ATOMIC IONS IN DIATOMIC MOLECULES: FROM CaO to ZnO: INSIGHT OR DISASTER?

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The electronic structure of CaO may be understood in terms of one valence electron on Ca^+ in the field of a -1 point charge and one p-hole on O^-, the π-hole and σ-hole orientations of which are split by a combination of Pauli repulsion and quadrupole interactions with the Ca^+ atomic ion. CaF is an excellent model for the effect of a -1 point charge on Ca^+. NaO is an excellent model for the effect of a +1 point charge on O^-. This (CaF, NaO) model for CaO accounts for all features of the non-$^1\Sigma^+$ states of CaO, including the ordering of electronic states, spin-orbit and lambda-doubling constants, and perturbation matrix elements.

Zn^+ differs from Ca^+ primarily by a filled and core-like 3d subshell. However, the significantly larger effective nuclear charge seen by the valence orbitals (4s and 4p) of Zn^+ causes these orbitals to be much more compact than those on Ca^+. The splitting between the lowest lying ZnO π-hole ($^3\Pi$) and σ-hole ($^3\Sigma^+$) states is observed in anion photoelectron spectra and *ab initio* calculations to be respectively 1.562(12) and 1.3(1) eV, about **ten times larger** than between the corresponding CaO states. If this larger splitting in ZnO cannot be explained by a simple Rittner-like model, serious doubts would be raised about the validity of the atomic-ions-in-diatomic molecule model, despite its remarkable success for CaO.