

Charge displacement analysis: A new general method to estimate atomic charges in molecules and clusters

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Abstract

A new method, termed CDA, for charge distribution analysis, to estimate net charges of atoms in molecules or clusters is proposed. The method is based on well defined physical quantities and avoids many of the shortcomings of the Mulliken population analysis while keeping the idea that charge or electronic density on atoms is defined through their basis functions. Several examples, including the CH₄ molecule, bulk MnO and chemisorption of O and CN on Cu(100), are presented.

Keywords: Charge displacement analysis; Atomic charges; Methane; Manganese oxide; Chemisorption; Copper

1. Introduction

Understanding chemical reactivity in general and the mechanisms of heterogeneous catalysis in particular is one of the main goals of modern theoretical chemistry. In pursuing this objective, a very useful concept is that of net atomic charges on molecular or model systems. Atomic charges are related to basic chemical concepts such as electronegativity, nucleophilic or electrophilic reactions, and reactivity indexes. Mulliken population analysis and several closely related variant methods have been, and remain today, widely used as the most common approach to assign charges on atoms and determine bonding character, using the gross charges

and the decomposition of molecular orbitals into atomic components. It is accepted that, except for pathologic cases, these procedures lead to reliable qualitative data. However, it has also been shown that, especially in compounds containing transition metal atoms, the Mulliken analyses may fail seriously. There are several examples of standard molecular calculations which result in atomic charges contrary to the conclusions of more sophisticated studies, and even contrary to chemical intuition. These include: the study of the ionicity of bulk NiO by Chang et al. [1], the study of Ni(CO)₄ by Spangler et al. [2], and the study of the AlCO molecule by Bauschlicher and Bagus [3]. All these examples have been recently reviewed by Bagus et al. [4], showing that, in all cases, a feature responsible for the unrealistic results are the large orbital overlaps. In this case, the arbi-

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trary equal division of the overlap population introduces large uncertainties and makes the gross populations meaningless. Thus, the Mulliken analysis is strongly basis set dependent; it gives more reliable results for minimal basis sets, for which it was initially proposed. However, assigning net charges to the atoms in a molecule or in a model system is so useful that Mulliken analysis is nowadays broadly used albeit without the necessary care to avoid artifacts arising, especially with large basis sets routinely used in the every day research work.

Several approaches have been proposed to avoid the problems associated to the Mulliken analysis. Many of these methods are based on numerical integration of the electron density on space regions associated to atoms [5,6]. Other methods try to derive atomic charges from the molecular electrostatic potential maps [7]. All these methods involve rather intricate computations and will not be further discussed here. A different estimate of the net charge of atoms in molecules, which is not basis set dependent, has fewer artefacts, and which keeps a level of computational simplicity similar to Mulliken analysis, was introduced by Nelin et al. [8]. This procedure makes use of orbitals projections and has been used extensively as an alternative to Mulliken analyses to study the ionicity of bulk metal oxides [4,9,10] and of adsorbates in chemisorption cluster model calculations [11–20]. However this method is not free of problems because if the overlap between different fragments is considerable the method is only able to give bounds to the ionicity. Another different procedure to obtain approximate charges is based on the analysis of dipole moment curves [8]. It has been shown that the slope of the dipole moment curve for small displacements of an atom around its equilibrium position is a measure of the ionicity of a bond. The basic idea is very simple: for an ideal ionic molecule A^+B^- the slope of the dipole moment curve must be 1 and its curvature 0. This method has been extensively used to characterize the nature of the bond in chemisorption of atoms

[11–13] or molecules [14,16] on metals, oxides [17] and semiconductor surfaces [18,20]. However, this simplified model does not include the effects of the polarization of each fragment due to the presence of the other. In general, this effect decreases the absolute magnitude of the dipole moment. This is the reason why the value of the dipole moment is not a good measure of the ionicity, whereas the slope of the dipole moment curve can give a better estimate of the bond ionicity. Unfortunately, even the slope of the curve is subjected to uncertainties arising from the intra-unit polarization. For a dominantly ionic bond, the intra-unit polarization effect on the dipole moment curve can be taken into account by substituting one of the subunits by a point charge. From the comparison between the real and the model system a more precise estimate of the net charge can be obtained.

