Resonating Hartree-Fock Ground State in Carbon Mono-Oxide

Akira IGAWA and Hideo FUKUTOME*

Department of Mathematics, Tokyo Denki University, Tokyo 101
*Department of Physics, Kyoto University, Kyoto 606

(Received May 7, 1988)

The ground state of carbon mono-oxide with increased bond length has an unusual electron correlation which is never obtained by a single unrestricted Hartree-Fock (UHF) wave function. Dissociating CO has three UHF states which converge to the correct dissociation limit, two of them are of axial spin density wave (ASDW) type and another is of axial spin wave (ASW) type. One of them, ASDW_1, bifurcates from the restricted Hartree-Fock (RHF) ground state, but the other two, ASDW_2 and ASW, which have lower energies than ASDW_1, do not bifurcate from ASDW_1 and RHF but cross with RHF. Configuration analysis shows that none of them contains all the essential configurations in the ground state wave function. However, a superposition of projected ASDW_1 and ASDW_2 (or ASW) wave functions gives a good approximation to the ground state, showing that it is in resonance of the two UHF states, namely two different kinds of collective correlation are resonating. The resonating UHF ground state is shown to originate from the double well structure of the UHF variational energy surface which yields two UHF states with nearly degenerate energies.

§ 1. Introduction

Dissociation of a chemical bond is a basic process in chemical reactions. The electronic process involved in a bond dissociation, however, is by no means simple. It is well known that the restricted Hartree-Fock (RHF) theory is unable to correctly describe dissociation of a chemical bond even of the simplest kind, the single bond of H_2. Electron correlation is essential in the electronic process of a bond dissociation and in many cases a rather complicated configuration mixing with a number of multiple, including more than double, excitations is needed to correctly describe it by the configuration interaction (CI) method.

It has been shown that the unrestricted Hartree-Fock (UHF) theory is able to correctly describe the dissociation processes of the chemical bonds of different natures,^1^ the single bond of H_2,^2^ the double bond of olefin,^3^ the triple bond of N_2^4^ and the triplet bond of O_2.\(^^5\) The UHF theory provides reasonable physical description for the electronic processes in the bond dissociations which involve rather complicated electron correlation effects. The UHF wave function projected to the state with the correct spin and spatial symmetries, the projected UHF (pUHF) wave function, contains all the electronic configurations of essential importance.

We discuss in this paper the ground state of carbon mono-oxide, CO, with varying interatomic distance \(R\) that has a quite unusual electronic structure from the UHF theoretical viewpoint. A very brief account of the problem was given in Ref. 1. Various ab-initio calculations^9,10^ of CO have been made showing a complicated character of electron correlation. Nagashima and Yamamoto^10^ pointed out that the character of the wave function of CO far from equilibrium strongly depends on the level of the basis set used and the level of configuration mixing included. Our study
will disclose the novel nature of the electron correlation in CO. In § 2, we show that there are several UHF solutions at increased R which are not interconnected to each other but converge to the correct atomic ground state C(3P)+O(3P) in the dissociation limit $R \to \infty$. In § 3, we make the configuration analysis of the pUHF wave functions of these UHF solutions. We show that none of the pUHF wave functions covers all the essential electronic configurations in the wave function which survive at $R \to \infty$. However, if we make a linear superposition of the appropriate two pUHF wave functions, namely a resonating UHF wave function, then all the important configurations are included, and a reasonable approximation for the ground state wave function is obtained in spite of a widely spread configuration mixing in the intermediate stage of the dissociation. In § 4, we investigate the reason why a resonating UHF wave function is necessary to approximate the exact wave function. We show that it is due to the unusual double minima structure of the UHF variational energy functional.

In the following UHF and CI calculations, we use the INDO model. We desire to obtain low lying UHF solutions including unstable ones, to study their instabilities and to compare them with CI wave functions making projection. We use the simple semi-empirical model for which we have a computer program for such a comprehensive UHF study, since we do not yet have such an ab-initio program unfortunately. UHF solutions are calculated by the direct optimization algorithm with secured convergence. We use the notations for the types of UHF solutions and their instabilities proposed by one of the authors. CI calculations are made using the program developed in Ref. 15).

