GREEN'S FUNCTION CALCULATION OF SURFACE PHONONS IN IONIC CRYSTALS

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INTRODUCTION

How can a paper on the Green's function method applied to surface lattice dynamics fit to a workshop on "Ab-initio calculation of phonon spectra"? We think that the answer comes out from the very essence of the method. All what happens at the free surface of a solid, such as the change of force constants, of atomic equilibrium positions, of electronic structure, is due to intrinsic properties of the bulk Hamiltonian manifesting themselves through the symmetry breaking. Thus a full knowledge of the dynamical structure of the bulk, regardless whether obtained ab-initio or in a phenomenological way, should be sufficient to account for all the surface intrinsic dynamical properties. In the Green's function (GF) method applied to surface problems the bulk dynamical structure is the basic ingredient, whereas the perturbation of an intrinsic surface, induced by the symmetry breaking, turns out to be fully described by the corresponding change in the translational invariance (TI) and rotational invariance (RI) sum rules.

The elements of the unperturbed, bulk, GF matrix contain all the information we need on both bulk dynamics and surface perturbation. Thus the GF method, in the form it has developed, is just a formal procedure to transfer to the surface all what we know, a priori, in the ideal lattice with cyclic boundary conditions. The idea of considering the surface as a perturbation of a perfect cyclic

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lattice dates back to the work of I.M. Lifshitz and L.M. Rozenzweig [1] and was occasionally applied to crystal lattices with short-range interaction [2-4]. The GF technique has been implicitly considered of practical use as far as the perturbation effect is restricted to a small number of surface atomic layers, a requirement which is satisfied only in short-range force constant models. Clearly, in ionic crystals, the surface perturbation extends deeply into the bulk. In a previous paper, appeared in 1973, one of us considered a NaCl ionic slab and the symmetry transformation from a slab of increasing thickness to a semiinfinite lattice with a single surface [5]. According to that work the symmetrized perturbation appropriate to the single-surface semiinfinite lattice has the important property that the Coulomb part of the perturbation is completely screened. Maradudin and Sham, starting from a microscopic description, gave a sound demonstration of the intrinsic difference between a slab and a semiinfinite lattice, with regard to the Coulomb interaction in the long wavelength limit, showing that its contribution to the dynamical matrix is screened in the latter case [6].

The fast exponential decay of the Coulomb contribution inside the crystal allowed for the substitution of the actual perturbation with an effective short-range perturbation matrix, whose elements are defined in terms of the static bulk Green's function through the translational and rotational invariance conditions [5,7].

A similar situation was already met, fifteen years ago, in the theory of local and resonant vibrations in imperfect crystals [8,9], another problem originally approached by Lifshitz [10]. The perturbation due to a substitutional defect in an ionic lattice is never perfectly short-range due to the local change of electronic structure and related parameters such as polarizabilities and Szigeti charge. Thus Benedek and Nardelli introduced the concept of effective short range force constant, defined in terms of the static bulk Green's functions through the stability condition of the defect configuration [8]. The Green's function approach to the surface dynamics of ionic crystals, briefly reviewed in this paper, was based on that same idea.

THE GREEN'S FUNCTION METHOD FOR SURFACE VIBRATIONS

Definitions

We consider first a crystal slab formed by N layers, with N→∞, whose force constant matrix

$$\phi = \phi_0 + \Lambda$$  \hspace{1cm} (1)

is the sum of the force constant matrix $\phi_0$ corresponding to the lattice with three-dimensional (3D) cyclic boundary conditions and