

Atomic Charges in Some Copper Compounds Derived from XPS Data

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Linear relationships between the core electron binding energies and atomic charges previously derived in our laboratory have been tested on XPS data for Cu_2O , CuO , $\text{Cu}(\text{NO}_3)_2$ and CuFeS_2 , as well as for CuF_2 and CuCl_2 . Atomic charges are obtained by combining these relationships with literature data on binding energies. This results in $q_{\text{Cu}} = +0.38$ for Cu_2O ; $q_{\text{Cu}} = +1.02$ for CuO , $q_{\text{Cu}} = +1.37$ for $\text{Cu}(\text{NO}_3)_2$, $q_{\text{Cu}} = +0.15$ for CuFeS_2 , $q_{\text{Cu}} = +2.05$ for CuF_2 and $q_{\text{Cu}} = +1.04$ for CuCl_2 . These values are compared to recent theoretical estimates from the literature, giving $q_{\text{Cu}} = +0.38$ for Cu_2O and $q_{\text{Cu}} = +0.60$ for CuO . The agreement is strikingly good for Cu_2O . A calculated value of q_{Cu} for CuF_2 is $+1.44$ and for CuCl_2 $+1.10$. For $\text{Cu}(\text{NO}_3)_2$ theoretical calculations of q_{Cu} give values between 1.38 and 1.77 . For CuFeS_2 , similarly, $q_{\text{Cu}} = +0.07$ has been reported. The purpose of this paper is to test and demonstrate the usefulness of the relations between core binding energies and charge. The agreement in most cases between experimental and theoretical charge values is therefore worth noting.

It was first observed by Siegbahn *et al.*¹ that the binding energies of core electrons exposed by XPS (ESCA) are related to the chemical situation of the atoms in question. This 'chemical situation' may be described in terms of formal oxidation states,¹ by the external potential acting on the atom,² or by the 'effective charge' of the atoms as calculated by population analysis of the orbitals obtained from quantum-chemical models.^{3–5} Several analytical expressions have been proposed relating the binding energy, E_b , of core electrons of an atom to the effective charge, q , of that atom.^{2,6,7} In a series of investigations (e.g. Ref. 8) we have used the simplest possible of these expressions (also suggested in Siegbahn's early work)¹ – viz. that of the linear relationship of eqn. (1). This equation is based on

$$E_b = kq + E_{b0} \quad (1)$$

least-squares regression analysis between binding energy values and theoretically derived charges. The latter were obtained with *ab initio* techniques using Mulliken population analysis. In all investigations that imply the use of eqn. (1) two fundamental considerations have been our guiding principles.

First, it was considered necessary to use a good internal standard to calibrate the spectra properly.⁹ This standard is the C1s binding energy of the carbons in a phenyl group (Ph) incorporated in the compound to be investigated. By supplying additional information from IR intensity measurements of the C–H stretching vibration, we could eliminate any chemical influence on the phenyl carbons in the

compounds studied. Thus, for example, Cl could be measured in $(\text{Ph}_4\text{P})\text{ClO}_4$, $(\text{Ph}_4\text{P})\text{Cl}$ and PhCl , and the binding energies calibrated against the carbon 1s binding energy as said above.

Secondly, we have used theoretical charge values only for those light elements for which estimations of charge, e.g. via Mulliken population analysis,¹⁰ may be made with some accuracy. This means that for the heavy elements, especially the transition metals, with increasingly diffuse wavefunctions describing the electron distribution, we have used indirect methods of charge estimation. This means that we have prepared compounds such as $(\text{Ph}_4\text{P})_2\text{MCl}_4$, $(\text{Ph}_4\text{P})_2\text{M}(\text{SCN})_6$ and $(\text{Ph}_4\text{P})_3\text{MF}_6$, where the ligands of the complex anions contain only such elements that have already been characterized by eqn. (1), i.e. they contain only relatively light elements. This gives us the charges of the atoms of the ligands, and thus we obtain the charge of the central metal atom, assuming no charge transfer between the cation and the anion. We thus avoid the difficulties contained in calculating charge populations for diffuse orbitals discussed by Schaefer.¹¹ Our techniques are described in detail in Ref. 8 or 12. About 20 elements are presently characterized in this way. It turns out that the linear relationship (1) describes the results for heavy elements as well as for the light ones.

