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# Multiconfiguration self-consistent field (MCSCF) theory for excited states\*

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An exact MCSCF theory is proposed for excited states belonging to the same symmetry species and is illustrated by actual application to some of the excited states of the CN radical.

## I. INTRODUCTION

Excited bound states of atomic and molecular systems, though of considerable experimental interest, particularly in astrophysics, are not as widely explored as the corresponding ground states. The obvious reason for this shortcoming is that no formalism of sufficiently general validity exists in the literature for treating excited states of the same symmetry as a lower state, apart from a straightforward configuration-interaction (CI) procedure. The CI method<sup>1</sup> is, however, not quite as reliable as one usually finds the self-consistent-field methods to be, unless the basis set is large enough and a very large number (often of the order of thousands) of configurations are employed. Methods<sup>2</sup> which, in effect, screen out configurations that are unimportant in the context of excitation energies rather than the total absolute energy, have been proposed and applied to different systems. While these latter methods are successful in many important cases and have been reported to be highly efficient with a small basis set, they have not been extended to cases where the Hartree-Fock is open shell and, in particular, those cases involving charge transfer.

We have in the recent<sup>3</sup> past found the MCSCF method cast in the OVC formalism to be very successful in the investigation of the ground states of molecular systems. To extend the theory to excited states let us consider the difficulties that can arise. Convergence can now be a serious problem (which it is not for the ground state) owing to two probable sources of instability: First, since we shall be concerned often with singly excited states, single excitations in the sense of additional configurations are often going to be of major importance. This, therefore, requires that improved convergence techniques should be introduced to deal with single excitation if and when they become important. Such excitations are notoriously difficult to converge with the presently available methods.<sup>4</sup> Second, lack of any other constraint than just the requirement that the excited state in question should correspond to a certain root in the secular equation in the CI part of the MCSCF may allow the orbitals of the excited state to "overreadjust" in the course of iterations.

We shall present below a formalism that will counter the two sources of instability mentioned above. We illustrate our method in Sec. IV by application to some of the excited states of the CN radical as discussed by Schaeffer.<sup>1</sup>

## II. FORMULATION OF THE MCSCF PROBLEM FOR EXCITED STATES

We assume the  $n$ th excited wavefunction of a certain symmetry species to be of the form,

$$\Psi^{(n)} = \sum_a A_a^{(n)} \Phi_a, \quad (1)$$

where  $\Phi_a$ 's are the configurations. The corresponding secular equation is given by

$$|\mathcal{H}_{ab} - E\delta_{ab}| = 0, \quad (2)$$

where  $\mathcal{H}$  is the total Hamiltonian and

$$\mathcal{H}_{ab} = \langle \Phi_a | \mathcal{H} | \Phi_b \rangle$$

are the matrix elements.

The conventional MCSCF process consists of (1) forming the matrix elements using the given vectors and solving Eq. (2) to obtain  $A_a^{(n)}$  and (2) using these mixing coefficients to construct and solve the Fock equations for the orbitals and repeating this process until convergence. For the ground state in a given symmetry species each of the above two steps reinforce each other in lowering the energy, and the resulting MCSCF process, except in the cases of bad initial choice of vectors, is likely to be stable. For the excited states, however, the two steps do not necessarily reinforce each other, and it is therefore essential that the coupling of the two steps is somehow built into the solution of the Fock equations.

The solution of the Fock equations is most conveniently done in two steps: (1) Perform rotational transformations among the occupied vectors to match the Lagrangian multipliers; and (2) obtain increments of the vectors outside the space spanned by the vectors. Obviously since the second step involves excitation only to the virtual states, the roots of the secular equation (2) usually retain the order in which they occur to start with, since the excitations into virtual vectors can only lead to more or less uniform improve-

ment. In the step No. (1), however, in those cases where the orbital energies of the occupied vectors are similar—valence states of molecules, for example—the stability is likely to be poor. Thus it is in this part of the calculation that one need introduce the change of the mixing coefficients explicitly in the Fock equations. This is easily obtained by observing that the second-order change in the total energy is given by (see Appendix)

$$\Delta E^{(2)} = \sum_{i \neq n} \left[ \left( \sum_{ab} A_a^{(n)} A_b^{(i)} \delta \langle \Phi_a | \mathcal{H} | \Phi_b \rangle \right)^2 / (E_n - E_i) \right], \quad (3)$$

where the summation goes over all the solutions of the

secular equation (2) except the  $n$ th, and  $\delta \langle \Phi_a | \mathcal{H} | \Phi_b \rangle$  is the change in the matrix element  $\mathcal{H}_{ab}$  due to the change in the vectors.

