

Charge decomposition analysis of the chemisorption bond

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Abstract

Charge decomposition analysis (CDA) has been applied to study the interaction of CO and NH₃ on several metal surfaces. For NH₃ chemisorption, CDA predicts a large donation from the NH₃ lone pair to the surface and a vanishing contribution for the backdonation. However, for CO chemisorption, CDA predicts the σ -donation to be larger than the π -backdonation, contrary to other methods. CDA overestimates the extent of the σ -donation because of its large overlap with the metal orbitals compared with the overlap of the π orbitals. The same situation is found in Ni(CO)₄. Therefore, the CDA method should only be applied to the investigation trends. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Charge decomposition analysis (CDA) is a partitioning scheme to analyse donor–acceptor interactions. It was developed by Dapprich and Frenking [1] as a quantitative expression of the well-known Dewar–Chatt–Duncanson (DCD) model [2,3] which describes the metal–ligand interactions in terms of donation and backdonation chemical mechanisms. In the CDA method the molecular orbitals, either Hartree–Fock or Kohn–Sham, of a given donor–acceptor complex (AB) are transformed to the non-orthogonal basis provided by the superposition of the orbitals of A and B. In practice the molecular orbitals of A, B and AB are all obtained in the same basis set of contracted Gaussian-type functions so that expressing those of AB in terms of the superposition of orbitals of A and B requires only a change

of the basis set. In the new basis set it is possible to write the total density in terms of the overlap matrix between the orbitals of the A and B units, hereafter denoted as S^{AB} , and decompose the occupation of each orbital, typically 2 or 0 (except when the natural orbitals of an explicitly correlated wavefunction are used), of the complex into the contributions due to A or B or to the charge transfer between A and B, cf. Ref. [1]. This interesting yet simple idea permits the extent of donation or backdonation contributions in the DCD theoretical model for metal–ligand interactions to be quantified. The CDA method has proven to be very useful for estimating the *relative* strength of charge donation and backdonation in a series of transition metal–carbonyl complexes [4,5].

In the case where an adsorbate interacts with a metal surface, it has been proposed that the DCD model can be invoked in order to explain some special features, such as the red-shift of CO chemisorbed on transition metal surfaces. The extension of the DCD to metal surfaces was first sug-

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gested by Blyholder [6]. However, it has been recently shown that, contrary to the assumption of the Blyholder model, the σ -donation also contributes to the red-shift of CO chemisorbed on low index platinum surfaces [7,8]. This analysis of the interaction of CO with platinum surfaces follows the previous work of Bagus and co-workers [9–12]. These authors studied in detail several aspects of the adsorbate–surface interaction by means of another partition technique, named constrained space orbital variation (CSOV) method [13]. This is an energy decomposition analysis similar in spirit to the energy partition introduced earlier by Morokuma [14,15], but that avoids the double counting of the interactions inherent to this first decomposition method. The first applications of the CSOV decomposition were devoted to the analysis of the chemisorption bond [16], but it has also been applied to metal–ligand interactions [17] and to problems in solid state physics [18]. Nevertheless, the main field of application of CSOV still concerns chemisorption and related properties [16]. The CSOV technique is similar in spirit to CDA described above, but the partition is carried out in terms of variationally obtained energy contributions rather than in terms of charge contributions. It has been pointed out before, that the energy contributions of the σ and π interactions may not have the same ratio as the changes in σ and π orbitals [4]. We were interested in the relative size of the energy and charge contributions to the chemisorption bond of CO on a metal surface. This Letter is devoted to the study of the performance of the CDA method in describing the different contributions to the chemisorption bond. To this end several model systems involving different adsorbates – CO and NH_3 – and different transition metal surfaces – Cu(100), Ag(100), Pd(100) and Pt(111) – are chosen. The chemisorption bond is analysed by means of the CDA method and results compared to those arising from the CSOV analysis, complemented with the use of the projection operator techniques.