Test of the E_b vs. q relationships

Obviously, it is of great interest for us to look for systems that can be used to test these relationships. One possibility appeared recently by combining calculations of the charge distribution of copper oxides with data from experimental

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investigations on the core electron binding energies of these oxides. In a recent paper Ching *et al.*¹³ performed a band-structure calculation on Cu₂O and CuO. Their calculations also give the electron distribution around the atoms in question. Hence it may be possible to compare the results with other techniques, the results of which are expressed as 'effective charges' on the atoms. XPS data of these compounds have been carefully measured by Ghijsen *et al.*¹⁴ who also report a collation of similar investigations of other authors.¹⁵⁻²⁰ We have therefore considerable experimental material on which we can test some of our relations. The publication of these data made us look for other similar investigations. Here we will use the XPS data on CuF₂ and CuCl₂ given by van der Laan *et al.*²¹ and compare the results with theoretical data of Bauschlicher and Roos.²² Other investigations that we will use are the accurate XPS data of water-free Cu(NO₃)₂²³ and the population analysis of this compound by Hillier and coworkers.^{23,24} Similarly, CuFeS₂ has been studied by XPS²⁵ and theoretical charge estimates have been made.²⁶

Our relationships for Cu2p_{3/2},⁸ O1s,²⁷ Fe2p_{3/2},²⁸ S2p,²⁹ F1s,³⁰ Cl2p_{3/2}³¹ and N1s³² are given by eqns. (2)–(8), respectively (E_b in eV). Before testing these relationships, how-

$$E_b(\text{Cu}2p_{3/2}) = 1.52 q_{\text{Cu}} + 932.2 \quad (2)$$

$$E_b(\text{O}1s) = 4.23 q_{\text{O}} + 534.1 \quad (3)$$

$$E_b(\text{Fe}2p_{3/2}) = 6.4 q_{\text{Fe}} + 704.1 \quad (4)$$

$$E_b(\text{S}2p) = 3.38 q_{\text{S}} + 163.8 \quad (5)$$

$$E_b(\text{N}1s) = 7.00 q_{\text{N}} + 401.4 \quad (6)$$

$$E_b(\text{Cl}2p_{3/2}) = 4.25 q_{\text{Cl}} + 201.2 \quad (7)$$

$$E_b(\text{F}1s) = 4.28 q_{\text{F}} + 688.8 \quad (8)$$

ever, one must remark that they hold only for conditions under which they were established. This means that one should have available the same internal standard (a phenyl group with characterized infrared absorption intensity of the C–H stretching modes)^{9,27} as used in the previous investigations. This is obviously not the case for the substances under discussion. Therefore we must use a substitute method that has been tried in other cases and found to work well.^{33,34} We assume that there is an energy difference, a /eV, between the measured binding energy and the one that should result from our equation; a is assumed to be constant over the entire energy range.^{33,34}

As an instructive example we may consider experimental data of Cu2p_{3/2} and O1s in copper(II) oxide. The binding energies can be expressed as eqns. (9) and (10). The addi-

$$E_b(\text{Cu}2p_{3/2})_{\text{obs}} = 1.52 q_{\text{Cu}} + 932.2 + a \quad (9)$$

$$E_b(\text{O}1s)_{\text{obs}} = 4.23 q_{\text{O}} + 534.1 + a \quad (10)$$

$$q_{\text{Cu}} + q_{\text{O}} = 0 \quad (11)$$

tional requirement of eqn. (11), that the sum of the charges should equal zero, makes it possible to solve for the three unknowns.

Using the XPS data quoted by Ghijsen *et al.*,¹⁴ we have performed this calculation of the effective charges for Cu₂O and CuO. The results appear in Tables 1 and 2. The calculations for CuF₂, CuCl₂, Cu(NO₃)₂ and CuFeS₂ were made in an analogous way. The results are given in Tables 3–6.

Discussion

The data shown in Tables 1 and 2 give rise to some comments. First, one observes that the charge on the oxygen atom is in both cases around -1 , i.e. half way between the formal oxidation state II and 0. In making this comment, however, we must remember that the effective charges do not express very much about the degree of oxidation, but rather the degree of Lewis acid–base interaction. The difference between the oxidation states of Cu(I) and Cu(II) is born out splendidly in the XPS results, e.g. Ref. 14: the absence of a satellite corresponds to Cu(I), whereas the presence of a satellite corresponds to Cu(II). Nevertheless, the oxide ions of the compounds have almost the same charge.

