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Application of Extended Hückel Theory to X-ray Photoelectron Spectra of Transition Metal Complexes. Correlations between Electron Binding Energy and Calculated Atomic Charge in Iron and Sulfur Compounds

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ABSTRACT

Comparisons of iron and sulfur atomic charges, derived from extended Hückel calculations, with core electron binding energies determined from x-ray photoelectron spectroscopy yield good correlations for neutral molecules. The assumptions and limitations of such correlations are discussed briefly.

Central to the question of the electronic structure of a transition metal complex is its charge distribution. Although the charge is often used as a parameter in the calculation of electronic structure, it has become feasible only recently to measure a quantity directly related to the net atomic charge. Core electron binding energies (B.E.s), as measured by X-ray photoelectron spectroscopy, can be correlated with atomic charge.

We report such correlations between measured Fe3P electron B.E.s and, iron atomic charge calculated by means of the extended Hückel M.O. method. Compounds were chosen to represent a diversity of electronic environments. In particular, our interest in metalloproteins suggested a number of materials containing both iron and sulfur. A similar correlation has been established for the S2P electron B.E.s in representative sulfur compounds.

Theoretical interpretations of measured X-ray photoelectron chemical shifts have been attempted by other workers with varying degrees of success. Siegbahn et al. [1,2] have investigated simple sulfur, nitrogen, and carbon compounds. Fadley et al. [3] made the first attempt to explain chemical shifts in ionic compounds. Hendrickson et al. [4,5] have carried out semiquantitative calculations on nitrogen and phosphorous compounds. Jolly and Hendrickson [6] have related thermodynamic data to chemical shifts in electron binding energies. More recent approaches to interpretation of X-ray photoelectron spectra have been presented in several other papers. [7-9]

Several assumptions are made when attempting to correlate measured core electronic binding energies with a parameter calculated by means of the extended Hückel formalism. We have assumed that the experimental work function variations among solid samples are negligible. Electronic relaxation effects after removal of a core photoelectron are assumed to be constant, since this method of calculation neglects such effects. (Justification for this assumption is given in a report by Davis et al. [10].) The electrostatic potential contributed by the charge on surrounding ligands has not been included explicitly, but has been assumed to be included implicitly through the modifications of reference 15. (Attempts to include a simple point charge modification using a potential varying as q^2/r resulted in no improvement in the correlation.) Finally, we have assumed that the extended Hückel approximations are indeed applicable to the transition metal complexes studied here. A more explicit analysis of the approximations of the extended Hückel formalism and its use in calculating parameters of transition metal complexes has been described elsewhere [11,12].

In our present work both charge and binding energy were calculated using an extended Hückel method formulated by Hoffman [13,14], with modifications [15] to the Coulomb integrals and Slater exponents such that iteration to charge self-consistency could be obtained. This method does not include electron repulsion terms explicitly, and uses empirical parameters for evaluation of the elements of the secular determinant. (The size of the electronic systems considered in this paper renders impractical more sophisticated calculations at the present time.) Coulomb integrals were approximated by Valence Orbital Ionization Potentials [16] (choosing an electronic configuration of d^6sp for the iron atom). Off-diagonal elements of the secular determinant were approximated by Cusach's formula [17]. Slater-type orbitals [18] were used for the minimum basis set of wave functions. Charge values, made self-consistent to 0.05 charge units through iteration, were obtained by Mulliken's method of population analysis [19]. Coordinates, bond distances, and bond angles were obtained from appropriate literature sources, and, in some cases, Quantum Chemistry Program PROXYZ [20] was used to obtain suitable coordinates. Large molecular structures, such as iron phthalocyanine and the dithiocarbamates, were approximated by replacing peripheral carbon substituents with hydrogen atoms in a manner similar to that of Zerner et al. [21].

Table 1 lists the measured and calculated electron binding energies and calculated charges for a diverse series of iron and sulfur compounds. For a representative sampling of iron compounds, the Fe3P B.E.s were calculated by including the Fe3P electrons in the molecular orbital calculations and using the resulting one electron energies of the three lowest molecular orbitals as the Fe3P binding energies. Comparison of these B.E.s with the corresponding calculated charge shows a direct correlation between calculated B.E. and calculated charge. From this observation it seems reasonable to expect similar results for attempts to correlate measured electron B.E.s with either calculated charge or calculated electron B.E.s when using this extended Hückel method of calculation.

