Theor Chim Acta (1990) 77: 17–28

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Chimica Acta

An energy criterion for determining *d* orbital contribution to adsorbate bonding to a transition metal: CO/Fe_{12}

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(Received August 28, 1989; received in revised form October 23, 1989/Accepted October 26, 1989)

Summary. A new criterion is presented for determining the contribution of a particular class or group of orbitals to a chemical bond. The new criterion is the diatomic energy contribution of particular orbitals to a bond. In neglect to differential overlap methods the total energy may be decomposed entirely into monoatomic and diatomic terms. The contribution of the electrons in *d* orbitals to the diatomic energy terms, which are responsible for holding a molecule together, have been calculated for an Fe-Fe bond of Fe_{12} and for the Fe-C bond of CO absorbed at an on-top site of an Fe_{12} cluster. This direct measure of the *d* electron contribution to the total energy indicates that the *d* orbitals are responsible for only a small contribution to the Fe-Fe binding energy and to the binding energy for absorbed CO. This occurs, despite there being large *d* orbital attractive diatomic energy terms, because a careful analysis indicates repulsive terms balance the attractive terms.

Key words: *d* Orbitals — Transition metals — Carbon monoxide — Adsorption

1. Introduction

In catalysis by metals, the transition metals are often active catalysts whereas pretransition metals are seldom active catalysts. This fact has led to the proposal that *d* orbitals are important in bonding adsorbates to metal surfaces and in obtaining catalytic properties [1]. Early simple molecular orbital models of CO bonding to metals, which were quite successful in qualitatively discussing infrared band shifts, used *d* orbitals in the M-C-O π electron system, but the fact that the orbitals used were called *d* orbitals was not necessary to the model [2, 3].

In *ab initio* calculations and semi-empirical procedures designed to mimic *ab initio* methods, the importance assigned to *d* orbitals has been quite variable. As well as intrinsic differences in calculational results this variability is a result of using different criteria for determining the importance of *d* orbitals. It has been pointed out that in dealing with complex many electron systems there is generally no single unique way to analyze the bonding [4].

Among the earliest cluster calculations, EH (extended Hückel) calculations for H interacting with clusters of 8–10 Ni atoms indicated the Ni 4*s* orbitals were most important with some contribution from the 3*d* orbitals [5]. CNDO (complete neglect of differential overlap) calculations [6] for H adsorbed on 10 atom Ni clusters gave the Ni 4*s* and 4*p* orbitals as being primarily responsible for the Ni_{10}-H bonding with the *d* orbitals playing a relatively minor role. Subsequent less approximate calculations including HF (Hartree-Fock) [7, 8] and Xα [9] calculations also concluded that the 3*d* electrons play a minor role in directly establishing the Ni-H binding energy. In some cases the 3*d* orbitals were eliminited from the valence shell [7], while others found an important direct effect of 3*d* orbitals in bonding [10]. In the second and third transition series the M-H bond has been found to be primarly formed from *d* orbital interactions as shown in calculations for Pd_3H [11], Pd_4H [12] and Pd_xH [13] at the HF level, in Xα calculations for Pd_4H and Pt_4H [9], and in LSD (local spin density) calculations for Pd_xH [14].

For the interaction of CO with Ni in the first round of calculations, a semi-empirical (CNDO) procedure for CO adsorbed on Ni clusters [15] and SCF-HF (self consistent field-HF) results for NiCO [16] and $Ni(CO)_4$ [17] indicated that the metal-carbon bond was primarily formed from the Ni 4*s* and 4*p* orbitals with the 3*d* orbitals making only a minor contribution as judged by population analysis. In HF calculations that included Cl for NiCO the importance for $d\pi$ backbonding was noted [18, 19]. In SCF-Xα-SW (self consistent field-Xα-scattered wave) calculations the *s*, *p*, and *d* orbitals of Ni were found to make approximately equal contributions to the Ni-C bond of NiCO on the basis of populations in the molecular orbitals contributing to bonding [20]. Shifts in the *d* states were found to be important in determining the magnetic properties of Ni clusters with chemisorbed CO in LSD calculations [4]. In both LSD [21] and HF-CI (Hartree-Fock-configuration interaction) [22–24] calculations for Pd, Rh, and Pt interaction with CO, the importance of $d\pi$ bonding is indicated by population analysis and electron density contour maps.

