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Application of the Direct Configuration Interaction Method to the Ground State of O_2

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The Direct Configuration Interaction Method, originally due to Roos [1], has been implemented using the method of Lucchese and Schaefer [2], for open shell systems. As in the closed-shell case, the method is very efficient. Results are presented for a part of the potential energy curve of the O_2 $^3\Sigma_g^-$ ground state electronic configuration, together with several properties.

Key words: O_2, ground state of ~

1. Introduction

It is generally recognised [3] that the Direct Configuration Interaction Method, introduced by Roos [4] for closed-shell systems which have one dominant configuration, is a very efficient CI procedure. In this approach, the CI wavefunction consists of spin and symmetry adapted configuration state functions, which are obtained by making single and double excitations from a dominant configuration, the "root function", Φ_0.

$$\Psi = c_0\Phi_0 + \sum_{i}^{\binom{\text{all occupied and}}{\text{semi-occupied}}} \sum_{a}^{\binom{\text{all virtual and}}{\text{semi-occupied}}} c_{i\to a}\Phi_i^a \\ \sum_{i\geq j}^{\binom{\text{all occupied and}}{\text{semi-occupied}}} \sum_{a\geq b}^{\binom{\text{all virtual and}}{\text{semi-occupied}}} c_{ij\to ab}\Phi_{ij}^{ab} \tag{1}$$

Φ_i^a and Φ_{ij}^{ab} denote single and double replacement configurations where i, j refer to all singly and doubly occupied orbitals in the root function and a, b to all singly occupied and virtual orbitals.

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The method is especially suitable for calculations involving large CI expansions. To date, various groups of workers [1, 2, 3, 5] have been using the method for closed-shell systems with one dominant root function.

Fast convergence iterative methods [6–8] adopted to calculate the lowest roots of a large CI matrix depend upon constructing the vector $\boldsymbol{\sigma}$, where

$$\boldsymbol{\sigma} = \boldsymbol{H}\cdot\boldsymbol{c} \tag{2}$$

and $\boldsymbol{c}$ is the trial vector, either approximating to the exact eigensolutions of $\boldsymbol{Hc} = E\boldsymbol{c}$, or one of a series (e.g. the Krylov series) spanning the space of the exact eigensolution.

Roos [1] devised a direct CI approach which does not necessitate the construction of the matrix elements, one at a time, as in conventional CI methods [9, 10] but proceeds directly to the solution of the secular equations from a list of one- and two-electron integrals by construction of the vector in the form

$$\Delta\sigma_{ij\to ab} = \sum (pq \mid rs) A_{\mu\nu} c_{kl\to cd} \tag{3}$$

where $(pq \mid rs)$ represents the usual form of a two-electron integral over molecular orbitals. Similar equations involve one-electron integrals, single replacement functions and the root function Φ_0 [4]. $A_{\mu\nu}$ is a coupling matrix element analogous to projective reduction coefficients in Bonded Function CI for the configuration state functions $\Phi_\mu(\equiv\Phi_{ij}^{ab})$ and $\Phi_\nu(\equiv\Phi_{kl}^{cd})$.

In closed-shell systems there are only five distinct types of spin configuration and thus the extent of the coupling matrix table A is small. Extension to open-shell systems increases the number of spin configuration types enormously. Lucchese and Schaefer [2] have recently given a method for overcoming this problem.

2. The Direct CI Method for Open Shell Systems

Lucchese and Schaefer apply the method to triplet states, where the root function Φ_0 is of the form

$$\Phi_0 = \mathscr{A}[\phi_1^2\phi_2^2\phi_3^2\cdots\phi_n^2\phi_{n+1}^\alpha\phi_{n+2}^\alpha]. \tag{4}$$

Only those single and double replacements of Φ_0 which have nonzero Hamiltonian matrix elements with Φ_0 (i.e. those present in the first order interaction subspace) are included in the CI expansion. This restriction shortens the configuration list, typically by a factor of two (or more for large scale systems) at the expense of a negligible loss of correlation energy in most cases (usually of the order of 0.2%) [11]. The list of all these configurations is shown in Table IV of Ref. [2]. There are 21 distinct types of configuration present in the case of triplet spin states.

