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Applicability of SCF Theory to Some Open-Shell States of CO, N₂, and O₂*

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By working with the real functions π_x and π_y instead of π^+ and π^- , we show how to express the SCF Hamiltonians for the Σ states of the configurations $(\pi_u)^3(\pi_g)$, $(\pi_u)^2(\pi_g)^2$, and $(1\pi)^2(2\pi)$ of diatomic molecules in terms of the Coulomb and exchange operators only. With these results, we have used conventional SCF programs to solve for the wavefunctions of many interesting states of N₂, O₂, and CO, e.g., the $B^3\Sigma_u^-$ state of O₂. For many states, the SCF results are in good agreement with experiment. However, SCF theory runs into serious trouble if electron correlation is important in determining the relative locations of excited states.

I. INTRODUCTION

The Hartree-Fock model provides a useful description of the electronic structure of atoms and molecules. For closed-shell systems, the Hartree-Fock (HF) wavefunction is an antisymmetrized product of orthogonal spin orbitals which satisfy the pseudoeigenvalue equation

$$F\varphi_i = \epsilon_i\varphi_i, \quad (1)$$

where

$$F = h + \sum_{i=1}^N (2J_i - K_i). \quad (2)$$

h is the nuclear field plus kinetic energy operator for each electron, and J_i and K_i are the Coulomb and exchange operators associated with the doubly occupied orbital φ_i . For open-shell systems, the total wavefunction is, in general, a sum of Slater determinants. In these cases there are two complicating features which do not occur in the closed shell equations, Eqs. (1) and (2): (i) the off-diagonal Lagrange multipliers ϵ_{ij} cannot, in general, be eliminated by an appropriate unitary transformation and will therefore appear in Eq. (1), and (ii) it is not always possible to express the HF operator in terms of Coulomb and exchange operators only. For some types of open-shell

configurations the first difficulty can be handled by Roothaan's coupling operators¹ but the recently proposed Orthogonality Constrained Basis Set Expansion (OCBSE) method is much more convenient and general.² The second difficulty arises in systems with two or more open shells in which, in addition to the usual terms in the expression for the total energy, we have a term representing the interaction between two open shells. In the notation of Ref. 1, this is the term

$$I = 2ff' \sum_{mm'} I_{mm'}, \quad (3)$$

where m and m' refer to orbitals in the first and second open shells, respectively, and f and f' are the usual fractional occupations of the open shells. For example, in the $B^3\Sigma_u^-$ state of oxygen with the configuration $\pi_u^3\pi_g^2$, I would be

$$I(^3\Sigma_u^-) = 9J(\pi_u^+, \pi_g^+) - 3K(\pi_u^+, \pi_g^-) - K(\pi_u^+, \pi_g^+) - \langle \pi_u^-(1)\pi_g^+(2) | \pi_u^+(1)\pi_g^-(2) \rangle, \quad (4a)$$

where

$$\begin{aligned} & \langle \pi_u^-(1)\pi_g^+(2) | \pi_u^+(1)\pi_g^-(2) \rangle \\ & = \int \pi_u^{-*}(1)\pi_g^{+*}(2)(1/r_{12})\pi_u^+(1)\pi_g^-(2)d\tau. \end{aligned} \quad (4b)$$

Upon variation of the total energy, an integral such

as (4b) leads to an operator which cannot be expressed as a sum of Coulomb and exchange operators. All eight Σ states arising from the configurations $\pi_u^2\pi_g$ and $\pi_u^3\pi_g^3$ contain such integrals. The presence of such terms in the HF Hamiltonian matrix is a complicating factor in trying to set up a general computer program to treat open-shell states.

In this paper we show that by working with the real functions π_x and π_y instead of π^+ and π^- , we can write the energy expressions for Σ states of the configurations $(\pi_u)^3(\pi_g)$, $(\pi_u)^3(\pi_g)^3$ and $(1\pi)^3(2\pi)$ for diatomic molecules in terms of Coulomb and exchange integrals only. This means that the HF operator now contains only the Coulomb and exchange operators J_i and K_i . This is an immediately useful result for it allows us to solve correctly for the SCF solutions of the ${}^1\Sigma_u^+$, ${}^3\Sigma_u^+$, ${}^1\Sigma_u^-$, and ${}^3\Sigma_u^-$ states of N_2 and O_2 and the analogous states in CO. Many of these states are of spectroscopic interest, e.g., the $B^3\Sigma_u^-$ state of O_2 and the $b'{}^1\Sigma_u^+$ of N_2 . These calculations can be done using existing open-shell SCF programs. In the next section we discuss the algebraic identities which are used to express the interaction terms $I_{mm'}$ in terms of the J and K integrals. We also list the coefficients needed to set up the new HF matrices.