We shall consider the effect of the term (3) on the process of minimization of the energy under rotation of the vectors  $\mathbf{c}_k$  and  $\mathbf{c}_l$ . Under the rotation, let

$$\begin{aligned} \mathbf{c}_k \rightarrow \mathbf{c}_k' &= (\mathbf{c}_k + u_{kl} \mathbf{c}_l) (1 + u_{kl}^2)^{-1/2}, \\ \mathbf{c}_l \rightarrow \mathbf{c}_l' &= (\mathbf{c}_l - u_{kl} \mathbf{c}_k) (1 + u_{kl}^2)^{-1/2}. \end{aligned} \quad (4)$$

Then the equation determining  $u_{kl}$  is obtained by minimization of the following expression for the change in the energy neglecting the third and higher powers of  $u_{kl}$ :

$$\begin{aligned} \Delta F(u_{kl}) &= 2u_{kl} \mathbf{c}_k^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_l + u_{kl}^2 \mathbf{c}_k^+ \left[ \frac{\partial}{\partial u_{kl}} (\mathbf{F}_k - \mathbf{F}_l) \right] \mathbf{c}_l + u_{kl}^2 [\mathbf{c}_l^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_l - \mathbf{c}_k^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_k] \\ &\quad + u_{kl}^2 \sum_i \left[ \left( \sum_{ab} A_a^{(n)} A_b^{(i)} \frac{\partial \mathcal{H}_{ab}}{\partial u_{kl}} \right)^2 / (E_n - E_i) \right]. \end{aligned} \quad (5)$$

Thus

$$u_{kl} = \frac{-\mathbf{c}_k^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_l}{\mathbf{c}_l^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_l - \mathbf{c}_k^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_k + \mathbf{c}_k^+ \left[ \left( \partial / \partial u_{kl} \right) (\mathbf{F}_k - \mathbf{F}_l) \right] \mathbf{c}_l + \Delta_{kl}}, \quad (6)$$

where

$$\Delta_{kl} = \sum_i \left[ \left( \sum_{ab} A_a^{(n)} A_b^{(i)} \frac{\partial \mathcal{H}_{ab}}{\partial u_{kl}} \right)^2 / (E_n - E_i) \right] \quad (7)$$

is the principal term arising from the coupling between the CI secular equation and the Fock equations. The detailed derivation of Eqs. (3) and (5) is given in the Appendix.

The evaluation of  $\Delta_{kl}$ , which has to be carried out in every iteration and for many pairs of vectors, may, in general, be a costly process unless simplifications are made. To this end we observe that since the Fock equations represent the energy minimization conditions for single excitations, the change in the matrix elements between configurations differing from each other by double excitations is not likely to contribute to  $\Delta_{kl}$  significantly. Thus we shall be content with evaluation of  $\Delta_{kl}$  for only the diagonal ( $a=b$ ) terms and the off-diagonal ones involving single excitations. Also we shall neglect entirely the coupling between two pairs of vectors represented by the terms in the energy expression (3) proportional to the product of their rotational transformation coefficients. The expression for  $\Delta_{kl}$  including only the diagonal and single excitation terms and neglecting small exchange terms is as follows:

$$\Delta_{kl} = \sum_i [f_{i,kl}^2 / (E_n - E_i)], \quad (8)$$

where

$$\begin{aligned} f_{i,kl} &= \sum_a A_a^{(n)} A_a^{(i)} \mathbf{c}_k^+ (n_{ak} \mathbf{F}_{ak} - n_{al} \mathbf{F}_{al}) \mathbf{c}_l \\ &\quad + \sum_{a \neq b}^{\text{single}} A_a^{(n)} A_b^{(i)} n_{ab,kl} (\mathbf{c}_l^+ \mathbf{F}_{ab} \mathbf{c}_l - \mathbf{c}_k^+ \mathbf{F}_{ab} \mathbf{c}_k). \end{aligned} \quad (9)$$

The matrix  $\mathbf{F}_{ak}$  is the Fock operator for the  $k$ th vector obtained from the  $a$ th configuration and  $n_{ab,kl}$ 's are the one-electron vector coupling coefficients.