2. Model systems and computational details

The Cu(100), Ag(100), Pd(100) and Pt(111) surfaces were represented by finite $\text{Cu}_{14}(5, 4, 5)$, $\text{Ag}_{14}(5, 4, 5)$, $\text{Pd}_2(2, 0, 0)$ and $\text{Pt}_{13}(7, 3, 3)$ cluster

models, where the numbers in parentheses indicate the number of atoms in each layer. These cluster models correspond to sections of the bulk crystal and are constructed in such a way that the bulk geometry, i.e. distances and angles, is always preserved. Chemisorption of CO and NH_3 above these surfaces was modelled by placing the adsorbate at a geometry close to the one determined by experiment [19,20] or by previous calculations [21,22]. In the case of CO on Ag_{14} , the geometry of chemisorbed CO was that corresponding to CO on Cu(100) because of the lack of previous information. All cases correspond to a surface interaction with the adsorbate above an on-top surface site, except for the interaction of CO on Pd_2 , where the model used simulates interaction at a bridge site [22]. For the purposes of the present work, which analyses the chemisorption bond by means of the CDA method, the choice of a given geometry is not determinant provided it is reasonably close to the equilibrium. A summary of all geometrical parameters used in the calculations is reported in Table 1.

CDA of the chemisorption bond was carried out for electron densities obtained from ab initio calculations using either the Hartree–Fock method or the hybrid B3LYP [23,24]. Density functional theory (DFT) based approach which combines the single determinant Hartree–Fock exchange and Becke's gradient corrected (GC) exchange functional together with the GC correlation functional of Lee, Yang, and Parr [25] using three parameters obtained from a fitting in order to best reproduce the thermochemical energies for a wide set of organic molecules. The cluster metal atoms were treated differently, depending on whether they are directly involved in the interaction with the adsorbate or they represent environmental atoms. For the atoms directly interacting with the adsorbate a small core relativistic pseudopotential together with the standard LANL2DZ basis – [8s5p5d/3s3p2d] for Cu; [8s6p4d/3s3p2d] for Ag and Pd; [8s6p3d/3s3p2d] for Pt – was used, whereas for the remaining cluster atoms a larger core, leaving one valence electron, was utilised. The Cu and Ag one-electron pseudopotentials and basis sets – [4s3p/2s2p] for Cu and [3s3p/2s1p] for Ag – are those previously used by Bagus and co-workers [12], whereas that corresponding to Pt has been taken from Ref. [26] and its basis set is of [5s3p/2s1p]

Table 1

Summary of geometrical parameters used in the surface model calculations

Distances are in Å and angles in degrees. For CO the angle is M–C–O (except for CO on Pd₂ where an angle of 180° means CO is perpendicular to Pd₂) while for NH₃ it is the M–N–H one. The M–C and M–N distances refer to the nearest metal–carbon and metal–nitrogen distances

System	<i>d</i> (metal–metal)	<i>d</i> (M–C)	<i>d</i> (C–O)	Angle
Cu ₁₄ –CO	2.556	1.900	1.148	180
Ag ₁₄ –CO	2.883	1.900	1.148	180
Pd ₂ –CO	2.750	1.930	1.130	180
Pt ₁₃ –CO	2.775	1.900	1.148	180
	<i>d</i> (metal–metal)	<i>d</i> (M–N)	<i>d</i> (N–H)	Angle
Cu ₁₄ –NH ₃	2.556	2.275	1.003	107.2
Pt ₁₃ –NH ₃	2.775	2.164	1.016	108.6

quality. The basis set for CO is that previously used by Bagus and co-workers [12], a 4s3p non-segmented contraction of the Dunning 9s5p primitive set, and, finally, the basis set for ammonia is the standard 6-31G** previously used in Ref. [21].

The Hartree–Fock and B3LYP calculations were carried out using the GAUSSIAN-94 [27] and HONDO8.5 [28] computer codes implemented in several workstations. CDA was performed using the CDA 2.1 version of the code downloaded directly from the web [29]. Because of the rather unexpected results from CDA, the systems described above were also analysed with the CSOV method [13–15] and with the orbital projection techniques [30], as implemented in HONDO8.5.