§ 2. UHF solutions in dissociating CO

The INDO RHF wave function of CO is a closed shell configuration in the form of $|1\sigma^22\sigma^23\sigma^2\pi_x^2\pi_y^2\rangle$. The RHF molecular orbitals (MO) $1\sigma$ and $2\sigma$ are composed mainly of the $2s$ atomic orbitals (AO) of carbon and oxygen, respectively. They localize in the $2s$ AO's in the dissociation limit. In the UHF and CI wave functions, the excitations of the $1\sigma$ and $2\sigma$ MO's are involved with only small probabilities. They persist in the CI wave function even at $R \to \infty$ giving the atomic electron correlation. However, they are not essential in the molecular electron correlation at large R and disappear in the UHF wave function at $R \to \infty$. So we do not explicitly mention their contribution in the following UHF wave functions. The $3\sigma$ MO is the bonding orbital composed mainly of the $\sigma$ type $2p$ AO's, which are taken to be the $2p_z$ AO's, and it is denoted by $\sigma$. The antibonding RHF MO $4\sigma$ is denoted by $\sigma^\ast$. $\pi_x$ and $\pi_y$ are the $\pi$ type bonding MO's, and their antibonding partners are denoted by $\pi_x^\ast$ and $\pi_y^\ast$ as usual. The structures of the RHF MO's are shown in Fig. 1(a). $\sigma$ has larger MO weight on the carbon atom while $\pi_x$ and $\pi_y$ have larger MO weights on the oxygen atom. The RHF MO's localize in an atom when the interatomic distance R tends to $\infty$. $\sigma$ localizes in the carbon while $\pi_x$ and $\pi_y$ in the oxygen, so that the RHF electronic structure at $R \to \infty$ becomes as shown in Fig. 3(a). It is a mixture of the atomic states $C(1S)+O(1S)$ and $C(1D)+O(1D)$ which are higher in energy than the atomic ground state $C(3P)+O(3P)$. Thus, the RHF ground state does not give the
correct dissociation behavior. The RHF adiabatic potential is shown in Fig. 2.

When the interatomic distance $R$ is increased up to 1.445 Å, the RHF ground state becomes $^3ST_-$ unstable for the triplet $\pi \to \pi^*$ and $\sigma \to \sigma^*$ transitions with the $\Sigma^+$ spatial symmetry. An axial spin density wave (ASDW) solution, called ASDW, bifurcates from RHF as shown in Fig. 2. The orbitals of ASDW are of the form

$$
\phi_{\lambda^+} = \pi \cos \frac{\lambda^+}{2} + \pi^* \sin \frac{\lambda^+}{2},
$$

$$
\phi_{\lambda^-} = \pi \cos \frac{\lambda^-}{2} + \pi^* \sin \frac{\lambda^-}{2},
$$

$$
\phi_{\sigma^\pm} = \sigma \cos \frac{\lambda_\sigma}{2} - \sigma^* \sin \frac{\lambda_\sigma}{2},
$$

where the superscript $\pm$ denotes the spin state. Since the $\pi \to \pi^*$ transition with the $\Sigma^+$ symmetry occurs in the combination $\pi \pi^* + \pi^* \pi$, the $\pi$ and $\pi^*$ type orbitals $\phi_{\lambda^+}$ and $\phi_{\lambda^-}$ in ASDW still have the same MO coefficients. The spin polarization in the $\sigma$ orbitals $\phi_{\sigma^\pm}$ is very small because of the small contribution of the $\sigma \to \sigma^*$ transition in the instability and they remain to be of nearly closed shell. We show in Fig. 1(b)
the structures of the ASDW₁ orbitals. At $R \to \infty$, the mixing parameters $\lambda^+$, $\lambda^-$ and $\lambda_\sigma$ tend to $\pi$, $0$ and $\pi$, respectively. Consequently, two up spin $\pi$ electrons turn out to localize in the $2p_x$ and $2p_y$ AO's of the carbon atom, while the other two down spin $\pi$ electrons in those of the oxygen atom. The $\sigma$ electrons in the orbitals $\varphi_{\sigma}^\pm$ localize in the $2p_z$ AO of the oxygen atom making a $\sigma$ type lone pair on the contrary to the localization of the RHF orbital $\sigma$. The electronic structure of ASDW₁ at $R \to \infty$ is shown in Fig. 3(b). It correctly converges to the atomic ground state $C(3P) + O(3P)$.