A difference between our formulation and the one presented by these authors is that we only found it necessary to adopt two one-electron matrices, corresponding to Fock-type operators over α and β space-spin orbitals:

$$\begin{aligned}
\hat{f}^{(1)}(i) &= \hat{h}(i) + \sum_{j}^{\binom{\text{all doubly}}{\text{occupied}}} (2\hat{J}_j(i) - \hat{K}_j(i)) + \sum_{r}^{\binom{\text{all singly}}{\text{occupied}}} (\hat{J}_r(i) - \hat{K}_r(i)) \\
\hat{f}^{(2)}(i) &= \hat{h}(i) + \sum_{j}^{\binom{\text{all doubly}}{\text{occupied}}} (2\hat{J}_j(i) - \hat{K}_j(i)) + \sum_{r}^{\binom{\text{all singly}}{\text{occupied}}} (\hat{J}_r(i))
\end{aligned} \tag{5}$$

so that in the sum over λ in Tables I and III of Ref. [2] $\lambda = 1$ and 2 only. This obviously reduces computational time to a significant degree, and equally importantly, may decrease storage requirement for the coupling matrix elements in open-shell calculations.

The coupling matrix elements were determined, as suggested by these authors, by a "polished brute force" method involving a model calculation on a ten-electron system with five virtual orbitals. Each configuration state function is decomposed in terms of its constituent Slater determinants and the matrix elements are then calculated in terms of the Slater–Condon rules, over the two- and one-electron integrals.

There is a certain indeterminacy in the coupling matrices under some circumstances. This indeterminacy arises from an interdependence of various matrix elements within the Direct CI algorithm. An example is:

$$\langle \Phi_{ii}^{aa} | \hat{H} | \Phi_{kl}^{aa} \rangle = j_1(\mu, \nu, \rho)(ik \mid il) + k_1(\mu, \nu, \rho)(ik \mid il) \tag{6}$$

in which j_1 and k_1 are the coupling matrix elements required. Similarly

$$\begin{aligned}
\langle \Phi_{ii}^{ab} | \hat{H} | \Phi_{ki}^{cb} \rangle &= j_3(\mu, \nu, \rho)(ac \mid ik) + k_3(\mu, \nu, \rho)(ai \mid ck) \\
\langle \Phi_{ii}^{ab} | \hat{H} | \Phi_{ik}^{cb} \rangle &= j_6(\mu, \nu, \rho)(ac \mid ik) + k_6(\mu, \nu, \rho)(ai \mid ck).
\end{aligned} \tag{7}$$

Consideration of these and similar situations suggests simple rules to overcome these indeterminacies. Thus in the above cases the projective reduction coefficients $k_1(\mu, \nu, \rho)$, $j_6(\mu, \nu, \rho)$ and $k_6(\mu, \nu, \rho)$ were given the value zero.

Test calculations were performed on the triplet state of H_2O using a double zeta basis set employed by Shavitt and Rosenberg [12] in a singlet calculation on H_2O i.e. (O: $4s\ 2p$), (H: $2s$). Our full scheme was checked by expansion of a general CI eigenvector $\boldsymbol{c}$ into its constituent Slater determinants. The determinant CI eigenvector then input to a "CISD" (or UHFCI) [4, 5] direct CI program, followed by reconstruction of the resulting $\boldsymbol{\sigma}$ vector into the configuration state expansion terms. The eigenvector obtained by the two independent routes i.e. from the CISD program and from the open-shell CICS program were then compared. Other checks included a comparison with the values obtained using the Bonded Function CI [13] method, although the bonded function doubles plus singles replacement states expansion necessarily incorporates certain doubles outside the Hartree–Fock interaction subspace. The Bonded Function CI calculation was therefore only a check insofar as it gave a lower variational energy.

