[19]B. R. Cooper, H. Ehrenreich, and H. R. Philipp, Phys. Rev. **138**, A494 (1965).

[20]P. Drude, *The Theory of Optics* (Longmans, Green and Co., New York, 1902).

[21]W. Pimak and L. H. Fuchs, Phys. Rev. **95**, 22 (1954).

[22]W. Primak, Phys. Rev. **103**, 544 (1956).

[23]J. W. McClure and Y. Yafet, in *Proceedings of the Fifth Carbon Conference* (Pergamon, Oxford, England, 1962), p. 22.

[24]S. Ergun, in *Chemistry and Physics of Carbon*, edited by P. L. Walker, Jr. (Marcel Dekker, New York, 1968), Vol. 3, p. 45.

[25]R. L. Brodersen, Ph.D. thesis (MIT, 1972) (unpublished).

[26]G. Dresselhaus (unpublished).

[27]P. R. Schroeder, M. S. Dresselhaus, and A. Javan,

Phys. Rev. Letters **20**, 1292 (1968).

[28]H. R. Philipp, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (Wiley, New York, 1966), p. 408.

[29]E. Tosatti and F. Bassani, Nuovo Cimento **65**, 161 (1970).

[30]K. Kobayashi and Y. Uemura, J. Phys. Soc. Japan **25**, 404 (1968).

[31]A. Imatake and Y. Uemura, J. Phys. Soc. Japan **28**, 410 (1970).

[32]M. Anderegg, B. Feuerbacher, and B. Fitton, Phys. Rev. Letters **26**, 760 (1971).

[33]A. Balzarotti and M. Grandolfo, Phys. Rev. Letters **20**, 9 (1968).

[34]G. Gilat and L. J. Raubenheimer, Phys. Rev. **144**, 390 (1966).

[35]L. G. Johnson, Ph.D. thesis (MIT, 1973) (unpublished).

Localized Basis for Lattice Vibrations*

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For the case of electrons in a periodic lattice there exist extended basis functions (Bloch waves) and localized basis functions (Wannier functions). It is shown here that also for lattice vibrations there exists, in addition to the usual extended basis functions (normal modes), a set of localized basis functions. These are nontrivial only for lattices with several atoms per unit cell. Examples are worked out and discussed. These functions appear to be of interest for the treatment of defects and other problems calling for a localized description.

The electronic theory of solids has been largely developed in the language of Bloch functions, which are extended throughout the entire solid. While this approach has generally been eminently appropriate and successful, it has one drawback: The effective interactions between electrons are generally of short range and many interesting phenomena in solids, such as those associated with defects, are of a local character. For some purposes it is therefore somewhat unnatural, and also an obstacle to the application of physical or chemical intuition, to work in a representation of infinitely extended states. This drawback can be overcome by the use of localized Wannier functions[1] which span the same space as the extended Bloch functions.

For similar reasons it appears to be of interest to construct a localized orthonormal basis for lattice vibrations, which spans the same space as the well-known 'delocalized normal modes of the crystal lattice.[2] This will be done in the present paper.

The localized basis to be discussed is nontrivial only for lattices with more than one atom per unit cell. We therefore consider first a diatomic lattice in one dimension with lattice parameter a, masses M_1 and M_2, and two nearest-neighbor force constants α and β. The N lattice cells (with $N \to \infty$) are labeled by $l = -\frac{1}{2}N, \ldots, +\frac{1}{2}N - 1$; and the two atoms in each cell by $\kappa = 1, 2$ (see Fig. 1). It is well known[3] that the atomic displacements in a normal mode of vibration of wave number k and frequency ω have the form

$$w_{l,\kappa} = M_\kappa^{-1/2} u_\kappa e^{i(kla - \omega t)}, \tag{1}$$

where the coefficients u_κ satisfy the equations

$$\omega^2 u_\kappa(k) = \sum_{\kappa'=1}^{2} D\left(\begin{matrix} k \\ \kappa\kappa' \end{matrix}\right) u_{\kappa'}(k); \tag{2}$$

and the matrix

$$D\left(\begin{matrix} k \\ \kappa\kappa' \end{matrix}\right) \equiv \begin{pmatrix} \dfrac{\alpha + \beta}{M_1} & \dfrac{\alpha + \beta e^{-ika}}{(M_1 M_2)^{1/2}} \\[3mm] \dfrac{\alpha + \beta e^{ika}}{(M_1 M_2)^{1/2}} & \dfrac{\alpha + \beta}{M_2} \end{pmatrix}. \tag{3}$$

