhood of the transition point.

However, because of the symmetry breakdown at the transition point, properties which do not follow directly from the form of the potential energy curve can be calculated by this method for the range $0 < R < R_e$ only. This is obvious for the dipole moment (Fig. 2), which depends crucially on the symmetry properties of the wave function.

B. The MO model

The results of Table V show that the MO model leads to a satisfactory form of the potential energy curve, even though the dissociation limit does not correspond to HF subsystems. Therefore the relatively simple MO model used here is suitable for MCSCF calculations of spectroscopic constants, at least for this state. The MO CI results are slightly worse.

We find that for $R = \infty$ the valence shell MECE terms are mixed in slightly if an extended basis is used. This is caused by the distortion of the ungerade MO's with respect to their gerade counterparts (cf. the behavior of $\psi_5$ in the He$^*_2$ example). Since the corresponding energy lowering is small (~0.03 eV) the calculated $D_e$ value is only slightly affected.

VII MO MCSCF CALCULATIONS FOR VARIOUS STATES OF $O_2^+$

For the eight lowest lying states of $O_2^+$, the MO model was used in order to investigate the general usefulness of this model for the valence states of $O_2^+$. The results of these calculations are given in Table VI.

A comparison of the $D_e$ and $T_a$ values shows that slightly different results are obtained for the dissociation limits of states with different $L_z$ or $S^z$ eigenvalues dissociating into the same atomic states. For example, the $^1\Pi_u$ and $^3\Pi_u$ states which both dissociate into ground-state $O^1(3P) + O^1(3S)$ yield an energy difference of 0.016 eV at $R = \infty$. This may be explained by the fact that the MECE terms are different for each state. Consequently, there is a small inherent inaccuracy (0.02–0.08 eV) in the $T_a$ values. For four states, i.e., the $^3\Pi_u$, $^4\Pi_u$, $^5\Pi_u$, and $^5\Sigma_u$ states, the MCSCF calculations yield satisfactory results for the spectroscopic constants, corresponding to a correct overall form and relative position of the corresponding potential energy curves. The MO CI values for $D_e$ and $\omega_e$ are smaller than the MO MCSCF values (which are slightly smaller than the experimental data) indicating that the single excitations in the CI calculations are more important for large $R$ than for $R_e$.
For three states (\(1\Sigma^+_g, 1\Sigma^+_u\), and \(3\Sigma^+_u\); for the \(2\Pi_u\) state no experimental data are available), our method does not work very well. The \(D_a\) and \(\omega_e\) values are too small, whereas the \(R_a\) and \(T_e\) values are too large, leading e.g., to an incorrect ordering of the \(2\Sigma^+_u\) and \(2\Pi_u\) states. Since the calculated and experimental energy differences between the states at \(R = \infty\) appear to be approximately the same, our results indicate that MO MCSCF functions including only valence shell CSF's are inadequate for a correct description of the bonding for these states. This conclusion is supported by the fact that for these states virtually no valence shell MECF terms exist (only for the \(2\Sigma^+_u\) state there is one such CSF). Therefore our wave function is practically identical to the base wave function which does not yield acceptable results for any of the states considered.

Therefore we have also carried out VB CI calculations (1032 CSF's) and MO MCSCF calculations including some reorganization terms (12 and 17 CSF's) for the \(1\Sigma^+_g\) state. The occupations used in the MO model calculations are given in Table VII. For comparison, the proper dissociation function on MO basis contains 248 CSF's in this case of which a large part is not included in our calculations. The results (Table VIII) show that in the MO model the results are improved by adding the reorganization terms, but that the convergence with respect to enlarging the configuration set is rather slow. The results of the VB CI calculations are significantly better, but still not very good. (Since no comparable calculations were carried out for the \(2\Pi_u\), state, it is not possible to make any prediction about the ordering of the \(2\Sigma^+_u\) and \(2\Pi_u\) states at this level of approximation.)

From our results we conclude that in this case the sum of the reorganization effect and semi-internal correlations is rather strongly \(R\) dependent. However, other effects, such as correlations of the \(5\Sigma^+\) shells and orbital basis set effects, will also have to be taken care of if accurate results are required.

VIII. CONCLUSIONS

We have shown that the configuration sets needed for the base wave function and for the proper dissociation function are not identical for homonuclear diatomic ions with an odd number of electrons. The latter configuration set generally is so large, that the MCSCF method in this form is rather unwieldy. Moreover, the partitioning of the configuration space into subspaces corresponding to the proper dissociation function, molecular (extra) correlation energy (MECF) terms, atomic correlation terms and coupling terms between the latter two sets is not stable with respect to a complete variational optimization of the corresponding MCSCF function. Therefore this partitioning is only meaningful if the orbital basis is partitioned accordingly.