Finally we found that the implementation of a formula tape procedure enhanced both the speed and core storage characteristics of the method. Calculations in general ran using a fraction of Bonded Function CI disc requirement and are of the order of six times faster for small calculations. Hopefully, large scale calculations become comparatively faster for two primary reasons: *a*) projective reduction coefficients need not be computed during the "symbolic reference generation" stage of the CI calculation and b) datafile searching is unnecessary in forming the numerical matrix elements. Additional advantages of the method include:

1. At different geometries the same symbolic reference tape may be used, making it similar to that of conventional CI methods except that the algorithm used to generate the symbolic reference is much faster by the nature of direct CI.

2. The symbolic reference tape is much shorter than for similarly sized Bonded Function CI calculations due to a) lack of the additional CI configurations included in the Bonded Function method outside the first order Hartree–Fock interacting subspace, b) shift of the CI matrix diagonal element values to $-H_{00}$, the energy of the lowest SCF configuration, hence excluding many diagonal element references usually included in Bonded Function CI, c) use of Fock matrix elements, rather than the direct construction of the CI Hamiltonian reference from two electron integrals exclusively (as often implemented in conventional CI approaches), due to the division of the Hamiltonian in the form [4]

$$\hat{\boldsymbol{H}}_{\mu\nu} = \hat{\boldsymbol{F}}_{\mu\nu} + \hat{\boldsymbol{V}}_{\mu\nu} \tag{8}$$

where $\hat{\boldsymbol{F}}_{\mu\nu}$ and $\hat{\boldsymbol{V}}_{\mu\nu}$ are the Fock and fluctional matrices respectively.

3. The symbolic reference tape need not be "restructured" and is merely written and read sequentially giving terms of the form

$$\Delta\sigma_\alpha = (ij \mid kl)A(\mu)c_\beta \tag{9}$$

where α, β and μ form the symbolic reference, again reducing computation time and peripheral file storage requirements.

Consideration of points 2 and 3 above indicates that not only is the generation of the symbolic reference much faster for direct CI but that subsequent calculations involving the direct CI method require less computational effort than Bonded Function CI calculations. Other conventional CI methods may in fact allow greater flexibility of selection of the configuration state functions for inclusion in the CI expansion than the Bonded Function CI approach. They therefore have the capability of producing a shorter symbolic reference than Bonded Function CI, but in general these methods are somewhat slower again than the latter in generating a formula tape. In general, it would be preferable under all circumstances, and especially in dealing with large scale CI expansions, to avoid the use of a symbolic reference. The length of a formula tape is always considerably greater than the integral list and becomes intractable for use on small computers without large amounts of disc and or tape space being available. Indeed, in our present implementation the use of symbolic reference or use of "conventional" direct CI is permissible and is in general adopted for larger scale calculations or when retention of a formula tape is not required. This does however require of the order of two or three times longer (for open-shell systems) than calculations involving a symbolic tape.

During our investigations and implementation of the method, it became apparent that it was straightforward to extend this program to deal with other open-shell systems. This has now been done at Berkeley [14] and at Cambridge. Furthermore, implementation and inclusion of higher replacement effects is also straightforward for closed-shell systems and this is being done in Cambridge [15]. We believe this Direct CI method has much to commend it.

3. Results for the O_2 $^3\Sigma_g^-$ State

Sample calculations were performed using a (O: $4s2p1d$) contracted Gaussian basis set generating 3415 symmetry adapted configuration states in the direct CI method. The basis set employed was the standard Dunning [16] contraction of the Huzinaga [O: $9s5p$] basis [17], plus a Dunning [$2d$]–($1d$) contraction with an exponent of 2.01 [18].

Restricted Hartree–Fock calculations were first performed using the ATMOL3 [19] package to obtain SCF molecular orbitals. The CI was then performed using all 32 molecular orbitals including all single and double replacement configurations.