In this paper we will present a new method to assign charges on atoms in a molecule or a cluster representation of a surface or a bulk solid. As we will show, the method makes use of the atomic basis functions to define atoms, as in the Mulliken population analysis, but avoids the overlap problems and is much less basis set dependent. The method takes also advantage of the analysis of dipole moment curves but avoids the problem associated with intra-unit polarization. Illustrative examples concerning systems relevant to surface science and heterogeneous catalysis will also be presented.

2. Theoretical details

First, we assume that the net charge on atoms in a molecular system is associated with their basis set; this is like in the Mulliken population analysis. Consider displacement of an atom, and its basis set, from its equilibrium position like in the study of dipole moment curves but with the molecular orbitals fixed at those of the equilibrium; the only change allowed in the MO's is that arising from orthogonality because the

overlap matrix changes with the geometry change. Using these orthogonalized frozen MO's the resulting dipole moment is computed for several small displacements and expanded in a Taylor series around the equilibrium distance:

$$\mu_{\text{CDA}}(x) = M_0 + M_1(\Delta x) + M_2(\Delta x)^2 + \dots \quad (1)$$

where x indicates the direction of movement of the atom. As in the analysis of the dipole moment curves described above, M_1 gives a reliable measure of effective charge but now intraunit polarization is explicitly excluded because the MO's are fixed. The method appears to be simple and clean as will be shown later on several examples. Moreover, the CDA analysis can also be applied to individual orbitals or to groups of orbitals to obtain a measure of their occupation using the expression

$$\langle \phi_i | x | \phi_i \rangle = \langle x \rangle + M_1(\Delta x) + \dots \quad (2)$$

where M_1 is associated with the charge on ϕ_i .

We have to point out that CDA and Mulliken population analysis, MPA, are very similar in spirit. In fact, both of them are based on atom centered basis functions, the main difference appearing in the two center effects. In the MPA the $2C_i C_j \langle \chi_i^A | \chi_j^B \rangle$ overlap terms which represent the population shared by the orbitals χ_i^A and χ_j^B are arbitrarily assigned equally to $Q(A)$ and $Q(B)$, while in CDA, the overlap terms $2C_i C_j \langle \chi_i^A | x | \chi_j^B \rangle$ contributes to the total dipole moment without an arbitrary assignment.

Finally, we note that the CDA method is not free of artifacts arising from BSSE or from the orthogonalization of the molecular orbitals. However, these artifacts appear to be small. On the other hand, limitations due to the use of orthogonal orbitals may reflect real limitations in assigning very defined values to net charges. In the next section we will apply the CDA analysis to few selected test cases to illustrate the method, showing its capabilities and possible limitations.

3. Selected examples

3.1. Methane molecule

This is a rather simple case, useful to illustrate differences between the MPA and CDA analysis. For this molecule we use two different basis sets; Set A is C(6s, 4p)/H(4s, 2p) and set B C(4s, 3p)/H(4s, 1p). The MPA gives values of -0.07 for H (set A) and $+0.09$ (set B) but the overlap populations are $0.77e$ and $0.80e$ or about five times larger than the net charge, thus indicating that the MPA charge should not be trusted. To apply the CDA method we have displaced an H atom along the three-fold axis connecting C and this H (axis Z). We have also considered motions along X and Y, X being parallel to one of the legs of the equilateral triangle formed by the other three H atoms; the Y axis passes through the H atom and the apex opposite to this leg. Results are collected in Table 1. It is seen that for the larger basis sets the effective charge on H is estimated as -0.17 for the Z movement and -0.06 for the motion perpendicular to the bond; furthermore, the motion perpendicular to the bond does not have the curvature found for the motion along Z. Thus, it appears that the motion of H along X or Y has fewer artifacts and the X or Y results should be considered more reliable. The CDA results indicate that C–H is almost an ideal covalent bond with very little charge displacement towards H

Table 1
Results of the CDA analysis for CH₄

| Basis and axis | M_0 | M_1 | M_2 |
|----------------|-------|--------|--------|
| C(6/4)/H(4/2) | | | |
| Z | 0.0 | -0.168 | -0.125 |
| X | 0.0 | -0.063 | 0.0 |
| Y | 0.0 | -0.063 | 0.0 |
| C(4/3)/H(4/1) | | | |
| Z | 0.0 | -0.011 | -0.008 |
| X | 0.0 | +0.062 | 0.0 |
| Y | 0.0 | +0.062 | 0.0 |

M_0 , M_1 and M_2 are as defined in Eq. (1); the definition of coordinates is given in the text.

and that H is essentially neutral. We must remark that the overlap between the SCF wave functions with basis A and B is almost 1, indicating that both lead to the same physical description. Thus, the overall conclusion is that $Q(\text{H})$ is in the 0.0 ± 0.06 interval.