Upon increase of $R$ up to 1.453 Å, ASDW₁ becomes both $A_+M_+$ and $A_+M_-$ unstable for the spin unflipping transitions preserving and breaking the magnetic symmetry, respectively. These transitions have the $\Delta$ and $\Sigma^-$ spatial symmetries, respectively. However, no new UHF solution bifurcates from ASDW₁ at this instability point, but two other UHF solutions, one being of ASDW type called ASDW₂ and the other being of the axial spin wave type called ASW, already exist below ASDW₁ as shown in the inset of Fig. 2. Their energies are very close. ASDW₂ has a little lower energy than ASW. They cross with the RHF solution and disappear at the region with $R$ smaller than 1.43 Å. Therefore, these instabilities of ASDW₁ are neither interconnecting nor crossing. As will be shown in § 4, ASDW₁ is a local minimum of the UHF energy functional for $R$ smaller than this instability point but becomes a saddle point for the longer $R$. Thus, this instability is of the same character as a first order phase transition where a jump to another state with a discontinuous change of the energy takes place.

The orbitals of ASDW₂ are of the form

\[
\varphi_{x}^{\pm} = \pi_x \cos \frac{\mu_x^\pm}{2} + \pi_x^* \sin \frac{\mu_x^\pm}{2},
\]

\[
\varphi_{y}^{\pm} = \pi_y \cos \frac{\mu_y^\pm}{2} + \pi_y^* \sin \frac{\mu_y^\pm}{2},
\]

\[
\varphi_{\sigma}^{\pm} = \sigma \cos \frac{\mu_{\sigma}^\pm}{2} - \sigma^* \sin \frac{\mu_{\sigma}^\pm}{2}.
\]

The MO coefficients of the $\pi_x$ and $\pi_y$ type orbitals $\varphi_{x}^{\pm}$ and $\varphi_{y}^{\pm}$ are different owing to the fact that the mixing of the RHF orbitals to stabilize ASDW₂ has the $\Delta$ symmetry. The spin polarizations in the orbitals $\varphi_{x}^{\pm}$ and $\varphi_{\sigma}^{\pm}$ are large, but that in $\varphi_{y}^{\pm}$ is small so that the electrons in $\varphi_{y}^{\pm}$ are of nearly closed shell. At $R \to \infty$, $\mu_x^+$ and $\mu_\sigma^-$ tend to $\pi$, but $\mu_x^-$, $\mu_\sigma^+$ and $\mu_y$ to 0. Hence, two up spin electrons in $\varphi_{x}^{\pm}$ and $\varphi_{\sigma}^{\pm}$ turn out to localize in the $2p_x$ and $2p_y$ AO's of the carbon, and the other two down spin electrons in $\varphi_{x}^{-}$ and $\varphi_{\sigma}^{-}$ in those of the oxygen. The lone pair electrons in $\varphi_{y}^{\pm}$ localize in the $2p_y$ AO of the oxygen. Thus, ASDW₂ also converges to the atomic ground state $C(3P) + O(3P)$ at $R \to \infty$ as shown in Fig. 3(c). The $2p$ lone pair electrons of the oxygen atom is in the $\sigma$ orbital in ASDW₁, while in the $\pi$ orbital in ASDW₂. This difference makes ASDW₂ a little lower in energy than ASDW₁.

The orbitals of ASDW are of the form
\[ \phi_{\pm} = \pi \cos \frac{\nu_{\pi}}{2} + \pi^* \sin \frac{\nu_{\pi}}{2}, \]
\[ \phi_{\pm} = \pi \cos \frac{\nu_{\pi}}{2} + \pi^* \sin \frac{\nu_{\pi}}{2}, \]
\[ \phi_{\sigma} = \sigma \cos \frac{\nu_{\sigma}}{2} - \sigma^* \sin \frac{\nu_{\sigma}}{2}, \]
\[ (3) \]