Previous calculations on the O_2 molecule include those by Schaefer and Harris [20] using a minimal basis set to calculate a section of the potential energy curve. Schaefer later performed a calculation of higher accuracy [21]. More recently accurate first order subspace MCSCF-CI calculations on this state have been performed by Guberman [22]. Finally Saxon and Liu [23] performed a massive series of very accurate calculations on 62 valence states of O_2 for various internuclear distances, using first order MCSCF-CI wavefunctions again, but in this case with a more extended basis than that of Guberman. The only calculations which have attempted to obtain one-electron properties of interest were the series of calculations of Kotani *et al.* [24] in the 1950's using a very restricted CI expansion. The calculations reported here are in the middle of this range of accuracy, but we believe that they are of interest because they represent the implementation of a new method and because several property values, of which there are few theoretical predictions of magnitude, are given. The limited basis used and the necessity of adoption of a single root function should however be expected to produce inaccurate spectroscopic results. The properties we report are for the electric field gradient, q (to compare with ^{17}O nuclear quadrupole coupling values), the electric quadrupole moment, Θ and the electric hexadecapole moment, Φ (to compare with microwave spectroscopy line broadening measurements, infra-red multipole-induced dipole absorption spectra and birefringence measurements). Because property surfaces are becoming of increasing interest, we here give values for these properties over the range of the potential curve. Values, in atomic units (a.u.), are given in Table 1 for both SCF and CI wavefunctions.

Table 1. Potential energy surface and property surfaces (SCF and CI) for the $O_2\ {}^3\Sigma_g^-$ ground state configuration (in a.u.)

SCF values

R/Bohr	E(SCF)/Hartree	$q(z^2)$/a.u.	$\Theta(z^2)$/a.u.	$\Phi(z^4)$/a.u.
1.9	−149.553	1.224	−0.615	3.611
2.0	−149.604	1.268	−0.468	3.539
2.1	−149.629	1.330	−0.321	3.613
2.2	−149.637	1.406	−0.174	3.821
2.3	−149.632	1.488	−0.030	4.152
2.4	−149.619	1.576	+0.111	4.593
2.5	−149.600	1.664	+0.248	5.135
2.6	−149.576	1.750	+0.379	5.765
2.7	−149.551	1.832	+0.504	6.474

CI values

R/Bohr	E(CI)/Hartree	$q(z^2)$/a.u.	$\Theta(z^2)$/a.u.	$\Phi(z^4)$/a.u.
1.9	−149.861	1.192	−0.667	3.649
2.0	−149.921	1.245	−0.525	3.571
2.1	−149.957	1.326	−0.388	3.731
2.2	−149.974	1.344	−0.216	3.931
2.3	−149.978	1.410	−0.069	4.292
2.4	−149.974	1.478	+0.072	4.773
2.5	−149.961	1.586	+0.194	5.364
2.6	−149.949	1.624	+0.334	6.009
2.7	−149.932	1.692	+0.456	6.757

In Table 2 values for the spectroscopic constants obtained from a Dunham analysis [28] of the potential curve are presented and compared with other calculations and experimental results.

We note that our values for the equilibrium internuclear distance R_e, and consequently B_e, are in good agreement with experiment. The values for $\omega_e x_e$ and α_e are in reasonable agreement. The value for ω_e is predictably poor, but its error is in line with other *ab initio* calculations of harmonic constants obtained from single plus double replacement wavefunctions from a single root function [29]. To get better values a multi-root reference function, or similar technique of including higher-order replacements, would be desirable. The values for one of the best CI calculation to date, a careful and sophisticated calculation by Guberman [22], admittedly using a small basis, are also included in the table. This CI calculation, which involved a preliminary MCSCF calculation, included excitations out of many root functions into the first order Hartree–Fock interacting subspace. Our total energy is lower than that of Guberman's because his calculation did not freeze the 1*s* core orbitals and in consequence our value of R_e is somewhat better. It is a pity

Table 2. Values for spectroscopic constants and other properties for the $O_2\ {}^3\Sigma_g^-$ state from the CI calculations

