to a symmetry coordinate representation. The sum is over the three optically active symmetry coordinates *m*. The dimensionless Green's functions of the defect lattice can be expressed in terms of the Green's functions of the perfect lattice G:

$$G' = M\omega_L^2[1-G\delta]^{-1}G. \tag{5}$$

The required complex matrix elements of G have been calculated for this model.[1]

For a random distribution of impurities, the total absorption is just the sum of the absorption by isolated defects and by defect pairs, Eqs. (3) and (4), with

$$f_1 = f(1-f)^{12} \simeq f - 12f^2, \tag{6}$$

$$f_2 = \tfrac{1}{2}[12f^2(1-f)^{18}] \simeq 6f^2. \tag{7}$$

Here, the fraction of defect atoms f is assumed to be small.

Figures 3 and 4 show the infrared absorption due to the same number of charged impurities. In Fig. 3, the impurities are assumed isolated. In Fig. 4, they are assumed to occur only in pairs. A comparison of the two figures shows that the $\Delta M=0$ curve for defect pairs is enhanced at low frequencies and depressed at high frequencies. This is due to the coherent, in-phase motion of the impurities at low frequencies and to the out-of-phase motion at high frequencies. It is assumed that the motion of the isolated impurities is uncorrelated. Although the peaks of the resonance absorption for the three optically active symmetries occur at slightly different frequencies for $\Delta M/M=-4$, they are not resolved, and only a line broadening is observed.

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Walk-Counting Method, with an Application to Energy Bands and Impurity States in Close-Packed Lattices*

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Three formally equivalent problems of crystal physics (vibrations of arrays of masses with nearest-neighbor harmonic coupling, vibrations of arrays of coupled vibrators, and a generalization of Koster and Slater's theory of electronic states) are considered. The moments of the energy (or frequency) bands of pure crystals and the energy and amplitude functions of localized impurity states are expressed in terms of the numbers of closed or open walks on the crystal lattice. The method is applicable to aperiodic as well as periodic arrays, and is used to show that the level distribution in a pure crystal and the positions of impurity levels due to isolated impurities are, for the models considered, the same for all close-packed lattices, periodic or aperiodic. It is suggested that the walk-counting method is a more useful computational resource than has previously been recognized.

I. INTRODUCTION

IT has been observed repeatedly that calculation of the *n*th moment of the frequency spectrum of a lattice of coupled masses or vibrators can be reduced to the summing of appropriately weighted contributions from the various closed walks of *n* steps on the lattice. The method has been applied to disordered linear chains by Domb, Maradudin, Montroll, and Weiss[1] and by Deltour,[2] but it has been little used in deriving concrete results for problems of higher dimensionality. It is the purpose of this paper to point out that there are contexts in which the walk-counting method is simple, convenient, and even powerful.

Attention will here be limited to three problems that are formally equivalent:

(a) The vibrations of a lattice of masses with equal harmonic couplings of nearest neighbors only. This is treated in the approximation, common when the effects of imperfections in lattices were first under investigation,[3] in which the *x*, *y*, and *z* components of the mass displacements are separable. (This is, of course, less general than the harmonic approximation now commonly used.[4]) The equations of motion for the *x* components of the displacements are, in this model,

$$M_i x_i = \kappa \sum_{j(i)} (x_j - x_i), \quad \text{all } i \tag{1}$$

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* Work supported by National Science Foundation.

[1] C. Domb, A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Phys. Rev. **115**, 18 (1959).

[2] J. Deltour, Physica **32**, 762 (1966).

[3] E. W. Montroll and R. B. Potts, Phys. Rev. **100**, 525 (1955).

[4] A. A. Maradudin, E. W. Montroll and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963).

the sum being over all nearest neighbors j (however defined) of mass i.