In a paper with the partial title "A clear-cut analysis" it was pointed out that all population analysis for carbonyls is intrinsically unclear because, with the large overlap between metal and CO orbitals, "the assignment of charge to one or the other of these sets of orbitals is quite arbitrary" [25]. One analysis scheme which gives definite energies associated with charge redistribution in bond formation is the CSOV (constrained space orbital variation) method [25]. Starting with metal and ligand charge distributions frozen at values for the isolated components, the energy lowering associated with changing the charge distribution for various types of orbitals (σ, π, metal, ligand) to that in the bound molecule is calculated to determine the energetic importance of various types of interaction. These results have established $d\pi$ interactions as among the most important for Fe, Ni, and Cu interactions with CO [25–28].

In this paper a new criterion is presented for determining the contribution of a particular class or group of orbitals to a chemical bond. The new criterion is the diatomic energy contribution of particular orbitals in a particular bond (any diatomic atom pair) to the total molecular energy. It is a unique feature of NDO (neglect of diatomic overlap) type procedures that the total energy can be divided up entirely into monoatomic and diatomic energy terms [29]. Here this method is applied to determining the contribution of *d* orbitals to the binding energy of CO adsorbed on a cluster of 12 iron atoms.

2. Calculational procedure

The details of the MINDO/SR semi-empirical SCF method used here, as well as its ability to handle a wide variety of compounds including large metal clusters, have been reported previously [30–34]. The MINDO/SR (modified intermediate neglect of differential overlap/SR) procedure is parameterized to give bond energies and lengths for selected reference compounds in agreement with experimental values and explicitly includes electron-electron repulsions. The decomposition of the total energy into monoatomic and diatomic energy terms is used to put the effect of one adsorbate on another on a firm quantitative basis. Specific expressions for this partitioning have been given [29].

The computer program used was obtained by modifying the QCPE Program 290 by Rinaldi with the changes by Schmidling [35] to incorporate MINDO/3. Automatic geometry optimization is done with analytically calculated gradients. The inclusion of transition metals, symmetry [36], and selective molecular orbital filling further enhance MINDO/SR.

Parameters selected to give reasonable properties to FeH, FeO, $Fe(CO)_5$, $HFe(CO)_4^-$, $(CO)_3FeCHO^-$, $CH_3Fe(CO)_4^-$, $(CO)_3FeC(O)CH_3^-$, HFe_{12}, $COFe_{12}$ and OFe_{12} are given in Table 1. The Clementi and Roetti [37] double ξ basis for the Fe 3*d* orbitals and the de Brouckere [38] *d* orbital energy and Slater-Condon parameters are used. Small adjustments in the literature parameter values were made to obtain better agreement between calculated and experimental properties for the above referenced compounds. The *s*, *p* and *d* orbitals all use the same β parameters.

The geometric arrangement of the atoms is shown in Fig. 1. Calculations were done with the Fe cluster atom positions fixed as in the bulk [39] with a nearest neighbor distance of 2.48 Å and a next nearest distance of 2.86 Å. The atoms on the top layer are next nearest neighbors to each other and nearest neighbors to bottom layer atoms. In order to get a cluster large enough to represent several types of binding sites on a Fe(100) plane and small enough that calculations could be done in a reasonable length of time a 12 atom cluster was chosen. A state with multiplicity 39 was found to give the lowest energy. The multiplicity 39 corresponds to a d^7 configuration with 3 unpaired electrons per atom. No magnetic data for small iron clusters are available. The atomic

Table 1. Parameters for iron

a. Orbital exponents [37]