where \( \pi = (\pi_x + i \pi_y)/\sqrt{2} \) and \( \pi^* = (\pi_x^* - i \pi_y^*)/\sqrt{2} \) are the complex \( \pi \) orbitals and subscript \( \pm \) denotes the orbital angular momentum \( L_x = \pm 1 \) around the molecular axis. In the ASW orbitals \( \phi_{\pm} \) and \( \phi_{\sigma} \) are spin polarized but \( \phi_{\pm} \) are of nearly closed shell. At \( R \to \infty \), \( \nu_{\pi} \) and \( \nu_{\sigma} \) tend to \( \pi \), but \( \nu_{\pm} \), \( \nu_{\sigma} \) and \( \nu_{\pm} \) to 0. Hence, the two up spin electrons in \( \phi_{\pi} \) and \( \phi_{\sigma} \) turn out to localize in the \( 2p_\pi \) and \( 2p_\sigma \) AO's of the carbon and the two down spin electrons in \( \phi_{\pi} \) and \( \phi_{\sigma} \) in those of the oxygen. The lone pair electrons in \( \phi_{\pm} \) localize in the \( 2p_\pm \) AO of the oxygen. Thus, in ASW the carbon tends to the atomic ground state \( C(3P) \) with \( L_z = 1 \) and the oxygen to \( O(3P) \) with \( L_z = -1 \) as shown in Fig. 3(d). Hence, ASW also converges to the correct atomic ground state at \( R \to \infty \). In ASW, the polarization of the orbital angular momentum, that is, the localization of the positive and negative components of the orbital angular momentum density toward different atoms, takes place as well as the polarization of spin.

Thus, we have three UHF solutions in CO at large \( R \), ASDW\(_1\), ASDW\(_2\) and ASW, all of which converge to the correct atomic ground state in the dissociation limit. ASDW\(_2\) is of the lowest energy at large \( R \)'s as seen in Fig. 2. However, ASDW\(_2\) does not connect continuously with RHF but crosses with it which is the HF ground state near the equilibrium bond length. No UHF solution to connect RHF and ASDW\(_2\) exists. We shall disclose in the following why such a pathological situation arises in the UHF description of CO.

\[ \S 3. \text{ Configuration analysis of the UHF wave function} \]

To see how the UHF solutions ASDW\(_1\), ASDW\(_2\) and ASW approximate the exact ground state wave function, we make configuration analysis of their wave functions. We expand the UHF wave functions into RHF configurations composed of the RHF MO's and pick up the configurations with the \( 1\Sigma^\pm \) symmetry and the core \( 1\sigma^2 2\sigma^2 \). We neglect the configurations arising from the excitations of the electrons in the \( 1\sigma \) and \( 2\sigma \) orbitals. Thus obtained pUHF wave functions with the normalized norm are denoted as \( \Phi(p\text{ASDW}_1) \), \( \Phi(p\text{ASDW}_2) \) and \( \Phi(p\text{ASW}) \). We compare them with the valence electron full CI wave function \( \Phi(\text{CI}) \) in which \( 1\sigma \) and \( 2\sigma \) are regarded as a core. \( \Phi(p\text{ASDW}_2) \) and \( \Phi(p\text{ASW}) \) are almost the same wave functions with very similar distributions of the RHF configurations. Hence, we do not consider here \( \Phi(p\text{ASW}) \).

Table I shows the RHF configurations contained in the pUHF wave functions. \( \Phi(\text{CI}) \) is comprised of thirty configurations, and twenty four of them are contained in the pUHF wave functions. All the rest configurations are related to \( \sigma \to \pi^* \) and \( \pi \to \sigma^* \) transitions and their weights in \( \Phi(\text{CI}) \) are very small. We show in Figs. 4(a) and (b)
Table I. The RHF configurations contained in the pUHF wave functions

