On the Relationship between Molecular Core Binding Energies and Atomic Charges

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Summary The linear relationship between molecular core binding energies (as measured by *X*-ray photoelectron spectroscopy or calculated by an "*ab initio*" SCF–LCAO method) and the Mulliken gross atomic charges is restored if the interatomic Madelung potential is taken into account.

RECENTLY, Barber and Clark have published communications[1–3] in which they demonstrated that the simple linear relationship between the binding energies of the molecular core electrons and the atomic charges, as observed earlier,[4,5] breaks down in several examples. These authors have measured the binding energies of carbon 1*s* and nitrogen 1*s* electrons in acetonitrile and in three nucleic acid bases, adenine, cytosine, and thymine, by *X*-ray photoelectron spectroscopy. They showed that the experimental core ionization energies are linearly related to the orbital energies calculated[6] by an "*ab initio*" SCF–LCAO method, as can be expected from Koopmans' theorem. Thus photoelectron peaks can be assigned to ionizations of specific carbon or nitrogen atoms. The authors emphasize, however, that no linear relationship exists between the core electron binding energies and the Mulliken atomic charges on the ionized atoms. In some cases even higher binding energies correspond to more negative atoms.

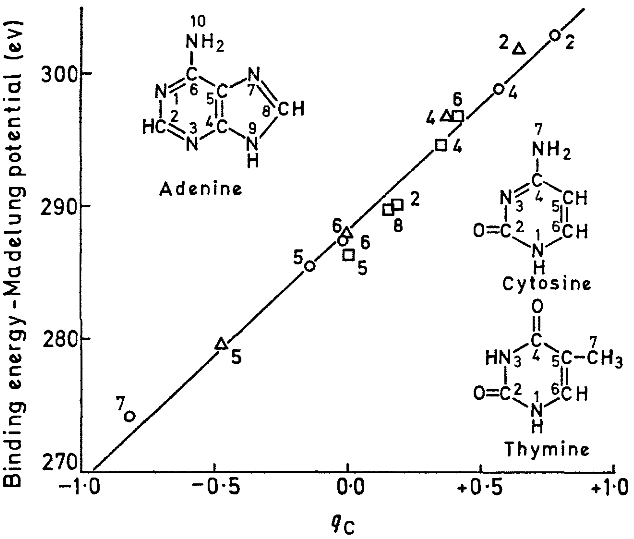

FIGURE 1. *Binding energy for the carbon* 1s *level, corrected for the effect of the interatomic Madelung potential, of adenine* (□), *thymine* (○), *and cytosine* (△) *against atomic charges.*

I report that the linear relation between the core ionization energy of an atom in a molecule and the Mulliken gross charge on this atom is restored if the Madelung potential due to the other atoms in the molecule, considered as point charges, is taken into account.† Following Gelius *et al.*[7] the binding energy of a core electron on atom *i*, E_i is given by:

$$E_i = \alpha + \beta q_i + \sum_{j \neq i} q_j/R_{ij},$$

where α and β are constants for the inner shell studied (α should be corrected for the work function of the sample), q_i is the Mulliken gross charge on atom *i* and R_{ij} is the distance between the nuclei *i* and *j*. Siegbahn *et al.*[4] introduced this Madelung potential to explain their observation that, generally, the shifts in binding energies with charge are smaller in molecules or solids than in isolated atoms.

With this formula I have tried to correlate the binding energies determined experimentally by Barber and Clark.[1–3] No charges on nitrogen or hydrogen were indicated for acetonitrile,[1] but it is easily found that the Madelung potentials on the carbon atoms have different sign, counteract the effects of the atomic charges, and can be sufficiently large to explain the very small difference in binding energy measured. The results for the molecules adenine, thymine, and cytosine, the Mulliken gross atomic charges of which were taken from Mely and Pullman[6] and the structures from Spencer,[8] and Barker and Marsh,[9] are shown in Figures 1 and 2. The experimental binding energies have been corrected for the effect of the interatomic Madelung potential and plotted against the atomic charges. A least-square fit through all carbon and all nitrogen points yields

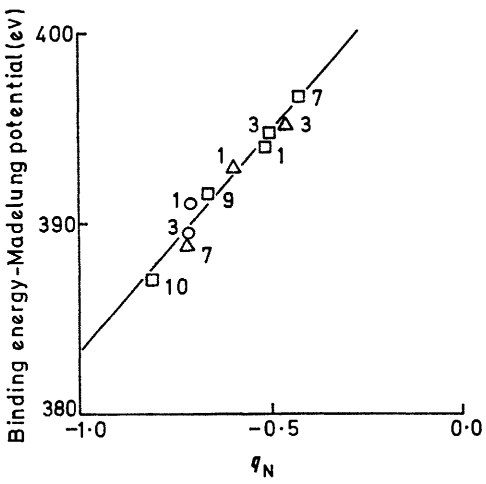

FIGURE 2. *Binding energy for the nitrogen* 1s *level, corrected for the effect of the interatomic Madelung potential of adenine* (□), *thymine* (○), *and cystosine* (△) *against atomic charges.*

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† Since the examples treated are crystals composed of neutral molecules, the "Madelung potential" was restricted to a summation over atomic charges within one molecule.

a 1*s* binding energy of 288·2 and 406·3 ev respectively for the neutral atoms and a charge dependence of 19·0 and 23·1 ev/unit charge respectively for the isolated atoms. This is in reasonable agreement with literature values for the experimental binding energies of 288 and 403 ev (ref. 4, p. 230) and the calculated shifts of 18·8 and 20·7 ev/unit charge (ref. 4, p. 84). Drawing straight lines through the points of different molecules separately, as Barber and Clark have done, would fit the results even more closely.

Although I agree with Barber and Clark that a linear relationship between the *X*-ray photoelectron spectroscopy shifts and the atomic charges is not "*a priori*" obvious, I think it can be concluded that for the examples given such a relation exists if the Madelung potential is added. This is convenient as, at least for the interpretation of an *X*-ray photoelectron spectrum, an "*ab initio*" SCF–LCAO calculation including all innershell orbitals need not be carried out, but a semi-empirical MO method applied to the valence electrons might suffice.

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