Figure 1 shows the plot of measured Fe3P B.E. vs. calculated charge; the line drawn through the points is a least squares fit to the data from neutral molecules. From this plot, it is apparent that the data point positions of formally charged ionic complexes depart from those of neutral molecules in a relatively consistent manner. There are two important factors which contribute to this variance with neutral molecule data. One factor is the lattice potential effect, and the other is the overemphasis of covalency in ionic molecules when using the extended Hückel method.

Also shown in Figure 1 is a plot of measured S2P B.E. vs. calculated charge. Sulfur d orbitals were not used in these calculations; however, when d orbitals were included for representative sulfur compounds, no significant improvement in the correlation was observed.

It should be noted that if unrestricted *ab initio* calculations (including relaxation effects) were possible for the compounds we have investigated, there would be no reason to expect a *simple* charge vs. B.E. correlation (even if there were no solid state effects on the electron binding energy). The observation that our calculations show reasonable correlations between atomic charge and measured B.E. (with the exception of ionic iron complexes) indicates that the assumptions made in establishing these correlations are relatively good. However, the correlations are admittedly somewhat artificial since the simple extended Hückel calculations are insensitive to some important contributions to electron energy, which include relativistic, electron correlation, and relaxation effects. (In fact, the observation that the calculated Fe3P B.E.s of the neutral iron molecules are consistently higher than the measured B.E.s is an expected result of this insensitivity.) Nevertheless, until ab initio calculations can be applied easily to large electronic systems, semi-quantitative methods, such as used here, may be very useful aids in understanding structural and bonding phenomena.

We are very grateful to Dr. D. N. Hendrickson for making the Hoffman extended Hückel program available to us, and for his valuable advice when beginning this work.

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Table 1

Measured and calculated electron binding energies and calculated charges for a diverse series of iron and sulfur compounds. Spectra were produced and analyzed in the Berkeley iron-free electron spectrometer [22]. The widths at half maximum of the Fe3P and S2P photoelectron lines are about 2.6 eV and 2.4 eV, respectively. The relative binding energies are reproducible to about 0.2 eV, and charges are self-consistent to 0.05 charge units. Published synthetic procedures were followed in the preparation of compounds 2, 13, 15, 18, and 25. Compounds 14, 9, and 16 were obtained from Dr. H. H. Wickman, Dr. D. N. Hendrickson, and Dr. J. B. Neilands, respectively. All other compounds were obtained from commercial sources. FeS and $KFeS_2$ gave broad, ill-defined iron photoelectron spectra which were too ambiguous to assign a definite measured binding energy.

Table 1 (continued)

No.	Molecule	Measured Fe3P B.E. (eV)	Calculated Fe3P B.E. (eV)	Calculated iron charge	Measured S2P B.E. (eV)	Calculated sulfur charge
1	$FeF_6^{\equiv}$ (K_3FeF_6)	57.7	56.0	+1.81		
2	$FeO_4^{=}$ (K_2FeO_4)	57.7	56.1	+1.79		
3	$Fe(H_2O)_6^{+3}$ ($Fe_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot 24H_2O$)	56.6		+1.51		
4	$Fe(H_2O)_6^{+2}$ ($FeSO_4(NH_4)_2SO_4\cdot 6H_2O$)	54.2		+0.86		
5	$Fe(CN)_6^{-3}$ ($K_3Fe(CN)_6$)	55.0		+1.24		
6	$Fe(CN)_6^{-4}$ ($K_4Fe(CN)_6$)	54.0		+1.03		
7	Fe(metal)	52.0	52.4(def.)	0(def.)		
8	$Fe(C_5H_5)_2$	53.7	54.5	+1.00		
9	$Fe(C_5H_5)_2^{+}\cdot(NO_2)_3C_6H_2O^{-}$	54.9		+1.36		
10	$Fe(CO)_5$	54.0	54.7	+1.02		
11	$Fe_2(CO)_9$	54.6		+1.30		
12	FeS_2	53.0	53.3	+0.45	161.5	-0.22
13	$Fe(S_2CNEtEt)_3$	53.5		+0.95	161.5	-0.3
14	$FeBr(S_2CNEtEt)_2$	54.0	54.1	+0.82	161.4	-0.3
15	$Fe(S_2C_6H_3CH_3)_2^{-}\cdot N(n\text{-}C_4H_9)_4^{+}$	53.2		+0.29	161.4	-0.43
16	Ferrichrome A	54.9	55.5	+1.53		
17	Hemin Cl	54.2		+1.04		
18	Fe^{+3}Cl Phthalocyanine	54.4		+1.46		
19	$SO_4^{=}$				167.8	+1.86
20	$SO_3^{=}$				166.4	+1.40
21	CH_3SOCH_3				165.5	+0.70
22	CH_3SSCH_3				162.7	-0.13
23	CH_3SH				162.7	+0.09
24	FeS			+0.43	160.7	-0.43
25	$KFeS_2$			+0.35	161.1	-0.46