(b) The internal vibrations of an array of molecular vibrators with centers of mass fixed in a rigid lattice, subject to next-neighbor coupling potentials proportional to $(r_i-r_e)(r_j-r_e)$, r_i and r_j being the instantaneous nuclear separations of molecules i and j and r_e the equilibrium value of these separations. In the first approximation, as concerns the internal vibrations only, one may consider solid H_2 as an example of such a system.[5] The ortho- and para-H_2 molecules may be regarded as harmonic oscillators with excitation energies somewhat different because of their different rotational states. In discussing the infrared[6] and Raman[7] spectra due to vibrational excitation of a single H_2 molecule, one can describe the state of the crystal in which only molecule i is vibrationally excited by

$$|\mathbf{R}_i\rangle = |\varphi_i(1;r_i)\prod_{j\neq i}\varphi_j(0;r_j)\rangle, \qquad (2)$$

and a stationary state τ of the system of coupled vibrators by

$$|\tau\rangle = \sum_i U_\tau(\mathbf{R}_i)|\mathbf{R}_i\rangle, \qquad (3)$$

where $U_\tau(\mathbf{R}_i)$ is the amplitude for excitation of molecule i in state τ. Let one species of molecule, appearing at sites $\mathbf{R}_\rho$, be regarded as an impurity in a matrix of molecules of the other species, with excitation energy differing from that of the matrix molecules by an amount W. Since coupling of the vibrators is weak in H_2 and W is small, one can treat the energy band of the singly excited states τ by neglecting interaction with states having other numbers of excited molecules. The Schrödinger stationary state equation is then equivalent to a set of difference equations,

$$-\tfrac{1}{2}\epsilon'\sum_{\mathbf{d}_i} U_\tau(\mathbf{R}_i+\mathbf{d}_i)+W\sum_\rho \delta(\mathbf{R}_i,\mathbf{R}_\rho)U_\tau(\mathbf{R}_\rho) = E_\tau U_\tau(\mathbf{R}_i), \quad (\text{all } i) \qquad (4)$$

where $\mathbf{d}_i$ runs over all displacements from site i of the lattice to its nearest-neighbor sites, ϵ' is a constant measuring the strength of the coupling between nearest molecules, and E_τ is the energy of the state, measured from the energy of the "pure" crystal with vibrational coupling absent. Equation (4) forms a basis for discussion of the band (or bands) of singly excited vibrational states of the pure crystal, and of the associated impurity states due to presence of a second species of molecule.

(c) A generalization of Koster and Slater's theory of electronic states in an imperfectly periodic lattice,[8] which is based on description of the perturbed wave functions in terms of Wannier functions $a(\mathbf{r}-\mathbf{R}_i)$ and neglect of matrix elements of the unperturbed one-electron Hamiltonian H between Wannier functions centered about atoms more remote than nearest neighbors. Assuming that there are unique values for the matrix elements

$$\langle a(\mathbf{r}-\mathbf{R}_i)|H|a(\mathbf{r}-\mathbf{R}_i)\rangle = \mathcal{E}(0), \qquad (5)$$

$$\langle a(\mathbf{r}-\mathbf{R}_i)|H|a(\mathbf{r}-\mathbf{R}_i-\mathbf{d}_i)\rangle = \mathcal{E}(1), \qquad (6)$$

and that the only matrix elements of the perturbation potential V that need be retained are

$$\langle a(\mathbf{r}-\mathbf{R}_\rho)|V|a(\mathbf{r}-\mathbf{R}_\rho)\rangle = V(0), \qquad (7)$$

where $\mathbf{R}_\rho$ denotes any site occupied by an impurity, one may write

$$\mathcal{E}(1)\sum_{\mathbf{d}_i} U_\tau(\mathbf{R}_i+\mathbf{d}_i)+V(0)\sum_\rho \delta(\mathbf{R}_i,\mathbf{R}_\rho)U_\tau(\mathbf{R}_\rho) = [E-\mathcal{E}(0)]U_\tau(\mathbf{R}_i), \text{ all } i. \qquad (8)$$

Equation (1) gives rise to equations having the same general form as Eqs. (4) and (8) if one restricts attention to normal mode vibrations. We identify each mass i by its equilibrium position $\mathbf{R}_i$, and assume that all masses are M, except for impurity masses M' with equilibrium positions $\mathbf{R}_\rho$. We assume that each mass has p nearest neighbors. Let $U(\mathbf{R}_i)$ denote the amplitude of the x displacement of mass i. Then

$$-M\omega^2U(\mathbf{R}_i) = -p\kappa U(\mathbf{R}_i)+\kappa\sum_{\mathbf{d}_i} U(\mathbf{R}_i+\mathbf{d}_i) +(M'-M)\omega^2\sum_\rho \delta(\mathbf{R}_i,\mathbf{R}_\rho)U(\mathbf{R}_\rho), \text{ all } i. \qquad (9)$$