<table>
<thead>
<tr>
<th>Configuration(^a)</th>
<th>No. of excitation</th>
<th>Coefficient of conf. mixing(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\Phi(\text{pASDW}_1))</td>
</tr>
<tr>
<td>A (\sigma^<em>\pi^</em>)</td>
<td>0</td>
<td>(e)</td>
</tr>
<tr>
<td>B (\pi^<em>(\sigma\sigma^</em>\pi\pi^*)_1)</td>
<td>2</td>
<td>(l^i)</td>
</tr>
<tr>
<td>C (\pi^<em>(\sigma\pi\pi^</em>)_2)</td>
<td>2</td>
<td>(e^*)</td>
</tr>
<tr>
<td>D (\sigma^<em>(\pi\pi^</em>\pi\pi^*)_1)</td>
<td>4</td>
<td>(e^*)</td>
</tr>
<tr>
<td>E (\sigma^<em>(\pi\pi^</em>\pi\pi^*)_2)</td>
<td>4</td>
<td>(e^*)</td>
</tr>
<tr>
<td>f (\sigma^<em>(\pi\pi^</em>))</td>
<td>1</td>
<td>(l^i)</td>
</tr>
<tr>
<td>g ((\sigma\sigma^<em>)\pi^</em>)</td>
<td>1</td>
<td>(l^i)</td>
</tr>
<tr>
<td>h (\sigma^<em>(\pi\pi\pi\pi^</em>)_1)</td>
<td>2</td>
<td>(m^i)</td>
</tr>
<tr>
<td>i (\sigma^<em>(\pi\pi\pi\pi^</em>)_2)</td>
<td>2</td>
<td>(m^i)</td>
</tr>
<tr>
<td>j (\sigma^<em>\pi^</em>\pi^<em>\pi^</em>)</td>
<td>2</td>
<td>(m^i)</td>
</tr>
<tr>
<td>k (\sigma^<em>\pi^</em>\pi^*)</td>
<td>2</td>
<td>(m^i)</td>
</tr>
<tr>
<td>l ((\sigma\sigma^<em>\pi\pi^</em>\pi\pi^*)_1)</td>
<td>3</td>
<td>(l^i)</td>
</tr>
<tr>
<td>m ((\sigma\sigma^<em>\pi\pi^</em>\pi\pi^*)_2)</td>
<td>3</td>
<td>(l^i)</td>
</tr>
<tr>
<td>n (\sigma^<em>\pi^</em>\pi^<em>(\pi\pi^</em>))</td>
<td>3</td>
<td>(m^i)</td>
</tr>
<tr>
<td>o ((\sigma\sigma^<em>)\pi^</em>\pi^*)</td>
<td>3</td>
<td>(m^i)</td>
</tr>
<tr>
<td>p (\sigma^<em>\pi^</em>(\pi\pi^*))</td>
<td>3</td>
<td>(m^i)</td>
</tr>
<tr>
<td>q (\pi^<em>(\sigma\sigma\pi\pi^</em>))</td>
<td>4</td>
<td>(m^i)</td>
</tr>
<tr>
<td>r (\sigma^<em>\pi^</em>\pi^<em>\pi^</em>)</td>
<td>4</td>
<td>(m^i)</td>
</tr>
<tr>
<td>s (\sigma^<em>\pi^</em>\pi^*)</td>
<td>4</td>
<td>(m^i)</td>
</tr>
<tr>
<td>t (\sigma^<em>\pi^</em>\pi^<em>(\pi\pi^</em>))</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

a) Four configurations are not listed because of their very small weights in both \(\Phi(\text{pUHF})\) and \(\Phi(\text{CI})\).

b) \(e\): essential at \(R \sim R_c(1.43 \text{Å} \sim 1.5 \text{Å})\)

\(e^*:\) essential at \(R \to \infty\).

\(l^i:\) large \((0.6 \sim 0.3)\) but transient.

\(m:\) medium \((0.3 \sim 0.1)\) at \(R \sim R_c\).

\(m^i:\) medium but transient.

The others are small \((<0.1)\).

c) Two singlet excitations.
d) Two triplet excitations coupled to singlet.
e) Three singlet excitations.
f) One singlet and two triplet excitations coupled to singlet.

the \(R\) dependence of the CI coefficients of \(\Phi(\text{pASDW}_1)\) and \(\Phi(\text{pASDW}_2)\), respectively. We show in Fig. 5(a) also those of \(\Phi(\text{CI})\). Table I and these figures show that \(\Phi(\text{CI})\) at \(R \to \infty\) contains four RHF configurations, two being doubly excited and the other two being quadruply excited. Nagashima and Yamamoto\(^{10}\) also showed that both double and quadruple excitations are important in the ab-initio CI wave function in the ground state of CO far from equilibrium. At \(R \to \infty\), however, \(\Phi(\text{pASDW}_1)\) contains only the two quadruply excited configurations, and \(\Phi(\text{pASDW}_2)\) only the two doubly excited ones. Therefore, neither \(\Phi(\text{pASDW}_1)\) nor \(\Phi(\text{pASDW}_2)\) is able to correctly approximate \(\Phi(\text{CI})\) at \(R \to \infty\) though they represent the atomic ground state \(C(3P) + O(3P)\).

