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A New Method Analyzing Large and Strongly Interacting Reaction Systems

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A new method is presented to analyze the various interactions in reaction systems. The method is especially suited for large and strongly interacting systems where other analyzing methods are not practical. The method could isolate the particular interaction from the whole interaction by a procedure termed the partial diagonalization of the bond order matrix. The usefulness of the method is exemplified by the adsorption of CO on Pt and W surfaces. The interactions on the W surface are much stronger than those on the Pt surface, which is consistent with the experimental data. The role of individual interactions for the weakening of the C–O bond and the formation of the Pt–C and W–C bonds is discussed separately.

Key words: Interaction analysis – Strong interaction – large reaction system.

1. Introduction

One of the main subjects in quantum chemistry has been the elucidation of the electronic processes in chemical reactions, that is, the various interactions caused by the approach of more than two molecules. A useful treatment of the reaction system is to represent these interactions in terms of molecular orbitals (MO's) of the constituent molecules in the system, and several methods for the analysis have been proposed; the perturbation expansion method [1–3], the configuration analysis [4–5] and the interaction energy decomposition analysis [6–8]. These methods have been applied to rather small systems which interact weakly or moderately each other. It is possible in principle to employ the methods to large

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and strongly interacting systems, but many expansion terms and the complicated decomposition of the energy are required. Furthermore, various interactions appear in combined form in the individual expansion terms. So the simple and clear picture of the methods seems to be diminished.

In this article we present a new method to analyze the interactions, which is applicable to large and strongly interacting systems without any practical difficulties. To illustrate the usefulness of the method, the adsorption of CO on Pt (111) and W (110) surfaces is examined. Definite differences between the two metals have been reported. CO is adsorbed associatively on Pt, but a fission of the C–O bond occurs on W [9, 10]. This implies the existence of strong interactions on the W surface. The treatment of the surface necessitates the inclusion of several surface atoms into the reaction system, and the system becomes rather large. Furthermore, the adsorption of CO on transition metals becomes of great interest in catalytic chemistry and surface physics. So these systems seem to be a good example to show the advantages of the present method.

2. Method of Analysis

The MO ψ's of the reaction system are expanded using the MO ϕ's of the constituent molecules, which are referred to as the subsystems A and B, as Eq. (1) shows

$$[\psi_o, \psi_v] = [\phi_{A-o}, \phi_{B-o}, \phi_{A-v}, \phi_{B-v}]C \tag{1}$$

where bracket means the raw vector and C is the coefficient matrix. Let the system be composed of n MO's and the number of occupied MO's be m. The subscripts "o" and "v" mean the occupied and vacant MO's respectively. The bond order matrix P is constructed in terms of ϕ,

$$P = 2C_oC_o^\dagger, \tag{2}$$

where the matrix C_o is derived from C by replacing the elements corresponding to the vacant MO ψ_v's by zero. The elements in P have the following meanings: The diagonal element means the net electron density on the MO ϕ under the interactions between subsystems. The offdiagonal element is the indication of the mixing between ϕ's. Since every mixing is caused by some quantum chemical interactions, these elements are considered to be a representation of the interactions, and so they are classified into several blocks as shown in Fig. 1. The exchange (EX) interaction mixes ϕ_{A-o}'s and ϕ_{B-o}'s, or ϕ_{A-v}'s and ϕ_{B-v}'s, respectively. The polarization (PL) interaction mixes ϕ_{A-o}'s and ϕ_{A-v}'s, or ϕ_{B-o}'s and ϕ_{B-v}'s. The charge transfer (CT) interaction mixes ϕ_{A-o}'s and ϕ_{B-v}'s, or ϕ_{B-o}'s and ϕ_{A-v}'s. These three interactions are not completely independent from each other. For example, if the CT and PL interactions are all allowed, the EX interaction also occurs to some degree. However it is always possible to isolate one interaction of the three.

The density matrix for the system is written in two ways as Eq. (3)

$$[\phi]P[\phi]^\dagger = [\psi]D[\psi]^\dagger, \tag{3}$$

where D is a diagonal matrix and has m 2's and $(n-m)$ 0's in the diagonal. We interpret the equivalence in the two representations as follows. On the left hand side of Eq. (3), the mixings, that is, the interactions between the MO ϕ's are all represented by P, whereas on the right hand side all the interactions are transferred into the MO ψ's. This gives a possibility to construct a set of MO ρ's which represents only the particular interaction and the other interactions are left in the resulting bond order matrix. The MO ρ's and the transformation matrix T are introduced in Eq. (4)

$$[\rho]=[\phi]T. \tag{4}$$

Insertion of $TT^{-1}=1$ into the left hand side of Eq. (3) leads to Eqs. (5) and (6)

$$[\phi]TT^{-1}P(TT^{-1})^{\dagger}[\phi]^{\dagger}=[\rho]Q[\rho]^{\dagger} \tag{5}$$

$$Q=T^{-1}P(T^{-1})^{\dagger}, \tag{6}$$

where Q is the bond order matrix represented in terms of ρ. By a suitable matrix T, a particular block in P can be converted to a zero-block, that is, a partial diagonalization of P is achieved. For example, let the CT interaction from ϕ_{A-o} to ϕ_{B-v} be allowed, then only ϕ_{A-o} and ϕ_{B-v} are mixed by T, and new MO ρ' and ρ'' are obtained. We hereinafter refer to this ϕ_{A-o}-ϕ_{B-v} block as the