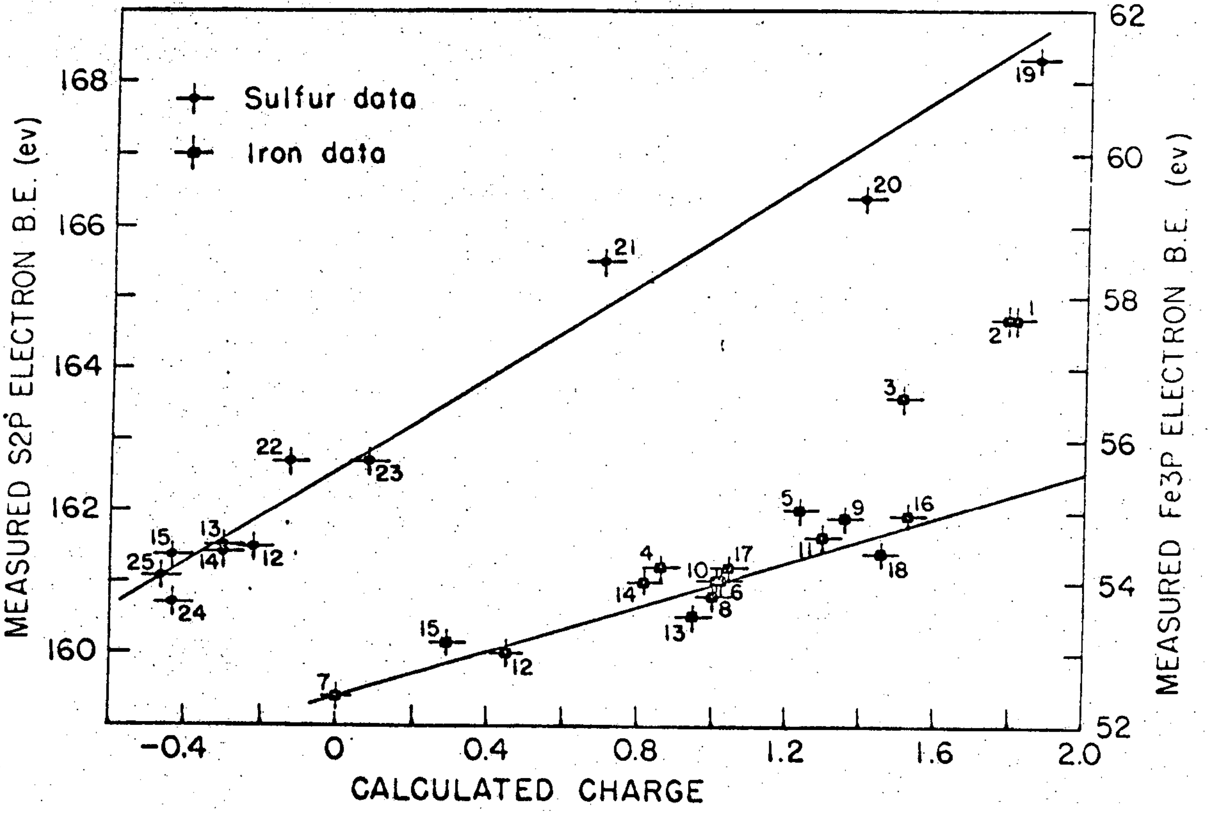

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Figure Caption

Plot of measured Fe3P B.E. and S2P B.E. vs. calculated charge in iron and sulfur compounds chosen to represent a diversity of electronic environments. The line drawn through the iron data points is a least squares fit to the data from neutral molecules. The numbers associated with the data points correspond to the compounds listed in Table 1.

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