there is a limit to the accuracy. However, use of spectroscopic data for evaluating atomic energies will help, but is not at all essential from a theoretical point of view.

In a forthcoming paper, we shall discuss how our approach can be simplified for application to more complicated systems. We shall consider the accuracy of further approximation by comparing with the corresponding simplification in the orbital approach.

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Electronic Structure and Binding Energy of Carbon Monoxide

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1. INTRODUCTION

THE most accurate method of determining dissociation energies of diatomic molecules is from the analysis of their band spectra. In favorable cases, when this analysis is unambiguous, values accurate to within 0.001 ev may be obtained [e.g., O_2 Herzberg (1950)[1]]. However, for many molecules of thermochemical interest the analysis of the spectra is ambiguous and leads to several possible values for the dissociation energy. One of the most important examples of this is provided by the carbon monoxide molecule. Here the spectroscopic data are consistent with just three values for $D_e(\mathrm{CO})$, namely, 9.28 ev [Herzberg (1950)], 9.74 ev [Hagstrum (1947)], and 11.24 ev [Gaydon (1947)].

In this situation, relatively crude estimates of the dissociation energy may be of value in distinguishing between the possible spectroscopic values. Various experimental techniques have been employed for this purpose; for example, mass-spectrometric analysis of the ions resulting from the electron bombardment of carbon monoxide [Hagstrum (1951, 1955)] and the direct thermochemical measurement of the latent heat of sublimation of graphite [Chupka and Inghram (1953, 1955)], this quantity being related to $D_0(\mathrm{CO})$ by well-established thermochemical quantities.

In this paper two theoretical calculations of the binding energy and ground state wave function of carbon monoxide are described. The first is an *ab initio* orbital calculation and the second employs the intra-atomic correlation correction (ICC), introduced by the author [Hurley (1956a, 1958a)], as a necessary modification of the method of atoms in molecules [Moffitt (1951)], The orbital calculation (Sec. 2) is carried out in such a way as to facilitate the transition to the ICC theory in later sections. The key quantity in this transition is the transformation matrix T [Eq. (2.21)].

2. ORBITAL CALCULATION

(a) Atomic Orbitals

The basic atomic orbitals are taken as orthogonalized Slater-type functions centered on the carbon and oxygen nuclei.

$$\begin{aligned}
\sigma\text{-type}\quad & \phi_1 = k_O = (\zeta_1^3/\pi)^{\frac{1}{2}} \exp(-\zeta_1 r_O),\\
& \phi_2 = k_C = (\zeta_2^3/\pi)^{\frac{1}{2}} \exp(-\zeta_2 r_C),\\
& \phi_3 = s_O = N_1\{(\zeta_3^5/3\pi)^{\frac{1}{2}} r_O \exp(-\zeta_3 r_O) - \alpha_1 k_O\},\\
& \phi_4 = s_C = N_2\{((\zeta_4^5/3\pi)^{\frac{1}{2}} r_C \exp(-\zeta_4 r_C) - \alpha_2 k_C\},\\
& \phi_5 = \sigma_O = (\zeta_5^5/\pi)^{\frac{1}{2}} z_O \exp(-\zeta_5 r_O), \qquad (2.1)\\
& \phi_6 = \sigma_C = (\zeta_6^5/\pi)^{\frac{1}{2}} z_C \exp(-\zeta_6 r_C),\\
x\text{-type}\quad & \phi_7 = x_O = (\zeta_5^5/\pi)^{\frac{1}{2}} x_O \exp(-\zeta_5 r_O),\\
& \phi_8 = x_C = (\zeta_6^5/\pi)^{\frac{1}{2}} x_C \exp(-\zeta_6 r_C),\\
y\text{-type}\quad & \phi_9 = y_O = (\zeta_5^5/\pi)^{\frac{1}{2}} y_O \exp(-\zeta_5 r_O),\\
& \phi_{10} = y_C = (\zeta_6^5/\pi)^{\frac{1}{2}} y_C \exp(-\zeta_6 r_C).
\end{aligned}$$

Here (x_O, y_O, z_O), (x_C, y_C, z_C) are Cartesian coordinates centered on the oxygen and carbon nuclei; the z axes are directed inwards along the internuclear axis and the $x, (y)$ axes on the two centers are parallel:

$$r_O = (x_O^2 + y_O^2 + z_O^2)^{\frac{1}{2}}, \quad r_C = (x_C^2 + y_C^2 + z_C^2)^{\frac{1}{2}}.$$

The orbital exponents ζ have values which minimize the energy of the ground state dissociation products $\mathrm{O}(s^2p^4, {}^3P)$, $\mathrm{C}(s^2p^2, {}^3P)$ [Roothaan (1955)].

$$\begin{aligned}
&\mathrm{O}: \quad \zeta_1 = 7.66, \quad \zeta_3 = 2.25, \quad \zeta_5 = 2.23,\\
&\mathrm{C}: \quad \zeta_2 = 5.67, \quad \zeta_4 = 1.61, \quad \zeta_6 = 1.57. \qquad (2.2)
\end{aligned}$$

All the basic atomic integrals involving the orbitals (2.1) were evaluated for the equilibrium nuclear separation $R = 2.1319$ atomic units (a.u.) [Herzberg (1950)], and are listed in Appendix II.

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[1] References are given in alphabetical order in the Bibliography.

(b) Valence-Bond Basis

As in previous calculations on the ground states of the first-row hydrides [Hurley (1958b)], the valence-bond basis functions were chosen from an expansion of the self-consistent field molecular orbital function. This single determinant wave function Ω^t may be expressed as the antisymmetrized product of a wave function for the ten σ electrons and a wave function for the four π electrons,

$$\Omega^t = \mathcal{A}\Omega^\sigma\Omega^\pi, \tag{2.3}$$

where

$$\Omega^\sigma = |\sigma_1\bar{\sigma}_1\sigma_2\bar{\sigma}_2\sigma_3\bar{\sigma}_3\sigma_4\bar{\sigma}_4\sigma_5\bar{\sigma}_5| \tag{2.4}$$

and

$$\Omega^\pi = |\pi_x\bar{\pi}_x\pi_y\bar{\pi}_y|. \tag{2.5}$$

The form of Eq. (2.3) enables us to consider the expansions of Ω^σ and Ω^π separately.

Each of the molecular orbitals $\sigma_1\cdots\sigma_5$ appearing in Ω^σ is some linear combination of the σ-type atomic orbitals $\phi_1\cdots\phi_6$ [Eq. (2.1)]. If this single determinant is now expanded in terms of valence-bond functions, and if all functions not showing two electrons in each of the inner shell orbitals $\phi_1(=k_{\mathrm{O}})$ and $\phi_2(=k_{\mathrm{C}})$ are discarded, the following set of valence-bond wave functions is obtained:

$$\Psi_1{}^\sigma = \begin{bmatrix} s_{\mathrm{O}} & s_{\mathrm{C}} & \sigma_{\mathrm{O}} \\ |0 & |0 & |0 \\ s_{\mathrm{O}} & s_{\mathrm{C}} & \sigma_{\mathrm{O}} \end{bmatrix},$$

$$\Psi_2{}^\sigma = 2^{-\frac{1}{2}}\begin{bmatrix} s_{\mathrm{O}} & s_{\mathrm{C}} & \sigma_{\mathrm{O}} \\ |0 & |0 & | \\ s_{\mathrm{O}} & s_{\mathrm{C}} & \sigma_{\mathrm{C}} \end{bmatrix},$$

$$\Psi_3{}^\sigma = 2^{-\frac{1}{2}}\begin{bmatrix} s_{\mathrm{O}} & s_{\mathrm{C}} & \sigma_{\mathrm{O}} \\ |0 & | & |0 \\ s_{\mathrm{O}} & \sigma_{\mathrm{C}} & \sigma_{\mathrm{O}} \end{bmatrix},$$

$$\Psi_4{}^\sigma = \begin{bmatrix} s_{\mathrm{O}} & s_{\mathrm{C}} & \sigma_{\mathrm{C}} \\ |0 & |0 & |0 \\ s_{\mathrm{O}} & s_{\mathrm{C}} & \sigma_{\mathrm{C}} \end{bmatrix},$$

$$\Psi_5{}^\sigma = 2^{-\frac{1}{2}}\begin{bmatrix} s_{\mathrm{C}} & s_{\mathrm{O}} & \sigma_{\mathrm{O}} \\ |0 & | & |0 \\ s_{\mathrm{C}} & \sigma_{\mathrm{C}} & \sigma_{\mathrm{O}} \end{bmatrix}, \tag{2.6}$$

$$\Psi_6{}^\sigma = 2^{-\frac{1}{2}}\begin{bmatrix} s_{\mathrm{O}} & \sigma_{\mathrm{O}} & \sigma_{\mathrm{C}} \\ |0 & | & |0 \\ s_{\mathrm{O}} & s_{\mathrm{C}} & \sigma_{\mathrm{C}} \end{bmatrix},$$

$$\Psi_7{}^\sigma = 2^{-\frac{1}{2}}\begin{bmatrix} s_{\mathrm{C}} & s_{\mathrm{O}} & \sigma_{\mathrm{C}} \\ |0 & | & |0 \\ s_{\mathrm{C}} & \sigma_{\mathrm{O}} & \sigma_{\mathrm{C}} \end{bmatrix},$$

$$\Psi_8{}^\sigma = 2^{-\frac{1}{2}}\begin{bmatrix} s_{\mathrm{O}} & \sigma_{\mathrm{O}} & \sigma_{\mathrm{C}} \\ | & |0 & |0 \\ s_{\mathrm{C}} & \sigma_{\mathrm{O}} & \sigma_{\mathrm{C}} \end{bmatrix},$$

$$\left(\Psi_9{}^\sigma = \begin{bmatrix} s_{\mathrm{C}} & \sigma_{\mathrm{O}} & \sigma_{\mathrm{C}} \\ |0 & |0 & |0 \\ s_{\mathrm{C}} & \sigma_{\mathrm{O}} & \sigma_{\mathrm{C}} \end{bmatrix}\right),$$

$$\left(\Psi_{10}{}^\sigma = \begin{bmatrix} s_{\mathrm{O}} & \sigma_{\mathrm{O}} & \sigma_{\mathrm{C}} \\ |0 & |0 & |0 \\ s_{\mathrm{O}} & \sigma_{\mathrm{O}} & \sigma_{\mathrm{C}} \end{bmatrix}\right).$$

Here the generalized notation for valence-bond structures introduced by McWeeny (1954) has been used. The inner-shell orbitals k_{O}, k_{C}, which are doubly occupied in all the wave functions, have been omitted. In order to define the structures appearing in Eq. (2.6) uniquely, we must specify the ordering of the orbitals in the elementary determinants (McWeeney). In Eq. (2.6) and all subsequent equations, the natural ordering

$$\begin{bmatrix} 1 & 3 & \cdots \\ 2 & 4 & \cdots \end{bmatrix}$$

is employed.