Equations (4), (8), and (9) can all be brought to the form

$$\lambda U(\mathbf{R}_i) = \sum_{\mathbf{d}_i} U(\mathbf{R}_i+\mathbf{d}_i)+\gamma_0\sum_\rho \delta(\mathbf{R}_i,\mathbf{R}_\rho)U(\mathbf{R}_\rho), \qquad (10)$$

where the last sum is over impurities only. In the several cases one has the following equivalences:

Case (a):

$$\lambda = p-(\omega^2/\omega_0^2), \quad \gamma_0 = \frac{M'-M}{M}\frac{\omega^2}{\omega_0^2}, \qquad (11a)$$

where $\omega_0^2=\kappa/M$;

Case (b):

$$\lambda = -2E/\epsilon', \quad \gamma_0 = -2W/\epsilon'; \qquad (11b)$$

Case (c):

$$\lambda = [E-\mathcal{E}(0)]/\mathcal{E}(1), \quad \gamma_0 = V(0)/\mathcal{E}(1). \qquad (11c)$$

An equivalent form, to be used later, is

$$U(\mathbf{R}_i) = \alpha U(\mathbf{R}_i)+\beta\sum_{\mathbf{d}_i} U(\mathbf{R}_i+\mathbf{d}_i) +\gamma\sum_\rho \delta(\mathbf{R}_i,\mathbf{R}_\rho)U(\mathbf{R}_\rho), \qquad (12)$$

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[5] J. Van Kranendonk, Physica **25**, 1020 (1959).

[6] V. F. Sears and J. Van Kranendonk, Can. J. Phys. 42, 980 (1964).

[7] H. M. James and J. Van Kranendonk, following paper, Phys. Rev. **164**, 1159 (1967).

[8] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); **96**, 1208 (1954).

where

$$\begin{aligned}\alpha&=-c/(\lambda-c)\,,\\ \beta&=1/(\lambda-c)\,,\\ \gamma&=\gamma_0/(\lambda-c)\,,\end{aligned}\tag{13}$$

c being an arbitrarily chosen constant that may even vary with the state under consideration.

The notation in Eqs. (4), (8), and (10) is chosen to permit consideration of cases in which not all sites of the lattice are equivalent, and the set of displacements $\mathbf{d}_i$ is different for different i. This includes cases in which (quite aside from the presence of impurities) the lattice is not a perfectly periodic one. In these latter cases one can not derive Eq. (8) using arguments involving Wannier functions, but must regard Eq. (8) as defining a mathematical model for the variation of the amplitudes $U_\tau(\mathbf{R}_i)$ of electronic states in the lattice.

Special attention will here be given to close-packed lattices. This term will comprise all lattices formed by a compact stacking of hexagonal-close-packed planes of molecules, whether they occur with the $ABABAB\cdots$ alternation of the hexagonal-close-packed lattice, with the $ABCABC\cdots$ alternation of the cubic-close-packed lattice, with a periodic stacking having a longer period, or with an aperiodic alternation such as $ABACACBAC\cdots$, subject only to the condition (essential for compact stacking) that like plaes should not follow each other. For all such structures $p=12$.

II. LATTICES WITHOUT IMPURITIES

If the lattice is periodic and impurities are absent, standard methods lead quickly to a full description of the energy (or frequency) bands. If all sites are equivalent, the set of displacements $\mathbf{d}_i$ is the same for all i. Equation (10), with $\gamma_0=0$, then has solutions

$$U(\mathbf{R}_i)=U_0\exp(i\mathbf{k}\cdot\mathbf{R}_i)\,,\tag{14}$$

with

$$\lambda(\mathbf{k})=\sum_{\mathbf{d}}\exp(i\mathbf{k}\cdot\mathbf{d})\,.\tag{15}$$

If the sites are inequivalent, but can be divided into sublattices τ of equivalent sites, one has solutions of the form

$$U(\mathbf{R}_i)=C_\tau\exp(i\mathbf{k}\cdot\mathbf{R}_i)\,,\quad(\mathbf{R}_i\text{ on sublattice }\tau)\tag{16}$$

where

$$\lambda C_\tau=\sum_\nu C_\nu S_{\tau\nu}\,,\quad(\text{all }\tau)\tag{17}$$

with

$$S_{\tau\nu}=\sum_{\mathbf{d}_{\tau\nu}}\exp(i\mathbf{k}\cdot\mathbf{d}_{\tau\nu})\,,\tag{18}$$

the sum being over displacements from a site on sublattice τ to all its nearest-neighbor sites on sublattice ν. The requirement of compatibility for Eqs. (17) leads to the familiar secular equation

$$|S_{\tau\nu}-\lambda\delta_{\tau\nu}|=0\,,\tag{19}$$

from which one obtains the energies or frequencies for given $\mathbf{k}$.