When one or more of the roots of secular Eq. (2) are very close to that corresponding to the excited state under consideration, the second-order perturbation expression (3) is no longer valid. In those cases where the lower states in actuality are sufficiently separated in energy from the one in question, but owing to the deficiency in wavefunction, happen to be close to the latter, one possible way out is to take into account an adequate number of excitations such as to allow the lower roots to describe the lower states well enough. It is also essential to modify the second-order perturbation series for nearly degenerate roots in the following manner: Suppose that the  $n$ th excited state of a given symmetry is under investigation and the  $m$ th energy in an MCSCF iterative cycle happens to be very close to the  $n$ th. Let us consider the manner in which these states are going to mix under the rotation  $u_{kl}$  of the vectors  $\mathbf{c}_k$  and  $\mathbf{c}_l$  as defined in (4). Let the diagonal energies be given as a function of the rotation by

$$\begin{aligned} E_n(u_{kl}) &= E_n(0) + 2N_n u_{kl} + D_n u_{kl}^2, \\ E_m(u_{kl}) &= E_m(0) + 2N_m u_{kl} + D_m u_{kl}^2. \end{aligned} \quad (10)$$

Let the off-diagonal element be  $u_{kl}K$ . The correspond-

ing secular equation has the following roots:

$$\lambda = \frac{1}{2}(E_n(u_{kl}) + E_m(u_{kl}) \pm \{[E_n(u_{kl}) - E_m(u_{kl})]^2 + 4u_{kl}^2 K^2\}^{1/2}). \quad (11)$$

Let  $E_m(u_{kl}) > E_n(u_{kl})$ . Setting to zero the derivatives of  $\lambda$  with respect to  $u_{kl}$  one has

$$\Delta_n(u_{kl}) = \delta_{nm}(u_{kl}) + \{[E_n(u_{kl}) - E_m(u_{kl})]^2 + 4u_{kl}^2 K^2\}^{-1/2} \times \{-\delta_{nm}(u_{kl})[E_m(u_{kl}) - E_n(u_{kl})] + u_{kl} K^2\}, \quad (12)$$

where

$$\Delta_n(u_{kl}) = N_n + D_n u_{kl}, \quad \delta_{nm}(u_{kl}) = \frac{1}{2}[(N_n - N_m) + (D_n - D_m)u_{kl}]. \quad (13)$$

Thus

$$\Delta_n(u_{kl}) = [2\delta_{nm}(u_{kl})[\varepsilon_m(u_{kl}) - E_m(u_{kl})] + u_{kl} K^2] \times [\varepsilon_m(u_{kl}) - \varepsilon_n(u_{kl})]^{-1}, \quad (14)$$

where  $\varepsilon_m$  and  $\varepsilon_n$  are the higher and the lower roots of the secular equation in question. If we, therefore, assume that the vectors  $\mathbf{c}_k$  and  $\mathbf{c}_l$  are near convergence,  $\varepsilon_n(u_{kl})$  can only be a function of square and higher powers of  $u_{kl}$  while  $\varepsilon_m(u_{kl})$  can also depend linearly on  $u_{kl}$  according to essentially the term  $2N_m u_{kl}$  in Eq. (10). Since  $N_m$  can be substantial, Eq. (14), rather than a simple second-order perturbation expression is obviously the appropriate procedure.

### III. IMPROVED ITERATIVE SOLUTION OF THE FOCK EQUATIONS

For greater stability of the iterative process of solution of the Fock equations, it is necessary to consider the terms involving higher powers of  $u_{kl}$  in Eq. (5) than the second. Correcting to second order in  $u_{kl}$  [i.e., third in Eq. (5)] and neglecting some small coupling terms, Eq. (6) becomes

$$C u_{kl}^2 + D u_{kl} + N = 0, \quad (15)$$

where

$$C = -2\mathbf{c}_k^+ (\mathbf{F}_l - \mathbf{F}_k) \mathbf{c}_l, \quad D = \mathbf{c}_l^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_l - \mathbf{c}_k^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_k + \mathbf{c}_k^+ [(\partial/\partial u_{kl})(\mathbf{F}_k - \mathbf{F}_l)] \mathbf{c}_l + \Delta_{kl}, \quad N = \mathbf{c}_k^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_l, \quad (16)$$

with  $\Delta_{kl}$  defined by Eq. (7).

It is sometimes necessary, in particular when single excitations are present, to consider the coupling between the steps (1) and (2) of the iterative solution of the Fock equations discussed above. Consider the Fock equation in the context of single excitations,

$$\mathbf{M}_i' \mathbf{c}_i = \sum_j \epsilon_{ij} \mathbf{S} \mathbf{c}_j, \quad (17)$$

where

$$\mathbf{M}_i' = \mathbf{F}_i' - \sum_j [\mathbf{S} \mathbf{c}_j (\mathbf{F}_i' \mathbf{c}_j)^+ + \mathbf{F}_i' \mathbf{c}_j (\mathbf{S} \mathbf{c}_j)^+], \quad (18)$$