The wave functions $\Psi_9{}^\sigma$ and $\Psi_{10}{}^\sigma$ will interact with the functions $\Psi_1{}^\sigma$ and $\Psi_4{}^\sigma$ even for infinite nuclear separation, and are therefore omitted from the basis. If included, these wave functions would have a small effect on the result of the orbital calculation, but almost no effect on the result of the ICC calculation [cf. Hurley, (1959) and Sec. 4(e)].

The remaining eight valence-bond functions (2.6) are represented as a row vector

$$\Psi^\sigma = [\Psi_1{}^\sigma\cdots\Psi_8{}^\sigma]. \tag{2.7}$$

We consider also a set of orthogonalized valence-bond functions

$$\Theta^\sigma = [\Theta_1{}^\sigma\cdots\Theta_8{}^\sigma], \tag{2.8}$$

which are obtained from (2.6) by replacing the basic atomic orbitals $k_{\mathrm{O}}(\phi_1)\cdots\sigma_{\mathrm{C}}(=\phi_6)$ by Schmidt orthogonalized atomic orbitals $\theta_1\cdots\theta_6$ defined by the equations

$$\theta_q = \sum_{p=1}^{6}\phi_p t_{pq}, \quad (q=1\cdots6), \tag{2.9}$$

where

$$\int\theta_p\theta_q dv = \delta_{pq}$$

and

$$t_{pq}=0 \quad (p>q).$$

The nonzero elements of the matrix t are given in Table I. The basic functions (2.7) and (2.8) are related by a matrix transformation

$$\Theta^\sigma = \Psi^\sigma T^\sigma, \quad \Psi^\sigma = \Theta^\sigma S^\sigma, \quad S^\sigma = (T^\sigma)^{-1}. \tag{2.10}$$

Table I. Schmidt orthogonalized atomic orbitals.

A. σ orbitals [Eq. (2.9)]					
t_{11}	1.00000	t_{23}	−0.05017	t_{36}	−0.99910
t_{12}	−0.00009	t_{24}	0.02401	t_{44}	1.10994
t_{13}	0.00000	t_{25}	−0.09942	t_{45}	−0.43873
t_{14}	−0.05605	t_{26}	0.10222	t_{46}	0.64369
t_{15}	0.02216	t_{33}	1.00126	t_{55}	1.07903
t_{16}	−0.15355	t_{34}	−0.47897	t_{56}	−0.62722
t_{22}	1.00000	t_{35}	0.19383	t_{66}	1.41082
B. π orbitals [Eq. (2.15)]					
$t_{77}=t_{99}$	1.00000				
$t_{78}=t_{9,10}$	−0.28099				
$t_{88}=t_{10,10}$	1.03873				

The elements of the matrix S^σ may be obtained from the equations [Hurley (1958a)]

$$S_{ij}^\sigma=\int \Theta_i^\sigma \Psi_j^\sigma dt.$$

Alternatively, the expansion formulas for valence-bond structures developed by McWeeny (1954) may be used. In the latter method, the matrices T^σ and S^σ are evaluated independently in terms of the matrices t [Eq. (2.9)] and $s(=t^{-1})$. The relation

$$S^\sigma T^\sigma=1$$

then provides a useful numerical check.

With the ordering of the functions Ψ^σ and Θ^σ defined by Eq. (2.6), the triangular form of the matrices t and s implies that the matrices T^σ and S^σ are also triangular:

$$T_{ij}^\sigma=S_{ij}^\sigma=0 \quad (i>j). \tag{2.11}$$

In the same way, the single determinant function Ω^π [Eq. (2.5)] is expanded in terms of the valence-bond basis

$$\Psi^\pi=[\Psi_1^\pi \cdots \Psi_6^\pi], \tag{2.12}$$

with

$$\Psi_1^\pi=\begin{bmatrix} x_\mathrm{O} & y_\mathrm{O} \\ |0 & |0 \\ x_\mathrm{O} & y_\mathrm{O} \end{bmatrix},$$

$$\Psi_2^\pi=\tfrac{1}{2}\left\{\begin{bmatrix} x_\mathrm{O} & y_\mathrm{O} \\ |0 & | \\ x_\mathrm{C} & y_\mathrm{C} \end{bmatrix}+\begin{bmatrix} x_\mathrm{O} & y_\mathrm{O} \\ | & |0 \\ x_\mathrm{C} & y_\mathrm{O} \end{bmatrix}\right\},$$

$$\Psi_3^\pi=2^{-\frac{1}{2}}\left\{\begin{bmatrix} x_\mathrm{O} & y_\mathrm{C} \\ |0 & |0 \\ x_\mathrm{O} & y_\mathrm{C} \end{bmatrix}+\begin{bmatrix} x_\mathrm{C} & y_\mathrm{O} \\ |0 & |0 \\ x_\mathrm{C} & y_\mathrm{O} \end{bmatrix}\right\}, \tag{2.13}$$

$$\Psi_4^\pi=\tfrac{1}{2}\begin{bmatrix} x_\mathrm{O} & y_\mathrm{O} \\ | & | \\ x_\mathrm{C} & y_\mathrm{C} \end{bmatrix},$$

$$\Psi_5^\pi=\tfrac{1}{2}\left\{\begin{bmatrix} x_\mathrm{C} & y_\mathrm{O} \\ |0 & | \\ x_\mathrm{C} & y_\mathrm{C} \end{bmatrix}+\begin{bmatrix} x_\mathrm{O} & y_\mathrm{C} \\ | & |0 \\ x_\mathrm{C} & y_\mathrm{C} \end{bmatrix}\right\},$$

$$\Psi_6^\pi=\begin{bmatrix} x_\mathrm{C} & y_\mathrm{C} \\ |0 & |0 \\ x_\mathrm{C} & y_\mathrm{C} \end{bmatrix}.$$

The orthogonal basis

$$\Theta^\pi=[\Theta_1^\pi \cdots \Theta_6^\pi] \tag{2.14}$$

is obtained by replacing the atomic orbitals

$$\phi_7(=x_\mathrm{O})\cdots\phi_{10}(=y_\mathrm{C})$$

by the Schmidt orthogonalized orbitals [Table I(B)]

$$\theta_q=\sum_{p=7}^{8}\phi_p t_{pq} \quad (q=7,\,8)$$

$$\theta_q=\sum_{p=9}^{10}\phi_p t_{pq} \quad (q=9,\,10) \tag{2.15}$$

$$t_{pq}=0 \quad (p>q).$$

Again the bases (2.12) and (2.14) are related by a triangular matrix transformation

$$\Theta^\pi=\Psi^\pi T^\pi, \quad \Psi^\pi=\Theta^\pi S^\pi, \tag{2.16}$$

with

$$T_{ij}^\pi=S_{ij}^\pi=0 \quad (i>j).$$

The valence-bond basis functions for the ground state of carbon monoxide are now obtained as antisymmetrized products of the functions Ψ_i^σ [Eq. (2.7)] and Ψ_j^π [Eq. (2.12)]:

$$\tilde{\Psi}_{(i,j)}=\mathfrak{A}\Psi_i^\sigma\Psi_j^\pi \quad (i=1\cdots 8;\, j=1\cdots 6). \tag{2.17}$$

This basis of forty-eight functions is represented as a row vector $\tilde{\Psi}$ with inverse dictionary ordering:

$$\tilde{\Psi}=[\tilde{\Psi}_{(1,1)},\tilde{\Psi}_{(2,1)},\cdots,\tilde{\Psi}_{(8,1)},\tilde{\Psi}_{(1,2)},\cdots,\tilde{\Psi}_{(8,6)}]. \tag{2.18}$$

Similarly, the orthogonalized valence-bond basis

$$\tilde{\Theta}=[\tilde{\Theta}_{(1,1)},\, \tilde{\Theta}_{(2,1)},\, \cdots,\, \tilde{\Theta}_{(8,6)}], \tag{2.19}$$

is constructed from the functions Θ_i^σ (2.8) and Θ_j^π (2.14):

$$\tilde{\Theta}_{(i,j)}=\mathfrak{A}\Theta_i^\sigma\Theta_j^\pi \quad (i=1\cdots 8;\, j=1\cdots 6). \tag{2.20}$$