	ξ_1	C_1	ξ_2	C_2
4*s*	1.1[a]	1.0	—	—
4*p*	1.1[a]	1.0	—	—
3*d*	6.06828	0.40379	2.61836	0.71984

b. Core parameters (eV) [38]

W_{ss}	W_{pp}	W_{dd}
−102.13	−74.57	−129.29[a]

c. Slater-Condon parameters (eV) [14]

	(3*d*, 3*d*)	(3*d*, 4*s*)	(3*d*, 4*p*)	(4*s*, 4*s*)	(4*s*. 4*p*)	(4*p*, 4*p*)
F^0	17.72786[a]	13.20528[a]	10.07614	13.02842[a]	9.58363	8.28028
F^2	8.41423		0.67693		2.45289	
F^4	5.10633					
G^1			0.25098		2.20164	
G^2		1.38466				
G^3			0.16581			

d. Bond parameters

Bond	Fe-Fe	Fe-C	Fe-O	Fe-H
β	.273	.729	1.710	.418
α	.382	1.571	3.515	1.517

[a] Value different from reference value

magnetic moment of bulk Fe is 2.22 Bohr magnetrons [40], so a state of such high multiplicity is expected.

An on-top site has an atom or molecule adsorbed directly over atom #7. For CO in an on-top site the Fe(7)–C–O group is linear with the axis perpendicular to the plane of the top layer of atoms.

3. Results and discussion

The published [31] calculational results using MINDO/SR show that the breakdown of the adsorption energy into monoatomic and diatomic terms indicates a complex interaction in which a large Fe-C diatomic energy term of 325 kcal/mole for CO in an on-top site is needed to obtain a net adsorption energy of 23 kcal/mole because of destabilizing the C-O bond and Fe-Fe bonds in Fe_{12} and a destabilization from monoatomic energy terms. The cluster *d* band is shifted by adsorbate-adsorbent charge transfer even though the *d* orbitals overlap only very weakly with the adsorbate. While the interaction of CO with its nearest neighbor dominates the interaction energy, the interaction energy with the other cluster atoms is necessary for a quantitative account of adsorption and can be as large as the net adsorption energy. The binding energies give the increased stability of the adsorption complex Fe_xCO over the sum of the energies for the separated CO and Fe_x cluster. The calculated binding energies, which vary from 14–28 kcal/mole for different surface sites, compare well with the experimental adsorption energies for CO on the Fe(100) face, which vary from 13 to 26 kcal/mole [41, 42]. In the bare Fe_{12} cluster and in all $Fe_{12}CO$ complexes the configuration of all Fe atoms is d^7, i.e., the total *d* orbital population does not change with CO adsorption. In this paper the diatomic energy terms are further broken down into *sp* and *d* contributions. In a future communication the breakdown into σ and π contributions will be given.

The calculational results relevant to considering the Fe-Fe bond in a bare Fe_{12} cluster are given in Table 2. The term $E\mu\mu$ is the attraction of the electronic charge in atomic orbital μ on atom A for the core of atom B. The term $E\mu\nu$ contains the repulsion of the electronic charge in orbital μ on atom A for the electronic charge in orbital ν on atom B and it also contains the attractive resonance term which is usually relatively small. The conclusions that may be drawn from this data to assess the relative contribution of *sp* and *d* orbital interactions are not immediately evident. The bond orders indicate only a small contribution to the bonding by the *d* orbitals. On the other hand the $E\mu\mu$ term for the attraction of electrons in *d* orbitals on one atom for the core of the bonding atom is quite large, thus suggesting a large diatomic energy contribution for the *d* orbital electrons. It is the resolution of this apparent contradiction that takes carful consideration. The real question is not the magnitude of *d* orbital diatomic terms but whether or not the net result of the *d* electron attractive and repulsive terms is a stabilizing effect.