This rather curious situation arises from the existence of a lone pair on the oxygen atom. The lone pair can be in two distinct positions, that is, in the \(\sigma\) type AO and the \(\pi^*\) type AO. The two positions correspond to the electronic structures of ASDW\(_1\) and ASDW\(_2\) at \(R \to \infty\), respectively (Figs. 3(b) and (c)). The difference in the
Fig. 4. The $R$ dependence of the normalized coefficients of the RHF configurations in $\Phi(p\text{ASD}W_1)$(a) and $\Phi(p\text{ASD}W_2)$(b). The configurations are marked by the symbols defined in Table I. The same notation is used in Figs. 5 and 8.

Fig. 5. The $R$ dependence of the normalized coefficients in $\Phi(\text{CI})(a)$ and $\Phi(\text{rUHF})(b)$.

direction of the lone pair leads to an essential difference in the molecular electronic structure. We note that the resonance of the two electronic structures of Figs. 3(b) and (c) will be of essential importance also in the valence bond description of CO at large $R$.

$\Phi(\text{CI})$ has a widely spread CI weight distribution over many configurations in the intermediate stage of the dissociation though only the four configurations survive at $R \to \infty$. Neither $\Phi(p\text{ASD}W_1)$ nor $\Phi(p\text{ASD}W_2)$ is a good approximation of $\Phi(\text{CI})$ also in the intermediate stage as seen in Figs. 4(a), (b) and 5(a). As a result of this the use
of the natural orbitals\textsuperscript{160} of ASDW\textsubscript{1} or ASDW\textsubscript{2} as the MO bases of the CI expansion does not lead to an improvement of the wide distribution of the CI weight.

Since $\Phi(p_{ASDW_1})$ and $\Phi(p_{ASDW_2})$ respectively have only two complementary configurations among the four essential configurations at $R \to \infty$, it is necessary to superpose them to get a wave function correctly approximating $\Phi(\text{CI})$ at $R \to \infty$. Therefore, we construct a wave function in the form

$$\Phi(r_{\text{UHF}}) = C_1 \Phi(p_{ASDW_1}) + C_2 \Phi(p_{ASDW_2}).$$  \hspace{1cm} (4)

The wave function $\Phi(r_{\text{UHF}})$ contains all the important configurations of $\Phi(\text{CI})$ in all range of $R$. Since $\Phi(r_{\text{UHF}})$ is a superposition of the two pUHF wave functions, it is called the resonating UHF (rUHF) wave function. We determine the mixing coefficients $C_1$ and $C_2$ so as to minimize the norm of $\Phi(r_{\text{UHF}}) - \Phi(\text{CI})$. We show in Fig. 5(b) the $R$ dependence of the CI coefficients of $\Phi(r_{\text{UHF}})$ and in Fig. 6 those of $C_1$ and $C_2$. To see quantitatively the degree of the resemblance of $\Phi(p_{ASDW_1})$, $\Phi(p_{ASDW_2})$ and $\Phi(r_{\text{UHF}})$ to $\Phi(\text{CI})$, we show in Fig. 7 the $R$ dependence of the norm of the difference of these wave functions. Norms of both $\Phi(p_{ASDW_1}) - \Phi(\text{CI})$ and $\Phi(p_{ASDW_2}) - \Phi(\text{CI})$ increase in the region of $R > 1.5\text{Å}$ and have large values at $R \to \infty$. However, that of $\Phi(r_{\text{UHF}}) - \Phi(\text{CI})$ has values about 0.2–0.3 in the intermediate region $1.5\text{Å} < R < 2.3\text{Å}$, where $\Phi(\text{CI})$ has a widely spread CI weight distributions over many configurations, and tends to 0 in $R > 2.3\text{Å}$. We see from Figs. 5 and 7 that $\Phi(r_{\text{UHF}})$ is a reasonable approximation of $\Phi(\text{CI})$ in the region $R > 1.5\text{Å}$. In the region of small $R < 1.5\text{Å}$ near the bifurcation point of ASDW\textsubscript{1} and the crossing point of ASDW\textsubscript{2} with RHF, $\Phi(r_{\text{UHF}})$ turns out not to be a good approximation. We note that $\Phi(r_{\text{UHF}})$ becomes meaningless in the region of $R$ below the vanishing point of ASDW\textsubscript{2}. $\Phi(p_{ASDW_2})$ is the major component of $\Phi(r_{\text{UHF}})$. This seems because $\Phi(p_{ASDW_2})$ has lower energy than $\Phi(p_{ASDW_1})$. Thus, the ground state of dissociating CO cannot be approximated by a single UHF wave function but can be approximated by a superposition of two UHF wave functions, namely, by a resonating UHF wave function.