These methods fail if the lattice is aperiodic, as is the most general close-packed lattice. One must then be content with calculation of the moments of the energy or frequency distribution. A direct calculation of these moments is also desirable for some purposes, even when the lattice under consideration is periodic. For such calculations it is convenient to use the following approach. We note that Eq. (10) can be reduced to the matrix form

$$\lambda\mathbf{U}=\mathbf{\Lambda}\mathbf{U}\,,\tag{20}$$

where $\mathbf{U}$ is a column matrix of the $U(\mathbf{R}_i)$, and $\mathbf{\Lambda}$ is a square matrix in which the element Λ_{ij} is 1 if sites i and j are next neighbors, and is 0 otherwise. If these matrices are finite, one has the familiar theorem that

$$\sum_\tau\lambda_\tau^n=Tr(\mathbf{\Lambda}^n)=\sum_i\sum_{i_2}\cdots\sum_{i_n}\Lambda_{i,i_2}\Lambda_{i_2,i_3}\cdots\Lambda_{i_n,i}\,.\tag{21}$$

The terms on the right with given i contribute 1 to the sum for each walk of n steps on the lattice that begins and ends on site i. We denote the total number of such closed walks by $P_n(\mathbf{R}_i;\mathbf{R}_i)$. Dividing both sides of this equation by N, which is at the same time the number of lattice sites and the number of eigenvalues λ_τ, we obtain

$$\langle\lambda^n\rangle=\langle P_n(\mathbf{R}_i;\mathbf{R}_i)\rangle_i\,.\tag{22}$$

That is, the nth moment of the distribution of values of λ is equal to the average, over all sites i in the lattice, of the number of closed walks of n steps beginning and ending on site i.

As an application of this theorem it will be shown that, for the models here under consideration, all close-packed lattices give rise to the same over-all distribution of energies or frequencies. This is somewhat surprising, since the energy levels in question may be associated, in the ordinary approach, with one energy band (fcc lattice) or with two bands (hcp lattice), or with many bands.[9] In the aperiodic cases, the association of energy levels into bands through the propagation vector falls away, but there remains a band of energies (in the sense of a distribution of finite width) that is the same as for the periodic structures. Band structure, in this latter sense, need not be lost, or even seriously modified, by loss of certain types of periodicity in the system.

To prove these statements it is only necessary to supplement Eq. (22) by a proof that $P_n(\mathbf{R}_i;\mathbf{R}_i)$ is the same for every n and for every site $\mathbf{R}_i$ in any close-packed lattice.[10] Let us choose an arbitrary starting

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[9] The near but not exact equality of the frequency distributions for hcp and fcc lattices of masses with a somewhat different coupling has been studied by C. Isenberg and C. Domb, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon Press, Inc., New York, 1965), p. 141.

[10] It has been noted by C. Domb and M. F. Sykes, [Proc. Phys. Soc. (London) **B70**, 896 (1957)], that this equality exists in the case of hcp and fcc lattices, but the author is not aware of any published proof.

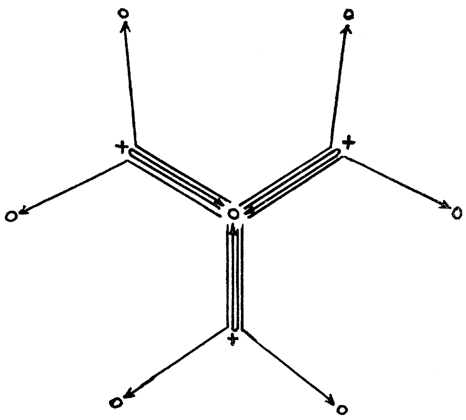

FIG. 1. ○, sites on hexagonal-close-packed plane A. +, sites on plane B, above plane A. Arrows indicate walks from central A site to plane B and back to plane A.