The 48×48 transformation matrices T and S relating the bases (2.18) and (2.19),

$$\tilde{\Theta}=\tilde{\Psi}T, \quad \tilde{\Psi}=\tilde{\Theta}S, \quad S=T^{-1}, \tag{2.21}$$

are now just the direct products of the 8×8 matrices T^σ, S^σ and the 6×6 matrices T^π and S^π:

$$T=T^\sigma\times T^\pi, \quad S=S^\sigma\times S^\pi; \tag{2.22}$$

that is,

$$\left.\begin{aligned} T_{(i,k)(j,l)}&=T_{ij}^\sigma T_{kl}^\pi \\ S_{(i,k)(j,l)}&=S_{ij}^\sigma S_{kl}^\pi \end{aligned}\right\} \quad (i,j=1\cdots 8;\, k,l=1\cdots 6).$$

These matrices are completely triangular in the sense that

$$T_{(i,k)(j,l)}=S_{(i,k)(j,l)}=0 \text{ unless } i\leq j \text{ and } k\leq l. \tag{2.23}$$

This property of the transformation matrices, which stems from the use of Schmidt orthogonalized atomic orbitals, is very convenient for calculations employing the intra-atomic correlation correction. It permits us to truncate the bases (2.18) and (2.19) simultaneously without destroying the linear dependence between them. For example, Eq. (2.23) shows that the first functions in each basis are simply multiples of each other:

$$\tilde{\Theta}_{(1,1)}=\tilde{\Psi}_{(1,1)}T_{(11,11)}.$$

If we had used some other transformation to orthogonalize the basic atomic orbitals, it would have been impossible to truncate the bases in this way. Thus, if Löwdin's (1950) symmetrical orthogonalization had been employed the expansion of $\tilde{\Theta}_{(1,1)}$ would have involved all 48 of the functions $\tilde{\Psi}_{(i,j)}$ together with 12 wave functions constructed from the functions Ψ_9^σ and Ψ_{10}^σ [Eq. (2.6)].

The importance of this truncation of the basis in ICC calculations lies in the treatment of highly ionized states of the dissociation products. Thus the full valence-bond basis (2.18) includes many states of the ions C^{2-}, C^{3-}, C^{4-}. It is clearly impossible to obtain reliable experimental estimates of the energies of these states. In a previous calculation of the binding energy of N_2 [Hurley (1956b)], this difficulty was circumvented by using an extrapolation technique to dispense with empirical estimates of the energies of various states of the ions N^{2-} and N^{3-}. Nevertheless, the presence of these states in the total wave function led to some uncertainty in the final results.

Here it is possible to eliminate these troublesome states entirely. First it is shown that they have a negligible effect on the total energy in the orbital calculation. These states are then omitted from the ICC calculations by truncating the bases in accordance with Eq. (2.23).

Of course, it is always possible to truncate the basis in an ICC calculation after transforming the full energy matrix explicitly into the valence-bond basis, regardless of what process of orthogonalization is employed. However, this is a much less efficient procedure than exploiting the properties of Schmidt orthogonalization.

(c) Energy Matrix

The energy matrix $\tilde{H}(\Theta)$ in the basis of orthogonalized valence-bond functions (2.19) was evaluated by using McWeeny's (1954) generalization of the cycle-diagram method. This somewhat arduous task was greatly simplified by taking full advantage of the special reductions in the formulas which result from the factorization of the wave functions into antisymmetrized products of Θ_i^σ $(i=1\cdots 8)$ and Θ_j^π $(j=1\cdots 6)$ [Eq. (2.20)]. In this way the 48×48 matrix $\tilde{H}(\Theta)$ may be evaluated with little more work than is required for one 8×8 matrix and one 6×6 matrix. As these special reductions are simple examples of McWeeny's (1960) recent analysis of density matrices for generalized product functions, they are not discussed further.

(d) Total Energy and Binding Energy

The total molecular wave function $\tilde{\Omega}$ and energy $\tilde{E}$ in the orbital calculation are now given by the usual secular equations,

$$\tilde{\Omega} = \tilde{\Theta}\tilde{\Gamma}$$

$$\det\{\tilde{H}(\Theta) - \tilde{E}1\} = 0 \quad \text{(lowest root)} \tag{2.24}$$

$$\{\tilde{H}(\Theta) - \tilde{E}1\}\tilde{\Gamma} = 0.$$

The binding energy $\tilde{D}_e$ is obtained from the equation

$$\tilde{D}_e = \tilde{W}_G - \tilde{E}, \tag{2.25}$$

where $\tilde{W}_G$ is the total energy of the ground state $O(s^2p^4, {}^3P)C(s^2p^2, {}^3P)$ of the dissociation products calculated by using the atomic orbitals (2.1).

Table II. Total energy and binding energy (orbital calculation).

Basis functions	$\tilde{E}$ (a.u.)	$\tilde{D}_e$(ev)[b]
23 terms[a] $C^{2+}O^{2-}$, $C^{+}O^{-}$, CO, $C^{-}O^{+}$	-112.437	7.45
39 terms $C^{2+}O^{2-}\cdots C^{2-}O^{2+}$	-112.438_4	7.50
48 terms $C^{2+}O^{2-}\cdots C^{4-}O^{4+}$	-112.438_5	7.50
SCFMO [Moser (1960)]	-112.343	4.9
SCFMO [Ransil (1960)]	-112.344	4.9[c]

[a] See Table III.
[b] 1 a.u. = 27.210 ev.
[c] Relative to $C(s^2p^2, {}^3P)$, $O(s^2p^4, {}^3P)$ calculated with optimum Slater functions [Hurley (1959)].

The results obtained from Eqs. (2.24) and (2.25) by using different numbers of functions in the basis (2.19) are shown in Table II. The results of self-consistent field molecular orbital calculations [Moser (1960), Ransil (1960)] are shown for comparison. The orbital exponents ($\zeta_1=7.7$, $\zeta_3=\zeta_5=2.275$, $\zeta_2=5.7$, $\zeta_4=\zeta_6=1.625$) used by Ransil differ slightly from those of Eq. (2.2), which were also used by Moser.

We see from Table II that the binding energy obtained by Ransil and Moser is increased by about 2.5 ev by the 23-term valence-bond calculation. However, the further reduction in energy brought about by all the chemically unreasonable structures involving more than one negative charge on the carbon nucleus is very small. The 23-term basis, which was used in the subsequent calculations, is specified in detail in Sec. 3 (Table III).

(e) Validity of Valence Coupling

Even the full valence-bond basis (2.18) contains only a small fraction of the total number of ${}^1\Sigma^+$ wave functions which can be constructed from the basic atomic orbitals (2.1). Indeed, an application of the correlation rules of Wigner and Witmer (1928) to all possible states of the dissociation products (subject to the restriction that the inner-shell orbitals k_O, k_C are both doubly occupied) shows that a complete basis for the ${}^1\Sigma^+$ ground state of carbon monoxide contains 177 terms. The additional functions are of two types:

(i) Functions with the same orbital assignments as the functions (2.18) but with different spin couplings. In the valence-bond basis, the spin coupling is always between electrons in orbitals of the same symmetry type (σ, x, or y). The relaxation of this restriction leads to a large number of additional functions which show spin couplings between orbitals of different symmetries.

Additional functions of this type must be included if we wish to resolve the valence-bond basis functions in terms of approximate composite functions [Moffitt (1954)]. This would be important for a calculation at large nuclear separations since it would lead to dissociation products in true stationary states rather than in the valence states which result from the basis (2.18) (cf. Table III).

However, the effect of these extra functions on the energy of the ground state at the equilibrium nuclear

TABLE III. Wave functions for the 23-term calculations.

Basis functions[a]		Dissociation products				Coefficients in total wave function					
		Ionicity	Valence states[b]			Orbital calculation			ICC calculation		
Ψ_i	Ψ_i^σ,Ψ_i^π	C^{n+}	C	O	$(W_i-\tilde{W}_i')$[c]	$\tilde{\Gamma}(\Theta)$	$\tilde{\Gamma}(\Psi)$	$\tilde{\nu}$	$\Gamma(\Theta)$	$\Gamma(\Psi)$	ν
1	1,1	2	s^2V_0	$s^2p^6V_0$	−0.6184	0.3883	−0.0025	−0.001	0.5063	0.0566	0.020
2	2,1	1	s^2pV_1	$s^2p^5V_1$	−0.2453	0.2804	0.0904	0.029	0.2868	0.1283	0.048
3	3,1	2	spV_0	$s^2p^6V_0$	−0.5992	−0.1301	−0.0225	0.007	−0.2002	−0.0922	0.037
4	4,1	0	$s^2x^2V_0$	$s^2x^2y^2V_0$	−0.0746	0.0722	0.0677	0.012	0.0708	0.0503	0.010
5	5,1	1	s^2pV_1	sp^6V_1	−0.4784	0.0547	0.0322	0.011	0.0591	0.0720	0.033
6	6,1	1	sx^2V_1	$s^2p^5V_1$	−0.2505	0.0643	0.0524	0.013	0.0701	0.0875	0.026
7	7,1	0	$s^2x^2V_0$	sp^5V_0	−0.2087	−0.0146	−0.0338	0.010	−0.0208	−0.0146	0.005
8	1,2	1	s^2pV_1	$s^2p^5V_1$	−0.2454	0.6350	0.1490	0.085	0.6092	0.2805	0.168
9	2,2	0	s^2xyV_2	$s^2x^2yzV_2$	−0.0102	0.3434	0.3053	0.188	0.2793	0.1642	0.099
10	3,2	1	$sp^2V_1^*$	$s^2p^5V_1$	−0.2658	−0.2025	−0.1342	0.083	−0.2289	−0.2346	0.154
11	4,2	−1	$s^2x^2yV_1$	$s^2x^2yV_1$	0.0027	0.0515	0.0392	0.012	0.0506	0.0503	0.015
12	5,2	0	s^2xyV_2	sp^5V_2	−0.1393	0.0608	0.1035	0.075	0.0421	0.0305	0.023
13	6,2	0	sx^2yV_2	$s^2x^2yzV_2$	−0.0574	0.0646	0.1565	0.071	0.0549	0.1040	0.047
14	7,2	−1	$s^2x^2yV_1$	$sp^4V_1^*$	−0.1031	−0.0033	−0.0090	0.005	−0.0272	−0.0749	0.040
15	1,3	0	$s^2x^2V_0$	$s^2x^2y^2V_0$	−0.0746	0.1691	0.1184	0.035	0.1392	0.0836	0.024
16	2,3	−1	$s^2x^2yV_1$	$s^2x^2yV_1$	0.0027	0.0516	0.0666	0.020	0.0454	0.0546	0.015
17	3,3	0	$sp^3V_0^*$	$s^2x^2y^2V_0$	−0.1419	−0.0475	−0.0891	0.028	−0.0467	−0.0840	0.025
18	5,3	−1	$s^2x^2yV_1$	$sx^2y^2V_1$	−0.0754	0.0049	0.0107	0.004	0.0085	0.0186	0.006
19	1,4	0	s^2xyV_2	$s^2x^2yzV_2$	−0.0102	0.3333	0.2360	0.114	0.2420	0.1483	0.064
20	2,4	−1	s^2xyzV_3	s^2xyzV_3	0.0702	0.1100	0.1489	0.071	0.0804	0.0946	0.039
21	3,4	0	$sp^3V_2^*$	$s^2x^2yzV_2$	−0.0959	−0.0924	−0.1690	0.084	−0.0853	−0.1542	0.071
22	5,4	−1	s^2xyzV_3	sx^2yzV_3	−0.0132	0.0139	0.0304	0.018	0.0149	0.0326	0.017
23	1,5	−1	$s^2x^2yV_1$	$s^2x^2yV_1$	0.0027	0.0550	0.0886	0.026	0.0407	0.0656	0.016