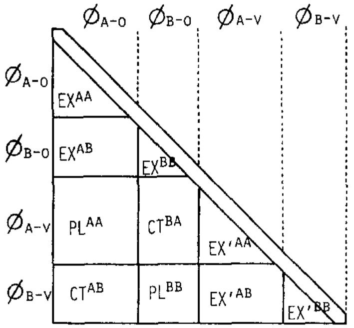
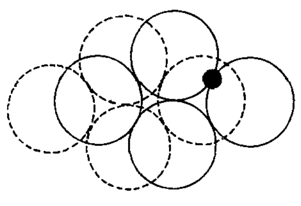
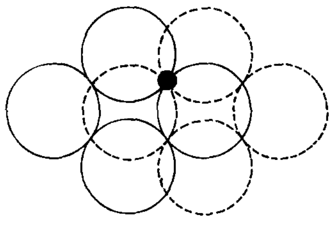


Fig. 1. Various blocks in the bond order matrix P. Only the lower triangle is shown. EX and EX′ mean the exchange interactions among the occupied ϕ's and the vacant ϕ's, respectively. PL and CT are the polarization and charge transfer interactions, respectively. Superscripts AA and BB indicate that the interaction occurs within a subsystem, and AB and BA between subsystems. Notice that CT^{AB} and CT^{BA} are the reverse CT interactions of each other



CO on Pt(111)



CO on W(110)

Fig. 2. MUC's used for the adsorption of CO on the Pt (111) and W (110) surfaces. The surface atoms are shown by large solid and dashed circles for the first and second layer atoms, respectively. CO molecule is adsorbed on the bridge sites normal to the surfaces and the sites are shown by small full circles.

transferred interaction block (TIB). Thus, the interaction represented by the TIB in P is transferred into ρ through T. Conversely, T is determined so that the TIB may become the zero-block.

In general, T is not unitary due to the non-orthogonality of ϕ's between the subsystems with the overlap matrix S, as written in Eq. (7)

$$\langle[\phi]^{\dagger}[\phi]\rangle = S. \tag{7}$$

So T is obtained in two steps, and it is convenient to rewrite T as the product of two matrices, V and U

$$T = VU, \tag{8}$$

where U is unitary but V is not. Only ϕ's concerning the TIB are orthogonalized as Eqs. (9) and (10), since complete orthogonalization mixes all ϕ's

$$[\omega] = [\phi]V \tag{9}$$

$$\langle[\omega]^{\dagger}[\omega]\rangle = V^{\dagger}SV = R, \tag{10}$$

where R is the overlap matrix in terms of ω. The TIB in S is changed to the zero-block in R by transformation matrix V. The bond order matrix Q in Eq. (6) is rewritten as Eq. (11) by substitution of Eq. (8)

$$Q = U^{\dagger}V^{-1}P(V^{-1})^{\dagger}U. \tag{11}$$

The TIB in $V^{-1}P(V^{-1})^{\dagger}$ is changed to the zero-block by U. Thus, whole transformation matrix T is obtained. In the actual calculation of V and U, Jacobi's two-by-two rotation procedure seems to be most suitable to delete the particular offdiagonal elements, where V is normalized so that overlap matrix R has unity as diagonal elements. So the present analyzing method may be termed the partial diagonalization method of the bond order matrix.

The obtained ρ's are the MO's of the system where only particular interaction is allowed. The calculation of the electronic structure of the system using ρ's is very useful to discuss the relative importance of the individual interactions. The "occupied" ρ's are taken to be the m ρ's which have larger fraction of ϕ_{A-o}'s and ϕ_{B-o}'s. So the present analysis is effective so long as the occupied and vacant ρ's are definitely separated.

