Lattice Vibrations in Crystals with Molecular Impurity Centers*

MAX WAGNER

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

(Received 5 June 1963)

The Green's function formalism of Lifshitz and others for the calculation of lattice vibrations in impure crystals is restricted to disturbed lattices with an unchanged number of particles (monatomic impurity centers). A method is given here which reduces the problem of polyatomic impurities to the Lifshitz formalism. This is achieved by means of a molecular Green's function which describes the influence of the molecular particles as an effective disturbance among the lattice particles, excluding the molecular coordinates themselves.

THE lattice vibrations of a disturbed crystal can be calculated by a method first developed by Lifshitz.[1] The idea in this method is to reduce the many-dimensional problem ($\sim 10^{23}$) to effectively few dimensions using a Green's function, defined in ideal lattice-mode representation. The method has been used extensively by numerous authors[2] and proved especially effective in some new developments by Krumhansl[3] and Klein.[4] Its use has been restricted, however, to monatomic impurity centers, i.e., to cases where there are no new degrees of freedom. The aim of this paper is to show that the method is easily extended to molecular impurity centers.

If a molecule of $s+1$ masses m_ν replaces a regular lattice atom at $\mathbf{n}=0$, we may transform the molecular variables to a new set $(x_0{}^i, \xi_1{}^i, \cdots, \xi_s{}^i)$, where $(x_0{}^i)$ gives the position of the molecular center of the mass. The $\xi_\nu{}^i$ may be chosen rather arbitrarily, but they must diagonalize the kinetic energy, with an associated effective mass μ_ν. Let us add $x_0{}^i$ and the molecular mass $M_0 = m_1 + m_2 + \cdots m_s$ to the other lattice coordinates $x_n{}^i$ and masses $M_n{}^{(0)}$ ($M_n{}^{(0)} = $ ideal masses), thus establishing a $3N$ system as in the ideal case. Then, there is a natural way of looking at the problem: (a) The "lattice system" is characterized by a $3N \times 3N$ matrix $H_{nm}{}^{ij} = H_{nm}{}^{(0)ij} + H_{nm}{}^{(1)ij}$, where $H_{nm}{}^{(0)ij}$ is the ideal matrix. (b) The "molecular system" is characterized by a $3s \times 3s$ matrix $h_{\nu\mu}{}^{ij}$. (c) The interaction between the two systems is defined by a $3N \times 3s$ matrix $R_{n\nu}{}^{ij}$. (d) The disturbance extends only to a small number r of lattice sites $\mathbf{n}$ around the origin, which implies that $H_{nm}{}^{(1)ij}$ and $R_{n\nu}{}^{ij}$ are (practically) zero outside this region. (e) We may expect, therefore, the reduction of this kind of problem using Green's functions. We introduce the substitutions,

$$z_n{}^i = (M_n{}^{(0)})^{1/2} x_n{}^i,$$

$$\zeta_\nu{}^i = \mu_\nu{}^{1/2} \xi_\nu{}^i,$$

[1] I. M. Lifshitz, Nuovo Cimento 3, Suppl. A1, 716 (1956).
[2] J. A. Krumhansl, Suppl. J. Appl. Phys. 33, 307 (1962); this is a review article with more complete references.
[3] J. A. Krumhansl, Phys. Rev. (to be published). See also short report given at the St. Louis Meeting, 1963 [Bull. Am. Phys. Soc. 11, 207 (1963)].
[4] M. V. Klein, Phys. Rev. 131, 1500 (1963). See also short report given at the St. Louis Meeting, 1963 [Bull. Am. Phys. Soc. 11, 207 (1963)].

$$L_{nm}{}^{ij} = (M_n{}^{(0)} M_m{}^{(0)})^{-1/2} H_{nm}{}^{(0)ij},$$

$$\alpha_{\nu\mu}{}^{ij} = (\mu_\nu \mu_\mu)^{-1/2} h_{\nu\mu}{}^{ij},$$

$$B_{n\nu}{}^{ij} = (M_n{}^{(0)} \mu_\nu)^{-1/2} R_{n\nu}{}^{ij},$$

$$A_{nm}{}^{ij}(\omega^2) = \omega^2 (1 - M_n/M_n{}^{(0)}) \delta_{ij} \delta_{nm} \delta_{0n}$$
$$+ (M_n{}^{(0)} M_m{}^{(0)})^{-1/2} H_{nm}{}^{(1)ij}. \quad (1)$$

