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DERIVATION OF PHONON DISPERSION RELATIONS FROM ELECTRONIC STATES IN INSULATORS

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(Received 8 August 1968)

The electronic contribution to the force constants of lattice vibrations in insulators is studied in a Green's-function formalism. Results of an application of the method to LiF are given where the one-electron spectrum has been treated in the tight-binding approximation.

During the last years a number of articles have been published on the calculation of phonon dispersion curves for metals.[1-5] In contrast to this only a few attempts have been made to treat insulators by taking the contribution of the electrons to the force constants explicitly into account.[6-9] The difficulties associated with an application of the Born-Oppenheimer approximation to insulators have, instead, been avoided by pointing out the formal equivalence between calculations using electronic states and phenomenological force-constant models.[10,11] Numerical calculations were so far based on these models.

This Letter proposes a systematic way for the derivation of the dispersion relations in the harmonic Born-Oppenheimer approximation and gives preliminary results for the application of the method to LiF.

According to Born and Huang[12] the electronic contribution to the harmonic interatomic force constants is given by

$$\varphi(jj')=\frac{d}{dR(j)}\frac{d}{dR(j')}\langle H_{\mathrm{el}}\rangle. \tag{1}$$

Here the index j comprises the number of the unit cell l, the number of a particular lattice particle in the cell s, and the direction in which this particle is displaced from equilibrium α. $d/dR(j)$ denotes the corresponding derivative, and H_{el} is the electronic Hamiltonian:

$$H_{\mathrm{el}}=\sum_i\left[\frac{\hbar^2}{2m}\frac{d^2}{d\vec{r}_i^{\,2}}+V(\vec{r}_i)\right]+\tfrac{1}{2}\sum_{i,j}{}'v(\vec{r}_i-\vec{r}_j).$$

The summation runs over all electrons and the term $i=j$ is excluded from the second sum. H_{el} depends on the lattice configuration through the electron-ion potential $V(\vec{r})$. The Coulomb interaction between the electrons is denoted as $v(\vec{r}-\vec{r}')$. The derivatives in formula (1) are to be taken at the equilibrium position of the ions.

We specify the average over the electronic Hamiltonian to be performed with the ground-state electronic wave function. Thus, temperature dependence is not included in the treatment although there is no principal objection to a generalization of the formulas using temperature-dependent Green's functions.

With the aid of the Hellman-Feynman theorem Eq. (1) can be rewritten as

$$\varphi(jj')=[d/dR(j)]\langle dH_{\mathrm{el}}/dR(j')\rangle. \tag{2}$$

Introducing the electronic Green's function by

$$G(12)=(-i)\langle T[\psi(1)\psi^\dagger(2)]\rangle,$$

where the variables 1 and 2 stand for space and time coordinates of the respective particles, T means time ordering of the quantities in the brackets, and $\psi(1)$ and $\psi^\dagger(2)$ are fermion annihilation and creation operators in the Heisenberg picture, we get from Eq. (2)

$$\varphi(jj')=(-i)\int d\tau\left[\frac{dG(11^+)}{dR(j)}\frac{dH_{\mathrm{el}}}{dR(j')}+G(11^+)\frac{d}{dR(j)}\frac{d}{dR(j')}H_{\mathrm{el}}\right]. \tag{3}$$

Here the symbol 1^+ means that an infinitesimal time argument $\epsilon>0$ has been added to t_1 to insure the correct order of the field operators in the Green's function.

The first term of Eq. (3) can be calculated by considering the equation of motion for the Green's function:

$$LG(11')=\delta(1-1')-i\int d\tau_2\, v(\vec{r}-\vec{r}_2)G(121'2^+)|_{t_1=t_2}. \tag{4a}$$

Here L is a single-particle operator defined by

$$L=i\hbar d/dt-(\hbar^2/2m)d^2/d\vec{r}^2-V(\vec{r}),$$

and

$$G(1234)=\langle T[\psi(1)\psi(2)\psi^\dagger(3)\psi^\dagger(4)]\rangle$$

is the two-particle Green's function. We now differentiate Eq. (4a) with respect to $R(j)$ and solve for $G(11')$ by using the adjoint equation

$$L^+G(1''1')=\delta(1''-1')-i\int d\tau_2\, v(\vec{r}-\vec{r}_2)G(1''s^-1'2)|_{t_1=t_2}. \tag{4b}$$

If we define the mass operator M of the electronic system by the relation

$$(-i)\int d\tau_2\, v(\vec{r}-\vec{r}_2)G(121'2^+)=\int d2\, M(12)G(21'),$$

the following result is obtained:

$$\frac{dG(11')}{dR(j)}=\int d1''\, G(11'')\left[\frac{dV(1'')}{dR(j)}G(1''1')+\int d2\frac{dM(1''2)}{dR(j)}G(21')\right]. \tag{5a}$$

Since the mass operator can be expressed in terms of one-electron Green's functions and the Coulomb interaction between the electrons, Eq. (5a) is really a linear integral equation for the electronic response $dG(11')/dR(j)$. By expanding the mass operator in terms of one-electron lines and the antisymmetrized electron-electron interaction,

$$U(121'2')=(-i)v(\vec{r}_1-\vec{r}_2)[\delta(1-1')\delta(2-2')-\delta(1-2')\delta(2-1')],$$

we get for the lowest order terms

$$dG(11')/dR(j)=\int d2\, G(12)[dV(\vec{r}_2)/dR(j)]G(21')+\int d2d2'd3d3'\, G(12)U(233'2')G(2'1')dG(33')/dR(j)+\cdots.$$