In Secs. III and IV we give the SCF results for most of the low-lying excited states of N_2 , O_2 , and CO. For N_2 and CO, these calculations are all done at the ground state geometry, but for O_2 we give results at a few internuclear distances for the $B^3\Sigma_u^-$ and $A^3\Sigma_u^+$ states. The SCF results for the ${}^1\Sigma_u^+$ states of N_2 and ${}^3\Sigma_u^-$ states of O_2 answer some important questions concerning the relative locations of valence and Rydberg states of the same symmetry in the HF approximation compared to the positions of the corresponding states in the observed spectrum. For example, we show that in a basis with only valence atomic orbitals there is no bound ${}^1\Sigma_u^+$ state arising from a $\pi_u \rightarrow \pi_g$ transition in N_2 in the HF approximation. Expansion of the basis to include Rydberg orbital character gives well defined Rydberg states but still no bound valence states. This is contrary to experiment where the π_g orbital of the $b'{}^1\Sigma_u^+$ state is known to be strongly antibonding. We show that there is a simple explanation for this behavior, namely, that changes in correlation energy are important in establishing the ordering of these excited states. A very similar case arises in comparing the valence $B^3\Sigma_u^-$ state of O_2 with configuration $(\pi_u)^3(\pi_g)^3$ and a Rydberg state of the same symmetry with the configuration $(\pi_u)^3(1\pi_g)^2(2\pi_g)$.

II. THE SCF HAMILTONIANS

For open-shell systems the SCF wavefunction is, in general, a sum of Slater determinants. For many open-shell states it is possible to write the expression for the total energy in terms of the familiar one-

electron, Coulomb, and exchange integrals of closed shell SCF theory. In such cases, if one partitions the occupied spatial orbitals into Q shells each containing the set of orbitals $\{\phi_q\}$, the energy is given by

$$E = 2 \sum_{q=1}^Q f_q \sum_{\phi_i \in \{\phi_q\}} h_i + \sum_{q=1}^Q \sum_{p=1}^Q f_q f_p \sum_{\phi_i \in \{\phi_q\}} \sum_{\phi_j \in \{\phi_p\}} \times (2a_{qp}J_{ij} - b_{qp}K_{ij}). \quad (5)$$

Here f_q is the fractional occupation of shell q , a_{qp} and b_{qp} are elements of a symmetric matrix specifying the interactions between shells q and p , and h_i , J_{ij} , and K_{ij} are defined as follows:

$$h_i = \langle \phi_i | h | \phi_i \rangle, \quad (6a)$$

$$J_{ij} = \langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_i(1)\phi_j(2) \rangle, \quad (6b)$$

$$K_{ij} = \langle \phi_i(1)\phi_j(2) | 1/r_{12} | \phi_j(1)\phi_i(2) \rangle. \quad (6c)$$

The numbers a_{qp} and b_{qp} must be determined for each specific state. Requiring that the energy be stationary with respect to variations of the orbitals, we obtain the HF equation for each shell,

$$F_q \phi_i = \epsilon_i \phi_i, \quad (7a)$$

$$F_q = h + \sum_{p=1}^Q f_p \sum_{\phi_j \in \{\phi_p\}} (2a_{qp}J_{ij} - b_{qp}K_{ij}). \quad (7b)$$

The off-diagonal Lagrange multipliers, ϵ_{ij} , needed to preserve orthogonality between orbitals ϕ_i and ϕ_j are not explicitly shown in Eq. (7a) since we assume that these equations are to be solved by the OCBSE method.² In this method the orthogonality of a given orbital to all others is achieved by requiring the variations to be orthogonal to the other orbitals.

Clearly, if the energy, Eq. (5), cannot be written only in terms of the integrals h_i , J_{ij} , and K_{ij} , then the resulting SCF equations, Eqs. (7), will contain operators which cannot be expressed in terms of the Coulomb and exchange operators. The resulting equations would be more complicated to solve numerically, requiring an SCF program which would have to manipulate the additional integrals necessary for the calculation. Huzinaga has stated that the energy expressions for some important excited Σ states of diatomic molecules cannot be written in terms of J and K integrals alone.¹ These would include the $b'{}^1\Sigma_u^+$ state of N_2 and the $B^3\Sigma_u^-$ of O_2 . However, if the wavefunctions of the configuration $(1\pi)^n(2\pi)^m$ are expressed in terms of the real functions π_x and π_y instead of the complex functions π^+ and π^- , the terms in the energy expression which are not obviously J and K integrals are of only three types:

$$I_1 = \langle 1\pi_x(1)2\pi_x(2) | 1/r_{12} | 1\pi_y(1)2\pi_y(2) \rangle, \quad (8a)$$

$$I_2 = \langle 1\pi_x(1)1\pi_y(2) | 1/r_{12} | 2\pi_x(1)2\pi_y(2) \rangle, \quad (8b)$$

$$I_3 = \langle 1\pi_x(1)1\pi_y(2) | 1/r_{12} | 2\pi_y(1)2\pi_x(2) \rangle. \quad (8c)$$