The approach taken here is to obtain the *sp* electron contributions by putting the *d* electrons into the core and obtaining the *d* electron contributions by removing the *sp* electrons and the core charge due to the presence of *sp* electrons. The bond between nearest neighbor atoms 1 and 7 is typical of Fe-Fe bonds and so an analysis for only this bond is presented. The core charge that balances the valence electrons is $+8$. Placing the *d* electrons in the core leaves the *sp* electrons interacting with $+1$ cores. The values for diatomic energy terms considering only the *sp* electrons are in the first column of Table 3. The $E\mu\nu$ term for *sp*-*sp* electron repulsion is unaffected by the core charge so it has the same value in Table 3 as in Table 2. Since the $E\mu\mu$ term is proportional to the core charge and the core charge considering only *sp* electrons is $+1$ instead of the original $+8$, the $E\mu\mu$ (*sp*) term is given by $(1/8)(-2.7730) = -0.3466$ in Table 3, where -2.7730 is the original $E\mu\mu$ (*sp*) term from Table 2. The core repulsion term CR, is proportional to the product of the core charges, originally $8 \times 8 = 64$. For the *sp* only core, CR is proportional to $1 \times 1 = 1$. Thus, taking the original CR of 12.5250 from Table 2, the CR (*sp* only) is given by $(1/64)(12.5250) = 0.1957$ in Table 3.

Table 2. Populations, bond orders, and diatomic energies of atoms 1 and 7 of the bare Fe_{12} cluster

Orbital populations

Fe atom	s	p_x	p_y	p_z	d_z2	d_{xz}	d_{yz}	$d_x2_{-y}2$	d_{xy}	Σsp	Σd
1	0.659	0.077	0.092	0.073	1.055	1.747	1.503	1.197	1.496	0.901	6.998
7	0.659	0.092	0.077	0.073	1.055	1.503	1.747	1.197	1.496	0.901	6.998

Bond order

Atom pair	*sp-sp*	*sp-d*	*d-d*	Total
1-7	0.64	0.01	0.00	0.65

Diatomic energies (atomic units)

Atom pair	$E\mu\mu$		$E\mu\nu$			Core repulsion	Diatomic energy
	sp	*d*	*sp-sp*	*sp-d*	*d-d*		
1-7	−2.7730	−22.3094	0.0761	2.4787	9.9421	12.5250	−0.0605

Table 3. Separate *sp* and *d* diatomic energies (atomic units) for Fe-Fe bond

	sp(only)	*d*(only)	Residual terms		Total
$E\mu\nu$	0.0761	9.9421	*sp-d*	2.4787	12.4969
$E\mu\mu$	−0.3466	−19.5207	*sp*	−2.4264	
			d	−2.7887	−25.0824
CR	+0.1957	9.5895		2.7398	12.5250
net	−0.0748	+0.0109		0.0034	− 0.0605

Similarly, when only the *d* electron contributions are considered the values in the second column of Table 3 are obtained. Again $E\mu\nu$ (*d-d*) is unaffected by core charge so the value from Table 2 is taken directly. The core charge to balance the 7*d* electrons is +7. Thus $E\mu\mu$ (*d*) is given by (7/8)(−22.3094) = 19.5207, where −22.3095 is the total value for $E\mu\mu$ (*d*) given in Table 2. The value of CR (*d* only) becomes [(7 × 7)/64][12.5250] = 9.5895.

The terms in the first two columns of Table 3 do not add up to the total diatomic terms because of *sp-d* cross terms. These are listed in column 3 for residual terms. The $E\mu\nu$ (*sp-d*) term again comes unchanged from Table 2. The $E\mu\mu$ (*sp*) residual is the attraction of the *sp* electrons for the +7 core due to the *d* electrons, i.e. (7/8)(−2.7730) = −2.4264. The $E\mu\mu$ (*d*) residual is the attraction of the *d* electrons for the +1 *sp* core, i.e. (1/8)(−22.4094) = −2.7887. The residual CR is the cross core repulsions, i.e. {[(1 × 7) + (7 × 1)]/64}{12.5250} = 2.7398. The totals in Table 3 now match the totals in Table 2. The residual terms are seen to make only a negligible contribution and so may be ignored in further analysis.

