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A Concise Representation of Adsorbate-Surface Interactions. I. Formulation and Model Calculation for Adsorption of CO on Cu(100) Surface

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A method is presented to clarify the concepts of the chemisorptive bonds among many chemisorptive interactions. The eigenfunctions of the system are transformed into new orbitals, and the chemisorptive interactions are represented in terms of a few transformed orbitals. To show the usefulness of the present method, the adsorption of CO on the Cu(100) surface is examined within the CNDO/2 approximation. The σ donation and the π type interaction is clearly visualized, and the information of the spatial extent of the chemisorptive interactions is also obtained.

Key words: Chemisorption – MO calculation – Localized orbital.

1. Introduction

Adsorption of atoms and small molecules on well-defined solid surfaces is one of the most exciting fields in surface physics and catalytic chemistry. Many theoretical calculations are so far devoted to the elucidation of the adsorbate-surface interactions, that is, the structure of adsorbed species, the electron redistribution between the adsorbate and surface, and so on. The cluster model and the slab model are both widely employed. There is, however, a common

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problem for the two models. In order to draw more exact description on the interactions, more surface atoms, that is, more surface orbitals, have to be taken into consideration. This requirement results in the enlargement in the size of the cluster or of the fundamental region determined by the periodic boundary conditions in the slab model. In the calculation with a large number of the surface orbitals, however, another problem arises except for the limitation of computer storage. The adsorbate-surface interactions occur between the adsorbate orbitals and many surface orbitals, and the individual orbital interactions certainly to some degree contribute to the formation of chemisorptive bonds and to the weakening of the bonding within the adsorbate. Therefore it becomes difficult to elucidate the concept of the chemisorptive bonds.

In this article we present a method to construct a new set of orbitals from the set of the eigenfunctions of the system which are called as the canonical orbitals. The chemisorptive interactions are more effectively represented by a small number of these transformed orbitals. The usefulness of the present method is exemplified in the adsorption of CO on the Cu(100) surface with the slab model of the surface. The analysis reveals the qualitative feature of CO adsorption, that is, the σ donation and the π back donation as well as the information on the extent of the chemisorptive bonds.

2. Method

2.1. Molecular Unit Cell and Bloch Molecular Orbitals

In the investigation of adsorption at low coverage within the framework of the slab model, it is convenient to consider the molecular unit cell (MUC) for the unit of the translation parallel to the surface. The MUC consists of several surface atoms and usually one adsorbate, and this model is a simple modification of the slab model. The MUC model was firstly employed by Messmer et al. for the adsorption on graphite [1]. Recently the authors extensively applied this model to the adsorption on the transition metal surfaces with steps and kinks [2–4]. To represent the chemisorption systems at low coverage, larger area of the MUC is required, and the wave vector could be confined to less points in the reciprocal lattice space for the MUC. In the extreme case along this line, the wave functions are calculated only at the Γ point. In the subsequent discussion, the method is presented for this case without any lack of generality and with advantage of easy understanding and simple notation. Then the area of the MUC becomes equal to the fundamental region determined by the periodic boundary conditions. The orbitals for the chemisorption system could be dealed with in the same manner as usual molecular orbitals (MOs) within each MUC, and so they are referred to as the Bloch molecular orbitals (BMOs) in this article.

2.2. Construction of Interaction Localized Orbitals

The BMOs for the chemisorption system are the eigenfunctions for the corresponding Fock operator, and spread over the whole MUC. The BMOs, ψ are represented by linear combination of the atomic orbitals (AOs), χ in the MUC as Eq. (1).

$$\psi_i = \sum_r^N \chi C_{ri} \qquad (i = 1, 2, \ldots N), \tag{1}$$

where C is the expansion coefficients and N the number of AOs in the MUC. Another set of orbitals, ρ is defined in Eq. (2).

$$\rho_l = \sum_i^M \psi_i U_{il} \qquad (l = 1, 2, \ldots M), \tag{2}$$

where U is the coefficient matrix for the transformation, and the number of ρ is equal to that of the occupied BMO, M. The orbital, ρ is determined so that the expectation value of ρ for the operator F^{AS} may take an extremum (maximum or minimum), as shown in Eq. (3), and the operator F^{AS} is the part corresponding to the adsorbate-surface interactions in the Fock operator which has determined the BMOs.