TABLE I. Coefficients for the configuration $\pi_u^3\pi_g^3$.^a

State	$q=$	σ	π_{uz}	π_{uy}	π_{gz}	π_{gy}
All states	f_q	1	3/4	3/4	1/4	1/4
	$(a_{\sigma q}, b_{\sigma q})$	(1, 1)	(1, 1)	(1, 1)	(1, 1)	(1, 1)
	$(a_{\pi_{uz}q}, b_{\pi_{uz}q})$	(1, 1)	(8/9, 8/9)	(8/9, 8/9)	b	b
$^3\Sigma_u^+$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(1/3, 4/3)	(5/3, 4/3)		
$^1\Sigma_u^+$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(1/3, -4)	(5/3, 20/3)		
$^3\Sigma_u^-, ^1\Sigma_u^-$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(5/3, 4/3)	(1/3, 4/3)		
$^3\Delta_u$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(1, 4/3)	(1, 4/3)		
$^1\Delta_u$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(1, 4/3)	(1, -4)		

^a The coefficients not explicitly listed can be found by a transformation $x \rightarrow y$ in the row and column labels. A blank space indicates no interaction.

^b These coefficients vary from state to state and can be found lower in the table by utilizing the symmetry of a_{pq} and b_{pq} .

TABLE II. Coefficients for the configuration $\pi_u^3\pi_g^3$.^a

State	$q=$	σ	π_{uz}	π_{uy}	π_{gz}	π_{gy}
All states	f_q	1	3/4	3/4	3/4	3/4
	$(a_{\sigma q}, b_{\sigma q})$	(1, 1)	(1, 1)	(1, 1)	(1, 1)	(1, 1)
	$(a_{\pi_{uz}q}, b_{\pi_{uz}q})$	(1, 1)	(8/9, 8/9)	(8/9, 8/9)	b	b
$^3\Sigma_u^+$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(11/9, 4/3)	(7/9, 4/3)	(8/9, 8/9)	(8/9, 8/9)
$^1\Sigma_u^+$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(11/9, 4/9)	(7/9, 4/9)	(8/9, 8/9)	(8/9, 8/9)
$^3\Sigma_u^-$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(7/9, 4/9)	(11/9, 20/9)	(8/9, 8/9)	(8/9, 8/9)
$^1\Sigma_u^-$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(7/9, 4/3)	(11/9, -4/9)	(8/9, 8/9)	(8/9, 8/9)
$^3\Delta_u$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(1, 4/3)	(1, 4/9)	(8/9, 8/9)	(8/9, 8/9)
$^1\Delta_u$	$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(1, 4/9)	(1, 4/3)	(8/9, 8/9)	(8/9, 8/9)

^a The coefficients not explicitly listed can be found by the transformation $x \rightarrow y$ in the row and column labels.

^b These coefficients vary from state to state and can be found lower in the table by utilizing the symmetry of a_{pq} and b_{pq} .

TABLE III. SCF results for the excited states of N₂.^a

State	Description ^b	E_{SCF} (a.u.)	ΔE_{exp} ^c (eV)	ΔE_{SCF} (eV)	ΔE_{fc} (eV)
$X\ ^1\Sigma_g^+$		-108.8877	0.0	0.0	0.0
$B\ ^3\Pi_g$	$\sigma_g \rightarrow \pi_g$	-108.6064	8.1	7.66	7.78
$a\ ^1\Pi_g$	$\sigma_g \rightarrow \pi_g$	-108.5408	9.3	9.44	9.72
$A\ ^3\Sigma_u^+$	$\pi_u \rightarrow \pi_g$	-108.6613	7.8	6.16	6.22
$^1\Sigma_u^+$	Rydberg ^d	-108.3633		14.27 ^d	...
$a'\ ^1\Sigma_u^-$	$\pi_u \rightarrow \pi_g$	-108.5813 ^e	9.9	8.34	8.38
$^3\Delta_u$	$\pi_u \rightarrow \pi_g$	-108.6211	8.5	7.26	7.31
$^1\Delta_u$	$\pi_u \rightarrow \pi_g$	-108.5565	10.3	9.01	9.05
$X\ ^2\Sigma_g^+$	N ₂ ⁺	-108.3059	15.6	15.83	17.05
$A\ ^2\Pi_u$	N ₂ ⁺	-108.3063	17.1	15.82	16.97

^a At an internuclear distance of 1.094 Å.

^b This describes the excitation relative to the ground state configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$.