$\mathbf{F}_i'$  being the Fock operator for the vector  $\mathbf{c}_i$ , which in the presence of single excitations is of the form,

$$\mathbf{F}_i' = \mathbf{F}_i + \sum_j \mathbf{F}_{ij} | \mathbf{c}_j \rangle \langle \mathbf{S} \mathbf{c}_j |. \quad (19)$$

Then if  $\delta \mathbf{c}_i$  be the increment in  $\mathbf{c}_i$ ,

$$\delta \mathbf{c}_i = -(\mathbf{M}_i' - \epsilon_i \mathbf{S})^{-1} (\mathbf{M}_i' + \mathbf{F}_i') \mathbf{c}_i \quad (20)$$

provided we neglect the coupling of the increments of the occupied vectors among themselves. While a full treatment of the coupling is costly and probably unnecessary, we have found the following partial treatment of the coupling successful: First, in performing the rotational transformations among the occupied vectors in order to match the Lagrangian multipliers, the changes in the parts of the Fock operator arising from the single excitations are important and have to be included. Also we modify Eq. (20) to

$$\delta \mathbf{c}_i = -(\mathbf{M}_i'' - \epsilon_i \mathbf{S})^{-1} (\mathbf{M}_i'' + \mathbf{F}_i'') \mathbf{c}_i^{\text{rot}}, \quad (21)$$

where

$$\mathbf{F}_i'' = \mathbf{F}_i' + \sum_j u_{ij} \mathbf{F}_{ji} \quad (22)$$

and

$$\mathbf{M}_i'' = \mathbf{F}_i'' - \sum_j [\mathbf{S} \mathbf{c}_j^{\text{rot}} (\mathbf{F}_i'' \mathbf{c}_j^{\text{rot}})^+ + (\mathbf{F}_i'' \mathbf{c}_j^{\text{rot}}) (\mathbf{S} \mathbf{c}_j^{\text{rot}})^+], \quad (23)$$

and the vectors  $\mathbf{c}_i^{\text{rot}}$  are those resulting from the rotation among the occupied vectors,  $\{u_{ij}\}$  being the transformation matrix. The additional term in Eq. (22) reflects the change in  $\mathbf{F}_i \mathbf{c}_i$  due to change in the vector  $\mathbf{c}_j$ ,  $j \neq i$ , which, as can be readily seen,  $\mathbf{F}_i$  defined by Eq. (19) cannot by itself yield. It is to be noted that unless the second term on the right-hand side of Eq. (22) is comparable to the first one, the modifications mentioned above are not likely to be much help. When single excitations happen to be dominant, however, the second term can, in certain cases, be as large as the first for not too small  $|u_{ij}|$ . A similar treatment can also be devised for excitations other than single but it is readily seen that for reasonable input vectors the corrections are not likely to be significant in regard to the convergence of the iterative process. Further, while computing these corrections for single excitations involves no new contraction of the supermatrices, such computations for other types of excitations requires new contractions which are expensive.

### IV. RESULTS ON THE EXCITED STATES OF THE CN RADICAL

For illustrating the theories proposed we selected the states of the CN radical belonging to the symmetries  $^2\Sigma^+$  and  $^2\Pi$ . Apart from a fair amount of relevant

TABLE I. Mixing coefficients and energies for the three  $^2\Sigma^+$  states and four  $^2\pi$  states of the CN radical. Energy is given in hartrees and the internuclear separation  $R$  in bohrs.