3.2. Ionic character of bulk MnO

The second example of application of the CDA method concerns the ionicity of MnO. Use of orbital projections shows that MnO is dominantly ionic while involving a small amount of covalent bonding between the metal 3d and the O 2p orbitals [4]. We will now apply the CDA to MnO and compare the results with the results in [4]. The cluster model we use is $[\text{MnO}_6]^{10-}$ embedded in a set of point charges, PC's, whose values have been optimized to reproduce, in the cluster region, the Madelung potential of a perfect ionic crystal with +2 cations and -2 anions (See Fig. 1). Further information about details of the calculations may be found in [21,22]. In an O_h symmetry point group, the electronic configuration of this cluster is (cores) $t_{2g}^6 e_g^4 t_{2g}^3 e_g^2$, where $t_{2g}^3 e_g^2$ are dominantly Mn 3d orbitals. The MPA gives occupations for the e_g^2 subsystem of 2.15, which gives an idea of covalent character and for the t_{2g}^3 subsystem the MPA occupation is 2.80, which is less than the expected value of 3. Further, the total charge on Mn^{2+} is +1.50,

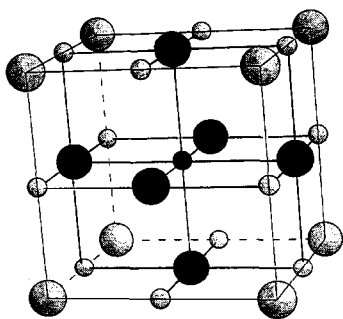


Fig. 1. Schematic representation of the $[\text{MO}_6]$ cluster model used to represent bulk MnO. The one Mn atom and the six O atoms explicitly included in the cluster are shown with dark shadings.

rather far from the expected value of $\approx +2$. A detailed analysis of the partial occupations shows that the overlap population for t_{2g}^3 is -0.56 while the net charge is 3.08. As shown in [4], negative overlap populations are consistent with anti-bonding interactions and, therefore, the arbitrary division of the overlap population introduces large uncertainties in the MPA charges.

As explained in the previous section for CH_4 we have displaced the Mn atom in two ways with respect to the O atoms; one displacement involves moving the Mn atom directly towards one of the six equivalent O atoms while the other displacement involves moving the Mn atom towards the center of two O atoms. For both displacements, the slope of the CDA curves were 2.00, to be compared with a value of 1.9 from the projection analysis. The contributions of the 3d Mn orbitals were found to be 3.01 for the t_{2g}^3 and 1.93 for the e_g^2 , which compares very well with 2.96 and 1.92, respectively, as obtained by means of the orbital projection operator technique. The total populations for the 3d shell and the subtotals for t_{2g}^3 and e_g^2 are extremely close to their nominal values of 5, 3, and 2, respectively, for an ideal ionic crystal. The small deviations can be due to a very small covalent contribution, which is slightly larger for the e_g symmetry. Considering that the t_{2g} orbitals are not directed towards the O atoms, this is an expected result. These analyses are fully consistent with the dipole moment curves which show a nearly perfect linear behavior, thus indicating a high ionicity. However, the value for the slope of the SCF dipole moment curve is far from being -2. This is because the motion of the electronic charge due to the change of the separation of the subunits is opposed to the change in μ due to the motion of the nuclei. This is a strong limitation of the simple dipole moment analysis which is overcome by the CDA. It may be argued that imposing +2 and -2 point charges around the cluster could force the high ionic character. As a test case, we have removed the point charges and considered an

isolated, or 'in vacuo', $[\text{MnO}_6]^{10-}$ cluster model. This is an ideal case for CDA because it is very difficult to treat the highly polarizable free O^{2-} . The CDA curve obtained is now $\mu_{\text{CDA}}(x) = 2.22x - 0.24x^2$ and the populations of the e_g^2 and t_{2g}^3 do not change. These results show that the ionicity does not depend critically on the environment, because the charge on the metal atom does not decrease. However, the charge cannot be greater than 2 and the curve is not linear. This is a limitation of the CDA, which can be due to the orthogonalization of diffuse $\text{O}(2p)$ orbitals to Mn 3s and 3p.