Property	Experimental	This calc. (CI)	Guberman[a]
$R_e/\text{Å}$	1.207[b]	1.214	1.222
B_e/cm^{-1}	1.446[b]	1.430	–
ω_e/cm^{-1}	1580[b]	1720	1584
$\omega_e x_e/\text{cm}^{-1}$	12.07[b]	9.576	12.87
α_e/cm^{-1}	0.016[b]	0.011	0.015
$q(z^2)/\text{a.u.}$	-1.32[c]	-1.407	–
$\Theta(z^2)/\text{a.u.}$	-0.299[d]	-0.077	–
	0.223[e]		
	0.253[f]		
$\Phi(z^4)/\text{a.u.}$	2.945[e]	4.267	–
	8,755, 8.2312[f]		
	21.242[g]		
D_e/eV	5.21[b]	3.24	5.20
$E(\text{min})/\text{Hartree}$	–	-149.9783	-149.8050

[a] See Ref. [22]. [b] See Refs. [25, 26]. [c] See Ref. [27].
[d] See Ref. [30]. [e] See Ref. [31]. [f] See Refs. [32, 33].
[g] See Ref. [34].

Conversion Factors
Quadrupole moment, 1 a.u. = $4.486613 \times 10^{-40}\ \text{cm}^2$
Hexadecapole moment, 1 a.u. = $1.256378 \times 10^{-60}\ \text{cm}^4$
Electric field gradient, 1 a.u. = $9.7171 \times 10^{21}\ \text{Vm}^{-2}$

that accurate calculations, such as those of Guberman, were not extended to calculate interesting one-electron properties.

The values for the electric field gradient, quadrupole moment and hexadecapole moment, obtained by vibrational averaging, using the determined spectroscopic constants from the calculated potential energy surface, are in as good agreement as might be expected with the experimentally observed values, within the restriction of the basis. A more accurate calculation, of the order of that of Saxon and Liu would be required to verify the results. It should be noted that use of the observed spectroscopic constants for the $O_2\ {}^3\Sigma_g^-$ state made a negligible difference to the calculated properties. Additional calculations involving variation of the polarization exponent by 10% in either direction also made a negligible difference to the calculated property values. There is considerable room for uncertainty in the observed values of the multipole moments, especially the hexadecapole moment, as the values for these quantities were obtained from fits to multipole-induced-dipole far infra-red absorption spectra (or microwave spectra) and induced-birefringence measurements. The naturally small magnitude of the quadrupole moment [30, 31] makes an accurate estimation of its value particularly difficult. The quadrupole moments derived from pressure-induced far infra-red absorption results are somewhat lower, in general, than those obtained directly from the induced birefringence experiments of Buckingham *et al.* [30]. Admittedly such collision-induced data produces values for moments which vary significantly, depending as such analyses do, upon the O_2–O_2 inter-molecular potential chosen [32, 33, 34] and upon collision diameter values used. In consequence, the calculated values of the hexadecapole moment vary enormously in the range 21×10^{-60} cm^4 to 3×10^{-60} cm^4, being highly dependent upon the quadrupole values adopted. The usual method of approach to account for discrepancies in the line shapes between experimental and theoretically predicted absorption spectra which include only the quadrupole-induced-dipole term is to add in the comparatively smaller contribution due to hexadecapole-induced-dipole effect by a procedure such as "least-squares-fit" [33, 34]. This approach, however, becomes unstable in this case as the quadrupole and hexadecapole effects are of similar magnitude owing to the size of the quadrupole moment in O_2. The strong dependence of the quadrupole moment upon the separation, evident from the property surface data, gives a large vibrational dependence in the quadrupole value (a first derivative of 3.03653 a.u.), indicating a need for careful vibrational averaging of the quadrupole moments. The electric field gradient calculation of Miller and Townes [27], being derived from the magnetic hyperfine structure of the microwave spectrum of $^{16}O^{17}O$, is again prone to some degree of error, and so we believe that our calculated value, while agreeing well with that of experiment, is probably a better estimate of the true value.

The value for the dissociation energy is very similar to that obtained by Hay [35] in a calculation using an equivalent basis set with conventional CI on only the equilibrium geometry of O_2, but falls short of the best calculated values as a result of lacking "size consistency" over the full surface.

In summary, these calculations demonstrate the ease of this direct CI method. The poor value obtained for ω_e illustrates the restrictions on its application: it is not capable of producing a good potential energy surface over a wide range because of the need to include one or more additional root functions.

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