$^2\Sigma^+$ States: mixing coefficients				
Configurations (Core)*	$X\ ^2\Sigma^+$ ( $R=2.21$ )	$B\ ^2\Sigma^+$ ( $R=2.21$ )	$E\ ^2\Sigma^+$ ( $R=2.75$ )	
$4\sigma^2 5\sigma 1\pi^4$	0.94581	0.18555	-0.16602	
$4\sigma^2 5\sigma 1\pi^3 2\pi$	-0.12561	-0.29324	-0.67964	
$4\sigma^2 5\sigma 1\pi^2 2\pi^3$			0.21717	
$4\sigma 5\sigma^2 1\pi^4$	-0.14706	0.91438	-0.65804	
$4\sigma 1\pi^4 2\pi^2$			0.05795	
$4\sigma 5\sigma^2 1\pi^3 2\pi$	-0.12770	0.09966		
$4\sigma 5\sigma^2 1\pi^2 2\pi^3$		0.18321	0.16431	
$4\sigma^2 5\sigma 1\pi^2 2\pi^2$	0.22776			
Total energy	-92.32008	-92.19001	-91.98583	
$^2\pi$ States: mixing coefficients				
Configurations (Core)*	$A\ ^2\pi$ ( $R=2.21$ )	$D\ ^2\pi$ ( $R=2.75$ )	$H\ ^2\pi$ ( $R=2.75$ )	$^2\pi(\text{IV})$ ( $R=2.75$ )
$4\sigma^2 5\sigma^2 1\pi^3$	0.95575	0.10962	-0.09652	0.06236
$4\sigma^2 5\sigma^2 1\pi^2 2\pi$	0.24113	0.99053	0.61147	-0.80776
$4\sigma^2 5\sigma^2 1\pi 2\pi^2$	0.15895		0.20989	-0.20537
$5\sigma^2 1\pi^4 2\pi$	-0.04547	-0.00465	-0.04941	-0.20141
$4\sigma^2 5\sigma^2 2\pi^3$	-0.01842	-0.02116	0.02112	-0.02845
$4\sigma^2 1\pi^4 2\pi$	0.02347	-0.00645	0.72356	0.48226
$4\sigma^2 1\pi^3 2\pi^3$	0.01114	0.05088	0.13888	0.16374
$5\sigma^2 1\pi^3 2\pi^3$	0.00713	0.05744		0.02644
$(4\sigma 5\sigma) 1\pi^3 2\pi^2$			0.16312	
Total energy	-92.26219	-92.05104	-91.98645	-91.95870

TABLE II. Excitation energies for different excited states. The internuclear separation  $R$  is given in bohrs.  $R_e$ , which denotes the equilibrium separation, is also given in bohrs.

States	MCSCF values (eV)	Schaeffer's CI values (eV)	Experimental values (eV)
$B\ ^2\Sigma^+$	3.54 ( $R=2.176$ )	3.765 ( $R_e=2.3536$ )	3.193 ( $R_e=2.176$ )
$E\ ^2\Sigma^+$	8.79 ( $R=2.49$ )	7.856 ( $R_e=2.574$ )	7.334 ( $R_e=2.49$ )
$A\ ^2\pi$	1.50 ( $R=2.326$ )	1.883 ( $R_e=2.5$ )	1.146 ( $R_e=2.326$ )
$D\ ^2\pi$	7.32 ( $R=2.83$ )	$\sim 6.593$ ( $R_e=3.0$ )	6.755 ( $R_e=2.83$ )
$H\ ^2\pi$	8.71 ( $R=2.47$ )	7.807 ( $R_e=2.7$ )	7.556 ( $R_e=2.47$ )
$^2\pi(\text{IV})$	9.73 ( $R=2.89$ )	8.76 ( $R_e=2.89$ )	

experimental data, these states have already been thoroughly investigated by Schaeffer *et al.*<sup>1</sup> using CI techniques. While they have used a minimal basis set for the valence shells, our results are based on a fairly saturated set for the ground state Hartree-Fock of the CN radical. In Table I, the MCSCF configurations for various spectroscopic states along with their energies and mixing coefficients are listed. In Table II we present the excitation energies obtained from these wavefunctions. The corresponding Schaeffer's and experimental values are also shown. Since we have not calculated full potential curves, our values of excitation energies are derived from our values of total energies by a simple harmonic approximation to account for the discrepancy between the internuclear separations at which our calculations are done and the corresponding actual equilibrium values. Where experimental values for the vibrational constants and equilibrium separation are not available, Schaeffer's values are used. The occupied vectors along with the basis functions for the different states are shown in Table III.

The MCSCF excitation energies as shown in Table III are not decisively better than Schaeffer's CI values.