$$\lambda = \langle \rho | F^{AS} | \rho \rangle / \langle \rho | \rho \rangle. \tag{3}$$

The variational conditions, $\partial\lambda/\partial U_i = 0$ leads to Eq. (4), which is similar to the secular equation seen in usual MO theories.

$$\sum_j \langle \psi_i | F^{AS} | \psi_j \rangle U_{jl} - \lambda U_{il} = 0 \tag{4a}$$

or in simpler notation,

$$\sum_j (F_{ij}^{AS} - \delta_{ij}\lambda) U_{jl} = 0. \tag{4b}$$

The formulation up to here is free from the approximation in the particular MO method. The explicit formula for the operator F^{AS} is, however, given within the framework of the CNDO/2 approximation in Eq. (5), since the model calculation in the next section is carried out using this approximation.

$$\begin{aligned} F^{AS} = {} & \sum_{\mu}^{\text{ads}} |\mu\rangle \sum_{S}^{\text{sur}} (P_{SS} - Z_S)\gamma_{\mu S} \langle \mu| \\ & + \sum_{\nu}^{\text{sur}} |\nu\rangle \sum_{A}^{\text{ads}} (P_{AA} - Z_A)\gamma_{A\nu} \langle \nu| \\ & + \sum_{\mu}^{\text{ads}} \sum_{\nu}^{\text{sur}} (|\mu\rangle F_{\mu\nu} \langle \nu| + |\nu\rangle F_{\nu\mu} \langle \mu|), \end{aligned} \tag{5}$$

where μ and ν indicate the AOs, and A and S indicate the atoms, and "ads" and "sur" mean the adsorbate and surface regions, respectively. Other notations are those used by Pople et al. [5]. The ket and bra pick up the particular AOs in the BMO. In the representation of the F^{AS} in the *ab initio* method, the first and second terms in Eq. (5) should be rewritten in order to consider the multicenter interactions, while the third term is used intact. To evaluate the F_{ij}^{AS} elements, Eq. (1) is rewritten as Eq. (6).

$$|\psi_i\rangle = \sum_r^{\text{ads}} |r\rangle C_{ri} + \sum_t^{\text{sur}} |t\rangle C_{ti}, \tag{6}$$

where r and t mean the AOs. Multiplication of ψ_i and ψ_j to the right and left hands of Eq. (5) and integration over space gives Eq. (7).

$$\begin{aligned} F_{ij}^{AS} &= \sum_r^{\text{ads}} C_{ri}C_{rj} \sum_S^{\text{sur}} (P_{SS} - Z_S)\gamma_{rS} \\ &+ \sum_t^{\text{sur}} C_{ti}C_{tj} \sum_A^{\text{ads}} (P_{AA} - Z_A)\gamma_{At} \\ &+ \sum_r^{\text{ads}} \sum_t^{\text{sur}} (C_{ri}C_{tj} + C_{ti}C_{rj})F_{rt}. \end{aligned} \tag{7}$$

Since the F_{ij}^{AS} elements construct a symmetry matrix, as seen in Eq. (7), the eigenvalue, λ and eigenvector, U are obtained by usual diagonalization of the matrix.

Among the obtained orbitals, ρs, those with large negative values of λ are bonding strongly between the adsorbate and surface, and mainly responsible for the chemisorptive bonds. The other orbitals are nonbonding or antibonding in this region, but they seem to contribute to the bonding in the remaining regions of the system since these orbitals are also constructed from the occupied BMOs. Hereinafter, the ρs are tentatively referred to as the interaction localized orbitals (ILOs). The term "interaction localized" does not mean that the ILOs are spatially localized in the vicinity of the adsorption site, but means that the (chemisorptive) interactions are localized into a few ILOs. The spatial extent of the ILOs depends on that of the interactions, therefore the orbital pattern of the ILOs presents the information on the localizability of the interactions.

It is more convenient to represent the ILO in terms of the AO in the MUC rather than the BMO, as Eq. (8).

$$\rho_l = \sum_i^{M} \psi_i U_{il} = \sum_i^{M} \sum_r^{N} \chi_r C_{ri} U_{il}, \tag{8}$$

where the matrix CU is the desired expansion coefficients.