[a] There are 30 functions in the bases (2.18) (2.19) which show not more than one negative charge on the carbon atom. However, some of these are mixed with states of higher ionicity by the transformations (2.21) and are omitted from the Table. This mixing could be avoided by changing the order of ϕ_4 and ϕ_5 in the Schmidt orthogonalization.

[b] $sp^2V_1^* = \frac{1}{4}\,{}^2D + \frac{3}{4}\,{}^2P$, $sp^3V_0^* = \frac{1}{2}\,{}^1D^0 + \frac{1}{2}\,{}^1P^0$, $sp^3V_2^* = \frac{1}{4}\,{}^3D^0 + \frac{1}{2}\,{}^3S^0 + \frac{1}{4}\,{}^1D^0$, $sp^4V_1^* = \frac{1}{4}\,{}^2D + \frac{3}{4}\,{}^2P$, all other valence states are listed in terms of stationary states by Moffitt (1954).

[c] Relative to the ground state dissociation products C($s^2p^2,{}^3P$), O($s^2p^4,{}^3P$) for which $W_G - \tilde{W}_G' = -0.8013$.

separation is certainly small and probably very small (<0.05 ev). The effect on the total energy of three states of this type, derived by altering the spin coupling in the most important valence-bond functions (Table III), was estimated by second-order perturbation theory to be less than 0.01 ev.

(ii) Functions with orbital assignments which differ from those of the valence-bond functions (2.18). These functions arise from the molecular orbital configurations $\sigma^4\pi^6$, $\sigma^8\pi^2$, and $\sigma^2\pi^8$ and also from the functions Ψ_9^σ and Ψ_{10}^σ, which we have discarded. The effect of these functions on the total energy will be very small, except for those functions which represent atomic configuration interaction; for example, interaction between C(s^2p^2, ${}^3P$), C(p^4, ${}^3P$) or O$^+$(s^2p^3, ${}^2P$), O$^+$(p^5, ${}^2P$). This atomic configuration interaction will have an appreciable effect (~0.5 ev) on the total energy in the orbital calculation but almost no effect on the results of the ICC calculation [Hurley (1959)].

It appears therefore, that as far as the ICC calculation is concerned, the 23-term valence-bond basis for the ground state of carbon monoxide (Table III) is almost complete in the sense that additional functions constructed from the atomic orbitals (2.1) would affect the calculated total energy by less than 0.1 ev. However, this result has not been established as unequivocally as in the much simpler case of the first-row hydrides [Hurley (1958b, 1959), Krauss and Wehner (1958)].

3. INTRA-ATOMIC CORRELATION CORRECTION

In the ICC theory, the energy matrix H in the valence bond basis Ψ (2.18) is given by the equation [Hurley (1958a)]

$$H=\tilde{H}+\tfrac{1}{2}[\tilde{M}(W-\tilde{W}')+(W-\tilde{W}')\tilde{M}] \quad (\Psi \text{ basis}). \quad (3.1)$$

Here $\tilde{H}$, $\tilde{M}$ are the energy and overlap matrices calculated directly from the orbital wave functions, W is a diagonal matrix whose elements are the empirical energies of the appropriate dissociation products, and $\tilde{W}'$ is a similar matrix formed from the energies calculated for the dissociation products by using the orbital wave functions (2.18) with optimum values of the parameters $\zeta_1, \zeta_2, \zeta_3, \zeta_4, \zeta_5, \zeta_6$. That is, in calculating $\tilde{W}'$, these parameters are varied to minimize the energy of each state of the dissociation products.

In Eq. (3.1) the valence-bond basis is restricted to the 23 functions shown in Table III; the functions are specified by the values of i and j in Eq. (2.17) (column 2). The valence state corresponding to each function and the numerical value of the correction term $W_i - \tilde{W}_i'$ [Eq. (3.1)] are given in columns 3 and 4. The evaluation of these correction terms is described in Appendix I.

To simplify the calculations, Eq. (3.1) is transformed into the orthogonal valence-bond basis Θ (2.19), which in virtue of Eqs. (2.23) also contains just 23 functions with the same values of i and j as for the Ψ basis:

$$H(\Theta)=\tilde{H}(\Theta)+\tfrac{1}{2}\{(W-\tilde{W}')^0+(W-\tilde{W}')^{0\dagger}\}, \quad (3.2)$$

where

$$(W-\tilde{W}')^0=S(W-\tilde{W}')T. \quad (3.3)$$

Here and in all subsequent matrix equations, the matrices are for the truncated 23×23 basis of Table III; S and T are the transformation matrices of Eqs. (2.22); the symbol † denotes the Hermitian conjugate.

The coefficients of the total wave function in the orthogonal basis Θ are listed in Table III, column 5 (orbital calculation) and column 8 (ICC calculation). For the orbital calculation these coefficients $\tilde{\Gamma}(\Theta)$ are given by Eqs. (2.24), whilst for the ICC calculation, $\Gamma(\Theta)$ is given by the corresponding equations with $H(\Theta)$ replacing $\tilde{H}(\Theta)$:

$$\begin{gathered}\Omega=\Theta\Gamma(\Theta)\\ \det\{H(\Theta)-E1\}=0 \quad \text{(lowest root)}\\ \{H(\Theta)-E1\}\Gamma(\Theta)=0.\end{gathered} \quad (3.4)$$

The remaining columns of Table III give the coefficients of the total wave function in the valence-bond basis and the occupation numbers $\tilde{\nu}$, ν of the valence-bond structures. These quantities are determined from the equations

$$\tilde{\Gamma}(\Psi)=T\tilde{\Gamma}(\Theta), \quad \Gamma(\Psi)=T\Gamma(\Theta), \quad (3.5)$$

$$\begin{aligned}\tilde{\nu}_i&=\sum_j \tilde{\Gamma}_i(\Psi)\tilde{M}_{ij}\tilde{\Gamma}_j(\Psi)=\tilde{\Gamma}_i(\Psi)\sum_j S_{ji}\tilde{\Gamma}_j(\Theta),\\ \nu_i&=\sum_j \Gamma_i(\Psi)\tilde{M}_{ij}\Gamma_j(\Psi)=\Gamma_i(\Psi)\sum_j S_{ji}\Gamma_j(\Theta).\end{aligned} \quad (3.6)$$

In practice, the second form of Eqs. (3.6), which derives from the equation $\tilde{M}=S^{\dagger}S$, is the more convenient since the matrix S is triangular.

The values of the occupation numbers ν_i enable us to estimate the effect ΔE on the ICC total energy of any uncertainties ΔW_i in the empirical values of the valence-state energies. To first order, we have

$$\Delta E=\sum_i \nu_i\Delta W_i.$$

In the present calculation the only appreciable uncertainty of this kind arises from the states of O^{2-} (Ψ_1 and Ψ_3). For these states, the value -6.63 ± 0.3 ev [Morris (1957)] was used for the double-electron affinity of oxygen. The small values of ν_1 and ν_3 (Table III, final column) indicate that this uncertainty will have a very small effect (<0.05 ev) on the calculated total energy.

TABLE IV. Total energy and binding energy (23-term ICC calculation).

	Total energy (a.u.)	Binding energy D_e(ev)
ICC calculation	−113.368	>11.00
Spectroscopic	−113.377[a]	11.24[a]
	−113.322[b]	9.74[b]
	−113.305[c]	9.28[c]

[a] Gaydon (1947). [b] Hagstrum (1947). [c] Herzberg (1950).