TABLE III. Valence shell vectors

Vector labels	States \ Basis set $n l \zeta$	$\sigma$ vec						
		$1s(C)$ 9.153	$1s(C)$ 5.382	$2s(C)$ 1.428	$3s(C)$ 3.076	$2p(C)$ 1.15	$2p(C)$ 2.177	$2p(C)$ 5.152
$4\sigma$	$X^2\Sigma^+$ $R=2.2b$	0.0007	0.1443	-0.1073	-0.2280	0.0616	-0.1487	-0.0038
	$B^2\Sigma^+$ $R=2.2b$	0.0022	0.1194	-0.2748	-0.1723	0.0405	-0.0102	-0.0003
	$E^2\Sigma^+$ $R=2.75b$	-0.0039	-0.1600	0.4378	0.2282	-0.0458	0.0025	-0.0015
	$A^2\pi$ $R=2.28$	0.0008	0.0277	-0.0794	-0.0512	0.0413	0.0276	0.0013
	$D^2\pi$ $R=2.75b$	-0.0017	-0.1738	0.4591	0.2807	-0.0395	0.0721	-0.0019
	$H^2\pi$ $R=2.75b$	-0.0038	-0.1856	0.5134	0.2667	-0.0508	0.0259	-0.0018
	$^2\pi(IV)$ $R=2.75b$	-0.0040	-0.1542	0.5412	0.2081	-0.0862	-0.0549	-0.0045
$5\sigma$	$X^2\Sigma^+$ $R=2.2b$	0.0058	0.1218	-0.7809	-0.1318	0.2161	0.3806	0.0116
	$B^2\Sigma^+$ $R=2.2b$	0.0047	0.1300	-0.8328	-0.0925	0.2254	0.2937	0.0154
	$E^2\Sigma^+$ $R=2.75$	-0.0043	-0.0811	0.6165	0.0426	-0.2783	-0.3378	-0.0136
	$A^2\pi$ $R=2.2b$	0.0016	0.1498	-0.8112	-0.1889	0.2342	0.2011	0.0129
$5\sigma$	$D^2\pi$ $R=2.75b$	-0.0031	-0.0669	0.6672	0.0364	-0.2625	-0.3058	-0.0139
	$H^2\pi$ $R=2.75b$	-0.0042	-0.0735	0.6109	0.0350	-0.2649	-0.3010	-0.0132
	$^2\pi(IV)$	-0.0033	-0.0428	0.5300	-0.0088	-0.2535	-0.3053	-0.0127
Vector labels	States \ Basis set $n l \zeta$	$\pi$ vec						
		$2p(C)$ 1.15	$2p(C)$ 2.177	$2p(C)$ 5.152	$3d(C)$ 1.9	$3d(C)$ 2.7	$4f(C)$ 2.6	$2p(N)$ 1.352
$1\pi$	$X^2\Sigma^+$	-0.2843	-0.2855	-0.0117	-0.0305	-0.0068	-0.0106	-0.3684
	$B^2\Sigma^+$	-0.2308	-0.2381	-0.0102	-0.0403	-0.0065	-0.0095	-0.4216
	$E^2\Sigma^+$	-0.3163	-0.2166	-0.0132	-0.0476	0.0065	-0.0072	-0.4412
	$A^2\pi$	-0.1543	-0.2090	-0.0070	-0.0375	-0.0112	-0.0110	-0.4435
	$D^2\pi$	-0.1200	-0.1364	-0.0043	-0.0442	0.0039	-0.0086	-0.5539
	$H^2\pi$	-0.3714	-0.2556	-0.0150	-0.0342	0.0020	-0.0089	-0.3881
	$^2\pi(IV)$	-0.3026	-0.2247	-0.0120	-0.0413	0.0038	-0.0082	-0.4478
$2\pi$	$X^2\Sigma^+$	-0.4504	-0.4580	-0.0101	0.0126	0.0276	0.0123	0.3416
	$B^2\Sigma^+$	-0.5469	-0.3917	-0.0168	-0.0625	0.0416	0.0023	0.3150
	$E^2\Sigma^+$	-0.6116	-0.3031	-0.0265	-0.0659	0.0161	0.0072	0.4338
	$A^2\pi$	-0.5460	-0.4485	-0.0169	-0.1278	0.0433	0.0043	0.2406
	$D^2\pi$	-0.6553	-0.3804	-0.0241	-0.0007	-0.0027	0.0049	0.3591
	$H^2\pi$	-0.5539	-0.3062	-0.0214	0.0432	-0.0105	0.0034	0.5156
	$^2\pi(IV)$	-0.5911	-0.3355	-0.0227	0.0317	-0.0103	0.0044	0.4803

for different spectroscopic states.