Then, the eigenvalue equations of the two connected systems read:

$$(L + A(\omega^2) - \omega^2 I) \cdot z + B \cdot \zeta = 0, \quad (3N \text{ equations}), \quad (2a)$$

$$(\alpha - \omega^2 I) \cdot \zeta + \tilde{B} \cdot z = 0. \quad (3s \text{ equations}). \quad (2b)$$

Without the perturbation A and the coupling B each of the two systems defines a Green's function,

$$G(\omega^2) = (L - \omega^2 I)^{-1} = \sum_{k\lambda} \frac{z(k\lambda) z^\dagger (k\lambda)}{\omega_{k\lambda}{}^2 - \omega^2}, \quad (3a)$$

$$\gamma(\omega^2) = (\alpha - \omega^2 I)^{-1} = \sum_\kappa \frac{\zeta(\kappa) \zeta^\dagger (\kappa)}{\omega_\kappa{}^2 - \omega^2}, \quad (3b)$$

where $z(k\lambda)$, $\zeta(\kappa)$ denote the normalized eigenvectors, $\omega_{k\lambda}{}^2$, $\omega_\kappa{}^2$ the eigenfrequencies of the matrices L and α, respectively. It is easily verified that the total Green's functions for the combined system (2a)–(2b) is given by the single Green's functions (3a)–(3b) in the simple way:

$$G_t(\omega^2) = \begin{pmatrix} G(\omega^2) & 0 \\ 0 & \gamma(\omega^2) \end{pmatrix}. \quad (4)$$

It is not necessary, however, to use this $(3N+3s) \times (3N+3s)$ matrix, because the special structure of the system (2a)–(2b) allows the molecular coordinates ζ to be excluded. Using (3b) we can write (2b) in the form,

$$\zeta = -\gamma(\omega^2) \tilde{B} \cdot z. \quad (5)$$

M   f   M   f M/2   f'   M/2   f   M   f

−2   −1   0   +1
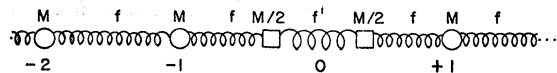
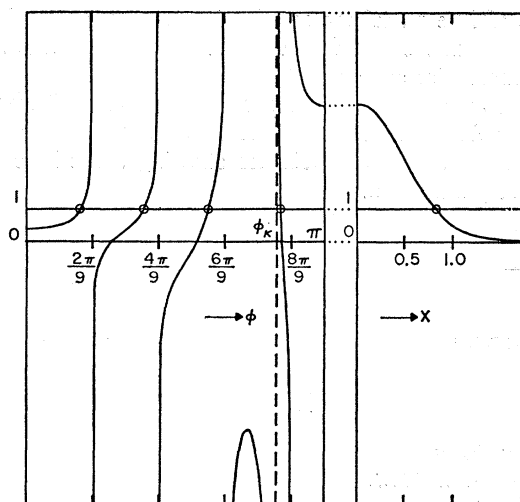FIG. 1. Uniform linear chain with a diatomic substitution at one single lattice site.

FIG. 2. The solutions of Eqs. (10a) and (10b) for $\omega_\kappa < \omega_L$ ($N=9$, $\varphi_\kappa = 0.84\pi$).

Introducing this expression for ζ in (2a) and multiplying from the left by $G(\omega^2)$, Eq. (2a) takes the form,

$$z = -G(\omega^2)[A(\omega^2) - B\gamma(\omega^2)\tilde{B}] \cdot z \qquad (6)$$

and the molecular coordinates are thus removed. Now A and B can be written as

$$A = \begin{pmatrix} a & 0 \\ 0 & 0 \end{pmatrix}, \quad B = (b,0), \qquad (7)$$

where a is a $3r \times 3r$ and b a $3r \times 3s$ matrix, both extending only over the r lattice sites involved around the molecule. Hence, the eigenvalue equation, extracted from the system (6), reads:

$$D(\omega^2) = \mathrm{Det}(I + g(\omega^2)[a - b\gamma(\omega^2)\tilde{b}]) = 0, \qquad (8)$$

which is a determinant of rank $3r$. $g(\omega^2)$ is the $3r \times 3r$ matrix of $G(\omega^2)$ which belongs to the r involved lattice points. It is seen that the old Lifshitz matrix $I + g(\omega^2)a$ is supplemented by the additional matrix $-g(\omega^2)b\gamma(\omega^2)\tilde{b}$,
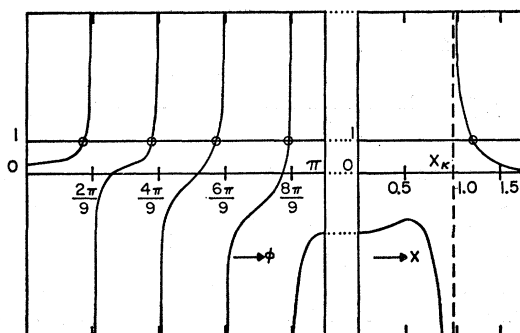