^c These values taken from R. S. Mulliken, in *Threshold of Space*, edited by B. Armstrong and A. Dalgarno (Pergamon, New York, 1957) and F. R. Gilmore, *J. Quant. Spectry. Radiation Transfer* **5**, 369 (1965).

^d This is not the $b'\ ^1\Sigma_u^+$ state which is known to have a strongly antibonding π_g orbital but is a Rydberg state with the configuration (core) $(\pi_u)^3(\sigma_g)^2n\pi_g$. No bound state of this symmetry is obtained with a purely valence basis. See text for discussion.

^e In the HF approximation the $B'\ ^3\Sigma_u^-$ and $a'\ ^1\Sigma_u^-$ states have the same energy. Experimentally, the $B'\ ^3\Sigma_u^-$ state lies at about 9.0 eV.

TABLE IV. SCF results for the excited states of CO.^a

State	Description ^b	E_{SCF} (a.u.)	ΔE_{exp}^c (eV)	ΔE_{SCF} (eV)	ΔE_{fc} (eV)	D_{exp}^d	D_{SCF}^d
$X^1\Sigma^+$		-112.6969	0.0	0.0	0.0	-0.114±0.005	0.528
$a^3\Pi$	$\sigma \rightarrow \pi^*$	-112.4977	6.3	5.42	5.80	±1.38	2.33
$A^1\Pi^e$	$\sigma \rightarrow \pi^*$	-112.3837	8.35	8.52	9.10	±0.03±0.08	1.29
$a^3\Sigma^+$	$\pi \rightarrow \pi^*$	-112.4492	8.2	6.74	7.65		-1.45
$I^1\Sigma^-$	$\pi \rightarrow \pi^*$	-112.3981 ^f	9.1	8.13	9.44		-1.11
$d^3\Delta$	$\pi \rightarrow \pi^*$	-112.4225	9.1	7.46	8.55		-1.28
$D^1\Delta$	$\pi \rightarrow \pi^*$	-112.3890	10.4	8.38	9.95		-0.95
$X^2\Sigma^+$	CO^+	-112.1990	14.1	13.55	15.18		

^a At an internuclear distance of 1.128 Å.

^b This describes the excitation relative to the ground state configuration $(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$.

^c See P. H. Krupenie, "The Band Spectrum of CO," Natl. Std. Ref. Data Ser., Natl. Bur. Std. (U.S.) 5, (1966).

^d In debyes. The dipole moment is positive if charge is transferred from carbon to oxygen, i.e., carbon is positive. The experimental values for the

$a^3\Pi$ and $A^1\Pi$ states are for the equilibrium distances on these states, i.e., 1.21 and 1.235 Å, respectively.

^e The total HF oscillator strength for this transition is 0.185 which is very close to experiment. See Ref. 11.

^f In the HF approximation the $e^3\Sigma^-$ and $I^1\Sigma^-$ states have the same energy. Experimentally the $e^3\Sigma^-$ state lies at about 8.9 eV.

Through various algebraic identities, I_1 , I_2 , and I_3 can all be expressed in terms of Coulomb and exchange integrals. The expression for I_1 can be obtained from the relationship

$$\langle 1\pi^-(1)2\pi^-(2) | 1/r_{12} | 1\pi^+(1)2\pi^+(2) \rangle = 0 = 2J(1\pi_x, 2\pi_x) - 2J(1\pi_x, 2\pi_y) - 4I_1. \quad (9)$$

Hence,

$$I_1 = \frac{1}{2} [J(1\pi_x, 2\pi_x) - J(1\pi_x, 2\pi_y)]. \quad (10)$$

Here π^+ and π^- are $(\pi_x + i\pi_y)/\sqrt{2}$ and $(\pi_x - i\pi_y)/\sqrt{2}$, respectively. Similarly I_2 can be found from

$$\langle 1\pi^-(1)1\pi^-(2) | 1/r_{12} | 2\pi^+(1)2\pi^+(2) \rangle = 0 = 2K(1\pi_x, 2\pi_x) - 4K(1\pi_x, 2\pi_y) - 2I_2. \quad (11)$$

Hence,

$$I_2 = K(1\pi_x, 2\pi_x) - 2K(1\pi_x, 2\pi_y). \quad (12)$$

Finally, I_3 is just an exchange integral

$$I_3 = K(1\pi_x, 2\pi_y). \quad (13)$$

These results for I_1 , I_2 , and I_3 can now be used to write the energy expressions for the open-shell Σ states of the configuration $(1\pi)^n(2\pi)^m$ in terms of J and K integrals only. With the resulting coefficients a_{qp} and b_{qp} , calculations can be done for these states using existing open-shell SCF programs. Tables I and II give these coefficients for the various states of the configuration $\pi_u^3\pi_g$ and $\pi_u^2\pi_g^3$, respectively. These states include many of the valence excited states of N_2 and O_2 . All the results for the $\pi_u^3\pi_g$ configuration are applicable to CO also, although the π orbitals no longer have g or u symmetry. The results for the Δ states are not new but are included for completeness.

