Charges and Multipoles in Condensed Matter: Their Relevance for Macroscopic Polarization and Infrared Spectra

Raffaele Resta

Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany;
INFM – Dipartimento di Fisica Teorica, Università di Trieste, I–34014 Trieste, Italy.*
<resta@ts.infn.it>

We start from the important example of oxygen ions in oxides: what is their charge? The formal value is -2: this also coincides with the charge actually transported by oxygen in liquids (e.g. in electrolithic cells). As for solids, the degree of ionicity is often "measured" by attributing a (noninteger) charge to each ion: for oxygen the modulus of this charge is expected to be 2 in the extreme ionic limit, and somewhat lower in partly covalent oxides. However, the static charge "belonging" to a given ion in a condensed system is *not* a measurable quantity, and can be defined only by means of some arbitrary model and/or theory: for instance, the concept of Mulliken charge is very popular in quantum chemistry.

A concept rooted in a more solid ground is that of dynamical (alias infrared) charge: it is an observable quantity, which by definition measures the coupling between electric fields and ionic displacements, ergo it measures the macroscopic polarization induced by sublattice displacements when dealing with lattice dynamics, piezoelectricity, and ferroelectricity. The dynamical charges also provide the oscillator strength of infrared (IR) active modes, thus dominating the IR spectra.

In the last decade there have been sweeping advances in electronic structure theory, allowing the study of the dynamical charges from first principles. Unexpected—and sometimes conterintuitive—results have emerged: for instance the dynamical charge of oxygen can be as large as 7 in modulus in some oxides. Some calculations will be presented, and the physical mechanisms responsible for the nontrivial results will be discussed.

Very recently, Pasquarello and Resta (unpublished) have generalized the concept of atomic dynamical charge by defining the dynamical monopole and dipole for a molecule in condensed—either solid or liquid—molecular phase. In the low frequency IR region, dominated by intermolecular modes (translational and librational), such monopole and dipole are responsible for the shape of the spectrum. For an isolated molecule the dynamical monopole and dipole both coincide with the static ones: the changes occurring when embedding a given molecule in a condensed environment carry in compact form outstanding information about the intermolecular interactions. These changes are particularly dramatic when the interactions between molecules in the condensed phase are strong: first-principle results for the case of liquid water will be presented. The dynamical multipoles quantitatively probe the importance of hydrogen bonding and account for the very strong low-frequency IR activity of water.

* Permanent address.