![Fig. 6. The $R$ dependence of the mixing coefficients of $\Phi(p_{ASDW_1})$ and $\Phi(p_{ASDW_2})$ in $\Phi(r_{\text{UHF}})$.

![Fig. 7. The $R$ dependence of the norm of the difference between $r$(or $\rho$)UHF and CI wave functions.](image-url)
The resonating UHF wave function has a connection with the first excited state with the $^1\Sigma^+$ symmetry. We define the wave function $\Phi^*(\text{rUHF})$ which is orthogonal to $\Phi(\text{rUHF})$ by

$$\Phi^*(\text{rUHF}) = D_1\Phi(p\text{ASDW}_1) + D_2\Phi(p\text{ASDW}_2),$$

where the mixing coefficients $D_1$ and $D_2$ are determined by the orthogonality to $\Phi(\text{rUHF})$. We show in Figs. 8(a) and (b) the $R$ dependence of the CI coefficients in the first $^1\Sigma^+$ excited state $\Phi^*(\text{CI})$ obtained by the CI calculation and those in $\Phi^*(\text{rUHF})$, respectively. As shown by the norm of $\Phi^*(\text{rUHF}) - \Phi^*(\text{CI})$ in Fig. 7 also, the distribution of the CI coefficients in $\Phi^*(\text{rUHF})$ nicely resembles to that of $\Phi^*(\text{CI})$ in the region $R > 2.0\,\text{Å}$. Therefore, $\Phi^*(\text{CI})$ can be approximated by $\Phi^*(\text{rUHF})$ at large $R$'s. The difference between the two wave functions becomes large in the region of smaller $R$'s. This is because $\Phi^*(\text{rUHF})$ does not contain enough amount of the configurations $\sigma^2\pi^4$, $(\sigma\sigma^*)\pi^4$ and $\sigma^2\pi^2(\pi\pi^*)$ which are the most important configurations in the region.

§ 4. Structure of the UHF variational energy surface and the origin of the resonating UHF ground state

In the dissociations of the single bond of $\text{H}_2$, the double bond of olefin, the triple bond of $\text{N}_2$ and the triplet bond of $\text{O}_2$, the single UHF ground state wave function contains all the important configurations in the full CI wave function which are essential to attain the correct dissociation limit. In the dissociation of $\text{CO}$, however, a single UHF wave function is by no means able to correctly approximate the ground state. It is correctly described only by a superposition of the two UHF states, ASDW$_1$ and ASDW$_2$, namely, by a resonating UHF wave function.

Such an unusual nature of the ground state originates from the unusual structure
of the UHF variational energy surface. As shown in §2, the UHF state ASDW₁, which bifurcates from RHF, becomes unstable at $R = 1.453 \text{Å}$ but no new UHF state bifurcates from the instability point. The two UHF states ASDW₂ and ASW with lower energies already exist prior to the instability. They do not bifurcate from ASDW₁ and RHF but cross with RHF. We can show also that ASDW₁ once becomes unstable at $R = 1.453 \text{Å}$ but again becomes stable at $R$ larger than $1.71 \text{Å}$.