The net diatomic energies in Table 3 indicate that the Fe-Fe bond is due entirely to electrons in *sp* orbitals. The numerical value for the *d* diatomic energy gives a small destabilizing influence, however, this may be zero within the calculational accuracy of the method. These bonding results are in accord with band theory calculations and experimentally measured band widths which give a narrow *d* band superimposed on a *sp* band broadened by bonding interactions.

The calculated properties for CO adsorbed at an on-top site of the Fe_{12} cluster are given in Table 4. The values are all quite reasonable and do not contradict any known experimental facts. In considering the *d* orbitals' contribution to the Fe-C bond, Table 4 shows only 4% of the total bond order is due to the *d* orbitals, which indicates only a small *d* contribution as judged by bond orders. However, in the diatomic energy terms there are large attractive terms due to the *d* orbitals. In terms of diatomic energies, the relative *sp* and *d* contributions will have to be judged on the basis of a careful analysis of the balance of the stabilizing and destabilizing terms of each type.

The contribution of the *sp* orbitals to the Fe–C bond is found by putting the *d* electrons into the Fe core. The diatomic energies for this case are listed in Table 5 under the column labeled *sp*(only). Since there are 7 *d* electrons, this puts the Fe *sp* electrons over a +1 core interacting with the C *sp* electrons over a +4 core. The electron-electron repulsive term plus resonance term, $E\mu\nu(Fe_{sp} - C_{sp})$ is

Table 4. Calculated properties for CO adsorbed on-top Fe_{12}

CO adsorption energy (−22.2 kcal/mole)

Charges (e)

C	O	CO	Fe_{12}	$Fe(7)/Fe_{12}CO$	$Fe(7)/Fe_{12}$
+0.24	−0.59	−0.36	+0.36	−0.02	+0.10

Orbital populations

Atom	s	p_x	p_y	p_z	d_z2	d_{xz}	d_{yz}	$d_x2_{-y}2$	d_{xy}	Σsp	Σd
Fe7	0.531	0.089	0.095	0.309	1.011	1.652	1.743	1.249	1.344	1.024	6.999
C	1.408	0.452	1.113	0.795						3.768	
O	1.849	1.532	1.788	1.423						6.591	

Bond orders

	Total	sp	d
CO (gas phase)	1.99		
CO (on-top Fe_{12})	1.56		
Fe(7)–C	1.10	1.06	0.04

Diatomic energies (atomic units)

$E\mu\mu$

Atom	s	p_x	p_y	p_z	d_z2	d_{xz}	d_{yz}	$d_x2_{-y}2$	d_{xy}	Σsp	Σd
Fe7	−0.4747	−0.0742	−0.0791	−0.2580	−0.9290	−1.5193	−1.6017	−1.1481	−1.2348	−0.8860	−6.4329
C	−2.5159	−0.7894	−1.9411	−1.3864	—	—	—	—	—	−6.6328	—

$E\mu\mu$

CFe	s	p_x	p_y	p_z	d_z2	d_{xz}	d_{yz}	$d_x2_{-y}2$	d_{xy}	Σ $(Fe_{sp}-C_{sp})$	Σ (Fe_d-C_{sp})
s	−0.0479	0.0261	0.0278	−0.2379	0.3164	0.5349	0.5639	0.4042	0.4348	0.2319	0.2542
p_x	0.0524	−0.0045	0.0087	0.0284	0.1028	0.1648	0.1772	0.1270	0.1366	0.0850	0.7084
p_y	0.1288	0.0201	−0.0142	0.0699	0.2528	0.4134	0.4340	0.3123	0.3360	0.2046	1.7485
p_z	0.0625	0.0144	0.0153	0.0303	0.1685	0.2953	0.3113	0.2231	0.2400	0.1225	1.2382
										0.1802	5.9493