3. Results and discussion

In the systems described above, the chemisorption bond can be understood quite easily from chemical intuition. In addition, some of the systems have previously been analysed in detail, at the Hartree–Fock level of theory, by means of the CSOV technique. The picture expected from both points of view is, because Cu, Ag and Pd are essentially d¹⁰ systems, that the interaction of the CO 5σ orbital with the metal d orbitals will be repulsive and that the only possible contribution will come from the delocalization of this orbital in the metal conduction band. However, this delocalization is energetically quite unfavourable because CO tends to maintain its molecular character. Therefore, the main contribu-

tion to the bonding of CO with the corresponding metal surfaces will be the backdonation from the d_π orbitals of the atom directly interacting with CO via the 2π* orbitals, and that the donation from the CO 5σ orbital should be much less important than the backdonation contribution [13]. It is worth pointing out here that earlier analysis of the interaction of CO with small Cu clusters by Post and Baerends, using rather small cluster models and the Xα method, points out a larger importance of the σ-donation contribution [31]. Recent work indicates that it is likely that this result arises from an overestimation of delocalization effects in the Xα method, rather than from a different picture in Hartree–Fock and DFT based methods [32]. In the case of the Pt surfaces, one would also expect a larger contribution from the σ-donation to the metal d orbitals because the configuration of Pt in the bulk is essentially d⁹s¹ [7,8,33]. Likewise, one can assume that the interaction of NH₃ with a metal surface will result essentially from the donation of the NH₃ lone pair to the metal conduction band with little (or no) contribution from π-backdonation [13].

For the case of NH₃ on metal surfaces, CDA is in agreement with chemical intuition and with the previous CSOV analysis. However, for the case of CO on metal surfaces CDA suggests that, except for CO on Pt₁₃, the interaction is dominated by σ-donation rather than from π-backdonation. The results of CDA of the Hartree–Fock and B3LYP electron densities are summarised in Tables 2 and 3, respectively. The CDA data are quite surprising because Cu, Ag and Pd have a d¹⁰ electronic configuration and,

Table 2

Relative contributions to the chemisorption bond obtained from CDA of Hartree–Fock wavefunctions
Values in **bold** stand for the largest contribution

System	Donation	Backdonation	Repulsion	Residual
Cu ₁₄ –CO	0.443	0.219	–0.336	0.016
Ag ₁₄ –CO	0.441	0.294	–0.424	0.014
Pd ₂ –CO	0.523	0.372	–0.274	0.012
Pt ₁₃ –CO	0.191	0.451	–0.431	0.033
Cu ₁₄ –NH ₃	0.201	–0.023	–0.188	0.000
Pt ₁₃ –NH ₃	0.191	–0.003	–0.323	0.008

hence, do not favour σ -donation interaction. Therefore, the results in Tables 2 and 3 may indicate that either the above chemical arguments do not provide a reliable description for the chemisorption bond, or that CDA is not adequate to interpret this particular chemical interaction.

In order to clarify the question about the importance of σ -donation and π -backdonation, we have further analysed the nature of the chemisorption bond in these systems by using the CSOV method and also a projection technique [30]. In the CSOV method each contribution to the bond is obtained from a variational calculation [13], rather than by decomposing the final density. The CSOV method has traditionally been applied to decomposition of Hartree–Fock energies but it has recently been applied to DFT based chemisorption cluster model calculations [32]. In the projection technique one computes the expectation value of the $\varphi\varphi +$ operator, $P_\varphi = \langle \Psi | \varphi\varphi + | \Psi \rangle$, on the wavefunction of the AB supersystem, φ being a given MO (Hartree–Fock

or Kohn–Sham) of a fragment and $|\Psi\rangle$ the Hartree–Fock wavefunction or the Kohn–Sham determinant used to obtain the B3LYP density. In the present cases we have chosen either the 5σ and $2\pi^*$ orbitals of CO or the $3a_1$ molecular orbital from NH₃ to carry out the projection. In the case of analysing the Hartree–Fock wavefunction, the molecular orbitals of A are obtained from a Hartree–Fock calculation of A at the same geometry A has in AB. Similarly, A and AB Kohn–Sham orbitals are used when the B3LYP density is analysed. The donation and backdonation contributions to the total energy obtained with the CSOV method, and by application of the projection operators, are displayed in Table 4 (Hartree–Fock calculations) and Table 5 (B3LYP calculations). In the CSOV analysis, the contribution to either donation or backdonation is given by the difference of two variational steps. In the projection technique, the precise value for the contribution to the donation is $2P_\varphi$, whereas the backdonation is directly given by P_φ . Results