The total energy E and the binding energy D_e which result from the 23-term ICC calculation are given in Table IV together with three spectroscopic values which have been put forward. The total energy is given by Eq. (3.4) and the binding energy by the equation

$$D_e=W_G-E, \quad (3.7)$$

where W_G is the experimental energy of the ground state dissociation products $O(^3P)$, $C(^3P)$. Since the ICC binding energy is calculated relative to the experimental energy of the dissociation products, it is a lower limit to the true value to within the accuracy of the approximation underlying the basic equation of the ICC theory (3.1). For the simple systems, H_2 [Hurley (1955, 1956a), Pauncz (1954), Arai (1957)], HeH^+ [Hurley (1956c), Evett (1956)], and Li_2 [Arai and Sakamoto (1958)], it has been shown that the errors underlying Eq. (3.1) are very small (<0.02 ev). Furthermore, calculations on the ground state of N_2 [Hurley (1956b)] and on a large number of states of the first-row hydrides LiH, BH, CH, NH, OH, and FH [Hurley (1958b, 1959), Krauss and Wehner (1958)] each lead to a total molecular energy which is above the experimental value, that is, to a binding energy D_e which is a lower limit to the true value.

However, more refined calculations on the ground state of FH [Krauss and Ransil (1960), Hurley (1960)], in which the orbital exponents are varied to minimize the total energy, show that under certain circumstances Eq. (3.7) may give binding energies which exceed the true value by 0.2–0.8 ev. This implies an error of at least this amount in Eq. (3.1). These calculations on HF have been analyzed, and it has been shown that the errors arise from discrepancies between Slater-type functions such as (2.1) and atomic and ionic Hartree-Fock functions. Such discrepancies, which are negligible for the simple systems mentioned above, sometimes lead to an overestimate of the correction for ionic states.

On the basis of this analysis, it is concluded that the uncertainty in the lower limit to the binding energy of carbon monoxide given in Table IV should not exceed 0.5 ev. Since a much larger uncertainty is needed to reconcile the ICC binding energy with either of the lower spectroscopic values, the present calculations indicate that the high value $D_e=11.24$ ev is correct.

This result is in accord with a direct determination of the heat of sublimation of graphite [Chupka and Inghram (1955)], which is linked to $D_0(CO)$ by well-established thermochemical quantities. Until recently it was thought that this high value for $D_0(CO)$ was inconsistent with electron-impact data [Hagstrum (1951)]. However, when these data were reanalyzed [Hagstrum (1955)] using a new value (1.45 ev) for the electron affinity of oxygen [Branscomb and Smith (1955)], most of the discrepancies disappeared and the high value for $D_0(\mathrm{CO})$ became generally accepted.

4. ANALYSIS OF THE TOTAL WAVE FUNCTION

The specification of the total wave functions by the coefficients $\tilde{\Gamma}(\Theta)$, $\tilde{\Gamma}(\Psi)$, $\Gamma(\Theta)$, and $\Gamma(\Psi)$ is not very convenient for physical interpretation or for the calculation of further properties. The most useful derived quantities for this purpose are the first-order density matrices $[\tilde{\rho}_{pq}]$, $[\rho_{pq}]$ for the orbital and ICC calculations, respectively. These may be defined from the expressions for the total charge densities $\tilde{\rho}$, ρ in terms of the basic atomic orbitals (2.1) [Löwdin (1955)]:

$$\tilde{\rho}=\sum_p \sum_q \tilde{\rho}_{pq}\phi_p\phi_q, \tag{4.1}$$

$$\rho=\sum_p \sum_q \rho_{pq}\phi_p\phi_q. \tag{4.2}$$

These density matrices were evaluated for the total wave functions of Table III and are given by the following equations:

$$[\tilde{\rho}_{pq}]=\begin{bmatrix}\tilde{\rho}^{\sigma} & 0 & 0\\ 0 & \tilde{\rho}^{x} & 0\\ 0 & 0 & \tilde{\rho}^{y}\end{bmatrix},\quad [\rho_{pq}]=\begin{bmatrix}\rho^{\sigma} & 0 & 0\\ 0 & \rho^{x} & 0\\ 0 & 0 & \rho^{y}\end{bmatrix}, \tag{4.3}$$

where[2]

$$\tilde{\rho}^{\sigma}=\begin{bmatrix}2.0040, & 0.0038, & 0.0119, & -0.0409, & -0.0553, & -0.0229\\ & 2.0109, & -0.0646, & 0.0178, & -0.0919, & -0.0571\\ & & 2.0015, & -0.3846, & -0.4296, & 0.0875\\ & & & 1.8764, & 0.0181, & -0.6283\\ & & & & 1.3645, & 0.6344\\ & & & & & 0.6364\end{bmatrix},$$

$$\tilde{\rho}^{x}=\tilde{\rho}^{y}=\begin{bmatrix}1.1472, & 0.6664\\ & 0.4923\end{bmatrix},$$

and

$$\rho^{\sigma}=\begin{bmatrix}2.0028, & 0.0039, & 0.0028, & -0.0275, & -0.0507, & -0.0168\\ & 2.0117, & -0.0639, & 0.0127, & -0.1021, & -0.0549\\ & & 1.9329, & -0.2871, & -0.3966, & 0.1364\\ & & & 1.7587, & 0.0204, & -0.7144\\ & & & & 1.4675, & 0.5787\\ & & & & & 0.6163\end{bmatrix},$$

$$\rho^{x}=\rho^{y}=\begin{bmatrix}1.2667, & 0.6504\\ & 0.3814\end{bmatrix}.$$

The matrices (4.3) enable us to calculate the expectation values $\langle\tilde{f}\rangle$, $\langle f\rangle$ of any one electron operator f for the ground state wave functions given by the orbital and ICC calculations

$$\langle\tilde{f}\rangle=\sum_p \sum_q \tilde{\rho}_{pq}f_{pq}, \tag{4.4}$$

$$\langle f\rangle=\sum_p \sum_q \rho_{pq}f_{pq}, \tag{4.5}$$

where

$$f_{pq}=\int \phi_p f \phi_q dv.$$

The net and gross atomic populations [$\tilde{N}(p)$, $\tilde{n}(p)$; $N(p)$, $n(p)$] and the overlap populations [$\tilde{n}(pq)$, $n(pq)$] for the orbital and ICC wave functions were derived from the matrices (4.3) by using the following equations [Mulliken (1955), Hurley (1958b)]:

$$\tilde{n}(p)=\tilde{\rho}_{pp},\quad n(p)=\rho_{pp},$$

$$\tilde{n}(pq)=2m_{pq}\tilde{\rho}_{pq},\quad n(pq)=2m_{pq}\rho_{pq},$$

$$\tilde{N}(p)=\tilde{n}(p)+\tfrac{1}{2}\sum_{q\neq p}\tilde{n}(pq),\quad N(p)=n(p)+\tfrac{1}{2}\sum_{q\neq p}n(pq),$$

where

$$m_{pq}=\int \phi_p\phi_q dv.$$

Since these populations are obtained so simply from the matrices (4.3) and the overlap integrals m_{pq} (Appendix II), they are not listed separately. The alternative expressions for the gross atomic populations $\tilde{N}(p)$, $N(p)$ in terms of the occupation numbers $\tilde{\nu}_i$, ν_i of the valence-bond structures [Hurley (1958b)],

$$\tilde{N}(p)=\sum_i \tilde{\nu}_i n_i(p),\quad N(p)=\sum_i \nu_i n_i(p), \tag{4.6}$$

provide a very useful check on the evaluation of the density matrices (4.3) and on the electron-population analysis. In Eqs. (4.6), $n_i(p)$ is the occupation number (0, 1 or 2) of the atomic orbital p in the valence-bond function Ψ_i (Table III, column 3).

The natural orbitals for the two calculations and their occupation number $\mathfrak{N}$ were obtained as the latent vectors and latent roots of the matrices (4.3) [Löwdin (1955)]. They are shown in Table V together with the self-consistent field molecular orbitals of Moser (1960).

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[2] These matrices are all symmetrical.

TABLE V. Natural orbitals and self-consistent field molecular orbitals.

Natural orbital	Occupation number $\mathfrak{N}$	Coefficients of atomic orbitals							
		k_O	k_C	s_O	s_C	σ_O	σ_C	$x_O(y_O)$	$x_C(y_C)$
$\tilde{\sigma}_1$	2	1	...	...	...	...	...	...	...
$\tilde{\sigma}_2$	2	...	1	...	...	...	...	...	...
$\tilde{\sigma}_3$	1.9998	−0.0069	−0.0302	0.8886	0.2573	−0.1722	−0.0712	...	...
$\tilde{\sigma}_4$	1.9967	−0.0320	−0.0118	−0.4230	0.8436	0.3970	−0.1240	...	...
$\tilde{\sigma}_5$	1.9809	−0.0258	−0.0650	0.1354	−0.3907	0.7000	0.5305	...	...
$\tilde{\sigma}_6$	0.0225	−0.1596	0.1347	−1.1317	0.9530	−0.9383	1.2994	...	...
$\tilde{x}_1(\tilde{y}_1)$	1.9424	...	...	...	...	...	...	0.7587	0.4777
$\tilde{x}_2(\tilde{y}_2)$	0.0576	...	...	...	...	...	...	−0.7094	0.9224
σ_1	2	1	...	...	...	...	...	...	...
σ_2	2	...	1	...	...	...	...	...	...
σ_3	1.9996	−0.0084	−0.0355	0.8991	0.2244	−0.1145	−0.0337	...	...
σ_4	1.9962	−0.0335	−0.0494	−0.2718	0.4475	−0.7581	0.1273	...	...
σ_5	1.9894	−0.0054	−0.0450	0.2740	−0.7907	0.3764	0.5289	...	...
σ_6	0.0149	−0.1612	0.1330	−1.1447	0.9813	−0.9101	1.3013	...	...
x_1	1.9717	...	...	...	...	...	...	0.7976	0.4249
x_2	0.0283	...	...	...	...	...	...	−0.6655	0.9478
SCFMO[a]									
$\phi_{1\sigma}$		1	...	...	...	...	...	...	...
$\phi_{2\sigma}$		...	1	...	...	...	...	...	...
$\phi_{3\sigma}$		−0.0245	−0.0573	0.7477	0.2198	0.2380	0.1558	...	...
$\phi_{4\sigma}$		−0.0320	−0.0209	−0.6355	0.5254	0.6349	0.0603	...	...
$\phi_{5\sigma}$		−0.0106	−0.0355	−0.0400	−0.7430	0.4515	0.5613	...	...
$\phi_{6\sigma}$		−0.1597	0.1358	−1.1416	0.9811	−0.9455	1.2836	...	...
$\phi_{1x}(\phi_{1y})$								0.7709	0.4617
$\phi_{2x}(\phi_{2y})$								−0.6962	0.9305

[a] Moser (1960).