FIG. 3. The solutions of Eqs. (10a) and (10b) for $\omega_\kappa > \omega_L$ ($N=9$, $x_\kappa = 1.0$).

written more explicitly for clarity as follows:

$$g(\omega^2)b\gamma(\omega^2)\tilde{b} \equiv \left(\sum_{l\nu\mu} g_{nl}b_{l\nu}\gamma_{\nu\mu}b_{\mu m} \right), \quad \begin{array}{l} l,n,m = 1,2,\cdots,3r; \\ \nu,\mu = 1,2,\cdots,3s. \end{array} \qquad (9)$$

In this formulation the eigenvalue determinant is of the same rank $3r$ as in the Lifshitz problem and $-b\gamma(\omega^2)\tilde{b}$ may be considered as an additional disturbance in the "lattice system."

We demonstrate the method for the very simple example of a monatomic linear chain where one lattice point is replaced by a "molecule" of two foreign atoms of equal mass $m = \frac{1}{2}M$. All properties are indicated in Fig. 1. Here we get two expressions for the determinant $D(\omega^2)$, due to the fact that the Green's function $g(\omega^2)$ has a different form for $\omega^2 < 4f/M$ (Wallis and Maradudin[5]) and for $\omega^2 > 4f/M$ (Montroll and Potts[6]). The even solutions are not altered by this special kind of "molecule," whereas the odd frequencies are given by the two equations,

$$\frac{\omega_L^2 \sin((N-2)\varphi/2)}{2(\omega_\kappa^2 - \omega^2) \sin(N\varphi/2)} = 1 \quad \text{for} \quad \omega^2 < \omega_L^2 \qquad (10a)$$

and

$$\frac{\omega_L^2(1 - e^{-2x})}{4(\omega^2 - \omega_\kappa^2) \sinh(x)} = 1 \quad \text{for} \quad \omega^2 > \omega_L^2, \qquad (10b)$$

with the abbreviations

$$\omega_L^2 = 4f/M,$$
$$\omega_\kappa^2 = (4f' + 2f)/M,$$
$$\omega^2 = \omega_L^2 \sin^2(\varphi/2) \text{ for } \omega^2 < \omega_L^2,$$
$$\omega^2 = \omega_L^2 \cosh^2(x/2) \text{ for } \omega^2 > \omega_L^2. \qquad (11)$$

The solutions of (10a) and (10b) are demonstrated graphically in Fig. 2 for $f' < \frac{1}{2}f$ and in Fig. 3 for $f' > \frac{1}{2}f$. As seen from the figures the number of solutions within the band is unchanged, but there is an additional solution above the band in both cases. For $\omega_\kappa < \omega_L$ there is some drastic change in the curves in the vicinity of $\omega_\kappa = \omega$ (Fig. 2) which might give rise to "phonon" resonances in this region. For $\omega_\kappa > \omega_L$ the new solution lies above the molecular frequency ω_κ (Fig. 3). It is, of course, true that this single example could have been treated also by the method of Montroll and Potts[6] as one of a chain of $N+1$ atoms of which two consecutive atoms differ from the rest in their masses and the "spring" joining them, or even by more elementary methods. But our treatment has the advantage of revealing most essential features of the three-dimensional case: (a) a drastic change in the vicinity of the molecular frequen-

[5] R. F. Wallis and A. A. Maradudin, Progr. Theoret. Phys. (Kyoto) 24, 1055 (1960).
[6] E. W. Montroll and R. B. Potts, Phys. Rev. 100, 525 (1955).

cies ω_κ which might culminate in additional solutions within the band in some cases and (b) new solutions outside the band.

The choice of the center-of-mass coordinates $x_0{}^i$ for the "lattice" is not the only possibility; we could have chosen, as well, any three coordinates of the molecule to which a single effective mass can be attached. In the case of interstitial masses, for instance, one may keep the old lattice coordinates, taking the interstitials as the molecular system ($\xi_\nu{}^i$).

The author wishes to express his thanks to Professor James A. Krumhansl for valuable discussions and to Professor Miles V. Klein for showing him his results before publication.