Table 3

Relative contributions to the chemisorption bond obtained from CDA of Kohn–Sham orbitals obtained from the hybrid B3LYP density functional theory based method

Values in **bold** stand for the largest contribution

System	Donation	Backdonation	Repulsion	Residual
Cu ₁₄ –CO	0.558	0.345	–0.274	0.016
Ag ₁₄ –CO	0.559	0.392	–0.361	0.014
Pd ₂ –CO	0.493	0.438	–0.123	0.033
Pt ₁₃ –CO	0.261	0.508	–0.389	0.022
Cu ₁₄ –NH ₃	0.319	–0.013	–0.206	–0.008
Pt ₁₃ –NH ₃	0.296	0.019	–0.277	0.009

Table 4

Magnitude of donation and back donation as measured from the CSOV decomposition, energy decrements in eV, and from the expectation value of the projection operator of the 5σ and $2\pi^*$ molecular orbitals of CO and the $3a_1$ of NH_3

Notice that in the projection technique the extent of donation is measured as $2\text{-}P(\text{orb})$, while back donation is directly given by $P(\text{orb})$. Both methods are applied to Hartree–Fock wavefunctions. Values in **bold** stand for the largest contribution.

System	CSOV		Projection	
	Donation	Backdonation	Donation	Backdonation
$\text{Cu}_{14}\text{-CO}$	−0.431	− 0.760	0.21	0.51
$\text{Ag}_{14}\text{-CO}$	−0.557	− 0.917	0.28	0.50
$\text{Pd}_2\text{-CO}$	−0.886	− 2.205	0.33	0.49
$\text{Pt}_{13}\text{-CO}$	−0.951	− 1.399	0.38	0.57
$\text{Cu}_{14}\text{-NH}_3$	− 0.230	−0.053	0.08	0.00
$\text{Pt}_{13}\text{-NH}_3$	− 0.522	−0.136	0.18	0.00

from both partitioning methods, CSOV and orbital projections, in Tables 4 and 5 clearly show that for the interaction of CO on all metal surfaces, the π -backdonation contribution is always considerably larger than the σ -donation. This holds for the energy contributions given by the CSOV method, as well as the charge interactions given by the projection technique. Thus, the results of the CSOV and projection methods for NH_3 on Cu and Pt surfaces agree with each other and, in this case, are consistent with the CDA data. In the case of the CO interactions with the metals, however, the CDA results are at variance with the other two methods. This indicates that the CDA picture of the interaction of CO with Cu, Ag and Pd model surfaces must be regarded with caution.

At this point it is worth pointing out that even in transition metal complexes, the CDA σ -donation

contribution appears to be more important than the one found by other methods of analysis. In the case of $\text{Ni}(\text{CO})_4$ and other metal carbonyls, Ehlers and co-workers [34] found that the σ -donation is considerably larger than the π -backdonation which contradicts an earlier analysis of the bond based on $X\alpha$ calculations [35] and with ab initio Hartree–Fock calculations by Bauschlicher and Bagus [17]. Bauschlicher and Bagus used different methods of wavefunction, including the CSOV method. The CSOV analysis unequivocally shows that the chemical bond in $\text{Ni}(\text{CO})_4$ arises essentially from the π -backdonation mechanism, in clear contrast with the picture based on orbital populations. In addition, Bauschlicher and Bagus have shown that when the metal basis set does not contain the 4s and 4p functions, the total energy is almost unchanged, but the σ -donation contribution nearly disappears. The

Table 5

Same as Table 4 but CSOV and projection methods are here applied to Kohn–Sham orbitals obtained from the hybrid B3LYP density functional theory based method

Values in **bold** stand for the largest contribution.