The eigenfrequencies are given by the quadratic secular equation

$$\left| D\left(\begin{matrix} k \\ \kappa\kappa' \end{matrix}\right) - \omega^2(k) \delta_{\kappa\kappa'} \right| = 0, \tag{4}$$

whose two solutions for each value of k are denoted by $\omega^2(\begin{smallmatrix} j \\ k \end{smallmatrix})$ $(j = 1, 2)$. These constitute the acoustic
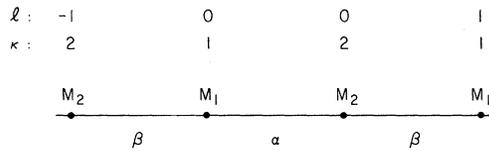
FIG. 1. Notation for the diatomic lattice l is the cell index; κ is the intracell index; M are the masses; α, β are the force constants.

and optical frequency branches, respectively. The corresponding orthonormal eigenvectors $u_\kappa\binom{j}{k}$ are obtained from Eq. (2) and the normalization condition

$$\sum_{\kappa=1}^{2} u_k^*\binom{j}{k} u_\kappa\binom{j'}{k} = \delta_{jj'} . \tag{5}$$

These conditions leave the phase of $u_\kappa\binom{j}{k}$ undefined. The functions

$$u_{l,\kappa}\binom{j}{k} \equiv N^{-1/2} u_\kappa\binom{j}{k} e^{ikla} \tag{6}$$

with $j = 1, 2$ and

$$k = (\pi/a)N^{-1}(-\tfrac{1}{2}N , \ldots , \tfrac{1}{2}N - 1) \tag{7}$$

evidently form a $2N$-dimensional orthonormal basis,

$$\sum_{l,\kappa} u_{l,\kappa}^*\binom{j}{k} u_{l,\kappa}\binom{j'}{k'} = \delta_{jj'} \delta_{kk'} . \tag{8}$$

In terms of these functions an arbitrary displacement function $f_{l,\kappa}$ of the $2N$ atoms can be linearly expressed.

For each branch j, we now replace the delocalized basis functions (6) by the following localized basis functions:

$$v_{l,\kappa}\binom{j}{m} \equiv N^{-1/2} \sum_k u_{l,\kappa}\binom{j}{k} e^{-ikma}$$

$$= N^{-1} \sum_k u_\kappa\binom{j}{k} e^{ik(l-m)a} , \tag{9}$$

where m denotes the index of the cell in whose neighborhood the displacements $v_{l,\kappa}$ are localized.

The orthonormality of the new basis,

$$\sum_{l,\kappa} v_{l,\kappa}^*\binom{j}{m} v_{l,\kappa}\binom{j'}{m'} = \delta_{jj'} \delta_{mm'} , \tag{10}$$

follows directly from the orthonormality of $u_{l,\kappa}\binom{j}{k}$, Eq. (8). Also, the second form of Eq. (9) shows that the different displacement patterns $v_{l,\kappa}\binom{j}{m}$ corresponding to a given band index j and to different m differ only by translation, i.e.,

$$v_{l,\kappa}\binom{j}{m} = v_{l-m,\kappa}\binom{j}{0} . \tag{11}$$

Equation (9) can be immediately inverted to give the normal-mode functions $u_{l,\kappa}\binom{j}{k}$ in terms of the

localized functions $v_{l,\kappa}\binom{j}{m}$;

$$u_{l,\kappa}\binom{j}{k} = N^{-1/2} \sum_m v_{l,\kappa}\binom{j}{m} e^{ikma} \tag{12}$$

or, equivalently,

$$u_\kappa\binom{j}{k} = \sum_m v_{0,\kappa}\binom{j}{m} e^{ikma} . \tag{13}$$

It remains to verify the localized character of the displacement $v_{l,\kappa}\binom{j}{0}$, i.e., that these displacements tend exponentially to zero as $|l| \to \infty$. This may be done in analogy to the corresponding demonstration for Wannier functions.[4] First one notes that the functions $\omega^2\binom{j}{k}$ constitute two branches of a single analytic function $f(k) = \omega^2(k)$ with branch points at those complex values of k at which the discriminant of the quadratic secular equation (4) for $f(k)$ vanishes:

$$k = (\pi/a)(2n+1) \pm ih_0 , \tag{14}$$

where

$$h_0 = \frac{2}{a} \cosh^{-1}\left\{ \frac{(\alpha+\beta)}{2(\alpha\beta)^{1/2}} \frac{1}{2}\left[\left(\frac{M_2}{M_1}\right)^{1/2} + \left(\frac{M_1}{M_2}\right)^{1/2}\right]\right\} .$$

Clearly $|h_0| > 0$ unless $M_1 = M_2$ and $\alpha = \beta$, which is the excluded monatomic case for which the two frequency branches touch; $\omega^2(k)$ is thus a periodic function of k which is analytic in a strip of finite width enclosing the real k axis.