The occupation numbers of the higher natural orbitals ($\tilde{\sigma}_6$, $\tilde{x}_2$, $\tilde{y}_2$; σ_6, x_2, y_2) provide an absolute measure of the departure of the total wave function from the form of a single determinant, that is, a measure of the irreducible configuration interaction which cannot be eliminated by a transformation of the one-electron functions. We see that, as in previous calculations, configuration interaction is much less important in the ICC calculation than in the orbital calculation.

The approximate equality of the higher natural orbitals $\tilde{\sigma}_6$, $\tilde{x}_2$, $\tilde{y}_2$ to the unoccupied molecular orbitals $\phi_{6\sigma}$, ϕ_{2x}, ϕ_{2y} ensures that the first term in the natural expansion of the total orbital wave function, namely,

$$|\tilde{\sigma}_1\alpha, \tilde{\sigma}_1\beta, \tilde{\sigma}_2\alpha, \tilde{\sigma}_2\beta, \tilde{\sigma}_3\alpha, \tilde{\sigma}_3\beta, \tilde{\sigma}_4\alpha, \tilde{\sigma}_4\beta, \tilde{\sigma}_5\alpha, \tilde{\sigma}_5\beta, \times \tilde{x}_1\alpha, \tilde{x}_1\beta, \tilde{y}_1\alpha, \tilde{y}_1\beta|, \quad (4.7)$$

is very similar to the self-consistent field function

$$|\phi_{1\sigma}\alpha, \phi_{1\sigma}\beta, \phi_{2\sigma}\alpha, \phi_{2\sigma}\beta, \phi_{3\sigma}\alpha, \phi_{3\sigma}\beta, \phi_{4\sigma}\alpha, \phi_{4\sigma}\beta, \times \phi_{5\sigma}\alpha, \phi_{5\sigma}\beta, \phi_{1x}\alpha, \phi_{1x}\beta, \phi_{1y}\alpha, \phi_{1y}\beta|. \quad (4.8)$$

Indeed, by using the techniques developed by Löwdin (1955), it is readily shown that the overlap between the functions (4.7) and (4.8) is simply

$$\left(\int \tilde{\sigma}_6\phi_{6\sigma}dv\right)^2 \left(\int \tilde{x}_2\phi_{2x}dv\right)^2 \left(\int \tilde{y}_2\phi_{2y}dv\right)^2 = (0.99949)^2(0.99985)^2(0.99985)^2 = 0.9984. \quad (4.9)$$

A close similarity between the functions (4.7) and (4.8) is expected on general grounds [Lödwin (1955)]. Thus, the large values of the overlap integrals (4.9) provide a valuable check on the consistency of the present orbital calculation with Moser's self-consistent field calculation.

On the other hand, there are quite large differences between the occupied self-consistent field orbitals $\phi_{1\sigma}\cdots\phi_{5\sigma}$ and the corresponding natural orbitals $\tilde{\sigma}_1\cdots\tilde{\sigma}_5$. This suggests that the orbital energies of self-consistent field functions are not very reliable guides in setting up a simple wave function to allow for configuration interaction. For example, it is to be expected that the double substitution $\phi_{5\sigma}^2 \rightarrow \phi_{6\sigma}^2$ would be considerably less effective than $\tilde{\sigma}_5^2 \rightarrow \tilde{\sigma}_6^2$ in lowering the total energy of the single determinant wave function.

5. DIPOLE MOMENT

Perhaps the simplest qualitative picture of the wave functions is that of resonance between the structures $C^{2+}O^{2-}$, $C^{+}-O^{-}$, $C=O$, $C^{-}\equiv O^{+}$ (Table VI). The occupation numbers of these structures are obtained from Table III by summing $\tilde{\nu}_i$ and ν_i for states of the same ionicity.

These results may be compared with the picture of Pauling (1940), which leaves out the structure $C^{2+}O^{2-}$ and gives equal weight to each of the other three. In constructing this picture Pauling made use of the fact that the dipole moment of carbon monoxide is almost zero. He considered only the formal moment μ_f, and it is clear that this will be zero if these three structures have equal weight. However, as Moffitt (1949) has pointed out, there is a large contribution to the moment from the carbon atomic dipole—so that a zero formal moment does not correspond to a zero total moment.

TABLE VI. Resonating structure and dipole moment (C^-O^+).

Structure	Orbital calculation	ICC calculation	Pauling
$C^{2+}O^{2-}$	0.006	0.057	0
C^+-O^-	0.221	0.428	$\frac{1}{3}$
$C=O$	0.617	0.367	$\frac{1}{3}$
$C^-\equiv O^+$	0.156	0.148	$\frac{1}{3}$
Dipole			
μ_f	$-0.42D$	$-2.13D$	0
μ_C	$2.94D$	$3.34D$	
μ_O	$-1.43D$	$-1.32D$	
μ_{CO}	$-0.08D$	$-0.25D$	
μ_t	$1.00D$	$-0.37D$	
$\mu_{SCFMO}{}^a=0.73D$, $\mu_{exptl.}=0.12D$			

[a] Ransil (1960).

We see this clearly from the present results (Table VI). For both calculations, the carbon atomic dipole μ_C is the largest single contribution. The oxygen atomic dipole μ_O is also fairly large, whilst the covalent dipole μ_{CO} is small. These dipole moments were evaluated by using the expressions (4.4), (4.5), the density matrices (4.3), and the dipole moment integrals (Appendix II). The contributions μ_f, μ_C, μ_O, μ_{CO} are obtained by an obvious grouping of the terms in Eqs. (4.4) and (4.5) [Hurley (1958)].

For the orbital calculation, the total moment is of the right sign but much too large; its value fits in well with that obtained by Ransil (1960) in a self-consistent field molecular orbital calculation.

The total moment from the ICC calculation is small but of the wrong sign. The relative values of the orbital and ICC moments are consistent with the results for the first-row hydrides [Hurley (1958b)]. Here also, the effect of the intra-atomic correlation correction is to alter the orbital moment in the right direction but by an amount which is rather too large. This overcorrection of the dipole moment is attributable, at least in part, to errors arising from the discrepancies between the Slater-type functions (2.1) and Hartree-Fock atomic orbitals [Hurley (1960)].

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APPENDIX I

The calculated and experimental energies of the stationary states of the atoms C and O and of the positive ions C^+, C^{2+}, O^+ were obtained from the tables of Roothaan (1955). The calculated and experimental energies of the stationary states of the negative ions C^-, O^-, and O^{2-} are given in Table VII. In all cases the calculated energies are those obtained by using the orbitals (2.1) with optimum values of the parameters $\zeta_1\cdots\zeta_6$ for each state.

The experimental energies of the negative ion states were obtained from the electron affinities EA(O) = 1.465 ±0.005 ev, EA(C) = 1.12±0.05 ev given by Branscomb, Burch, Smith, and Geltman (1958), the value −6.63 ±0.3 ev for the double-electron affinity of oxygen [Morris (1957)], and spectroscopic intervals extrapolated from the tables of Moore (1949).

TABLE VII. Energies of stationary states of the ions C^-, O^-, O^{2-} (a.u.).

State	Calc energy $\tilde{W}'$	Exptl. energy W
$C^-(s^2p^3, {}^4S^0)$	−37.5742	−37.8962
$, {}^2D^0)$	−37.4899	−37.8446
$, {}^2P^0)$	−37.4349	−37.8202
$O^-(s^2p^5, {}^2P^0)$	−74.3043	−75.1628
$O^-(sp^6, {}^2S)$	−73.5290	−74.6206
$O^{2-}(s^2p^6, {}^1S)$	−73.6202	−74.8653

The calculated and empirical energies of the valence states of Table III (column 4) are now obtained from the expressions for these states in terms of stationary states (Table III, footnote a). Since the additional valence-bond functions required to resolve the basis functions $\bar{\Psi}_i$ in terms of approximate composite functions are all orthogonal to the functions $\bar{\Psi}_i$, this procedure is equivalent to using a basis of approximate composite functions throughout the calculations [Hurley (1958b, Appendix)].

APPENDIX II

Atomic Integrals

(*a*) *One-Electron Integrals* (*Table VIII*)

Notation. Overlap integrals: $(ab)=\int abdv$,

Core integrals: $(afb)=\int afbdv$,

$$f=-\tfrac{1}{2}\nabla^2-(6/r_C)-(8/r_O).$$

Dipole moment integrals: $(a\mu b)=\int a\mu bdv$.