System	CSOV		Projection	
	Donation	Backdonation	Donation	Backdonation
$\text{Cu}_{14}\text{-CO}$	−0.590	− 1.167	0.27	0.71
$\text{Ag}_{14}\text{-CO}$	−0.711	− 1.305	0.33	0.68
$\text{Pd}_2\text{-CO}$	−1.261	− 2.918	0.45	0.72
$\text{Pt}_{13}\text{-CO}$	−1.188	− 1.737	0.43	0.67
$\text{Cu}_{14}\text{-NH}_3$	− 0.427	−0.046	0.12	0.00
$\text{Pt}_{13}\text{-NH}_3$	− 0.798	−0.144	0.23	0.00

excessive importance of σ -donation comes from the very large overlap between the CO 5σ orbital and the metal atomic orbitals, in the case of a carbonyl complex, or the surface conduction band orbitals, in the case of a metal surface. This overlap is, of course, responsible for the misleading results predicted by Mulliken populations analysis [17]. The projection operator technique used in this work is less sensitive to the overlap, and indicates that the importance of σ -donation is smaller than suggested by CDA.

We carried out additional calculations in order to clarify the strange CDA results concerning the relative size of σ -donation and π -backdonation in $\text{Ni}(\text{CO})_4$. To this end we calculated the atomic partial charge at the Ni atom given by the NBO method [36] at the B3LYP level, using the standard basis set II [34]. The results were compared with the results of a CDA calculation. The NBO method gave a positive partial charge of +0.333 e for the nickel atom. The CDA calculations predicted a $\text{OC} \rightarrow \text{Ni}(\text{CO})_3$ σ -donation of 0.439 e. The $\text{OC} \leftarrow \text{Ni}(\text{CO})_3$ π -backdonation was only 0.201 e. The results clearly show that the CDA method overestimates the extent of σ -donation relative to π -backdonation.

Systematic studies have shown that CDA is able to give a proper description of the *trend* of the σ -donation and π -backdonation along several series of complexes [4,5]. However, the results above suggest that the CDA method should not be employed to analyze the relative size of σ -donation and π -backdonation for a given compound. It is worth pointing out that a recent comparison of charge and energy decompositions in metal–carbonyl complexes [37] does also find that the importance of σ -donation and π -backdonation is different, depending on whether the energy or the charge is decomposed. The different contributions to the chemical bond are not physical observables and it possible to claim that the differences in the methods of analysis arise from different arbitrary partitioning. However, it is very important that the different methods of analysis produce a consistent picture of the chemical bond. The results presented here demonstrate that the CDA method may be used for the chemisorption bond as well as for molecular interactions. However, in both cases it holds that the CDA results should only be used to investigate the trends in the σ -donation and

π -backdonation along a series of ligands or metals, but not for the absolute values.

4. Conclusions

The charge decomposition analysis method has been applied to the study of the interaction of CO with Cu(100), Ag(100), Pd(100) and Pt(111) and of NH_3 with Cu(100) and Pt(111) surface cluster models. For the interaction of NH_3 with the Cu(100) and Pt(111) surface cluster models, the picture arising from the different methods of analysis – CDA, CSOV or projections – is the same, all methods predict the donation from the NH_3 lone pair as the largest contribution and give a vanishing contribution for the backdonation. However, for the interaction of CO on three of these metal surfaces – Cu(100), Ag(100) and Pd(100) – the CDA method predicts the σ -donation to be more important than the π -backdonation. This is contrary to chemical intuition and to the analysis of the chemisorption bond resulting from the CSOV energy decomposition method and from the use of projection operators. The inadequacy of CDA to properly describe the interaction of CO with a transition metal surface is related to the very large overlap of the CO 5σ orbital and the metal conduction band. The same failure of the CDA method was found for the metal–ligand interactions in $\text{Ni}(\text{CO})_4$. Consequently, the application of CDA to chemisorption problems has to be carried out with extreme care, focussing on trends along a series, and not on the particular ratio of different bonding mechanisms in a given compound.

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