If the orbital basis consists of orthogonalized (distorted) AO's the associated VB MCSCF function (i.e., the base wave function plus valence shell MECF terms) dissociates properly in \(C_{\infty v}\) symmetry. At \(R_i\) the VB and MO models lead to identical results, implying that the VB MCSCF function satisfies \(D_{\Sigma^-}\) symmetry for small \(R_i\).

It is shown that if the AO's on the two atoms are permitted to differ, this leads to a breakdown of the \(D_{\Sigma^-}\) symmetry and a consequent lowering of the energy for large \(RR = 1.65\) Å for the \(4\Pi_u\) state). Therefore, the VB MCSCF function leads to a discontinuity in the (first) derivative of the corresponding potential energy curve at some \(R > R_i\) and the VB MCSCF method (using \(C_{\infty v}\) symmetry) is thus not suited for the calculation of potential energy curves. The VB CI method yields satisfactory spectroscopic constants, although it is not accurate in the neighborhood of the transition point.

In the MO model, we have used the \(D_{\Sigma^-}\) base wave function, augmented with all \(D_{\Sigma^-}\) valence shell MECF terms, to calculate various spectroscopic constants for eight valence states of \(O_2\). For the lowest lying states, the neglect of semi-internal correlation effects and the reorganization effects appears to yield satisfactory results. This leads to the conclusion that it is sufficient to include only internal correlation effects for these states. For the higher states our MO MCSCF functions are less adequate. This may be understood by noting that these functions essentially contain only proper dissociation terms, because there is no room for MECF terms within the internal orbital space for these states.

For the \(4\Pi_u\) state we have also carried out MO CI calculations. The results are slightly worse than those obtained with the MO MCSCF method, indicating that by

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### TABLE VII. MO MCSCF configuration sets (including reorganization terms) for the \(1\Sigma^+_g\) state.

<table>
<thead>
<tr>
<th>Occupations</th>
<th>(n) (CSF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(3\Sigma^+_u)</td>
<td>1</td>
</tr>
<tr>
<td>(1\Sigma^+_u)</td>
<td>1</td>
</tr>
<tr>
<td>(1\Sigma^+_g)</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^a\) \(n\) (CSF) is the number of independent couplings per orbital configuration.

\(^b\) Base wave function \(\psi_2\), \(R = \) reorganization term.

### TABLE VIII. Spectroscopic constants for the \(1\Sigma^+_g\) state.

<table>
<thead>
<tr>
<th>Method</th>
<th>(n) (CSF)</th>
<th>(R_a) (Å)</th>
<th>(D_a) (eV)</th>
<th>(\omega_e) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>VB MCSCF</td>
<td>14</td>
<td>1.39</td>
<td>0.21</td>
<td>820</td>
</tr>
<tr>
<td>MO MCSCF</td>
<td>7</td>
<td>1.39</td>
<td>1.62</td>
<td>820</td>
</tr>
<tr>
<td>MO MCSCF (IR)</td>
<td>12</td>
<td>1.33</td>
<td>2.02</td>
<td>986</td>
</tr>
<tr>
<td>MO CI (1R)</td>
<td>566(^a)</td>
<td>1.37</td>
<td>2.22</td>
<td>930</td>
</tr>
<tr>
<td>MO CI (2R)</td>
<td>17</td>
<td>1.35</td>
<td>1.96</td>
<td>983</td>
</tr>
<tr>
<td>MO CI (2R)</td>
<td>833(^a)</td>
<td>1.37</td>
<td>2.12</td>
<td>904</td>
</tr>
<tr>
<td>VB CI</td>
<td>1032(^a)</td>
<td>1.32</td>
<td>2.11</td>
<td>1101</td>
</tr>
<tr>
<td>Exp.</td>
<td>1.28</td>
<td>2.60</td>
<td>1197</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The \(\omega_e\) values were calculated from the second derivative of \(E(R)\) at the interpolated equilibrium distance.

\(^b\) Since real \(\pi\)-MO's are used, CSF's of \(\Delta\) and \(\Gamma\) symmetry are included in the CI calculations.
including the single excitations the reorganization effect (for large \( R \)) is better described than the semi-internal correlation effects (for small \( R \)).

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We thank Dr. D. R. Williams for making available to us his computer program for the vibrational analysis of numerically given potential energy surfaces. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).