Secondly, one finds that the same or very similar charge values are obtained, whether the original data are well calibrated or not. The parameter a measures the level of reference. This may be higher or lower than the one we defined when using the phenyl group internal standard,⁹ but the deviation is always < 1 eV for all the solid samples. Compare especially the results from Refs. 17 and 18 in Table 1. The good agreement between charge values ob-

Table 1. Results on Cu₂O: experimental binding energies for Cu₂O together with atomic charges gained from eqns. (2) and (3).

$E_b(\text{Cu}2p_{3/2})_{\text{obs}}$ /eV	$E_b(\text{O}1s)_{\text{obs}}$ /eV	q_{Cu}	q_{O}	a /eV	Ref.
932.4	530.2	0.41	-0.82	-0.42	14
932.2	530.4	0.37	-0.74	-0.56	15
932.2	530.5	0.36	-0.72	-0.55	16
933.0	531.0	0.39	-0.78	0.21	17
932.5	530.5	0.39	-0.78	-0.29	18
932.0	529.9	0.40	-0.80	-0.81	19
Mean values:		0.39	-0.77		
Theoretical values of atomic charges					
		0.38	-0.77		13

Table 2. Results on CuO: experimental binding energies for CuO together with atomic charges gained from eqns. (2) and (3).

$E_b(\text{Cu}2p_{3/2})_{\text{obs}}$ /eV	$E_b(\text{O}1s)_{\text{obs}}$ /eV	q_{Cu}	q_{O}	a/eV	Ref.
933.2	529.2	1.03	-1.03	-0.56	14
933.6	529.7	1.01	-1.01	-0.13	15
933.2	529.9	0.90	-0.90	-0.37	16
933.8	529.6	1.06	-1.06	-0.01	18
933.5	529.5	1.03	-1.03	-0.27	19
933.8	529.5	1.08	-1.08	-0.04	20
Mean values:		1.02	-1.02		
Theoretical values of atomic charges					
		0.60	-0.60		13

tained for these two investigations, in spite of the variation in calibration procedure, supports the use of atomic charges rather than the use of straightforward binding energies as an interpretative tool for XPS data.

The value of a when relating to the measurements of gas-phase $\text{Cu}(\text{NO}_3)_2$, however, is much higher, as is usually found. This difference in a between gas-phase and solid-state data has been discussed in terms of the polarizability of the molecules in the gas-phase experiments in a recent paper.³⁵

Let us now compare our results with those of Ching *et al.*¹³ These authors report a Mulliken population analysis as well as direct integration of the calculated charge density function. The radial integration limit was taken as the distance of minimum charge density. For Cu_2O the result is $q_{\text{Cu}} = -0.07$ and $q_{\text{O}} = +0.13$ from the Mulliken analysis, which is obviously wrong in this case involving transition element atoms. The integration method gives $q_{\text{Cu}} = +0.58$ and $q_{\text{O}} = -0.57$. However, the latter method leaves 1.18 electrons 'in the interstitial region of the cell'.¹³ If these 1.18 electrons are evenly divided among the six atoms of the two formula units of the unit cell, an extra negative charge of 0.2 is given to every atom. Hence we arrive at $q_{\text{Cu}} = +0.38$ and $q_{\text{O}} = -0.77$ (Fig. 1). This estimate is in

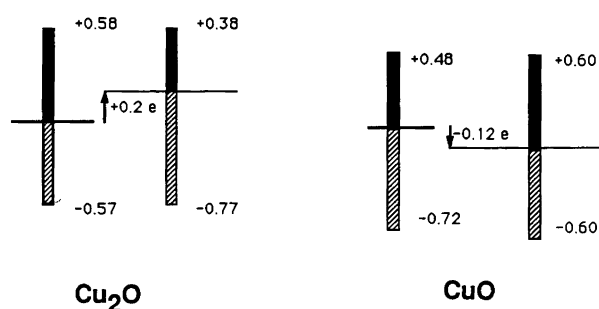


Fig. 1. Schematic representation of the data of Ching *et al.*¹³ and the atomic charges that result from these data after addition of 0.2 electrons per atom (Cu_2O) and subtraction of 0.12 electrons per atom (CuO).

perfect agreement with the experimental values given in Table 1.