3. Application to the CO-Pt (111) and CO-W (110) Interactions

The model for surfaces and the calculation method are similar to our previous work [11], and so only the outlines are written here. The surfaces are represented by the two layer slab model. The molecular unit cell (MUC) is used as the unit of the periodicity parallel to the surface. The MUC's contain eight surface atoms and one CO molecule and are illustrated in Fig. 2 together with the adsorption sites of CO. The eigenfunctions of the system are referred to as the Bloch molecular orbitals (BMO's) since they spread out over the MUC's and could be dealt with as usual MO's within each MUC. The CNDO/2 approximation is

Table 1. parameters for Pt and W atoms

	$\zeta_{s,p}$	ζ_d	$1/2(I+A)_s$	$1/2(I+A)_p$	$1/2(I+A)_d$	$-\beta_{s,p}$	$-\beta_d$
Pt	1.79[a]	2.31[b]	4.5	1.5	15.0	6.0	10.0
W	1.64[a]	1.75[b]	3.0	1.0	6.0	4.5	6.0

[a] See Ref. [13].
[b] See Ref. [14].

employed to calculate the BMO [12]. The parameters for the Pt and W atoms are estimated by the authors and are shown in Table 1. For the C and O atoms, the standard values by Pople et al. are used [12]. On account of the zero differential overlap approximation, some simplified features appear. The BMO's for the subsystems, that is, CO and the surface are orthogonal each other, and the transformation matrix T is reduced to a unitary matrix. The interaction among the occupied BMO's does not give rise to the net mixing, and so the non-zero offdiagonal elements in the EX and EX′ blocks in the bond order matrix P are explained only by the combination of more than two PL and CT interactions.

The electron density on the atomic orbitals (AO's) is shown in Table 2 for the adsorbate free Pt and W surfaces. Among the Pt 5d AO's, the d_{z^2}, d_{xz} and d_{yz} AO's are almost doubly occupied, and the d hole is mainly localized in the $d_{x^2-y^2}$ and d_{xy} AO's. In W, the 5d AO's contain 4.7 electrons and the d band is filled nearly half.

Table 2. Electron density on the AO's in the adsorbate free Pt and W surfaces

	Pt	W
s, p total	1.45	1.26
d_{z^2}	1.87	0.68
d_{xz}	1.94	0.53
d_{yz}	1.94	1.82
$d_{x^2-y^2}$	1.40	0.41
d_{xy}	1.40	1.30

Table 3. E_{AB} values (eV) for the C–O, Pt–C and W–C bonds under the particular interactions[a]

	Pt+CO			W+CO		
Allowed interaction	E_{CO}	$E_{Pt\text{-}C}(s, p)$	$E_{Pt\text{-}C}(d)$	E_{CO}	$E_{W\text{-}C}(s, p)$	$E_{W\text{-}C}(d)$
None	−75.2	0	0	−75.2	0	0
PL: within CO	−74.2	0	0	−69.0	0	0
CT: surface → CO	−73.4	−0.1	−3.7	−67.2	−0.4	−5.6
CT: CO → surface	−73.2	−7.4	−0.5	−70.5	−6.8	−7.1
CT: both	−71.4	−7.5	−4.3	−62.6	−7.2	−12.9
All	−70.6	−7.8	−5.0	−60.8	−7.8	−15.4

[a] Large negative values indicate strong bondings.

In the CNDO/2 approximation, the E_{AB} values are used as an index for the bond formation and weakening. Table 3 shows the formation of the nearest M–C (M = Pt or W) bonds and the weakening of the C–O bond in terms of the E_{AB} values when only particular interaction is allowed. The tabulated E_{AB} values do not include the electrostatic term to clarify the covalent nature of the chemisorption bonds. The $E_{\mathrm{M-C}}$ values are divided into the contributions from the $6s, p$ and $5d$ AO's. Following consequences are drawn from Table 3. The formation of the M–C bond comes from the CT interaction alone while the weakening of the C–O bond is ascribed to both the CT interaction and the PL interaction within CO. The PL interaction within the surface affects neither the M–C nor C–O bonds, and is not cited. In Pt, the contribution to the C–O bond weakening by each of the two CT interactions is larger than that by the PL interaction, while in W, the contribution decreases in the order of the CT interaction from the surface to CO, the PL interaction within CO and the CT interaction from CO to the surface.

The Pt $6s, p$ and $5d$ AO's seem to contribute to the formation of the Pt–C bond in a definitely different manner. The $6s, p$ and $5d$ AO's are responsible for the CT interactions from CO to the surface and from the surface to CO, respectively. This result is reasonable since the $6s$, p AO's are nearly vacant and the $5d$ AO's are almost occupied. The degree of the Pt–C bond formation is much larger in the CT interaction from CO to the surface, while the contribution to the C–O bond weakening is similar between the two CT interactions. Thus the formation of new bonds and the weakening of old bonds do not necessarily occur in parallel, but they depend on the shape of the individual orbitals within and between subsystems. Regarding the interactions on the W surface, the $5d$ AO's are responsible for both the two CT interactions, while the $6s$, p AO's only accept electrons from CO. This result is simply ascribed to the fact that the W d band is filled nearly half. The CT interaction of CO with the surface much more contributes to the W–C bond formation than the reverse CT interaction, but the former is less important for the C–O bond weakening. So the independent mechanism for the bond formation and weakening is suggested again. The sum of the two CT interactions closely approximates the result when both the CT interactions are allowed simultaneously, and is also semiquantitatively consistent with the result containing all the interactions. There, the $6s, p$ and $5d$ AO's explain the larger part of the M–C bond formation on the Pt and W surfaces, respectively. The stronger M–C bond formation and the larger weakening of the C–O bond are to be seen on the W surface, which agrees well with experimental results [9, 10].