III. EXCITED STATES OF N_2 AND CO

Tables III and IV give the results of SCF calculations on many of the interesting excited states of N_2 and CO. In addition to the states arising from the

$\pi \rightarrow \pi^*$ excitation, we also give results for the $\sigma \rightarrow \pi^*$ valence states and some ions. SCF results have already been reported for the $a^3\Pi$ state of CO^3 and the $X^2\Sigma_g^+$ and $A^2\Pi_u^4$ ions of N_2 , but the results for the other excited states are presented for the first time mainly due to the historical difficulties of expressing the open-shell SCF Hamiltonians of the $1^3\Sigma^+$ and $1^3\Sigma^-$ states in terms of Coulomb and exchange operators only.¹ The results of the previous section now allow us to carry out SCF calculations on these states in a simple and direct way. All the calculations except those for the $1^3\Sigma_u^+$ state of N_2 were done in a valence $[4s3p]$ contracted Gaussian basis derived from a $(9s5p)$ primitive basis on each atom.⁵ This basis gives an SCF energy close to the HF limit for the ground states, i.e., -108.9928 a.u. for N_2^4 and -112.7860 a.u. for CO.⁶ The effect of adding Rydberg-like $p\pi$ orbitals to the basis is estimated to be less than 0.001 a.u. on the total energy of the valence states listed. Although addition of a single $d\pi$ function to the basis in N_2 lowers the ground state energy by 0.071 a.u., the changes in excitation energies are much smaller, e. g., an increase of 0.27 eV for the $X^1\Sigma_g^+ \rightarrow A^3\Sigma_u^+$ transition.

The results are in good agreement with experiment except for the $b^1\Sigma_u^+$ state of N_2 and the $1^3\Sigma^+(1\pi \rightarrow 2\pi)$ of CO where there are some serious problems in attempting SCF calculations. We discuss these below. In most cases the SCF scheme underestimates the excitation energies since the excited states would usually have less correlation energy than the ground state. This is not so for some cases, for example, the $b^1\Sigma_u^+$ state of N_2 and the $B^3\Sigma_u^-$ of O_2 . The results in Column six of Tables III and IV are those in which only the excited orbital, e.g., π_g , is variationally determined and the core orbitals are taken from the ground state calculation. This approximation is quite good for N_2 but insufficient for CO, e.g., in the $1^1\Delta$ state of CO core contraction lowers the energy by

1.6 eV. Nesbet⁷ has computed the energy levels of all these states in the simple virtual orbital approximation. They are, in general, about 1 eV higher than our frozen-core results for N₂ but the discrepancy is less for CO.

The ${}^1\Sigma^+$ states of N₂ and CO are of special interest since they illustrate a serious problem with the SCF approach to some excited states. In N₂ the $b' {}^1\Sigma_u^+$ state is primarily a $\pi_u \rightarrow \pi_g$ transition with a vertical excitation energy of about 14.4 eV. Experimentally there is a strong perturbation of the $b' {}^1\Sigma_u^+$ state by the $c' {}^1\Sigma_u^+$ state, but this estimate of 14.4 eV for excitation to the $b' {}^1\Sigma_u^+$ is the deperturbed value of Geiger and Schroeder.⁸ A vibrational analysis shows the $b' {}^1\Sigma_u^+$ state to have a strongly antibonding π_g orbital and an equilibrium internuclear distance of 1.44 Å. In the SCF scheme no bound valence state exists which has such characteristics. In a [4s3p] Gaussian basis with only valence atomic orbitals,⁵ only π_g orbitals with positive eigenvalues result from the SCF iterative scheme. When very diffuse Rydberg-like atomic orbitals are added to the basis, i.e., p_x and p_z orbitals with exponents of 0.05, 0.015, 0.004, and 0.001, rapid convergence to a ${}^1\Sigma_u^+$ with a Rydberg-like π_g orbital results. This is a Rydberg state with an oscillator strength⁹ of 0.033 and a mean-squared displacement for the π_g orbital of $\langle \pi_g | x^2 | \pi_g \rangle = 50.2$ a.u.² (this is a $nd\pi$ orbital lying in the x - z plane where z is the molecular axis). The state is well described in the frozen core approximation using an ionic $A {}^2\Pi_u$ core, e.g., the energy lowering due to self-consistency is less than 0.01 eV. This state is then the first in a ${}^1\Sigma_u^+$ Rydberg series with the configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(\pi_u)^3(3\sigma_g)^2nd\pi_g$ and a HF excitation energy of 14.27 eV or 1.55 eV below the $A {}^2\Pi_u$ ion in the HF scheme. With this term value this state should be experimentally at about 15.6 eV, i.e., 1.55 eV below the true ionization potential. There

are many Rydberg transitions appearing in this region in the energy-loss spectrum of Geiger and Stickel.¹⁰