tors

$3d(C)$ 1.900	$3d(C)$ 2.700	$1s(N)$ 10.507	$1s(N)$ 6.346	$2s(N)$ 1.697	$3s(N)$ 3.715	$2p(N)$ 1.352	$2p(N)$ 2.555	$2p(N)$ 5.573	$3d(N)$ 1.402	$3d(N)$ 2.905
0.0262	-0.0233	-0.0031	-0.0890	0.3822	0.1119	-0.4442	-0.3101	-0.0283	-0.0423	-0.0196
-0.0090	-0.0035	-0.0045	-0.1379	0.5733	0.1737	-0.3102	-0.3161	-0.0193	-0.0089	-0.0015
0.0116	0.0012	0.0043	0.1238	-0.4940	0.1608	0.2811	0.2148	0.0185	0.0267	0.0077
0.0151	-0.0007	0.0047	-0.1034	0.6808	0.2485	-0.2757	-0.1733	-0.0181	-0.0184	-0.0030
0.0016	0.0097	0.0022	0.0349	-0.2243	-0.0518	0.3136	0.2138	0.0198	0.0540	0.0138
-0.0009	0.0056	0.0033	0.0797	-0.3678	-0.1078	0.2674	0.1931	0.0171	0.0393	0.0112
-0.0092	0.0016	0.0041	0.1445	-0.5669	-0.1889	0.1643	0.1351	0.0117	0.0199	0.0065
0.0528	0.0279	-0.0001	-0.0176	0.1228	0.0154	0.2496	0.1476	0.0131	0.0263	0.0140
-0.0047	0.0133	0.0	0.0321	-0.0573	0.0365	0.2921	0.1353	0.0168	0.0318	0.0054
0.0207	-0.0173	-0.0009	0.0002	0.0278	0.0011	-0.4130	-0.2161	-0.0246	-0.0498	-0.004
0.0128	-0.0007	-0.0058	-0.0385	0.0146	-0.0244	0.1072	0.0147	0.0053	0.0139	0.001
-0.0421	-0.0051	-0.0002	0.0315	-0.0700	-0.0344	-0.4267	-0.2224	-0.0253	-0.0608	-0.0096
-0.0364	-0.0064	-0.0012	-0.0021	0.0049	0.0092	-0.4412	-0.2499	-0.0264	-0.0544	-0.0101
-0.0355	-0.0070	-0.0016	-0.0147	0.1055	0.0243	-0.4799	-0.2730	-0.0291	-0.0612	-0.0110

tors

$2p(N)$ 2.555	$2p(N)$ 5.573	$3d(N)$ 1.402	$3d(N)$ 2.905	$4f(N)$ 2.80
-0.3014	-0.0234	-0.0346	-0.0213	-0.0089
-0.3354	-0.0265	-0.0241	-0.0119	-0.0092
-0.3082	-0.0274	-0.0271	-0.0120	-0.0049
-0.3839	-0.0271	-0.0449	-0.0192	-0.0063
-0.3766	-0.0334	-0.0312	-0.0126	-0.0032
-0.2844	-0.0245	-0.0242	-0.0129	-0.0073
-0.3111	-0.0282	-0.0202	-0.0127	-0.0068
0.4964	-0.0202	0.0133	-0.0085	-0.0122
0.4842	0.0144	-0.0312	-0.0539	-0.0008
0.3424	0.0252	-0.0097	0.0012	-0.0102
0.5120	0.0106	0.0016	-0.0256	-0.0169
0.1529	0.0213	-0.0284	-0.0046	-0.0075
0.2946	0.0320	-0.0201	0.0	-0.0013
0.2509	0.0298	-0.0243	-0.0014	-0.0021

This is primarily due to the rather restricted set of configurations our present computer program<sup>5</sup> can handle. The  $2\pi$  states are especially poorly represented, for while the proper description of the states under consideration over the whole significant range of internuclear separation one needs at least 35 configurations, we could afford only 17. In a future work on the CN states, we hope to correct for this deficiency.

One important feature that emerges from these calculations is that in most cases the convergence for the excited states is rapid once the ground state is converged, particularly for those excited states that can be characterized as single excitations from the lowest state. Thus, it may turn out to be less costly to do MCSCF on excited states than one may think.

## V. CONCLUSION

The above results indicate that the MCSCF procedure can be successfully applied to the case of valence excited states. While it is true that an exact MCSCF can be very much more expensive than the CI approach with a small basis set, the superiority of the former method in the case of large basis is certainly a great advantage. Thus, if higher accuracy of description of a given excited state rather than just the qualitative features of many excited states is what is looked for, the MCSCF method may always be the better approach.

## APPENDIX

Let us denote the Hamiltonian matrix  $\{\mathcal{H}_{ab}\}$  as  $\mathcal{H}$  and its first-order increment,  $\delta\mathcal{H}^{(1)}$ , due to a rotation of the vectors for the form given in Eq. (4). The corresponding change in the  $n$ th eigenvector  $\mathbf{A}^{(n)}$  is given to the first order by perturbation theory to be

$$\langle \delta \mathbf{A}^{(n)} | = \sum_{i \neq n} [\langle \mathbf{A}^{(n)} | \delta \mathcal{H}^{(1)} | \mathbf{A}^{(i)} \rangle / (E_n - E_i)] \langle \delta \mathbf{A}^{(i)} |.$$

\*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

<sup>1</sup>H. F. Schaeffer and T. G. Heil, J. Chem. Phys. **54**, 2573 (1971).

