The chemical bond overlap polarizability and covalency. Concepts and applications: from diatomic molecules to solids

The concepts of chemical bond overlap polarizability (OP) and ionic specific valence (ISV) have been introduced, about a decade ago (2002), in the context of the ligand field theory applied to lanthanide compounds. These concepts led to relevant conclusions on the interpretation of the non-spherical ligand field interaction in terms of covalency. They have also been explored in a more general context outside the scope of ligand field theory. Thus, they have proven to be useful in the case of diatomic molecules, allowing to establish a new covalency scale in excellent agreement with Pauling’s scale² and analytically quantifiable in terms of the OP.

An analysis on this subject in 2005, in which the overlap region is regarded as a localized plasmon-like mode of oscillation (chemical bond overlap plasmon - CBOP), characterized by the OP, has raised the possibility of absorption and inelastic scattering of radiation, specifically by the overlap region, in an oscillation mode distinguishable from the collective plasmon of the system. Predicted oscillator strengths and scattering cross sections for diatomic molecules are considerably high and can be measured in the UV up to the near soft-X-rays spectral regions². The possibility of detecting the CBOP in diatomic molecules by electron energy-loss measurements has also been analyzed⁴. Different treatments by using the Valence Bond Theory and a Localized Molecular Orbital approach have been evoked to describe de OP concept and the CBOP proposal, in polyatomic molecules and hydrogen bonding.

The CBOP has been shown as a promising tool for quantifying covalency also in solid-state materials, opening a way to classifying materials in terms of average covalent fractions. Interesting questions could be raised on possible relationships between macroscopic properties of materials and the OP concept. For instance, a good correlation has been found between the non-linear index of refraction (n³) and the OP, though the comparison has been made between the precursor diatomic molecule and the solid-state material. Some unassigned bands in the electron energy-loss and absorption spectra of crystalline alkaline-earth chalcogenides and some alkali and alkali-earth metals in solid-state systems have been discussed in terms of the CBOP, raising the possibility of new assignments alternative to exciton or band-to-band transitions.⁵

Refs (origin of the subject)