Sum Rule for Lattice Vibrations in Ionic Crystals

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It is shown that in lattices of tetrahedral symmetry with two ions to a unit cell, in the approximation of nearest neighbor repulsive interactions, for a given wave vector $\mathbf{q}$,

$$\sum_{i=1}^{6}\omega_i^2(\mathbf{q})=\frac{1}{\beta}\frac{18}{\bar{M}r_0},$$

where $\omega_i(\mathbf{q})$ = angular frequency of the ith mode for a given wave vector $\mathbf{q}$, $\bar{M}=m_+m_-/(m_++m_-)$, m_+ = mass of positive ion, m_- = mass of negative ion, r_0 = interionic distance, and β is the coefficient of compressibility. This theorem serves as a useful check on numerical work as well as a relation for the downward curvature of the optical modes at small q in terms of the speed of sound. In the limit of small q, this relation becomes the first Szigeti relation. A similar theorem is true for low-density electron gases where the electrons localize on a lattice. Here one can show that

$$\sum_{i=1}^{3}\omega_i^2(\mathbf{q})=\omega_{\mathrm{pl}}^2,$$

where $\omega_{\mathrm{pl}}^2=4\pi ne^2/m$, which is the classical plasma frequency. (This last relation was first derived by Kohn.)

IN computing the lattice vibration spectrum of ionic crystals, the model of nonpolarizable ions is often used. For this model, a general theorem on the sums of the squares of the angular frequencies $\omega_i(\mathbf{q})$ of all modes for a given lattice wave vector $\mathbf{q}$ is readily formulated. This theorem provides a powerful check on numerical work such as Kellermann's calculations on NaCl.[1]

As calculations have only been made on alkali halides, we shall restrict ourselves to the case of lattices of tetrahedral symmetry with two ions to a unit cell. The statement of the theorem is that in such lattices for nonpolarizable ions,

$$\sum_{i=1}^{6}\omega_i^2(\mathbf{q})=\frac{1}{\beta}\frac{18}{\bar{M}r_0}, \tag{1}$$

where $\bar{M}=m_+m_-/(m_++m_-)$, m_+ = mass of positive ion; m_- = mass of negative ion, r_0 = interionic distance, and β = coefficient of compressibility.

A special case of Eq. (1) is for very long wavelengths where all acoustic modes have zero frequency. The two transverse optical modes vibrate with the rest-strahl frequency ω_0 and the longitudinal mode vibrates with $(\epsilon_0)^{\frac{1}{2}}\omega_0$, where ϵ_0 is the static dielectric constant. In the usual notation we have $\epsilon_\infty=1$ for our nonpolarizable ionic model. In this case, Eq. (1) reads

$$(\epsilon_0+2)\omega_0^2=\frac{1}{\beta}\frac{18}{\bar{M}r_0}, \tag{2}$$

which is the first Szigeti relation.[2] The relation (1) which we shall prove is thus a generalization of the first Szigeti relation to all wavelengths in a nonpolarizable ionic lattice.

[1] E. W. Kellermann, Trans. Roy. Soc. (London) **A238**, 513 (1940).
[2] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954).

The proof of Eq. (1) follows immediately from the secular equation that determines the frequencies for a given $\mathbf{q}$. If $\boldsymbol{\varepsilon}$ is a six-vector, then the secular equation is

$$\omega^2(\mathbf{q})\boldsymbol{\varepsilon}(\mathbf{q})=\mathbf{G}(\mathbf{q})\cdot\boldsymbol{\varepsilon}(\mathbf{q}), \tag{3}$$

where the 6×6 tensor $\mathbf{G}$ may be labeled by the three orthogonal directions $\alpha,\beta=1,2,3$ and the index $+$ or $-$ for the positive or negative ion. The components are $G_{\alpha\beta}{}^{++}$, $G_{\alpha\beta}{}^{+-}$, and $G_{\alpha\beta}{}^{--}$. These have been worked out in detail by Kellermann, but to prove our theorem we only need the general form of the diagonal elements, i.e., $G_{\alpha\alpha}{}^{++}$, and $G_{\alpha\alpha}{}^{--}$. We split $\mathbf{G}$ into two parts, the part arising from the Coulomb forces being called ${}^{C}\mathbf{G}$ and the part from ionic overlap repulsion ${}^{R}\mathbf{G}$. Then

$${}^{C}G_{\alpha\alpha}{}^{++}=\frac{e^2}{m_+}\sum_{\mathbf{l}\neq0}\frac{\partial^2}{\partial x_\alpha{}^2}\frac{1}{|\mathbf{r}-\mathbf{a}_\mathbf{l}|}\exp(i\mathbf{q}\cdot\mathbf{a}_\mathbf{l}), \tag{4}$$

where $\mathbf{a}_\mathbf{l}$ = lattice vector. By Laplace's theorem, it is then seen that

$$\sum_{\alpha=1}^{3}{}^{C}G_{\alpha\alpha}{}^{++}=\sum_{\alpha=1}^{3}{}^{C}G_{\alpha\alpha}{}^{--}=0. \tag{5}$$

Equation (5) is the essential content of this paper for it says that the trace of $\mathbf{G}$ is determined by the repulsive forces alone, which is the verbal statement of Eq. (1).

