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Ab initio calculations for the 2s and 2p core level binding energies of atomic Zn, Zn metal, and Zn containing molecules

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Quantum chemical *ab initio* calculations have been performed for the 2s and 2p core level binding energies of atomic Zn, Zn clusters and a few Zn containing molecules. The calculations were performed by means of wave function based methods at different levels of approximation: Koopmans' theorem, frozen core hole approach, ΔSCF and ΔCASSCF approximations. Scalar relativistic corrections and spin–orbit coupling were included by means of perturbation theory. For atomic Zn, the calculated binding energies for the $2p_{1/2}$ and $2p_{3/2}$ core levels agree within 0.3 eV with experiment; for the 2s level there is a deviation of 3.5 eV which is due to a Coster-Kronig process not included in the present calculations. The calculated chemical shifts for various Zn clusters, from Zn_4 up to Zn_{87}, are decomposed into initial-state and final-state effects. The initial-state effects lead to larger binding energies and converge rapidly with increasing cluster size to shifts of +2.0 and +2.4 eV for 2s and 2p, respectively. The final-state effects lower the binding energies. They converge slowly, roughly proportional to $1/R$ (R being the cluster radius), to the value for Zn metal. Our final results for the atom-to-metal shifts, −2.7 eV both for 2s and 2p, agree fairly well with the experimental data, −2.9 eV. In the Zn containing molecules, the final-state effects are similar to those in the clusters, increasing slowly with increasing size of the ligand sphere. The initial-state effects, on the other side, depend strongly on the chemical properties of the ligands: They are positive for electron accepting ligands such as methyl and ethyl and in particular CF_3, but negative for the electron donating ligands NH_3 and pyridine.