Another useful representation is the expansion of the ILO by the BMO, ϕ for the adsorbate and surface subsystems, as Eq. (9).

$$\rho_l = \sum_i^{N} \phi_i T_{il} = \sum_i^{N} \sum_r^{N} \chi_r D_{ri} T_{il}, \tag{9}$$

where D is a block diagonal matrix. By equating Eqs. (8) and (9), the coefficient matrix, T is represented in terms of the D, C and U as Eq. (10).

$$T = D^{-1}\text{CU}. \tag{10}$$

To clarify the meaning of λ, λ of Eq. (3) is decomposed into three terms using Eqs. (5) and (8).

$$\lambda_l = \lambda_{l,e}^{A} + \lambda_{l,e}^{S} + \lambda_{l,c}, \tag{11a}$$

$$\lambda_{l,e}^{A} = \sum_{r}^{\text{ads}} [(\mathrm{CU})_{rl}]^2 \sum_{S}^{\text{sur}} (P_{SS} - Z_S)\gamma_{rS}, \tag{11b}$$

$$\lambda_{l,e}^{S} = \sum_{t}^{\text{sur}} [(\mathrm{CU})_{tl}]^2 \sum_{A}^{\text{ads}} (P_{AA} - Z_A)\gamma_{At}, \tag{11c}$$

$$\lambda_{l,c} = 2 \sum_{r}^{\text{ads}} \sum_{t}^{\text{sur}} (\mathrm{CU})_{rl}(\mathrm{CU})_{tl}F_{rt}. \tag{11d}$$

$\lambda_{l,e}^{A}$ represents the electrostatic interaction of the electron density in the adsorbate region within the lth ILO with the net charges on the surface, and $\lambda_{l,e}^{S}$ the reverse interaction. $\lambda_{l,c}$ represents the covalent interaction, that is, bonding, antibonding or nonbonding, between the adsorbate and surface, and it is most important for the discussion of the ILOs. Further the electron density in the adsorbate region in each ILO is defined in Eq. (12).

$$P_l = 2 \sum_{r}^{\text{ads}} [(\mathrm{CU})_{rl}]^2. \tag{12}$$

3. Model Calculation of CO on Cu(100)

3.1. Description of Chemisorption System and Calculation Procedure

The adsorption of CO on the Cu(100) surface is analyzed by means of the method discussed above. The MUC for the Cu(100) surface is taken to be the 6×6 regular square shown in Fig. 1. Three types of adsorption sites are considered. They are atop (A), bridged (B) and centered (C) sites. The nearest Cu—CO and C—O bond lengths are 1.82 and 1.15 Å, respectively. These values are taken to be equal to the Ni—CO and C—O bond lengths in the $\mathrm{Ni(CO)_4}$ complex. This seems to be reasonable since the differences in the metal-CO and C—O bond lengths among the transition metal carbonyl complexes are small (ca. 0.1 and 0.01 Å, respectively) [6, 7]. The Cu—Cu distance is 2.54 Å in the Cu crystal. Only the 4s AO is considered for Cu in this model calculation, and the electronic configuration is $4s^1$. The 3d AOs play a minor role in the adsorption

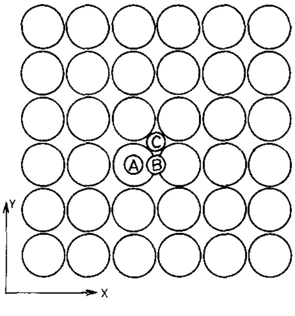

Fig. 1. MUC used for the Cu(100) surface. Three adsorption sites are shown by small circles

on Cu probably due to the complete occupation of the 3d shell [8, 9]. Though the 4p AOs contribute to the chemisorptive interactions to some degree, the qualitative feature seems to be invariant with or without the 4p AOs. The essential difference between Ni and Cu is the number of 3d electrons, and the size and nature of the 4s AO is considered to be similar to each other. So the parameters proposed by Blyholder for Ni are employed for the Cu 4s AO [10]. The standard values by Pople et al. are used for C and O [5].