One of the advantages of the present analysis is the separation of the CT and PL interactions, and the latter also contributes to the weakening of bonds within the subsystems to some degree. The analysis could be carried out to examine the contribution due to the mixing between any two BMO's in the subsystems. Before such a detailed analysis, however, it is instructive to know the important BMO's which are responsible for the formation and weakening of bonds. Some information is drawn from the changes in the electron density on the BMO's in

Table 4. electron density on the BMO's in CO under the PL or CT interaction

	Pt+CO		W+CO	
	PL	CT	PL	CT
6σ	0.007	0.008	0.005	0.006
$2\pi_y$	0.008	0.093	0.116	0.440
$2\pi_x$	0.001	0.059	0.100	0.357
5σ	1.996	1.863	1.995	1.688
$1\pi_y$	1.992	1.943	1.908	1.851
$1\pi_x$	1.999	1.946	1.876	1.881
4σ	1.999	1.928	2.000	1.853
3σ	1.998	1.954	2.000	1.909

CO when the PL or CT interaction is allowed. In Table 4, the large decrease of electron density from the occupied BMO's and the large accumulation of it into the vacant BMO's mean the strong interactions. In CO on the Pt surface, the PL interaction is much smaller than the CT interaction in conformity with the changes in the E_{CO} value shown in Table 3. For the CT interaction, the dominant change is the electron donation from the 5σ BMO to the surface, which is called the σ donation. On the W surface, the PL and CT interactions are much stronger than those on Pt. The PL interaction mainly occurs from the 1π BMO's to the 2π BMO's, and the contribution from the 5σ BMO is very small. On the contrary, a remarkable σ donation is seen in the CT interaction. Furthermore, the 3σ, 4σ and 1π BMO's considerably donate electrons to the surface, and the 2π BMO's accept more electrons from the surface.

The extent of the C–O bond weakening and the W–C bond formation is investigated when only the CT interaction is allowed between one or two BMO's in CO and the BMO's in the W surface. The results are shown in Table 5. In order to weaken the C–O bond, the CT interaction of the surface with the 2π BMO's is most important, and a secondary weakening is seen in the electron donation from the 1π and 3σ BMO's to the surface. The contribution by the 4σ and 5σ BMO's is negligible, for these BMO's are lone pair orbitals rather than bonding orbitals. On the contrary, the formation of the W–C bond is largely ascribed to the 5σ BMO as well as to the 2π BMO's, which have the large AO components

Table 5. E_{AB} values (eV) for the C–O and W–C bonds under the particular CT interaction

Allowed CT interaction	E_{CO}	$E_{\mathrm{W\text{-}C}}(s, p)$	$E_{\mathrm{W\text{-}C}}(d)$
surface → $2\pi_x$, $2\pi_y$	−67.3	−0.3	−5.4
5σ → surface	−75.0	−3.3	−3.3
$1\pi_x$, $1\pi_y$ → surface	−72.4	−1.0	−1.9
4σ → surface	−74.8	−2.1	−1.7
3σ → surface	−73.0	−1.2	−0.8

on the C atom. Thus, the role of the individual BMO's in CO is elucidated. These consequences are qualitatively consistent with the expectations based on the orbital patterns of the BMO's in CO, and the relative importance of the various interactions is, however, discussed quantitatively using the analysing method newly presented.

4. Conclusion

In this article, a new method is presented to analyze the various interactions in reaction systems. The principal advantage of the present method is its applicability to large and strongly interacting systems without any practical difficulties. The method is able to pick up only the particular interaction from the whole interaction and to estimate the relative importance of that interaction in the formation and weakening of chemical bonds. In the examination of the CO–Pt and CO–W surface interactions, the much stronger interactions are found in the latter, in conformity with experimental data. The PL interaction within CO considerably weakens the C–O bond on W, which is ascribed to the electron transition from the 1π to the 2π orbitals. In the CT interaction, the donation from the 5σ orbital of CO explains the larger part of the Pt–C and W–C bond formation, but its contribution to the C–O bond weakening is trivial. Much larger contribution by the $5d$ AO's in W than in Pt is responsible for the differences in the $5d$ AO electron density on the two metals. Thus, the present method seems to be especially suited for those systems where other methods are not practical due to strong interactions and the large size of the system.

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