To calculate the repulsive interactions, we use the work of Born and Huang (reference 2, Sec. 9), assuming only nearest neighbor repulsive interactions. Here

$${}^{R}G_{\alpha\alpha}{}^{++}=(1/3m_+)Z\nabla^2\phi_{\mathrm{repulsive}}\big|_{r=r_0}, \tag{6}$$

where Z is the number of nearest neighbors, r_0 the interionic distance. $\nabla^2\phi$ is easily expressed in terms of the compressibility. In fact

$$Z\nabla^2\phi_{\mathrm{repulsive}}\big|_{r=r_0}=18r_0/\beta. \tag{7}$$

From (5), (6), and (7), we find that the trace of the 6-tensor $\mathbf{G}$ is

$$\mathrm{tr}G=\frac{18r_0}{\beta}\left[\frac{1}{m_+}+\frac{1}{m_-}\right]. \tag{8}$$

By the invariance of the trace to orthogonal transformation this proves our theorem.

An interesting corollary of our theorem is the relation of the curvature downwards of the optical modes, as a function of wave number, to the speed of sound. If c_l and c_t are, respectively the longitudinal and transverse sound velocities, then for small $\mathbf{q}$ we have

$$\sum[\omega_{\text{optical}}]^2=(\epsilon_0+2)\omega_0^2-(2c_t^2+c_l^2)q^2. \tag{9}$$

An interesting application of these same ideas is in the calculation of the correlation energy of an electron gas in a uniform positive charge background at low density [i.e., (Bohr radius/interelectronic distance) $\ll 1$].[3,4] In this limit, the long-range Coulomb repulsion is the dominant contribution and the electrons will localize themselves on a lattice. The body-centered cubic lattice is most favorable.[5] In next approximation to the energy one must include the zero-point energy of the lattice. Here there are three modes per lattice wave vector $\mathbf{q}$. The forces on a given electron are the interelectronic Coulomb force and the interaction with the uniform background. Again let ${}^{C}G_{\alpha\beta}$ be the part of the frequency tensor arising from interelectronic repulsion. Further, let ${}^{B}G_{\alpha\beta}$ be the part of the frequency tensor arising from interaction with the background. We thus have

$${}^{B}G_{\alpha\beta}(\mathbf{q})=\frac{-e^2n}{m}\frac{\partial^2}{\partial x_\alpha\partial x_\beta}\int\frac{d\mathbf{r}'}{|\mathbf{r}-\mathbf{r}'|}, \tag{10}$$

where n is the mean number density of electrons. Because of spherical symmetry in the integral, the right-hand side of (10) vanishes for $\alpha\neq\beta$, and by Poisson's equation we thus have

$${}^{B}G_{\alpha\beta}(\mathbf{q})=\frac{1}{3}\frac{4\pi ne^2}{m}\delta_{\alpha\beta}=\tfrac{1}{3}\omega_{\mathrm{pl}}{}^2\delta_{\alpha\beta}, \tag{11}$$

where ω_{pl} is the classical plasma frequency. For the present problem, (11) supplies the stability role played by the ionic repulsive forces in the previous problem. Again we clearly have $\sum{}^{C}G_{\alpha\alpha}(\mathbf{q})=0$ by Laplace's theorem, so that

$$\sum_{\alpha=1}^{3}G_{\alpha\alpha}(\mathbf{q})=\sum_{L=1}^{3}\omega_t{}^2(\mathbf{q})=\omega_{\mathrm{pl}}{}^2. \tag{12}$$

This result was found independently some time ago by Kohn.[4] It is of importance for it gives an inequality for E_0, the correction to the lattice energy due to zero-point oscillations:

$$\tfrac{1}{2}\hbar\omega_{\mathrm{pl}}\leqslant E_0/N\leqslant\tfrac{1}{2}\sqrt{3}\hbar\omega_{\mathrm{pl}}, \tag{13}$$

where N is the total number of electrons. Rough estimates indicate that $E_0/N\cong 1.5\times\frac{1}{2}\hbar\omega_{\mathrm{pl}}$.

[3] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[4] W. Kohn has independently derived relation (12). Reference to this may be found in J. Bardeen and D. Pines, Phys. Rev. **99**, 1140 (1955). I am grateful to Professor Kohn for informing me of his results.

[5] W. Kohn (private communication).