The BMOs for the chemisorption system are made up of the thirty-six 4s AOs on the surface and the eight 2s and 2p AOs on CO. The number of occupied BMOs is twenty-three, and they are transformed into the ILOs.

3.2. *Results and Discussion*

The eigenvalue of the ILOs, λ_l is shown in Table 1 for the three sites of adsorption, where the ILOs are numbered in increasing order of λ_l. Table 1 also shows the values of $\lambda_{l,c}$ and P_l defined in Eqs. (11d) and (12), respectively. We are interested in the chemisorptive bonds which are to a great extent covalent nature between the adsorbate and surface, and so it is more adequate to use the $\lambda_{l,c}$ value as the criterion to pick up the important ILOs rather than the λ_l value itself. The ILO is tentatively regarded as the important ILO when the absolute value of $\lambda_{l,c}$, that is, $|\lambda_{l,c}|$ is larger than 0.5 eV. With this criterion, the $|\lambda_{l,c}|$ value of the important ILOs is also larger than one-sixteenth of the largest $|\lambda_{l,c}|$ value on each site. These ILOs are the ILOs-1 and -19 on the A site, the ILOs-1 to -3 and -19 on the B site, and the ILOs-1 to -3 and the ILOs-21 to -23 on the C site.

In the adsorption on the A site, the ILO-1 solely explains the bonding interaction between the adsorbate and surface, and the weak antibonding interaction appears in the ILO-19. The leading AO coefficients in the two ILOs are shown in Table 2. Their orbital patterns are also illustrated in Fig. 2. The ILO-1 is mainly

Table 1. λ_l, $\lambda_{l,c}$ (eV) and P_l values for the ILOs on the A, B, and C sites

Site		A				B				C	
ILO	λ_l	$\lambda_{l,c}$	P_l	ILO	λ_l	$\lambda_{l,c}$	P_l	ILO	λ_l	$\lambda_{l,c}$	P_l
1	−4.46	−6.07	0.98	1	−6.92	−8.52	1.24	1	−13.11	−11.78	1.38
2, 3	−1.22	−0.37	0.04	2	−2.32	−1.51	0.20	2, 3	−6.68	−5.60	0.96
4	−0.99	−0.00		3	−1.76	−0.75	0.10	4	−0.66	−0.16	1.50
~18	~−0.53	~0.00	$<10^{-4}$								
				4	−1.11	−0.10		5, 6	−0.26	−0.13	0.18
19	1.73	0.59	0.82	~18	~−0.43	~0.00	$<10^{-3}$				
								7	−0.15	±0.00	
20	4.31	0.01	2.00	19	0.70	0.73	0.46	~19	−0.05		$<10^{-3}$
21	4.35	0.13	1.98	20	3.85	−0.03	1.82	20	0.05	0.01	1.98
22, 23	4.38	0.20	1.96	21	4.36	0.25	1.96	21, 22	1.20	1.24	1.10
				22	4.52	0.37	1.94	23	1.80	2.33	0.64
				23	4.60	0.00	2.00				

composed of the 2s and $2p_z$ AOs on the C atom and the 4s AOs on the nearest and second nearest five Cu atoms. So the ILO-1 represents the σ type interaction between CO and the surface. The AO coefficients on the O atom are negligible, and so the CO moiety of the ILO-1 is not the same as the 5σ MO of free molecule. This rehybridization within CO is discussed later. The CO moiety of the ILO-19 resembles that of the ILO-1, but the interaction of CO with the surface is antibonding except for the slight bonding interaction with the nearest Cu atom. As a result of the two σ type interactions, the contribution to the CO-surface bonding by the second nearest Cu atoms is considerably decreased, which is visualized by superposing the ILO-1 and ILO-19 illustrated in Fig. 2a and b, respectively. Thus, the chemisorptive interactions as the disturbance by the adsorbate extend at least to the second nearest atoms, though the net bonding interactions are largely localized into only the nearest one Cu atom.