TABLE VIII. One-electron integrals.

p,q	$(\phi_p\phi_q)$	$(\phi_p f\phi_q)$[a]	$(\theta_p f\theta_q)$	$(\phi_p\mu\phi_q)$
1,1	1	−34.75659	−34.75659	−1.06595
1,2	0.00009	−0.00297	0.00002	−0.00004
1.3	0	−7.69622	0.35259	0
1,4	0.05050	−1.65416	−0.10150	−0.05010
1,5	0	−0.07029	−0.03414	0.05324
1,6	0.08579	−2.87949	−0.12450	−0.08550
2,2	1	−21.69807	−21.69807	1.06595
2,3	0.05011	−1.03235	0.02690	0.04312
2,4	0	−4.51873	0.25395	0
2,5	0.08313	−1.75901	−0.05195	0.07252
2,6	0	−0.11806	−0.06660	−0.06708
3,3	1	−10.95760	−9.75262	−1.06595
3,4	0.43044	−4.45051	0.13422	−0.12875
3,5	0	−0.82671	−0.90416	0.64963
3,6	0.50815	−5.53923	0.46304	−0.34175
4,4	1	−8.02746	−6.96866	1.06595
4,5	0.32824	−3.48869	−0.68772	0.17787
4,6	0	−1.36060	−0.65810	−0.91495
5,5	1	−9.57767	−9.36043	−1.06595
5,6	0.28880	−3.17960	0.41650	0.08235
6,6	1	−7.77696	−7.03055	1.06595
7,7	1	−9.06222	−9.06222	−1.06595
7,8	0.28880	−2.25027	0.20894	−0.06476
8,8	1	−6.74949	−6.68430	1.06595

[a] In this column only the integrals with p, q = 3, 4 are for the nodeless 25 functions ϕ_{3*}, ϕ_{4*}.

Here μ is the z coordinate of the electron relative to the center of the CO bond.

Orbitals: ϕ_p defined by Eqs. (2.1).

θ_p defined by Eqs. (2.9) and (2.15) (Table I).

(*b*) *Two-Electron Integrals* (*Table IX*)

Notation. $$[ab,cd]=\int\int a(1)b^*(1)(1/r_{12})\times c(2)d^*(2)dv_1dv_2,$$

$$\phi_{3*}=(\zeta_3{}^5/3\pi)^{\frac{1}{2}}r_O\exp(-\zeta_3r_O),\quad \theta_{3*}=\theta_3,$$

$$\phi_{4*}=(\zeta_4{}^5/3\pi)^{\frac{1}{2}}r_C\exp(-\zeta_4r_C),\quad \theta_{4*}=\theta_4,$$

$$\phi_{7*}=2^{-\frac{1}{2}}(\phi_7+i\phi_9),\qquad \theta_{7*}=2^{-\frac{1}{2}}(\theta_7+i\theta_9),$$

$$\phi_{9*}=2^{-\frac{1}{2}}(\phi_7-i\phi_9),\qquad \theta_{9*}=2^{-\frac{1}{2}}(\theta_7-i\theta_9),$$

$$\phi_{8*}=2^{-\frac{1}{2}}(\phi_8+i\phi_{10}),\qquad \theta_{8*}=2^{-\frac{1}{2}}(\theta_8+i\theta_{10}),$$

$$\phi_{10*}=2^{-\frac{1}{2}}(\phi_8-i\phi_{10}),\quad \theta_{10*}=2^{-\frac{1}{2}}(\theta_8-i\theta_{10}).$$

TABLE IX. Electron repulsion integrals.

pq,rs	$[\phi_p\phi_q,\phi_r\phi_s]$	$[\theta_p\theta_q,\theta_r\theta_s]$
11,11	4.78750	4.78750
12,11	0.00017	−0.00024
13*,11	0.67556	−0.44432
14*,11	0.15396	0.11929
15,11	0.00000	−0.04913
16,11	0.26991	0.19060
22,11	0.46907	0.46906
23*,11	0.02552	0.00272
24*,11	0.10275	−0.00130
25,11	0.04322	0.00509
26,11	0.01476	0.01545
3*3*,11	1.11739	1.12232
3*4*,11	0.35748	−0.14168
3*5,11	0.00000	0.05847
3*6,11	0.50408	−0.19522
4*4*,11	0.45309	0.43135
4*5,11	0.23360	0.10522
4*6,11	0.16903	0.11563
55,11	1.10765	1.13448
56,11	0.26100	−0.23597
66,11	0.53558	0.58787
12,12	0.00000	0.00000
13*,12	0.00003	0.00003
14*,12	0.00001	−0.00001
15,12	0.00001	0.00001
16,12	0.00001	−0.00002
22,12	0.00006	0.00002
23*,12	0.00000	−0.00000
24*,12	0.00001	−0.00000
25,12	0.00001	0.00000
26,12	0.00000	0.00000
3*3*,12	0.00008	−0.00002
3*4*,12	0.00003	0.00001
3*5,12	0.00002	0.00002
3*6,12	0.00005	0.00001
4*4*,12	0.00005	0.00001
4*5,12	0.00003	−0.00000
4*6,12	0.00002	0.00001
55,12	0.00009	−0.00001
56,12	0.00003	0.00001
66,12	0.00006	0.00001
13*,13*	0.12149	0.06895
14*,13*	0.02650	−0.01874
15,13*	0.00000	0.00771
16,13*	0.04636	−0.03009
22,13*	0.10849	−0.00001
23*,13*	0.00590	−0.00001
24*,13*	0.02377	0.00002
25,13*	0.00999	−0.00000
26,13*	0.00341	0.00000
3*3*,13*	0.24929	−0.01763
3*4*,13*	0.08080	0.00484
3*5,13*	0.00000	−0.00199
3*6,13*	0.11330	0.00779
4*4*,13*	0.10437	−0.00137
4*5,13*	0.05359	0.00001
4*6,13*	0.03835	−0.00192
55,13*	0.24731	−0.01043
56,13*	0.05963	0.00550
66,13*	0.12257	−0.00559
14*,14*	0.00588	0.00517
15,14*	0.00117	−0.00070
16,14*	0.01029	0.00755
22,14*	0.02398	0.00097
23*,14*	0.00131	0.00001
24*,14*	0.00525	−0.00001
25,14*	0.00222	0.00002
26,14*	0.00078	0.00006
3*3*,14*	0.05312	0.00457
3*4*,14*	0.01760	−0.00078
3*5,14*	0.00229	0.00287
3*6,14*	0.02464	−0.00245
4*4*,14*	0.02289	0.00079
4*5,14*	0.01221	−0.00040
4*6,14*	0.00854	0.00079
55,14*	0.05285	0.00299
56,14*	0.01385	−0.00174
66,14*	0.02697	0.00244
15,15	0.02500	0.02885
16,15	0.00196	−0.01623
22,15	0.01172	0.01226
23*,15	0.00071	0.00015
24*,15	0.00257	−0.00007
25,15	0.00120	0.00029
26,15	0.00074	0.00078
3*3*,15	0.00000	−0.00193
3*4*,15	0.00577	0.00711
3*5,15	0.03840	0.03518
3*6,15	0.00762	−0.00653
4*4*,15	0.00928	0.00522
4*5,15	0.01222	−0.00645
4*6,15	0.00533	0.00386
55,15	0.00000	0.00333
56,15	0.01812	−0.00543
66,15	0.01220	0.01358
16,16	0.01800	0.01909
22,16	0.04164	−0.00481
23*,16	0.00227	−0.00006
24*,16	0.00912	0.00003
25,16	0.00385	−0.00011
26,16	0.00136	−0.00031
3*3*,16	0.09257	0.00721
3*4*,16	0.03062	−0.00467
3*5,16	0.00378	−0.01412
3*6,16	0.04289	0.00008
4*4*,16	0.03978	−0.00154
4*5,16	0.02118	0.00279
4*6,16	0.01483	−0.00089
55,16	0.09213	0.00247
56,16	0.02402	0.00047
66,16	0.04687	−0.00357
22,22	3.54375	3.54375
23*,22	0.11009	−0.06451
24*,22	0.47079	−0.31667
25,22	0.19063	0.01270
26,22	0.00000	−0.07193
3*3*,22	0.46648	0.46506
3*4*,22	0.27694	0.08448
3*5,22	0.13706	0.11337
3*6,22	0.29523	0.04453
4*4*,22	0.80007	0.79968
4*5,22	0.30097	−0.03627
4*6,22	0.00000	0.03869
55,22	0.52276	0.50531
56,22	0.25542	0.08111
66,22	0.78055	0.83981
23*,23*	0.00426	0.00206
24*,23*	0.01802	0.00931
25,23*	0.00734	−0.00005
26,23*	0.00159	0.00412
3*3*,23*	0.02498	0.00222
3*4*,23*	0.01434	−0.00032
3*5,23*	0.00772	0.00121
3*6,23*	0.01606	−0.00013
4*4*,23*	0.03760	−0.00322
4*5,23*	0.01540	0.00128
4*6,23*	0.00325	0.00204
55,23*	0.02816	0.00254
56,23*	0.01424	−0.00078
66,23*	0.03721	−0.00154
24*,24*	0.08006	0.04736
25,24*	0.03106	−0.00236
26,24*	0.00000	0.01016
3*3*,24*	0.10182	−0.00167
3*4*,24*	0.05942	−0.00229
3*5,24*	0.02940	−0.00067
3*6,24*	0.06408	−0.00129
4*4*,24*	0.16940	−0.01131
4*5,24*	0.06378	0.00014
4*6,24*	0.00000	−0.00369
55,24*	0.11345	−0.00167
56,24*	0.05496	−0.00095
66,24*	0.16559	−0.00872
25,25	0.01265	0.00085
26,25	0.00269	0.00327
3*3*,25	0.04238	0.00444
3*4*,25	0.02440	0.00037
3*5,25	0.01312	0.00236
3*6,25	0.02727	0.00033
4*4*,25	0.06430	−0.00104
4*5,25	0.02625	0.00215
4*6,25	0.00535	0.00498
55,25	0.04781	0.00503
56,25	0.02419	−0.00091
66,25	0.06360	0.00094
26,26	0.01556	0.02498
3*3*,26	0.01378	0.01442
3*4*,26	0.00733	0.00127
3*5,26	0.00719	0.00738
3*6,26	0.01158	0.00220
4*4*,26	0.00000	−0.00747
4*5,26	0.00825	0.00857
4*6,26	0.02474	0.02225
55,26	0.01754	0.01539
56,26	0.01340	−0.00362
66,26	0.00000	−0.00108
3*3*,3*3*	0.81738	0.79659
3*4*,3*3*	0.29183	−0.06214
3*5,3*3*	0.00000	0.02518
3*6,3*3*	0.39355	−0.07265
4*4*,3*3*	0.43290	0.40348
4*5,3*3*	0.20717	0.08272
4*6,3*3*	0.13704	0.08778
55,3*3*	0.81373	0.80078
56,3*3*	0.21954	−0.10336
66,3*3*	0.48343	0.47870
3*4*,3*4*	0.12402	0.02860
3*5,3*4*	0.04250	0.03913
3*6,3*4*	0.15829	0.01807
4*4*,3*4*	0.22439	0.03610
4*5,3*4*	0.10617	−0.01718
4*6,3*4*	0.05497	0.00299
55,3*4*	0.29762	−0.05751
56,3*4*	0.11084	0.02611
66,3*4*	0.23725	0.03148
3*5,3*5	0.17984	0.16440
3*6,3*5	0.04948	−0.01919
4*4*,3*5	0.09442	0.05924
4*5,3*5	0.07833	−0.02123
4*6,3*5	0.03781	0.03058
55,3*5	0.00000	0.03459
56,3*5	0.10287	−0.00566
66,3*5	0.10585	0.09624
3*6,3*6	0.20842	0.03166
4*4*,3*6	0.25432	0.01253
4*5,3*6	0.12996	−0.00456
4*6,3*6	0.08415	0.00050
55,3*6	0.39947	−0.06824
56,3*6	0.14180	0.03205
66,3*6	0.27935	−0.00276
4*4*,4*4*	0.58488	0.56765
4*5,4*4*	0.21894	−0.02874
4*6,4*4*	0.00000	−0.01191
55,4*4*	0.45644	0.42492
56,4*4*	0.19557	0.03928
66,4*4*	0.57748	0.57238
4*5,4*5	0.10731	0.03255
4*6,4*5	0.04728	0.03428
55,4*5	0.22313	0.08780
56,4*5	0.11389	−0.02360
66,4*5	0.22689	−0.01597
4*6,4*6	0.12757	0.09503