Core repulsion CR(Fe–C) = 7.3440; net diatomic energy −0.4782

Table 5. Separate *sp* and *d* diatomic energies (au) for Fe-C bond

	sp(only)		*d*(only)		Total
$E\mu v$	$(Fe_{sp}-C_{sp}$	0.1802	$(Fe_{d}-C_{sp}$	5.9493	6.1295
$E\mu\mu$	$(C_{sp}-Fe_{core})$	−0.8291	$(C_{sp}-Fe_{core})$	−5.8037	−6.6328
	$(Fe_{sp}-C_{core})$	−0.8860	$(Fe_{d}-C_{core})$	−6.4329	−7.3189
CR		0.9180		6.4260	7.3440
Net		−0.6169		0.1387	−0.4782

unaffected by this change and so in Table 5 is unchanged from Table 4. Since the Fe core is changed from +8 to +1 for the *sp*(only) case, the value of $E\mu\mu(C_{sp}\text{-}Fe_{core})$ is given by $(1/8)(-6.6328) = -0.8291$, where −6.6328 is the $E\mu\mu(Csp)$ term from Table 4. Because the C core is unchanged, the $E\mu\mu(Fe_{sp}-C_{core})$ term is unchanged from Table 4. The core repulsion, CR, is proportional to the product of the core charges, 4 × 8, in Table 4, but for the *sp*(only) case is proportional to 1 × 4. Since the core repulsion is 7.3440 in Table 4, it becomes $(4/32)(7.344) = 0.9180$ for the *sp*(only) case in Table 5. The net diatomic stabilizing term in the *sp*(only) case is −0.6169 au.

To obtain the contribution of the *d* orbitals, the interaction of the Fe *d* electrons over their accompanying +7 core with the C_{sp} electrons and carbon +4 core is given in Table 5 under the *d*(only) column. The first term in the *d*(only) column is the electron-electron repulsion (slightly modified by a resonance term), $E\mu v(Fe_{d}-C_{sp})$, which is not affected by the core changes and so is taken unchanged from Table 4. The $E\mu\mu(C_{sp}-Fe_{core})$ term is the attraction of the C *sp* electrons for the Fe core which is now +7 rather than the +8 of the total calculation so that it becomes $(7/8)(-6.6328) = -5.8037$, where −6.6328 comes from Table 4. The $E\mu\mu(Fe_{d}-C_{core})$ attractive term is unchanged from Table 4. The core repulsion, CR, is now between +4 and +7 cores rather than +4 and +8 in the original calculation so CR becomes $(7/8)(7.3440) = 6.4260$. The net *d*(only) diatomic energy is a small destabilizing term of 0.1387 au. The chosen division into *sp* and *d* terms add up to give the total diatomic energy so there are no residual cross terms.

In considering the contribution of the electrons in *d* orbitals to the diatomic energy, the first two terms in the *d*(only) column of Table 5 represent the C *sp* electrons repulsion for the Fe *d* electrons and attraction to the accompanying Fe core to hold those *d* electrons. These two terms are seen to nearly cancel each other. The next two terms represent the C core attraction to the *d* electrons and repulsion for the Fe core due to the *d* electrons. Again these terms nearly cancel out. The *sp* electrons are seen to create the stabilizing diatomic energy which makes the Fe–C bond while the *d* electrons have a small destabilizing influence.