The question now arises as to where the valencelike $b' {}^1\Sigma_u^+$ state of N₂ is. The explanation is that in HF theory this valence state is calculated to be above the HF ionization potential and therefore in the continuum of the $A {}^2\Pi_u$ ion. Because of orthogonality requirements the state is also contaminated with lower-energy Rydberg components. This argument suggests a HF excitation energy of at least 15.8 eV and implies that the valence excited $b' {}^1\Sigma_u^+$ state has about 1.5 eV more correlation energy than the ground state. This is not unique as we will show that the $B {}^2\Sigma_u^-$ state of O₂ has 2.5–3 eV more correlation energy than the ground $X {}^3\Sigma_g^-$ state.

We also find no bound valencelike $\pi \rightarrow \pi^*$ state of ${}^1\Sigma^+$ symmetry for CO in the HF approximation and in fact such a state has not been observed. Lefebvre-Brion *et al.*¹¹ have shown that the $B {}^1\Sigma^+$ and $C {}^1\Sigma^+$ states (at 10.78 eV and 11.40 eV experimentally)¹² must be $\sigma \rightarrow \sigma^*$ excitation in which the σ^* orbital contains primarily M shell atomic functions. Calculations using the $X {}^2\Sigma^+$ ion core of CO and including Rydberg basis functions give ${}^1\Sigma^+$ states at 3.3 eV and 2.5 eV below the $X {}^2\Sigma^+$ ion. Using an ionization potential of 14.1 eV for this ion these states come out at 10.8 and 11.6 eV, respectively, in good agreement with experiment.¹² The calculated oscillator strengths of 0.031 and 0.082 for the transitions to the B and C states are in good qualitative agreement with the experimental values of 0.017 and 0.170.¹²

Dipole moments are also shown for CO in Table IV. The ground state dipole moment is opposite to the observed value and quite far from the HF limit of about 0.274 D.⁶ Hence, the calculated values should probably be viewed as representing only differences in dipole moments reliably. The Σ and Δ states are predicted to have large dipole moments in the same direction as the ground state (C^-O^+), which may be verified experimentally, while the Π states have large positive moments (C^+O^-). The dipole moment of the $a {}^3\Pi$ state (essentially the same value, 2.46 D, was obtained by Huo¹²) is very large and in qualitative agreement with experiment (1.38 D).

IV. EXCITED STATES OF O₂

Two important excited states of O₂ are the $A {}^3\Sigma_u^+$ and $B {}^3\Sigma_u^-$ states which are the upper states in the Herzberg bands ($A \rightleftharpoons X$) and Schumann–Runge bands ($B \rightleftharpoons X$), respectively. The transition $X \rightarrow B$ is dipole allowed with an oscillator strength of 0.193. These states arise from a $\pi_u \rightarrow \pi_g$ transition which leads to the relatively large increase of about 0.3 to 0.4 Å in equilibrium internuclear separation relative to the ground state. Robin and Kuebler¹³ have shown that the Schumann–Runge bands are unaffected by high

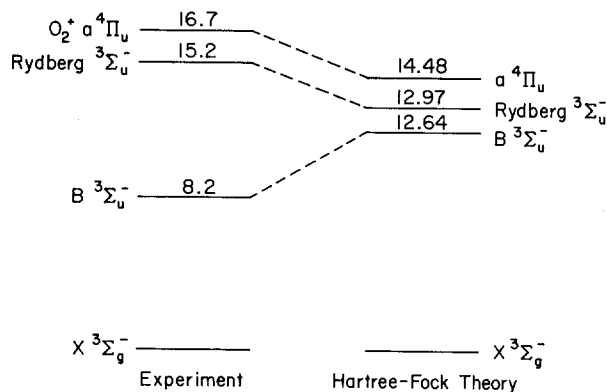


FIG. 1. Correlation between Hartree-Fock theory and experiment for the valence $B {}^3\Sigma_u^-[(\pi_u)^3(\pi_g)^3]$ and the Rydberg ${}^3\Sigma_u^-[(\pi_u)^3(\pi_g)^22\pi_g]$ states. See text for discussion.