For CuO a similar calculation was made by Ching *et al.*¹³ Their Mulliken population data are $q_{\text{Cu}} = +0.03$ and $q_{\text{O}} = -0.02$. Also in this case the result does not agree with chemical intuition, nor with the results of Table 2. Turning to the integration of the calculated charge density function, however, one finds charge values $q_{\text{Cu}} = +0.48$ and $q_{\text{O}} = -0.72$, which as the authors say 'overestimates the total charge within the cell by about one electron'. As the unit cell contains four CuO units the overestimate yields about 0.12 electrons per atom, evenly distributed. Subtracting these 0.12 electrons we arrive at a set of charge parameters that are numerically equal, agreeing with the stoichiometry of the compound, viz. $q_{\text{Cu}} = +0.60$ and $q_{\text{O}} = -0.60$ charge units (Fig. 1). These data should be compared to $q_{\text{Cu}} = +1.02$ from the XPS data of Table 2. The agreement is not very good, but nevertheless indicates the basic soundness of the two techniques. Hopefully the comparison may be used to further the theoretical treatment of CuO . From a close reading of their report,¹³ it seems that Ching *et al.* are more satisfied with the treatment of Cu_2O than with that of CuO . It is therefore pleasing to find a better agreement between our 'experimental' data and the theoretical ones for Cu_2O than for CuO .

Table 3. Results on $\text{Cu}(\text{NO}_3)_2$: experimental binding energies together with atomic charges gained from eqns. (2), (3) and (6).

$E_b(\text{Cu}2p_{3/2})_{\text{obs}}$ /eV	$E_b(\text{O}1s)_{\text{obs}}$ /eV	$E_b(\text{N}1s)_{\text{obs}}$	q_{Cu}	q_{O}	q_{N}	a/eV	Ref.
942.3	540.2	414.2	1.37	-0.46	0.68	8.02	23
Theoretical values of atomic charges							
q_{Cu}	$q_{\text{O}}(\text{chelate})$	$q_{\text{O}}(\text{terminal})$	q_{N}	$q_{\text{O}}(\text{mean})$	Ref.		
1.77	-0.59	-0.19	0.48	-0.46	23		
1.38	-0.43	-0.18	0.34	-0.35	24		

Table 4. Results on CuFeS₂: experimental binding energies for CuFeS₂ together with atomic charges gained from eqns. (2), (4) and (5).

$E_b(\text{Cu}2p_{3/2})_{\text{obs}}$ /eV	$E_b(\text{Fe}2p_{3/2})_{\text{obs}}$ /eV	$E_b(\text{S}2p)_{\text{obs}}$ /eV	q_{Cu}	q_{Fe}	q_{S}	a/eV	Ref.
932.5	708.8	162.4	0.15	0.72	-0.44	0.08	25
Theoretical values of atomic charges			0.07	0.58	-0.32		26

It was noted above that conventional Mulliken population analysis does not work very well for salt-like structures. Our eqns. (2)–(8) were, however, constructed from Mulliken-type population analyses of small discrete molecules or ions. It is reasonable, therefore, that the results obtained for the small discrete molecule Cu(NO₃)₂ should also be comparable to results from such theoretical calculations. This is born out by the comparison of experimental results and the theoretical calculations (Table 3). In particular, the early results of Garner *et al.*²⁴ are in extremely good agreement with ours. In contrast to this, the disagreement between our results and the Mulliken population analysis of Ching *et al.*¹³ on the copper oxides indicates the difficulty in applying the latter method to salt-like solid-state compounds. It is therefore very instructive to compare the charges arrived at by our empirical method for CuFeS₂ with values obtained from a theoretical calculation, (X α).²⁶ Probably the X α -technique facilitates a charge estimate in a useful way. It should be noted that the low value of q_{Cu} reported in Table 4 agrees well with the X-ray diffraction analysis³⁶ which indicates a low oxidation state on the copper atoms.

Turning to the results of the copper(II) halides, one immediately observes (Tables 5 and 6) that there is a fair agreement for CuCl₂ between experimental atomic charges and those from theory. On the other hand, our experimental results for CuF₂ indicate an almost completely ionic type of bond whereas the supposedly best theoretical calculation²² gives a much smaller polarity of the Cu–F bond. It might be mentioned here that earlier theoretical calcula-

tions by Larsson *et al.*³⁷ resulted in an almost completely ionic Cu–F bond. The discrepancy may be traced, in part, to the fact that the calculations are made for linear, discrete and free molecules, whereas the XPS data refer to solid salts. Furthermore, one should note that the crystal structure of CuCl₂ is of a layered, almost chain-like, type.³⁸ This indicates a rather high degree of covalency. Crystals of CuF₂, on the other hand, have a (distorted) rutile structure,³⁸ which is often associated with an ionic type of bonding, cf. Ref. 39. These trends are reflected in both the theoretical and experimental data.