Another different possible test of CDA is the comparison of the ionicity of a bulk Mn atom versus that of a surface one. Here, such a comparison has been carried out by means of the $[\text{MnO}_5]^{8-}$ cluster which simulates a surface cation in its environment. Again, we have moved the Mn atom and the slope of the CDA dipole moment curve is now 1.95. This result shows that the MnO oxide is essentially fully ionic at both surface and bulk.

3.3. Chemisorption of O on Cu(100)

The chemisorption of atomic oxygen on the Cu(100) surface has been widely examined from a theoretical point of view [11,13,23] and attention has been focused on accurate estimates of the charge on the oxygen atom. Orbital projection and dipole moment curves were used to assign a charge. Depending on basis sets or pseudopotentials used in those works, the quantitative results were slightly different although all the studies predict a large ionic bond with a

modest, but noticeable, covalent contribution. Here, we have applied the CDA method to the Cu_5O cluster, modelling the four-fold adsorption site. The five Cu atoms have been treated using an 11 electron ECP that explicitly leaves the $3d^{10}4s^1$ electrons and a double-zeta plus polarization basis set [24]. Oxygen has been treated at the all-electron level using a $[9s5p/4s3p]$ basis set. To be consistent we have also performed the analysis of dipole moment curves and the orbital projection technique. Results are presented in Table 2 and compared with [2] using an all-electron basis set for all the atoms and with [23], which uses ECP's for the core electrons of all the atoms. The MPA gives a value of -1 for the net charge on O. This value is in contrast with all the other measures, which give charges more negative than -1 . The value obtained using projections gives bounds on the anion charge of $-1.30 > q > -1.5$. The slope of the dipole moment is about -1 but it should be pointed out that for a test point charge of -1.0 , the slope of the dipole moment curve for the motion of the point charge parallel to the surface is -0.7 [8] or -0.75 [23], thus indicating that a point charge with larger magnitude than -1 is needed to represent the effective charge on O. The value given by the CDA, moving the O atom perpendicularly to the surface is -1.37 , and the curvature is zero. This value is near to the previous careful analyses using projection operators and properly calibrated SCF dipole moment curves. Moreover, we can exploit one of the capabilities of the CDA analysis which consists in moving the atom parallel to the surface, thus minimizing

Table 2
Results for O chemisorbed on the Cu_5 cluster model

| Reference | d_c | Q_{MPA} | Q_{Proy} | Q'_{Proy} | $M_{1,\text{dmc}}$ | M_{\perp} | $M_{\parallel}(\text{ })$ |
|-----------|-------|------------------|-------------------|--------------------|--------------------|-------------|----------------------------|
| This work | 1.75 | -1.02 | -1.59 | -1.27 | -1.14 | -1.37 | -1.37 |
| [8] | 1.9 | — | -1.55 | -1.33 | -1.17 | | |
| [20] | 1.70 | -0.98 | -1.52 | -1.28 | -0.97 | | |

The d_c , Q_{MPA} , Q_{proy} , Q'_{proy} , symbols stand for the equilibrium distance above the surface (in bohr), the Mulliken charge on O, the estimate of the charge by the projection operator method including the overlap correction. Likewise, $M_{1,\text{dmc}}$ is the slope of the dipole moment curve and M_{\perp} , $M_{\parallel}(\text{||})$ are the slopes of the CDA curves obtained moving the O atom perpendicular or parallel to the surface, respectively.

