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First-Principles Theory of Local Dielectric and Piezoelectric Properties of Insulators

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The first-principles theory of the linear dielectric and piezoelectric responses of bulk insulating crystals is by now well established. Typically, linear-response methods, implemented in the context of density-functional theory, are used to compute the electronic dielectric susceptibility and related response tensors, and these ingredients are then assembled in order to compute the lattice-mediated contributions to the dielectric and piezoelectric constants. These methods typically access only the linear responses evaluated at vanishing macroscopic electric field.

There is growing interest in the application of such methods, or extensions of them, to layered structures such as ferroelectric superlattices, ultrathin dielectric films, and nanoscale capacitors. Here one faces three challenges. First, one has to select an appropriate structural model for the study; typically this is an isolated slab (periodic in 2D and isolated along z), a periodically repeated slab in a supercell geometry, or a periodically repeated supercell used to study a superlattice geometry. Second, one is typically interested not only in the case of zero electric field or zero bias, but also in the full response curve (Q-V, C-V, piezoelectric, etc.) as a function of bias V or electric field E. Even if one is interested only in the case where the overall bias is zero, this often puts certain internal layers under a local electric field (due, e.g., to depolarization effects coming from charges at surfaces or interfaces). Thus, in order to understand the results, it is crucial to be able to understand the properties of the constituent layers in finite electric field. Third, one is often interested not just in the total dielectric or piezoelectric response, but also how this response can be decomposed into spatially local (e.g., layer-by-layer) contributions.

In this talk, I will review recent develeopments in theoretical methodologies that now allow all of these challenges to be overcome.

I first briefly review the development of methods that allow the treatment of bulk insulators in non-zero electric field. By carrying out such calculations for a series of E values, one can obtain an entire curve $P(E)$ curve, which we shall refer to as an electric equation of state (EES). Of course, it is straightforward to numerically invert this EES to obtain $E(P)$ as a second form of the EES. Using $D=E+4\pi P$, where D is the electric displacement field, one is then able to obtain four other forms of the EES, namely $D(E)$, $E(D)$, $D(P)$, and $P(D)$. Correspondingly, there are three energy functionals, the energy $E(P)$, the electric enthalpy $F(E)$, and the internal energy $U(D)$. The forms of the electric equation of state involving E as argument, namely $D(E)$ and

$P(E)$, are most naturally derived from the enthalpy $F(E)$, and similarly for the others. The three energy functionals are related by Legendre transformations. The relations between all of these quantities have been detailed in Ref. [1] (see also the supplement associated thereto). Practical first-principles methods for computing the properties of insulators at fixed E, fixed P, and fixed D have been given in Refs. [2-3], Ref. [4], and Ref. [1], respectively. The fixed-D methods turn out to be especially useful in thin-film, superlattice, and capacitor contexts.

I then survey some of the methods that are used to set up up structural models and to extract local dielectric and piezoelectric information, with examples drawn from the treatment of high-K and ferroelectric systems. For our purposes, we usually adopt periodic slab or supercell geometries and apply the finite-field methods mentioned above in the direction normal to the layers.

In the later parts, I will focus on the theory of ferroelectric superlattices and ultrathin capacitors in order to illustrate some of the ideas. For the superlattices, it is of special interest to resolve the local polar contributions. These can be shown to be a local function of chemical environment under appropriate circumstances, allowing for realistic modeling of complex superlattice structures based on reference calculations on a database of short-period structures [5]. Finally, local dielectric contributions can also be resolved for high-K or ferroelectric insulators in contact with metallic electrodes, allowing access to information about dielectric dead layers or about the minimum thickness for ferroelectric capacitor structures [6-7]. In particular, I will describe a study of the critical thickness for the appearance of ferroelectricity in capacitor structures composed of a small number N of unit cells of $BaTiO_3$ (BTO) or $PbTiO_3$ (PTO) sandwiched between $SrRuO_3$ (SRO) or Pt electrodes. The assumed geometry was one having a BaO or PbO termination of the oxide in contact with the electrode (thus there are actually N+1 BaO or PbO layers and N TiO_2 layers in the sandwich). I will then explain how, once we know the dielectric properties of the bulk perovskite, our methods allow us to predict the critical thickness for the appearance of ferroelectricity from a *single* superlattice calculation with an arbitrary number N of layers. In some cases, even a single layer can be ferroelectric.

References

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