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Calculation of the Exchange Splitting of N and O 1*s* Binding Energies in NO

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The splitting of the N and O 1*s* binding energies in NO due to ionization to either triplet or singlet states of the inner-hole-state ions is calculated from exchange integrals over the molecular orbitals from ground-state LCAO SCF MO wavefunctions in a "double-ζ" basis. Calculated splittings (in eV) of 1.26 (N_{1s}) and 0.77 (O_{1s}) are in reasonable agreement with experimental values of 1.5 and 0.7, respectively, suggesting that such a ground state only model will be useful for core energy splittings in paramagnetic molecules.

Although considerable electronic rearrangement occurs upon core-electron ionization [1], one would hope to understand "chemical shifts" of inner-shell binding energies (to be denoted here by ΔBE) on the basis of ground state molecular properties. Evidence is accumulating that this is a reasonable hope [2–5], and that for the most part errors involved in associating these *inter*-atomic ΔBE values with changes in negatives of core orbital energies from reasonably accurate *ab initio* LCAO SCF MO wavefunctions for closed-shell molecules effectively cancel for different molecular environments of an atom.

A related phenomenon is the occurrence of *intra*-atomic ΔBE's. These arise from ionization of a core electron from a paramagnetic molecule, to produce distinct states of the hole-state ion which differ in the coupling of the remaining unpaired core electron and the already unpaired valence electron(s). Beautiful examples of such splittings come from the experiments [6] on the well-known paramagnetic molecules NO and O_2. Because the overall environments of the states of the ion arising from a given core ionization are so similar, one might expect *a priori* that changes in rearrangement, correlation, and relativistic energies would be so similar that *intra*-atomic ΔBE's could be well described by use of the same ground state MO's for the different ionic states. A preliminarily investigation of the use of ground state MO's for such splittings has been described for NO and O_2 by Siegbahn *et al.* [7]. But both systems were studied *via* MO's built of minimum basis Slater orbitals, and only semiquantitative results were obtained. This is similar to the situation for *inter*-atomic ΔBE's [2–5, 8–9]. Though Siegbahn *et al.* indicated a plan to examine the splitting *via* direct calculations on the ions, we believe a more thorough investigation of the conceptually (and practically) simpler ground state approach is in order.

In this note we consider the splitting of both N and O 1*s* BE's in NO, using LCAO SCF MO's expanded in an essentially "double-ζ" gaussian basis [2, 10],

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which has already been shown [3, 5–8] to give a good accounting of *inter*-atomic ΔBE's. The formalism of the problem is well-known, and in the usual way leads to an energy splitting of $2K_{ij}$ between the triplet and singlet states formed from the same MO's when MO's ϕ_i and ϕ_j are each singly occupied. Here K_{ij} is the exchange integral

$$K_{ij} = \langle \phi_i(1)\, \phi_j(1) |\, 1/r_{12}\, | \phi_i(2)\, \phi_j(2) \rangle \;;$$

ϕ_i will be either the O_{1s} (1σ) MO or the N_{1s} (2σ) MO; and ϕ_j will be the 2π MO. Ground state MO's have been determined for the equilibrium internuclear distance of 1.15 Å (2.173 a.u.) by the Roothaan double-hamiltonian open-shell SCF formulation [11], as incorporated into the MOLE quantum chemistry system [12].

The relevant exchange integrals (in a.u.) are

$$K_{1\sigma 2\pi} = 0.01416$$

and

$$K_{2\sigma 2\pi} = 0.02316\,.$$

Corresponding calculated splittings are 0.77 eV for O_{1s} and 1.26 eV for N_{1s}, in reasonable agreement with the experimental values [7] of 0.7 eV and 1.5 eV, respectively. The earlier minimum basis calculations [7] gave the less satisfactory values of 0.68 eV and 0.88 eV.

The rather larger splitting for N_{1s} compared to O_{1s} is in accord with the larger concentration of the 2π MO on N: the mulliken gross atomic populations of this MO are 0.694 for N and 0.306 for O. One is warned, of course, not to take this literally, since the minimum basis 2π MO [13] gave quite similar gross populations of 0.65 for N and 0.35 for O, but rather different calculated ΔBE's. This is because the different basis functions give different electron-repulsion integrals contributing to K_{ij}, and furthermore the overlap populations are quite different: -0.463 for our 2π MO; -0.25 for the minimum basis one.

The important point here is that ground state MO's in a flexible molecular basis set have given a satisfactory accounting of the exchange splitting of core levels in a paramagnetic molecule, much as the usual chemical shifts are accounted for by Koopmans' theorem with such MO's [2–5].

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