point $\mathbf{R}_i$, and consider all walks that involve l steps within the same hexagonal plane, m steps up to planes above, and m steps down, in some specified order.[11] Such walks will always end on the plane on which they began; they will contain equal numbers of $A \rightarrow B$ steps up and $B \rightarrow A$ steps down, $A \rightarrow C$ steps up and $C \rightarrow A$ steps down, and so on. Let us consider the possible resulting displacements within the hexagonal plane. An $A \rightarrow B$ step up followed by a $B \rightarrow A$ step down can be realized in nine ways (see Fig. 1), of which three produce no net displacement and the other six produce net displacements equal to those from a site to each of its six neighbors in the same hexagonal plane. The result will be the same whether the $B \rightarrow A$ step follows the $A \rightarrow B$ step immediately in the sequence or not; it will also be the same for any pair of adjacent planes (BA, AC, CA, etc.). The set of possible displacements will thus be the same regardless of the starting point and the alternation of A, B, C planes; in particular, the number of *closed* walks will be independent of these factors. We now add up the number of closed walks for all orderings of the l in-plane steps, m steps up and m steps down, and for all choices of l and m such that $l+2m=n$. Since these last-named processes involve no reference to the ordering of the planes, the final result, $P_n(\mathbf{R}_i;\mathbf{R}_i)$, will be independent of $\mathbf{R}_i$ and of the alternation of planes. Q.E.D.

III. LOCALIZED STATES DUE TO ISOLATED IMPURITIES

The counting of closed or open walks on the lattice can be a useful means for calculating the energy and characterizing the spatial behavior of localized impurity states. It also provides an easy means of proving that, for the models here considered, the energy of a localized impurity state due to an isolated impurity is the same for all close-packed lattices. (This is not necessarily the case if the localized state is associated with several interacting impurities.)

We approach this problem by considering Eq. (12). Let $G(\mathbf{R}_i;\mathbf{R}_\rho)$ be a solution of

$$G(\mathbf{R}_i;\mathbf{R}_\rho)=\alpha G(\mathbf{R}_i;\mathbf{R}_\rho)+\beta\sum_{\mathbf{d}_i} G(\mathbf{R}_i+\mathbf{d}_i;\mathbf{R}_\rho)+\delta(\mathbf{R}_i;\mathbf{R}_\rho) \quad (23)$$

such that $G(\mathbf{R}_i;\mathbf{R}_\rho)\rightarrow 0$ as $|\mathbf{R}_i-\mathbf{R}_\rho|\rightarrow 0$. This function, which plays the role of a Green's function, will in general depend on $\mathbf{R}_\rho$ and $\mathbf{R}_i$ separately; it may be simply a function of $\mathbf{R}_i-\mathbf{R}_\rho$ for impurities at equivalent sites $\mathbf{R}_\rho$ in a periodic lattice. In any case, one can write a formal solution of Eq. (12) as

$$U(\mathbf{R}_i)=\gamma\sum_{\rho} G(\mathbf{R}_i;\mathbf{R}_\rho)U(\mathbf{R}_\rho),\ \text{all } i. \quad (24)$$

The constants $U(\mathbf{R}_\rho)$ associated with the impurity sites must satisfy the conditions

$$U(\mathbf{R}_\rho)=\gamma\sum_{\rho'} G(\mathbf{R}_\rho;\mathbf{R}_{\rho'})U(\mathbf{R}_{\rho'}),\ \text{all } \rho. \quad (25)$$

Consistency of these conditions determines the values of E or ω (on which α, β, γ depend) for which the solutions given by Eq. (24) exist. If there is only a single impurity, this condition becomes

$$1=\gamma G(\mathbf{R}_\rho;\mathbf{R}_\rho). \quad (26)$$

To determine G, one can use an iterative process. For simplicity, consider first the case $\alpha=0$. We construct an nth approximation to $G(\mathbf{R}_i;\mathbf{R}_\rho)$ as

$$G_n(\mathbf{R}_i;\mathbf{R}_\rho)=\beta\sum_{\mathbf{d}_i} G_{n-1}(\mathbf{R}_i+\mathbf{d}_i;\mathbf{R}_\rho),\ \mathbf{R}_i\neq\mathbf{R}_\rho, \quad (27\text{a})$$

$$G_n(\mathbf{R}_\rho;\mathbf{R}_\rho)=\beta\sum_{\mathbf{d}_\rho} G_{n-1}(\mathbf{R}_\rho+\mathbf{d}_\rho;\mathbf{R}_\rho)+1 \quad (27\text{b})$$

taking as the zeroth approximation

$$G_0(\mathbf{R}_i;\mathbf{R}_\rho)=\delta(\mathbf{R}_i;\mathbf{R}_\rho). \quad (28)$$