Vibrational Corrections to Nuclear Magnetic Resonance Second Moments*

D. E. O'REILLY AND TUNG TSANG

Argonne National Laboratory, Argonne, Illinois

(Received 2 May 1963)

The effect of rapid nuclear motions on the observable second moments of nuclear-magnetic resonance-absorption lines is considered by the method of lattice harmonics. An explicit formula is given in terms of time-averaged values of lattice harmonics. In the case of lattice vibrations in a cubic solid with a cubic point group at the nuclear site, the observable correction to the rigid lattice second moment is zero up to and including the second order in the relative nuclear amplitudes of vibration. In general, only the anisotropic vibrations contribute in second order to the observable second moment.

THE effects of nuclear motion on nuclear-magnetic resonance lines of nuclei in crystals are well recognized and generally referred to as "motional narrowing" since the nuclear motion produces a reduction in the observed resonance linewidth and moments. Denoting the truncated dipolar interaction Hamiltonian of Van Vleck[1] by $\mathfrak{K}$ and the total nuclear spin by $\mathbf{I}$, the second moment is proportional to the trace of $\langle[\mathfrak{K},I_x]^2\rangle$, where the angular bracket indicates the time average of the enclosed quantity. In the presence of nuclear motion which causes a time dependence of $\mathfrak{K}$ and which is rapid compared to the Larmor precession of the nuclei in the external magnetic field, $\langle[\mathfrak{K},I_x]^2\rangle$ may be rewritten as follows:

$$\langle[\mathfrak{K},I_x]^2\rangle=[\langle\mathfrak{K}\rangle,I_x]^2+\langle[\mathfrak{K}-\langle\mathfrak{K}\rangle,I_x]^2\rangle. \quad (1)$$

Equation (1) results since $\mathfrak{K}=\langle\mathfrak{K}\rangle+(\mathfrak{K}-\langle\mathfrak{K}\rangle)$ and $\langle[\langle\mathfrak{K}\rangle,I_x][\mathfrak{K}-\langle\mathfrak{K}\rangle,I_x]\rangle=0$. As pointed out by several authors,[2] the second term in (1) gives a contribution to the second moment in the far wings of the absorption line which is not observed in a conventional magnetic resonance experiment. In the following, we will refer to the second moment computed by taking the trace of $\langle[\mathfrak{K},I_x]^2\rangle$ and $[\langle\mathfrak{K}\rangle,I_x]^2$ as $M_2{}'$ and $M_2{}^{\mathrm{obs}}$, respectively. The experimentally measured second moment will correspond to $M_2{}^{\mathrm{obs}}$. $M_2{}^{\mathrm{obs}}$ has also been referred to as the "observable" part of the second moment.[2]

An alternative, but equivalent way of viewing the situation is to note that if a nuclear spin undergoes a periodic motion during which it experiences a range of local magnetic fields due to neighboring nuclei, and, further, if the period of this motion is very short compared to the period of Larmor precession, then the magnetic moment will respond only to the mean local field. Thus, in computing the mean square local field, the local field must first be time averaged corresponding to the first term of Eq. (1). The fourth moment is proportional to $\langle[\mathfrak{K},[\mathfrak{K},I_x]]^2\rangle$ which may be seen from arguments similar to those given above yields an observable part which is proportional to $[\langle\mathfrak{K}\rangle,[\langle\mathfrak{K}\rangle,I_x]]^2$ when the motion is fast.

For a rigid lattice, the dependence of the second moment on the orientation of the crystal under study may be conveniently expressed in terms of the lattice harmonics of the point group of the crystal[3] as follows (for only one magnetic nucleus per unit cell):

$$M_2=12\pi\gamma^4\hbar^2I(I+1)$$
$$\times\sum_k\sum_{L\alpha}\frac{[C(22L;00)]^2}{2L+1}\frac{X_L{}^{1\alpha*}(jk)}{r_{jk}{}^6}X_L{}^{1\alpha}(\theta,\phi), \quad (2)$$

where L takes on the values 0, 2, and 4, $C(22L;00)$ is a Clebsch-Gordan coefficient, $X_L{}^{1\alpha}$ denotes a lattice harmonic of order L belonging to the identity representation of the crystal point group, jk and (θ,φ) denote the respective orientations of the radius vector $\mathbf{r}_{jk}$ and the external magnetic field relative to the crystal coordinate system.

---

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[1] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

[2] See, for example, the review by A. Abragam, in *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. 10.

[3] D. E. O'Reilly and T. Tsang, Phys. Rev. 128, 2639 (1962).