Next, one must choose the phases of $u_\kappa\binom{j}{k}$ as a function of k such that these quantities become periodic functions of k (period $2\pi/a$) and are also analytic as functions of k in a strip of finite width enclosing the real k axis. By an argument completely analogous to that given in Ref. 4, one then ascertains that the corresponding localized functions $v_{l,\kappa}\binom{j}{0}$ decay exponentially with $|l|$.

We now treat explicitly two cases of special interest, each of which has a center of inversion.

A. "Molecular" Crystal $(M_1 = M_2 = M; \alpha > \beta)$

Here the two atoms of equal mass within each cell—the "molecule"—interact more strongly with each other than with the atoms in the neighboring cells. For this case the proper choices of phase are
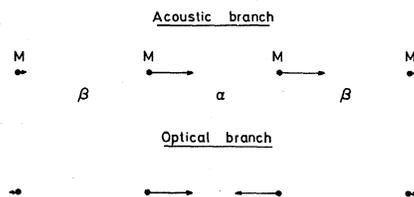
FIG. 2. Localized functions $v_{l,\kappa}$ for the molecular crystal; $M_1 = M_2 = M$; $\alpha/\beta = 2$.

Acoustic branch

M   2M   M   2M

α α α
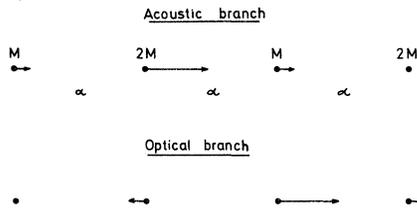
Optical branch

FIG. 3. Localized functions $v_{l,\kappa}$ for the ionic crystal;
$M_1/M_2=2$; $\alpha=\beta$.

$$u_{0,1}\begin{pmatrix} j \\ k \end{pmatrix} \pm u_{0,2}\begin{pmatrix} j \\ k \end{pmatrix} = \text{real and positive} , \qquad (15)$$

where the plus and minus signs refer, respectively, to the acoustic ($j=1$) and optical ($j=2$) branches. The corresponding localized functions $v_{l,\kappa}\binom{j}{0}$ are shown in Fig. 2 for the case $\alpha=2\beta$. The acoustic function suggests a uniform translation of the molecule, while the optical function suggests an internal vibration. (In Fact, when $\alpha/\beta \to \infty$, these descriptions become exact.) The symmetry properties of the $v_{l,k}\binom{j}{0}$ are evident from the figure.

B. "Ionic" Crystal $(M_1 > M_2 ; \alpha = \beta)$

Here the unit cell contains one heavy and one light atom, and all nearest-neighbor interactions are equal. For this case the proper choices of phase are

$$u_{0,1}\begin{pmatrix} 1 \\ k \end{pmatrix} = \text{real and positive (acoustic branch)} ,$$

$$\qquad (16)$$

$$u_{0,2}\begin{pmatrix} 2 \\ k \end{pmatrix} = \text{real and positive (optical branch)} .$$

The corresponding localized functions $u_{l,\kappa}\binom{j}{0}$ are shown in Fig. 3 for the case $M_1=2M_2$. It will be noticed that the acoustic and optical functions are concentrated on the heavy and light atoms, respectively. Symmetry properties are again evident from the figure.

For a monatomic lattice with atomic-site label l, the localized basis is simply

$$v_l(m) = \delta_{l,m} , \qquad (17)$$

describing the displacement of a single atom. Such a lattice has no structure internal to each cell and for this reason the basis functions are also structureless.

Generalizations to real three-dimensional lattices are possible. In this case the point $k=0$ and possibly other points are degenerate and the problem must be treated in a manner analogous to the treatment of Wannier functions for degenerate bands.[5]

In metals the interatomic forces have a long-range tail which exhibits Friedel oscillations. Under these circumstances the functions $\omega^2\binom{j}{k}$ have points of nonanalyticity (anomalies) for real k. As a result the functions $v_{l,\kappa}\binom{j}{0}$ will then not decay exponentially with $|l|$, as they did in our examples, but have long-range oscillatory tails similar to the Friedel oscillations of the interatomic forces.

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[1]G. Wannier, Phys. Rev. <u>52</u>, 191 (1937).
[2]In the same way one can construct a localized basis equivalent to spin waves.
[3]A. A. Maradudin, E. W. Montroll, and G. M. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963).
[4]W. Kohn, Phys. Rev. <u>115</u>, 809 (1959).
[5]J. Des Cloiseaux, Phys. Rev. <u>129</u>, A698 (1964); <u>135</u>, A685 (1964); <u>135</u>, A698 (1964); W. Kohn (unpublished).