Other ILOs are actually not important for the chemisorptive bond formation as indicated by their small $|\lambda_{l,c}|$ values ($|\lambda_{l,c}| < 0.4$) and their P_l values which are very close to zero or two. The ILOs-2 to -18 essentially spread into the surface, and the ILOs-20 to -23 are localized within the adsorbate. It is worth noting that the π type interactions, which appear in the ILOs-2 and -3, are negligible compared with the σ type interaction in the ILO-1 at the A site ($\lambda_{2,c}/\lambda_{1,c} = 0.06$). Thus the chemisorptive interactions are represented by only the two ILOs. This simple and clear description of the interactions is the principal advantage of the present method. In the representation in terms of the BMOs, in fact, the AO coefficients on CO appear in every BMO except for the prohibition by symmetry.

We discuss shortly the difference between λ_l and $\lambda_{l,c}$ in Table 1 which arises from the electrostatic interactions of the electron density in the ILO with the net charges in the system. Both λ_l and $\lambda_{l,c}$ show a similar trend for the ILOs-1 to -19. For the ILOs-20 to -23, the λ_l values are shifted to higher energies (ca.

Table 2. AO coefficients in the ILO-1 and -19 at the *A* site

AO[a]	ILO-1	ILO-19
(1)*s*	0.372	0.096
(2)*s*	0.295	−0.364
(3)*s*	0.076	−0.102
(4)*s*	0.029	−0.048
(5)*s*	−0.010	0.018
(*C*)*s*	0.578	0.471
(*C*)p_z	−0.389	−0.403
(0)*s*	0.011	−0.047
(0)p_z	0.027	0.144

[a] (1) to (5) mean the first to fifth nearest neighboring Cu atoms, respectively. AO coefficients on the more distant Cu atoms are smaller than those on the fifth nearest neighbors. (C) and (O) mean the C and O atoms of CO

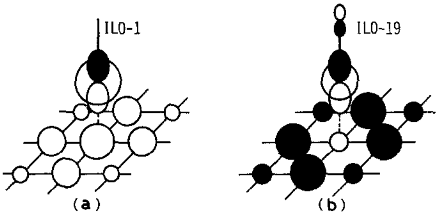

Fig. 2. The leading AO components in the ILOs-1 and -19 on the A site. The size of orbital lobe is qualitatively proportional to the magnitude of the AO coefficients. The illustrated AOs have the coefficients larger than 0.03 and 0.05 for the ILOs-1 and -19, respectively

4 eV) due to the electrostatic interactions than the corresponding $\lambda_{l,c}$ values. Although these ILOs are repulsive between the adsorbate and surface, they are nonbonding rather than antibonding in this region as mentioned above. One may ask why the ILOs are not constructed from the BMOs by using only the third term in the F^{AS} operator in Eq. (5). This type of transformation has also been examined, and the eigenvalues similar to $\lambda_{l,c}$ are obtained. The chemisorptive interactions are, however, less localized in the transformed orbitals. So the inclusion of the electrostatic interactions seems to be necessary to localize well the chemisorptive interactions.

For the adsorption on the B site, the orbital patterns for the ILO s-1, -2, -3 and -19 are illustrated in Fig. 3. The ILO-1 represents again the σ type bonding interaction. The two nearest and four second nearest Cu atoms largely participate in the interaction. The ILOs-2 and -3 represent the π type bonding interactions where the four second nearest atoms contribute more strongly to the bonding than the nearest ones. The ILO-19 represents the σ type antibonding interaction, which decreases the contribution to the net bonding by the second nearest Cu atoms as the adsorption on the A site. Thus, the superposition of the ILOs-1 and -19 in Fig. 3a and c, respectively shows again the net σ type bonding to be localized into the nearest two Cu atoms. The second nearest atoms are, however, more responsible for the π type bonding than the nearest atoms. The difference between the A and B sites is the enhancement of the π type interactions at the

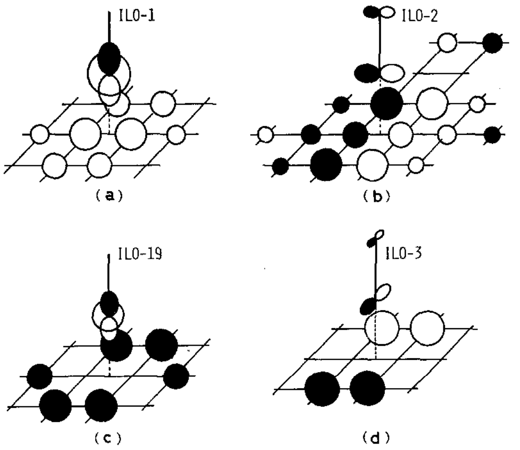

Fig. 3. The leading AO components in the ILO s-1, -2, -3 and -19 on the *B* site. The illustrated AOs have the coefficients larger than 0.06, 0.06, 0.06 and 0.10 for the ILO s-1, -2, -3 and -19, respectively. See caption of Fig. 2