Table 3
Results for CN chemisorption on the Cu₅ cluster model

| | Z_C | Z_N | M_0 | M_1 | M_2 | Q_C | Q_N | Q_{CN} |
|-----------|-------|-------|-------|-------|-------|-------|-------|----------|
| C-down | 3.705 | 5.936 | | | | -0.22 | -0.30 | -0.55 |
| Moving CN | | -4.77 | -0.85 | -0.02 | | | | |
| Moving C | | -4.77 | -0.46 | -0.07 | | | | |
| Moving N | | -4.77 | -0.37 | -0.04 | | | | |
| N-down | 5.839 | 3.609 | | | | -0.03 | -0.59 | -0.62 |
| Moving NC | | -4.58 | -1.02 | -0.01 | | | | |
| Moving C | | -4.58 | +0.23 | +0.18 | | | | |
| Moving N | | -4.58 | -1.24 | +0.14 | | | | |

The Z_C and z_N symbols represent the distances to the surface. The M_0 , M_1 , M_2 stand for the coefficients of the Taylor expansion of the CDA curve; cf. Eq. (1). Q are the MPA charges for C, N and CN. All distances are in bohr.

the artifacts associated with changes in the two-center dipole moment integrals. The value is then exactly the same, -1.37 . The overall result confirms the high ionicity of the bond and encourages to use this simply but powerful method to study different systems.

3.4. Chemisorption of CN on Cu(100)

As a last example, we have selected the chemisorption of CN on the Cu(100) surface. The CN molecule is known to chemisorb perpendicularly to the surface on top of a Cu atom. Previous theoretical work [25–27] has demonstrated that, for the C-down orientation, the bond between CN and a copper metal surface is essentially ionic. In this last case, the cluster used has five atoms (as in the Cu₅O system), but here it is oriented in such a way that one atom is in the first layer and four on the second one. The adsorbate is added at an on-top site and the two C-down and N-down possibilities have been considered. The basis set for Cu is the same as for the Cu₅O system. The C and N atoms are treated at the all-electron level and with a (11s6p1d/5s3p1d) basis set¹ [28]. Starting from the equilibrium distance, we have considered displacements of the CN molecule, by

keeping the CN equilibrium distance fixed and we have also considered individual displacements of the C and N atoms; the results are collected in Table 3. From these data, it would appear that the N-down bond has slightly more ionic character than the C-down one which indeed is also largely ionic. This is in full agreement with the estimate by Nelin et al. [8] based on dipole moment curves and projections for the CN–Cu and NC–Cu molecular complexes. Moreover, within our model and basis sets, these results are consistent with a larger interaction energy for the C-down case by about 0.18 eV. However, the difference in ionic character is very small, indicating again that both systems are largely ionic. It should be noted that the Mulliken charges are always less than the ones derived from CDA. Finally it is interesting to notice that it seems possible to use the CDA to assign net charges to both C and N on the chemisorbed CN molecule (See M_1 in Table 3). An important measure of the power of the CDA is the fact that the sum of the independently calculated charges on C and N, $Q(C)$ and $Q(N)$, is almost equal to the charge computed by moving the CN molecule rigidly, $Q(CN) \approx Q(C) + Q(N)$. As opposed to a Mulliken population analysis where the total charge is forced to be conserved through the arbitrary division of overlap charge, the CDA does not force $Q(CN)$ to be equal to the independent determination of $Q(C)$ and $Q(N)$; and this near equality is a test

¹ (TZ basis augmented with a polarization d function with an exponent of 0.72 for C and 0.98 for N).

of the small uncertainty of the CDA assignments.

4. Conclusions

A new method to estimate net charges of atoms on molecules or clusters has been presented. The method is simple, of general applicability and easy to use. It is based on well defined physical quantities. It uses the same strategy as for the analysis of the dipole moment curves obtained from fully variational calculations but avoids the polarization effects which is present in the variations from different distances and makes it difficult to relate the slope of the dipole moment curve to an atomic charge. The new method avoids many of the shortcomings of the Mulliken population analysis, while keeping the idea that charge or electronic density on atoms is defined through their basis functions. Moreover, the new method, termed CDA for charge distribution analysis, does not require numerical integrations of either electronic density or molecular electrostatic potentials for an arbitrary atomic region, nor does it need the external definition of an atomic region because an atom is simply defined by its atomic basis functions. The new CDA method will be applied in the near future to selected series of molecules and other chemical systems to provide further evidence of its capabilities. We hope this new CDA method will become a powerful method to analyze and understand heterogeneous catalysis, in particular, and chemical reactivity in general.

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