We truncate the series after the second term on the right and insert the approximate expression into Eq. (3). If we define the effective electron-electron interaction by

$$W(121'2')=U(121'2')+\int d3d3'd4d4'\, U(1233')G(34)G(3'4')W(44'1'2'),$$

we get for the force constants

$$\begin{aligned}\varphi(jj')+i\int d\tau\, G(11^+)\frac{d}{dR(j)}\frac{d}{dR(j')}V(\vec{r})\\ =-i\int d\tau\frac{dV(\vec{r})}{dR(j)}G(12)\frac{dV(\vec{r}_2)}{dR(j')}G(21^+)\\ +\int d\tau d\tau_4 d2d3d2'd3'\frac{dV(\vec{r})}{dR(j)}G(12)G(31^+)W(232'3')G(2'4)G(3'4^+)\frac{dV(\vec{r}_4)}{dR(j')}.\end{aligned} \tag{6}$$

So far we have not specified the potential and the wave functions. The formulas derived apply to any substance for which the Born-Oppenheimer approximation holds.

In order to use Eq. (6) as a basis for the explicit numerical calculation of the force constants of LiF,[13] the single-particle approximation was made. The electronic spectrum then enters the calculation via energy levels and eigenfunctions of an approximate one-electron Hamiltonian. Following the procedure of Slater and Koster,[14] the energy values were determined to give a band structure for the F$^-$ $2p$ valence and the Li$^-$ $2s$ conduction band of LiF (see Fig. 1) that reproduces the main features of the experi-

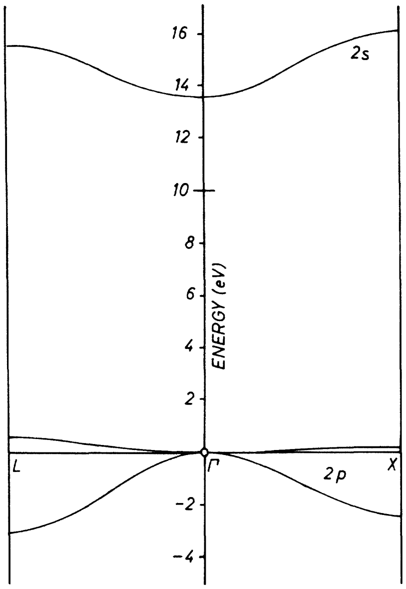

FIG. 1. Valence and conduction bands of LiF.

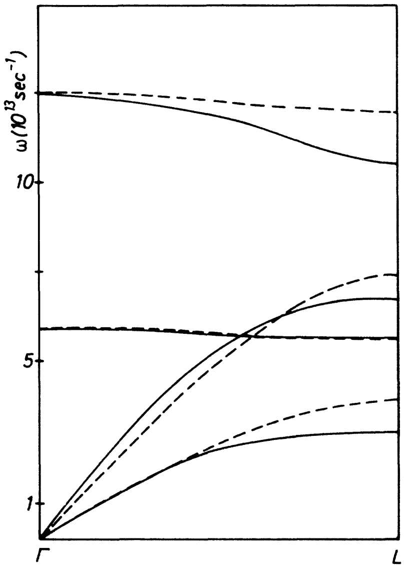

FIG. 2. Phonon dispersion curves for LiF in the (1, 1, 1) direction. Solid line: this paper. Broken line: results by Schröder and Nüsslein.

mental reflectivity spectrum given by Roessler and Walker.[15] The electron-ion potential was set up as a phenomenological potential. It includes that part of the electronic response that can be described by a rigid motion of the electrons with the displaced ion. The potential for each ion contains two parameters. Accordingly, Kellermann's[16] coefficients were used for the calculation of the Coulomb interactions between the ions. The matrix elements were calculated in the tight-binding approximation based on free-ion wave functions given by Clementi.[17] The orthogonalization procedure of Löwdin[18] was employed to first order in the overlap matrix elements and three- and four-center integrals were neglected.

By assuming the potential to be a superposition of the contributions of the different ions, the average over the second derivative of V in Eq. (6) can be eliminated because of the symmetry relation for translational invariance:

$$\sum_{ls}[\varphi(jj')+\varphi^{\mathrm{Coul}}(jj')]=0,$$

where $\varphi^{\mathrm{Coul}}(jj')$ is the Kellermann coefficient.

Figure 2 shows dispersion curves obtained for the (1, 1, 1) direction by our procedure. Two potential parameters which correspond to the screened ionic charges were used to fulfill the Lyddane-Sachs-Teller relation. The two other parameters describing the structure of the rigid part of the electronic charge were chosen to give good mean agreement of the calculated curves with the results of Schröder and Nüsslein[19] for 0 °K. For room temperature their model describes quite well the neutron-diffraction data measured by Dolling et al.[20]

The calculated result depends sensitively on the correct band structure. The dispersion curves did not give stable solutions, for instance, when the value of the energy gap was diminished from the experimental value of 13.6 eV by about 2 eV. For the (1, 0, 0) direction the result depends critically on the core regime of the ion potentials. Our simple model potential which neglected the electronic structure near the core did not yield satisfactory results in both symmetry directions. It is hoped, however, that an improved phenomenological potential and a better approximation for the one-electron wave functions will help to eliminate these shortcomings.

The present calculation, the results of which we have sketched, served as a test for different potential models. It also provided insight into the interrelation of phonon dispersion curves and the parameters of phenomenological force-constant models on one side and properties of the electronic states on the other.[21]

The authors acknowledge financial support by the Deutsche Forschungsgemeinschaft and technical assistance by Deutsches Rechenzentrum for carrying out the numerical calculations.

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