A possible concern about the contribution of *d* orbitals is the effect of the monatomic energies for the *d* orbitals. In examining this effect the sum of the changes in monatomic energy (as the adsorption bond is formed) due to *d* electrons on the Fe atom directly bonded to CO for on top adsorption between the bare cluster and the adsorption complex was +0.1221 au. This is small

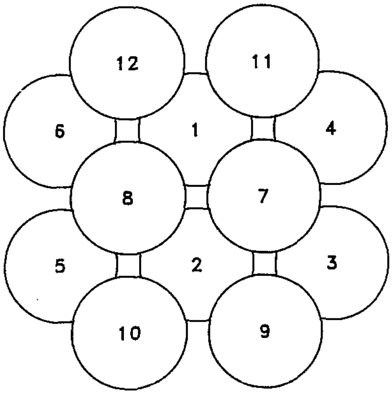

Fig. 1. Top view of Fe_{12} cluster

compared to the net *sp* diatomic energy given in Table 5 so it is concluded that the monatomic energy changes do not greatly affect conclusions about the importance of *d* orbitals.

The low bond orders for *d* orbitals in Fe-Fe bonds of Fe_{12} and for Tables 2 and 4 are in accord with the low contribution of *d* orbitals judged by the criterion of diatomic energies. The low *d* bond orders are a consequence of the *d* orbital basis set used giving little overlap with adjacent Fe orbitals and with ligand orbitals. The legitimacy of this basis set rests on it being a standard basis set from the literature. A more expanded *d* orbital basis set would be expected to place charge density in the same place but label it metal *d* rather than metal *p*. Thus there is a degree of arbitrariness in labeling orbital contributions. Questions about the validity of population analysis for transition metal compounds have been raised previously [25], but in that case the objection to population analysis was because of large overlap of metal and ligand orbitals allowing charge to be assigned arbitrarily to either metal or ligand orbitals. Here that objection does not occur because the overlap of our *d* orbitals is low. The concept of bond order was developed from experience with *sp* orbital bonding in first and second row elements where it has proven to be very useful. Continued experience with transition metal bonding is necessary to indicate if bond order is as useful a concept for *d* orbitals as it has been for cases using only *sp* orbitals.

Calculations have also been done for CO at two fold and four fold sites on the Fe_{12} cluster. As the number of Fe atoms bonding to the carbon atom are increased, the Fe-C equilibrium bond length increases. With this increased bond length, the *d* orbital overlap with carbon orbitals decreases and the *d* electron diatomic energies become less significant.

Since the diatomic energies do not indicate a major direct contribution to bond energies by electrons in *d* orbitals, the question of the role in chemisorption of *d* orbitals, which transition metal catalysis indicates is important, is raised. The *d* orbitals do furnish a mechanism for charge transfer even though the net *d* orbital population stays constant. The results of CSOV calculations referred to earlier indicate the necessity for charge rearrangement to form a stable chemisorbed CO molecule. While in the calculations here for the relatively small

Fe_{12} cluster the *d* orbital population remained constant, for an extended metal surface with a high density of *d* states at the Fermi level, the *d* band could more readily serve as a charge reservoir as needed.

The results here have been obtained with the semi-empirical MINDO/SR procedure which is parameterized to give correct overall energies and bond lengths. Although the general procedure has been to replace some integrals in a standard SCF claculation with empirical parameters, there have been no energy decompositions of *ab initio* SCF calculations against which the energy decomposition in this semi-empirical calculation could be tested. While there is no reason to believe that large terms such as $E\mu\mu$ would not correspond to those in a more exact calculation, it would be useful to have such a comparison.

4. Summary

In summary, the determination of atomic orbital populations in bonding molecular orbitals, drawing electron density contour maps, and calculating Mulliken bond orders all provide a qualitative picture of chemical bonding with which one can try to understand the relative contribution of various types of orbitals. The CSOV procedure gives the energy changes as charge redistribution occurs during bond formation. Here the ability of neglect of differential overlap methods to decompose the total energy entirely into monatomic and diatomic energy terms has been utilized to calculate the contribution of electrons in *d* orbitals to the diatomic energy terms which are responsible for holding a molecule together. This direct measure of the *d* electrons' contribution to the total energy in the molecule indicates that the *d* orbitals make only a small contribution to the binding energy for CO adsorbed on a 12 atom iron cluster.

Acknowledgements. Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society for partial support of this research and to the University of Arkansas for a computing time grant.

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