TABLE IX.—*Continued.*

pq,rs	$[\phi_p\phi_q,\phi_r\phi_s]$	$[\theta_p\theta_q,\theta_r\theta_s]$	pq,rs	$[\phi_p\phi_q,\phi_r\phi_s]$	$[\theta_p\theta_q,\theta_r\theta_s]$	pq,rs	$[\phi_p\phi_q,\phi_r\phi_s]$	$[\theta_p\theta_q,\theta_r\theta_s]$
55,4*6	0.14556	0.08185	77,4*4*	0.42053	0.39411	74*,82	0.00377	0.00208
56,4*6	0.07240	−0.02701	78,4*4*	0.13355	0.01868	84*,82	0.02474	0.02273
66,4*6	0.00000	−0.00414	88,4*4*	0.57748	0.56943	75,82	0.00253	0.00187
55,55	0.87284	0.87286	77,4*5	0.19847	0.07800	85,82	0.00760	−0.00252
56,55	0.23864	−0.11512	78,4*5	0.06050	−0.01170	76,82	0.00345	0.00144
66,55	0.51034	0.51105	88,4*5	0.21046	−0.02651	86,82	0.00000	0.00519
56,56	0.13159	0.05339	77,4*6	0.13192	0.08603	73*,73*	0.17984	0.17303
66,56	0.21412	0.02486	78,4*6	0.02985	−0.00021	83*,73*	0.03363	−0.01339
66,66	0.61451	0.63325	88,4*6	0.00000	0.01321	74*,73*	0.05372	−0.02444
			77,55	0.77876	0.77933	84*,73*	0.04295	0.03980
77,11	1.10765	1.10765	78,55	0.16336	−0.05092	75,73*	0.00000	0.01038
78,11	0.18434	−0.11975	88,55	0.42442	0.42068	85,73*	0.02278	0.01140
88,11	0.40899	0.42112	77,56	0.20891	−0.10507	76,73*	0.07857	−0.03374
77,12	0.00008	−0.00002	78,56	0.06133	0.01993	86,73*	0.02605	0.02658
78,12	0.00002	0.00001	88,56	0.18233	0.03604	83*,83*	0.01337	0.00846
88,12	0.00004	0.00001	77,66	0.46886	0.46782	74*,83*	0.01553	0.00818
77,13*	0.24731	−0.00914	78,66	0.13738	0.01076	84*,83*	0.03166	0.01857
78,13*	0.04231	0.00222	88,66	0.54827	0.56322	75,83*	0.00929	0.00721
88,13*	0.09458	−0.00055				85,83*	0.01365	−0.00221
77,14*	0.05261	0.00211	71,71	0.02500	0.02500	76,83*	0.01967	0.00738
78,14*	0.00918	−0.00031	81,71	0.00086	−0.00613	86,83*	0.01060	0.00763
88,14*	0.02069	0.00067	72,71	0.00005	0.00005	74*,74*	0.02063	0.00916
77,15	0.00000	−0.00088	82,71	0.00037	0.00037	84*,74*	0.02891	0.01003
78,15	0.00262	0.00307	73*,71	0.03840	0.03357	75,74*	0.00980	0.00821
88,15	0.00752	0.00684	83*,71	0.00448	−0.00487	85,74*	0.01392	−0.00269
77,16	0.09168	0.00310	74*,71	0.00934	−0.00685	76,74*	0.02794	0.00814
78,16	0.01597	−0.00194	84*,71	0.00415	0.00450	86,74*	0.01285	0.00396
88,16	0.03595	−0.00254	75,71	0.00000	0.00285	84*,84*	0.12757	0.12548
77,22	0.43810	0.43810	85,71	0.00262	0.00261	75,84*	0.01806	0.01000
78,22	0.15391	0.03677	76,71	0.01470	−0.01044	85,84*	0.03816	−0.01592
88,22	0.78055	0.78692	86,71	0.00304	0.00381	76,84*	0.02985	0.00550
77,23*	0.02336	0.00204	81,81	0.00003	0.00151	86,84*	0.00000	0.02106
78,23*	0.00795	−0.00010	72,81	0.00000	−0.00001	75,75	0.04704	0.04679
88,23*	0.03653	−0.00180	82,81	0.00002	−0.00008	85,75	0.01351	−0.00363
77,24*	0.09594	−0.00102	73*,81	0.00169	−0.00784	76,75	0.01201	−0.00996
78,24*	0.03344	−0.00027	83*,81	0.00024	0.00118	86,75	0.01060	0.01017
88,24*	0.16559	−0.00558	74*,81	0.00046	0.00165	85,85	0.01604	0.00748
77,25	0.03961	0.00386	84*,81	0.00025	−0.00102	76,85	0.01645	−0.00025
78,25	0.01352	−0.00005	75,81	0.00021	−0.00046	86,85	0.01070	0.00646
88,25	0.06247	−0.00080	85,81	0.00017	−0.00065	76,76	0.03918	0.01536
77,26	0.01184	0.01264	76,81	0.00070	0.00241	86,76	0.01762	0.00165
78,26	0.00345	0.00037	86,81	0.00018	−0.00086	86,86	0.03312	0.03545
88,26	0.00000	−0.00172	72,72	0.00005	0.00005			
77,3*3*	0.81373	0.80217	82,72	0.00076	0.00077	7*7*,7*7*	0.82580	0.82580
78,3*3*	0.16445	−0.05561	73*,72	0.00051	0.00050	7*8*,7*7*	0.16444	−0.06123
88,3*3*	0.40426	0.40297	83*,72	0.00045	0.00030	8*8*,7*7*	0.39393	0.39424
77,3*4*	0.28757	−0.06678	74*,72	0.00037	0.00016	7*8*,7*8*	0.04259	0.01516
78,3*4*	0.07137	0.01967	84*,72	0.00156	0.00139	8*8*,7*8*	0.13004	0.02263
88,3*4*	0.21472	0.04151	75,72	0.00031	0.00027	8*8*,8*8*	0.58139	0.58463
77,3*5	0.00000	0.02768	85,72	0.00060	−0.00003	9*7*,7*9*	0.09408	0.09408
78,3*5	0.02278	0.01740	76,72	0.00040	0.00010	9*8*,7*9*	0.01459	−0.01128
88,3*5	0.08547	0.06813	86,72	0.00035	0.00064	10*8*,7*9*	0.01164	0.01147
77,3*6	0.03837	−0.08190	82,82	0.01556	0.01635	9*8*,7*10*	0.00471	0.00399
78,3*6	0.08968	0.01630	73*,82	0.00423	0.00426	10*8*,7*10*	0.01029	0.00664
88,3*6	0.23868	0.01592	83*,82	0.00539	0.00382	10*8*,8*10*	0.06624	0.06699