To understand the origin of these unusual behaviors, we show in Fig. 9 the structure of the UHF variational energy surface along a path connecting ASDW₁ (or RHF) and ASDW₂ and how it changes with $R$. The path is obtained as the family of the canonical transformations $\exp[it\Lambda]$ with a parameter $0 \leq t \leq t_0$ from the Thouless canonical transformation\(^{17}\) $\exp[it_0\Lambda]$ transforming ASDW₁ to ASDW₂ where $\Lambda$ is a normalized antihermitian operator. The variational energy surface along the path is calculated by the method developed in Ref. 12). We see that in the region $R < 1.453 \text{Å}$ where the instability of ASDW₁ does not yet take place or even at shorter $R$'s where RHF is stable, ASDW₂ already exists as the minimum of another valley which is different from the valley to which ASDW₁ or RHF belongs. Therefore, both ASDW₁ (or RHF) and ASDW₂ are local minima in this region of $R$. In the region of $R$ beyond the instability threshold $R = 1.453 \text{Å}$ of ASDW₁, the hill separating ASDW₁ and ASDW₂ disappears and ASDW₁ turns out to be a saddle point and becomes unstable in the direction toward ASDW₂. Therefore, this instability of ASDW₁ is similar to the instability in a first order phase transition. Upon further increase of $R$ beyond $1.71 \text{Å}$, a hill separating ASDW₁ and ASDW₂ reappears and ASDW₁ again becomes locally stable. The hill persists until the dissociation limit $R \to \infty$. The double well structure with the energetically closely lying minima is the characteristic feature of the UHF variational energy surface of CO at large $R$'s.

It has been shown that Bose quantization of the time dependent Hartree-Fock (TDHF) amplitude gives an exact representation of a Fermion system.\(^{11,18}\) Accord-
ing to the quantized TDHF theory, the exact ground state is described by the quantal motion of the TDHF amplitude around the lowest energy minima of the UHF variational energy surface. In most systems, only one lowest energy minimum, that corresponds to the UHF ground state, exists in the UHF variational energy surface and other extremal points are separated from it by considerably large energy differences. In such a usual case, the ground state is well approximated by a single UHF wave function because the quantized TDHF motion is restricted near the lowest energy minimum. In CO at large $R$'s, on the other hand, the UHF variational energy surface has the double well structure with energetically closely lying minima, so that quantized TDHF motion extends over the regions around the two minima by quantum tunneling. Therefore, the exact ground state wave function cannot be approximated by a single UHF wave function, but the superposition of the UHF wave functions corresponding to the minima is necessary to correctly approximate it. Since ASW is little distinguishable from ASDW$_2$ after projection to the $^1\Sigma^+$ symmetry, the superposition of ASDW$_1$ and ASDW$_2$ is sufficient to have a reasonable approximation.

Thus, the resonating UHF character of CO at large $R$'s arises from the double well structure of the UHF variational energy surface. The necessity of the two reference states was demonstrated also in a coupled cluster calculation. The existence of the two nearly degenerate UHF states ASDW$_1$ and ASDW$_2$ at large $R$'s seems to be due to the existence of a lone pair of $p$ electrons on the oxygen as seen from their electronic structures at $R \to \infty$ shown in Fig. 3. There may be the possibility of the resonating UHF ground state in other chemical reaction systems with lone pair electrons. For instance, we found very complicated UHF situation in the insertion-addition reaction $\text{CH}_2+\text{F}_2 \rightarrow \text{CH}_2\text{F}_2$ which suggests possible occurrence of the resonating UHF ground state in this system. It is an interesting future problem to find other systems whose ground state is of resonating UHF type.

We have established that a novel and new kind of collective electron correlation, the resonating UHF ground state, appears in the diatomic molecule CO at large $R$'s. The conventional prescription of Fermion many body theory assumes that there is a Slater determinant which reasonably approximates the ground state. We have shown that this assumption may not be valid even in a simple diatomic molecule. As seen from the result in §3, the rUHF wave function of CO at intermediate $R$'s has a configuration distribution which is of nearly valence electron full CI level. Such a complicated wave function from the CI point of view may arise from resonance of different kinds of collective correlation. Therefore, if the resonating UHF ground state appears in a larger system, the CI method will be unable to correctly describe it, unless a prescription to give correct multi-references including highly multiple excitations are provided. Thus, we need to develop a new many body method to describe such a system. One of the authors (H.F.) has developed a general theory of resonating UHF approximation in which the UHF Slater determinants and their mixing coefficients are variationally determined. The theory will be described in a separate paper.

We finally note that the rUHF type ground state may arise also in nuclei in the transition region between the spherical and highly deformed shapes. In these nuclei, the spherical superconductive state and deformed UHF state may have nearly
degenerate energies and resonance may take place between them. If such is the case, we need to make a completely new approach to collective excitations in those nuclei.

Acknowledgements

We would like to thank Professor S. Iwata and Dr. O. Nomura for allowing us to use the CI program developed by them.

References