<sup>2</sup>T. Shibuya, J. Rose, and V. McKoy, J. Chem. Phys. **58**, 500 (1973).

<sup>3</sup>G. Das and A. C. Wahl, J. Chem. Phys. **56**, 1769 (1972).

<sup>4</sup>Consider an MCSCF process involving excitations of the kind  $a(1\sigma^2 2\sigma) + b(1\sigma 2\sigma^2)$ . It is easily seen that if the rest of the excitations are weak,  $1\sigma$  and  $2\sigma$  are not directly coupled in the sense that they can not mix into each other by virtue of the rotational transformation. As can be seen by doing some algebra, remembering that  $a$  and  $b$  are obtained by solving a CI secular equation,  $C_{1\sigma}^+(\mathbf{F}_{1\sigma} - \mathbf{F}_{2\sigma})C_{2\sigma} \approx 0$ , where  $\mathbf{F}_{1\sigma}$  and

The corresponding second-order perturbed energy is given by

$$\Delta E_n^{(2)} = \sum_{i \neq n} [\langle \mathbf{A}^{(n)} | \delta \mathcal{H}^{(1)} | \mathbf{A}^{(i)} \rangle^2 / (E_n - E_i)], \quad (\text{A1})$$

which is exactly what Eq. (3) is. The Hermitian property of the Lagrangian multipliers can be traced to the requirement that the energy remains stationary under the rotation of Eq. (4). One can write the change to the first order in energy due to this rotation,

$$\begin{aligned} \Delta E_1^{(1)} &= 2\delta \mathbf{c}_k^+ \mathbf{F}_k \mathbf{c}_k + 2\delta \mathbf{c}_l^+ \mathbf{F}_l \mathbf{c}_l \\ &= 2u_{kl} [\mathbf{c}_l^+ \mathbf{F}_k \mathbf{c}_k - \mathbf{c}_k^+ \mathbf{F}_l \mathbf{c}_l], \end{aligned} \quad (\text{A2})$$

whence the Hermitian property of the Lagrangian multipliers follows. If one analyzes the second-order change  $\langle \mathbf{A}^{(n)} | \delta \mathcal{H}^{(2)} | \mathbf{A}^{(n)} \rangle$  one finds this to be given by

$$\begin{aligned} \langle \mathbf{A}^{(n)} | \delta \mathcal{H}^{(2)} | \mathbf{A}^{(n)} \rangle &= u_{kl}^2 c_k^+ [(\partial / \partial u_{kl}) (\mathbf{F}_k - \mathbf{F}_l)] c_l \\ &+ u_{kl}^2 [c_l^+ (\mathbf{F}_k - \mathbf{F}_l) c_l - \mathbf{c}_k^+ (\mathbf{F}_k - \mathbf{F}_l) \mathbf{c}_k], \end{aligned} \quad (\text{A3})$$

where

$$\partial \mathbf{M} / \partial u_{kl} = \mathcal{L} t_{u_{kl} \rightarrow 0} \{ [\mathbf{M}(u_{kl}) - \mathbf{M}(0)] / u_{kl} \}. \quad (\text{A4})$$

Equation (A3) also parallels the first-order terms obtained<sup>3</sup> by expanding

$$\langle \mathbf{c}_k + u_{kl} \mathbf{c}_l | \mathbf{F}_k - \mathbf{F}_l + u_{kl} (\partial / \partial u_{kl}) (\mathbf{F}_k - \mathbf{F}_l) | \mathbf{c}_l - u_{kl} \mathbf{c}_k \rangle. \quad (\text{A5})$$

Thus matching of Lagrangian multipliers in the manner given in Ref. 3 can be replaced by an energetic language as given in Eq. (5) where, in addition, the second-order terms due to the first-order change in the mixing coefficient vector  $\mathbf{A}^{(n)}$  are included.

$\mathbf{F}_{2\sigma}$  are the Fock operators for the orbitals  $1\sigma$  and  $2\sigma$ . Convergence difficulties can, however, arise even in the ground state if the input vectors for  $1\sigma$  and  $2\sigma$  are far too crude and/or if  $a$  and  $b$  are large and comparable. For, in such circumstances, in the next iteration both vectors will try to draw corrections from the same part of the function space given by the basis set. The above considerations are true for both the ground and excited states so long as the other terms of the MCSCF are sufficiently weak.

<sup>5</sup>G. Das and A. C. Wahl, "BISONMC: A Fortran Computing System for Multi-configuration Self-Consistent Field (MCSCF) Calculations on Atoms, Diatoms, and Polyatoms," Argonne National Laboratory Report No. ANL-7955.