

## 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  $\text{Ca}^+$  in the field of a -1 point charge and one p-hole on  $\text{O}^-$ , the  $\pi$ -hole and  $\sigma$ -hole orientations of which are split by a combination of Pauli repulsion and quadrupole interactions with the  $\text{Ca}^+$  atomic ion. CaF is an excellent model for the effect of a -1 point charge on  $\text{Ca}^+$ . NaO is an excellent model for the effect of a +1 point charge on  $\text{O}^-$ . 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.

$\text{Zn}^+$  differs from  $\text{Ca}^+$  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  $\text{Zn}^+$  causes these orbitals to be much more compact than those on  $\text{Ca}^+$ . The splitting between the lowest lying ZnO  $\pi$ -hole ( $^3\Pi$ ) and  $\sigma$ -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-diatom molecule model, despite its remarkable success for CaO.