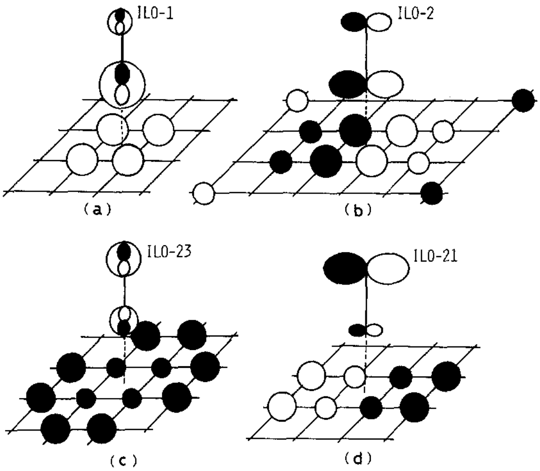

Fig. 4. The leading AO components in the ILO s-1, -2, -21 and -23 on the *C* site. The illustrated AOs have the coefficients larger than 0.05, 0.06, 0.12 and 0.10 for the ILOs-1, -2, -21 and -23, respectively. See caption of Fig. 2

B site ($\lambda_{2,c} = -1.51$, -0.37, $\lambda_{2,c}/\lambda_{1,c} = 0.18$, 0.06 for B, A sites), though the magnitude is still very small compared with that of the σ type interaction.

For the adsorption on the C site, we examine the ILOs-1 to -3 and the ILOs-21 to -23. Their orbital patterns are illustrated in Fig. 4 except for the ILOs-3 and -22, which degenerate by symmetry with the ILOs-2 and -21, respectively. The ILO-1 explains the σ type bonding interaction to the surface, and the four nearest Cu atoms are dominantly concerned with this interaction. The ILOs-2(3) and -21(22) represent the bonding and antibonding π type interactions, respectively. The ILO-21(22) compensates the small bonding interactions formed in the ILO-2(3) between CO and the second nearest Cu atoms. The ILO-23 is largely responsible for the bonding among the second nearest Cu atoms, and for the C—O bond in the adsorbate. The CO-surface interaction in the ILO-23 is weakly antibonding.

It is further instructive to represent the ILOs in terms of the BMOs for CO and the adsorbate-free surface. The special attention is given to the construction of the ILO in the region of the CO moiety. Table 3 shows the expansion coefficients for the ILOs which are responsible for the σ and π type interactions for the three sites. The BMOs for CO are essentially the same as the MOs for free molecule, and the notation of the MOs is used for the BMOs. The construction of the ILO-1 in the CO moiety is quite similar among the three sites, as is visualized in Fig. 5a. We easily recognize that the coefficient of the vacant 6σ BMO is very small in Table 3, and so the σ type interaction is essentially the σ donation from CO to the surface. The negligible AO coefficients on the O atom, which is mentioned in Fig. 2a, is understood as a result of the maximization of the orbital lobe on the C atom for the efficient σ donation. In the ILO-2 on the B and C sites, the $2\pi_x$ orbital mixes into the $1\pi_x$ orbital so that the $2p_x$ AO coefficient may be larger on the C atom than the O atom, as illustrated in Fig. 5b. This mixing is clearly favorable for the π type bonding interaction. Thus, the interaction through the ILO-2 includes both the π donation to the surface

Table 3. Expansion coefficients for the contribution to some ILOs from the adsorbate BMOs on the *A*, *B* and *C* sites[a]

Site BMO^{ILO}	*A* 1	*B* 1	*B* 2	*C* 1	*C* 2
6σ	−0.03	−0.03	0	−0.01	0
$2\pi_y$	0	0	0	0	0
$2\pi_x$	0	0	0.18	0	0.30
5σ	0.60	0.65	0	0.57	0
$1\pi_y$	0	0	0	0	0
$1\pi_x$	0	0	−0.26	0	−0.63
4σ	−0.33	−0.39	0	−0.43	0
3σ	0.12	0.20	0	0.42	0

[a] "0" means the exact null value by symmetry

and the π back donation to CO. The comparison among the three sites shows that the magnitude of the π type interactions increases in the order of the A, B and C sites. Therefore the C—O bond is weakened in this order, and this trend is widely known in the IR and ELS studies for the surface species and metal carbonyl complexes.