TABLE V. Some valence states of O₂.^a

State	Description	$E_{\text{SCF}}(R)$					Vertical excitation energy		R_e	
		1.0	1.207	1.42	1.60	1.80	Exp	SCF	Exp	SCF
$X^3\Sigma_g^-$	ground	-149.4670	-149.5758	-149.5211	-149.4411				1.21	1.21 \pm 0.02
$A^3\Sigma_u^+$	$\pi_u \rightarrow \pi_g$		-149.4276	-149.5057	-149.5027	-149.4745	6.2	4.03	1.52	1.49 \pm 0.04
$B^3\Sigma_u^-$ ^b	$\pi_u \rightarrow \pi_g$		-149.1110	-149.1558	-149.1254	-149.0701	8.3	12.64	1.60	1.4-1.5 ^c
$a^4\Pi_u$	O ₂ ⁺	-148.8244	-149.0437	-149.0617	-149.0246		16.7	14.48	1.38	1.34 \pm 0.02

^a In a [4s3p] Gaussian basis. See Ref. 5.^b The SCF value of the oscillator strength for the $X \rightarrow B$ transition is 0.87.^c Due to incorrect dissociation the potential energy curve begins rising steeply near equilibrium causing R_e to be underestimated.

pressures of inert perturbing gases indicating that the B state is a valence state. However, Taketa *et al.*¹⁴ have carried out π -electron calculations which show that the A state is adequately described in a minimum basis of valence atomic orbitals but that the B state comes out too high in energy. By allowing the orbital exponent of one π_g molecular orbital (MO) to take a different value from the other π_g MO's, variational calculations showed that the resulting outermost π_g orbital is much more diffuse than the other. We will show below that these calculations did not converge to the spectroscopic $B^3\Sigma_u^-$ state but to a Rydberg $^3\Sigma_u^-$ state with an electron configuration $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(\pi_u)^3(\pi_g)^2nd\pi_g$. In the π -electron approximation without exchange with the core, this Rydberg $^3\Sigma_u^-$ state has a lower energy than the valence state $[(\text{core})(\pi_u)^3(\pi_g)^3]$ in the SCF approximation. In fact, Fig. 1 shows that with reasonably accurate SCF results the $(\pi_u)^3(\pi_g)^3$ state is only 0.33 eV below the $(\pi_u)^3(\pi_g)^2nd\pi_g$ state. It is the inclusion of electron correlation which puts the valence state 6-7 eV below the Rydberg state. Recent extensive configuration interaction calculations^{15,16} confirm these conclusions.

Table V shows the results of SCF calculations on the $X^3\Sigma_g^-$, $A^3\Sigma_u^+$, and $B^3\Sigma_u^-$ states of O₂ and the $a^4\Pi_u$ state of O₂⁺ at several internuclear distances.

These are done using the coefficients of Table II. The vertical excitation energy for the A state is reasonable but the $^3\Sigma_u^+ - ^3\Sigma_u^-$ separation is far too large, namely 8 eV instead of the observed 2 eV. Inclusion of a single d function on each atom only lowers the excitation energy of the B state by 0.2 eV. This separation of 8 eV would be reduced considerably by including electron correlation. Comparison of minimum basis set SCF calculations with the complete minimal basis configuration interaction results of Schaefer and Harris¹⁷ shows that the $B^3\Sigma_u^-$ state has about 3 eV more correlation energy than the $X^3\Sigma_g^-$ state. From Table V we see that on the other hand the $A^3\Sigma_u^+$ state has 2 eV less correlation energy than the ground state. These two effects then reduce the SCF $^3\Sigma_u^+ - ^3\Sigma_u^-$ separation of 8 eV to about 3 eV.

To clarify the question of the relative location of the valence $^3\Sigma_u^-$ state and a Rydberg state of the same symmetry in the SCF approximation as compared to experiment, we have solved directly for the $^3\Sigma_u^-$ state with the configuration $(\text{core})(\pi_u)^3(\pi_g)^22\pi_g$. This state then has a singly occupied diffuse $2\pi_g$ orbital and a doubly occupied valence π_g orbital. There are four possible spin couplings for such a state¹⁴ but since only Rydberg states are of interest we can choose a state such that the core corresponds to the lowest state of O₂⁺ with the configuration $(\text{core})-$

TABLE VI. Coefficients for the $[(\pi_u)^3(\pi_g)^22\pi_g]^3\Sigma_u^-$ Rydberg state.^a

$q =$	σ	π_{uz}	π_{uy}	π_{gz}	π_{gy}	$2\pi_{gz}$	$2\pi_{gy}$
f_q	1	3/4	3/4	1/2	1/2	1/4	1/4
$(a_{\pi_{uz}q}, b_{\pi_{uz}q})$	(1, 1)	(8/9, 8/9)	(8/9, 8/9)	(1, 4/3)	(1, 4/3)	(1/3, -20/9)	(5/3, 44/9)
$(a_{\pi_{gz}q}, b_{\pi_{gz}q})$	(1, 1)	(1, 4/3)	(1, 4/3)	(1, 2)	(1, 2)	(1, -2/3)	(1, -2/3)
$(a_{2\pi_{gz}q}, b_{2\pi_{gz}q})$	(1, 1)	(1/3, -20/9)	(5/3, 44/9)	(1, -2/3)	(1, -2/3)	(1, -2/3)	

^a The other coefficients for the π_{uy} , π_{gy} , and $2\pi_{gy}$ orbitals can be obtained from the transformation $x \rightarrow y$ in the row and column labels. σ refers to the

closed shell core.