The possibility that the results for CuF₂ should be caused by an erroneous relationship, eqn. (8), may be ruled out from a sensitivity analysis: using two alternatives that are extreme relating to the data that were used for constructing³⁰ relationship (8), viz. $E_b(\text{F}1s) = 7.0 q_{\text{F}} + 691.0$ and $E_b(\text{F}1s) = 2.0 q_{\text{F}} + 687.0$, one obtains $q_{\text{F}} = -0.97$ and $q_{\text{F}} = -1.13$, respectively. Thus even these extreme variations in the coefficient of the relationship do not explain the observed high polarity. Furthermore, under all circumstances the fluoride charge should be not too far from that of the 'free' F⁻ ion that was used as one of the fixed points of the analysis³⁰ leading to eqn. (8). It should also be mentioned that the use of eqn. (8) for complexes of the type MF₆³⁻ led to q_{M} values that were very reasonable and in agreement³⁰ with trends found from the theory of *d-d* transition spectra.

In Fig. 2 we display the results reported in Tables 1–6. The line for total agreement ($q_{\text{exp}} = q_{\text{theor}}$) is drawn to indicate which results are the best ones. For example, one may easily observe that the calculations on Cu(NO₃)₂ from Ref. 24 are better than those of Ref. 23.

Table 5. Results on CuF₂: experimental binding energies together with atomic charges gained from eqns. (2) and (8).

$E_b(\text{Cu}2p_{3/2})_{\text{obs}}$ /eV	$E_b(\text{F}1s)_{\text{obs}}$ /eV	q_{Cu}	q_{F}	a/eV	Ref.
936.6	685.7	+2.05	-1.02	1.29	21
Theoretical values of atomic charges			+1.44	-0.72	22
		+1.3 ^a	-0.65 ^a		22
		+2.00	-1.00		37

^aEstimated by the present authors from an improvement suggested by Bauschlicher *et al.*²²**Table 6.** Results on CuCl₂: experimental binding energies together with atomic charges gained from eqns. (2) and (7).

$E_b(\text{Cu}2p_{3/2})_{\text{obs}}$ /eV	$E_b(\text{Cl}2p_{3/2})_{\text{obs}}$ /eV	q_{Cu}	q_{Cl}	a/eV	Ref.
934.6	199.8	+1.04	-0.52	0.82	21
Theoretical values of atomic charges			+1.10	-0.55	22
		+0.9 ^a	-0.45 ^a		22

^aEstimated by the present authors from an improvement suggested by Bauschlicher *et al.*²²

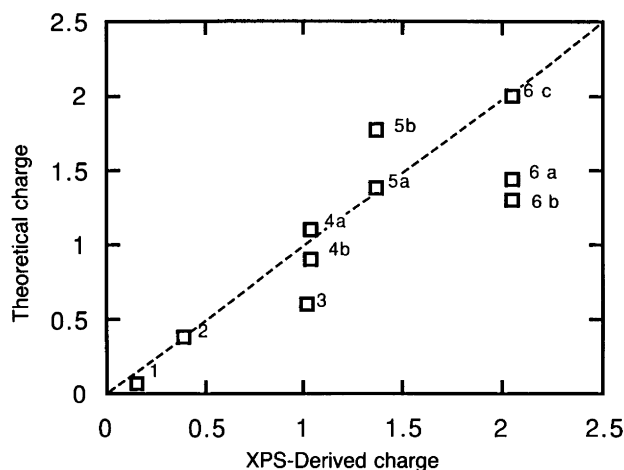


Fig. 2. A plot of the copper atom charges from theoretical calculations as a function of the experimental charges that we derive from XPS data: (1) CuFeS_2 (Table 4), (2) Cu_2O (Table 1), (3) CuO (Table 2), (4) CuCl_2 (Table 6; a and b describe different methods of calculation),²² (5) $\text{Cu}(\text{NO}_3)_2$ (Table 3; a = Ref. 24 and b = Ref. 23), (6) CuF_2 (Table 5; a and b describe different methods of calculation²² and c = Ref. 37). The line with slope 1.00 indicates complete correspondence.

Conclusion

In conclusion, one may note that the close agreement between experimental charge values and the theoretical ones found here and the similar agreement found previously^{33,34} indicate that the linear relations between core electron binding energies and atomic charges work well in a pragmatic sense. In particular, there is no significant trend in the deviations of our calculated copper charges from such charge values that are theoretically derived. Fig. 2 tries to bear this out. This means that the parameters of the eqns. (2)–(8) are not severely wrong, but can be used with confidence in further investigations.

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