The present calculation shows that the chemisorptive interactions are the largest at the C site. This result, however, does not necessarily indicate that the C site is the most stable since the relative stability among sites is determined by the total energy of chemisorption system.

From the discussion on the orbital pattern of the ILOs the following consequence is drawn. The chemisorptive interactions as the disturbance of the surface electronic states by the adsorbate extend at least up to the second nearest surface atoms. However, the net bonding interactions are largely localized into the first nearest surface atoms, since the interactions between CO and the distant surface atoms are considerably compensated over the ILOs.

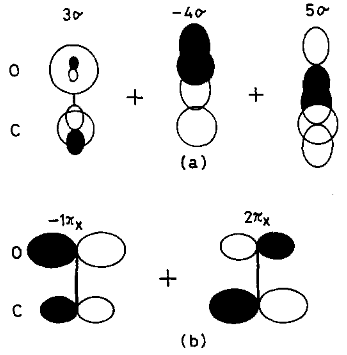

Fig. 5. Construction of ILOs in the CO moiety in terms of the BMOs for CO. (a) ILO-1, (b) ILO-2

4. Comparison with Other Localizing Methods

There are some methods to construct the spatially localized orbitals. The method of Edmiston and Ruedenberg seems to be adequate for the description of the covalent bonds and lone pairs [11], but it does not for the system including the metallic bonds. The Wannier functions are well suited for the description of the local electronic states in semiconductors or insulators [12]. The construction of the Wannier functions on metal surfaces is, however, inconvenient since it mixes the occupied and vacant orbitals through the summation over the Brillouin zone. In the method recently proposed by Whitten and Pakkanen, the orbitals localized on the particular atoms are constructed by maximizing the expectation value for the one-center Coulomb and exchange repulsion integrals on these atoms [13].

The present method is different from theirs in the following points. The orbitals to be transformed are not the surface orbitals before adsorption but the orbitals for the chemisorption system. The chemisorptive interactions themselves are employed as a criterion for the transformation. Only the chemisorptive interactions are localized into a few ILOs, whereas the delocalized nâture of the surface orbitals remains intact to a great extent. So, the present method seems much more natural than other localization methods.

Most recently, Fukui and co-workers presented analyzing methods, which represented the interactions among many MOs by those among the small and definite number of MOs [14, 15]. These MOs were determined iteratively in terms of a linear combination of MOs within each reactant molecule. In contrast to their methods, the present method uses the MOs in the reaction system, and the transformation to the ILO is performed without iterative calculations.

5. Conclusion

In quantum chemical studies on chemisorption, a large number of orbitals have to be taken into consideration. The BMOs, which are the eigenfunctions of the system in the MUC model, spread out over the whole region of the MUC, and the chemisorptive interactions are dispersed into many BMOs. So the BMOs are not convenient to elucidate the modes of "chemisorptive bonds". In this article the ILOs are constructed from the occupied BMOs by the unitary transformation. The chemisorptive interactions are effectively represented in terms of a few ILOs, otherwise the interactions appear in every BMO except for the prohibition by symmetry. The adsorption of CO on the Cu(100) surface is analyzed to show the usefulness of the present method. The orbital patterns of the ILOs visualize the σ and π donation and π back donation as well as the spatial extension of the chemisorptive bonds.

Recently Minot et al. pointed out the importance of the surface amplitude patterns constructed by the superposition of millions of surface orbitals [16].

The present work is also along this line, and further determines uniquely the important orbital patterns in the interactions with adsorbates.

Finally the present method is also applicable to any two systems interacting each other like the surface and the adsorbate.

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