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Hartree-Fock-Slater Calculations of the ESCA Chemical Shifts for Transition Metal Atoms

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Synopsis. Hartree-Fock-Slater calculations have been carried out for inner-shell orbitals of some transition metal atoms (Ni, Rh, and Pt), and the core ionization energies computed by the transition state approximation. It is found that the ionization energy shifts do not conform to the conventional charge-potential approximation; the electron populations in individual valence d and s orbitals need to be considered separately.

Recent developments in X-ray photoelectron spectroscopy (ESCA) have supplied a great amount of information on core-electron binding energies in atoms and molecules. The changes in the core-electron ionization potentials of an atom in given molecules relative to an appropriate standard are designated as chemical shifts. Siegbahn *et al.*[1] proposed that the shifts in ionization potential ΔE_i^A for core orbital i of atom A are related to the corresponding changes in atomic charge ΔQ_A by

$$\Delta E_i^A = k_i^A \Delta Q_A + \Delta V_A \quad (1)$$

where k_i^A is an adjustable parameter and the term ΔV_A denotes the change in the Coulomb potential at A due to the other atoms in the molecule. Implicit in Eq. 1 is the assumption that the core binding energy is a function of the initial state of the molecule; the reorganization energy upon ionization is assumed to be independent of the identity of atoms as long as they are in similar bonding environments. The charge-potential formula (1) has been applied extensively to series of compounds comprising first and second row atoms.[2] However, extention of the treatment to transition metal compounds is still lacking because of the great complexity of their bonding properties.

In the present article, we will deal with the core ionization potential shifts of transition metal atoms (Ni, Rh, and Pt) as well as some light atoms (C, N, and F) as the functions of atomic charge. The Hartree-Fock-Slater calculations have been carried out for these isolated atoms using the numerical technique. The transition state model[3] was employed to compute the energy difference between the ground state and an ionized state. The results justify the conventional charge-potential approximation for the case of light atoms but decisively indicate its breakdown for the transition metal atoms.

Method

The radial part of the Hartree-Fock wave equation for electrons in a free atom or ion has been solved numerically by Slater's X_α method.[4] A general procedure for numerical integrations as outlined by Pratt[5] was followed. The "exchange scaling parameter" α was chosen so that the statistical X_α total energy equals the configuration-averaged Hartree-Fock energy.[6]

In obtaining the ionization energies, we have invoked the concept of the "transition state," a hypothetical state of an atom or a molecule in which it is assumed that half an electron has been removed from the orbital in question.[4] The ionization energy E_i associated with the ith orbital is thus the negative of the ith one-electron orbital energy ε_i in the transition state.

Results and Discussion

The core ionization potentials of various atoms were calculated by varying the fractional occupation number of valence orbitals. We here direct our attention to the shifts ΔE_i of ionization potentials, taking the values for neutral atoms as standard ($Q=0$).

Figure 1 shows the shifts ΔE_{2p} of the core 2p orbital for a nickel atom with variations in the "valence-orbital net charges" Q(3d) and Q(4s). The charges were varied in the range between −0.3 and 0.9 of an electron, where the configuration of a neutral nickel atom is assumed to be $(\text{core})^{10}(3s)^2(3p)^6(3d)^8(4s)^2$. We see that ΔE_{2p} increases monotonically with increasing Q(3d)and Q(4s). Both plots appear to be slightly concave upward but may essentially be regarded as linear.

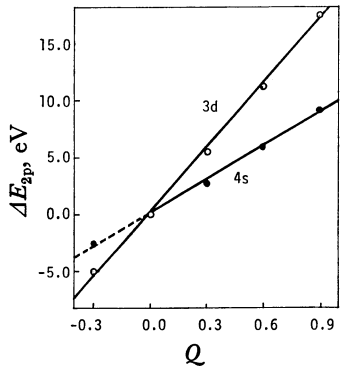

Fig. 1. Plots of the 2p-electron ionization energy shifts ΔE_{2p} of a nickel atom against the 3d as well as 4s orbital net charge.

The slopes for the two linear plots given in Fig. 1 differ clearly from each other. The slopes obtained by the least-squares treatments of the calculated data were $k_{2p}(3d)=18.76$ eV/e and $k_{2p}(4s)=9.84$ eV/e. The results suggest that, for a nickel atom, the effects of the 3d and 4s electron populations on the E_{2p} would have to be considered separately.

Some core-orbital k_i values obtained as above for the C, N, and F atoms as well as the Ni, Rh, and Pt atoms are summarized in Table 1. Two points are noteworthy with these k_i values. First, the shifts of E_{1s} for the light atoms do not depend on the origin of the charge; $k_{1s}(2s)$ is nearly equal to $k_{1s}(2p)$ for each atom. In other words,

Table 1. Exchange scaling parameters α and the calculated k_i values for atoms (eV/e)

Atom(core)[a]	α	Valence orbital	k_i	k_i(CNDO)[b]
C (1s)	0.75928	2s	16.46	21.9
		2p	16.53	
N (1s)	0.75197	2s	18.35	21.5
		2p	18.65	
F (1s)	0.73732	2s	21.96	27.6
		2p	21.81	
Ni (2p)	0.70896	3d	18.76	
		4s	9.84	
Rh (3d)	0.70217	4d	12.52	
		5s	8.21	
Pt (4f)	0.69306	5d	11.90	
		6s	8.10	

a) The orbitals denoted in parentheses show the core orbitals i from which an electron is removed upon ionization. b) Ref. 7.

the binding energy is little influenced by the difference in hybridization of valence orbitals.

Second, the k_i values calculated for the 2p, 3d, and 4s core orbitals of the Ni, Rh, and Pt atoms, respectively, all differ appreciably between the influencing d and s valence orbitals. Thus, the d orbital population exerts an apparently greater influence on the core binding energy of an inner-shell electron than does the valence s orbital population. In discussing the ESCA chemical shifts of transition metal atoms, therefore, we should look into the electron populations in individual d and s valence orbitals separately.

In Table 1 the values of k_{1s}[7] for the C, N, and F atoms in molecules obtained by fitting the observed 1s-electron chemical shifts to the CNDO/2 atomic charges are also listed. The k_{1s} (CNDO) values are uniformly greater than the Hartree-Fock-Slater k_{1s} values calculated. This may be attributed in part to the contraction of valence orbitals in molecules as a result of the accumulation of electronic charge in the bonding region.[8] The contraction should render the core orbitals in molecules more sensitive to the density of a valence electron than in isolated molecules.

Despite these numerical disagreements, the results of the present treatment of atoms lend support to the adequacy of the conventional charge-potential approximation for first-row atoms in molecules. The view that the k_{1s} values are quite different for the influencing 2s and 2p electrons[9] is thus unjustifiable. The better correlation of the two-parameter theory[9] to the shifts as compared with the conventional single-parameter treatment[1,7] is perhaps an artefact arising from the limited accuracy of the CNDO formalism itself. By contrast, it will be essential to resort to a multi-parameter treatment in interpreting the core-electron chemical shifts for transition metal atoms present in metal complexes.

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