$(\pi_u)^3(\pi_g)^2$. This is the $a^4\Pi_u$ state. The wavefunction for this Rydberg $^3\Sigma_u^-$ state is then

$$\begin{aligned} \Psi(^3\Sigma_u^-) &= \mathcal{A} \{ 3(\pi_{ux}\pi_{ux}\pi_{uy}2\pi_{gy} + \pi_{uy}\pi_{uy}\pi_{ux}2\pi_{gx})\alpha\beta\alpha\beta\pi_{gx}\pi_{gy}\alpha\alpha \\ &- (\pi_{ux}\pi_{ux}\pi_{uy}2\pi_{gy} + \pi_{uy}\pi_{uy}\pi_{ux}2\pi_{gx})\alpha\beta\beta\alpha\pi_{gx}\pi_{gy}\alpha\alpha \\ &- (\pi_{ux}\pi_{ux}\pi_{uy}2\pi_{gy} + \pi_{uy}\pi_{uy}\pi_{ux}2\pi_{gx})\alpha\beta\alpha\alpha\pi_{gx}\pi_{gy}(\alpha\beta + \beta\alpha) \}. \end{aligned} \quad (14)$$

In Eq. (14) \mathcal{A} is the antisymmetrizer and we do not show the sigma orbitals for convenience. The function, Eq. (14), reduces to that for the $(\pi_u)^3(\pi_g)^3$ configuration if the Rydberg orbital $2\pi_g$ is set equal to π_g . Table VI shows the a_{pq} and b_{pq} coefficients needed in the SCF calculations. The valence electron interactions are identical to those of the $a^4\Pi_u$ ion. The SCF energy for this Rydberg state is -149.0990 a.u. Its Rydberg character is reflected by its low oscillator strength of 0.001 and a very diffuse $2\pi_g$ orbital, e.g., with a matrix element $\langle 2\pi_g | x^2 | 2\pi_g \rangle = 60.1$ a.u.² compared to $\langle 1\pi_g | x^2 | 1\pi_g \rangle = 1.11$ a.u.² The Rydberg $^3\Sigma_u^-$ state is only 0.33 eV above the valence $B^3\Sigma_u^-$ state in the SCF approximation, whereas experimentally this $^3\Sigma_u^-$ state is about 7 eV above the $B^3\Sigma_u^-$. Electron correlation is responsible for a large part of this difference. Figure 1 illustrates these differences clearly.¹⁸ It is clear that in the π -electron approximation, without exchange, the Rydberg $^3\Sigma_u^-$ state lies below the $B^3\Sigma_u^-$ state, explaining why the calculation of Taketa *et al.*¹⁴ converged to the Rydberg state. The valence $(\pi_u)^3(\pi_g)^3$ state, which is constrained to have equivalent π_g orbitals certainly represents the major configuration of the Schumann-Runge state. For example, it indicates an equilibrium internuclear separation of about 1.4–1.5 Å¹⁹ compared to the experimental value of 1.6 Å. On the other hand the Rydberg $^3\Sigma_u^-$ state²⁰ has an SCF equilibrium separation of 1.34 Å, in good agreement with the experimental value which should be close to 1.38 Å of the $a^4\Pi_u$ state of O₂⁺.²¹ Other molecular properties which are sensitive to correlation, e.g., the oscillator strength can be expected to be in error since the $\pi_u \rightarrow \pi_g$ transition represents only about 80% of the Schumann-Runge band,^{15,16} most of the remainder being a $3\sigma_g \rightarrow 3\sigma_u$ contribution.²²

V. CONCLUSIONS

We have shown how to express the SCF Hamiltonians for many Σ states of diatomic molecules only in terms of the Coulomb and exchange operators of closed shell SCF theory. With these results we have been using conventional SCF programs to solve for the SCF wavefunctions for many interesting states of N₂, O₂, and CO, e.g., the $^3\Sigma_u^+$ states of N₂ and CO and the $A^3\Sigma_u^+$ and $B^3\Sigma_u^-$ state of O₂. On the whole the SCF results are in good agreement with experiment. However, we have shown that SCF theory runs into serious trouble if electron correlation is important in determining the relative locations of two excited states.

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