If $G_n(\mathbf{R}_i;\mathbf{R}_\rho)$ approaches a limiting form as $n\rightarrow\infty$, this limit will be a solution of Eq. (23).

One can think of $G_n(\mathbf{R}_i;\mathbf{R}_\rho)$ as representing the nth step in the generation of a distribution of weights $G(\mathbf{R}_i;\mathbf{R}_\rho)$. For any $\mathbf{R}_i$ it is constructed as the sum of weights at the sites neighboring $\mathbf{R}_i$ in the $(n-1)$st step, multiplied by β, plus an added weight 1 at the impurity site $\mathbf{R}_\rho$. This added weight will, in the next step, contribute an amount β to the weight at each site neighboring $\mathbf{R}_\rho$; after τ steps it will contribute to the weight at $\mathbf{R}_i$ an amount β^τ for each of the $P_\tau(\mathbf{R}_i;\mathbf{R}_\rho)$ distinct walks of τ steps from $\mathbf{R}_\rho$ to $\mathbf{R}_i$. The quantity $G_n(\mathbf{R}_i;\mathbf{R}_\rho)$ will be the sum of weights resulting from introduction of weight 1 at $\mathbf{R}_\rho$ in steps 0 to n:

$$G_n(\mathbf{R}_i;\mathbf{R}_\rho)=\sum_{\tau=0}^{n}\beta^\tau P_\tau(\mathbf{R}_i;\mathbf{R}_\rho). \quad (29)$$

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[11] This proof can be expressed in the language of generating functions, but that does not seem to add anything essential to the following statement of the ideas involved.

Passing to the limit, $n\to\infty$, one obtains[12]

$$G(\mathbf{R}_i;\,\mathbf{R}_p)=\sum_{\tau=0}^{\infty}\beta^\tau P_\tau(\mathbf{R}_i;\,\mathbf{R}_p). \tag{30}$$

The convergence properties of this expansion can be inferred from the known properties of random walks. If each site has p neighbors, there will be in all p^τ distinct walks of τ steps. The distribution of the endpoints of the walks will approach Gaussian form, for not too large $\mathbf{R}_i-\mathbf{R}_p$, as τ becomes very large. One thus has, for large τ,

$$P_\tau(\mathbf{R}_i;\,\mathbf{R}_p)\sim p^\tau\langle R^2\rangle^{-3/2}\exp\{-\tfrac{3}{2}|\mathbf{R}_i-\mathbf{R}_p|^2/\langle R^2\rangle\}\,, \tag{31}$$

where $\langle R^2\rangle$ is the mean square displacement due to a walk of τ steps, and is proportional to τ. For any fixed $\mathbf{R}_i$ and $\mathbf{R}_p$, as τ becomes large,

$$P_\tau(\mathbf{R}_i;\,\mathbf{R}_p)\sim p^\tau/\tau^{3/2}. \tag{32}$$

Thus the series in Eq. (30) converges if and only if $|p\beta|\leq 1$. If the series converges for $\mathbf{R}_i=\mathbf{R}_p$ it converges for all $\mathbf{R}_i$, and approaches 0 as $|\mathbf{R}_i-\mathbf{R}_p|$ increases; thus

$$U(\mathbf{R}_i)=\gamma G(\mathbf{R}_i;\,\mathbf{R}_p)U(\mathbf{R}_p) \tag{33}$$

describes a localized state of the system, provided, of course, that Eq. (26) is satisfied.

Unfortunately, the series in Eq. (30) does not converge in the whole range of interest. In the case of a cubic-close-packed lattice it is easily seen[7] that $\lambda(\mathbf{k})$ [Eq. (15)] ranges between 12 and -4. This, with Eq. (11), defines the range of energies (frequencies) of the unperturbed problem outside of which the energies of localized states will lie. In the present case ($\alpha=0$) it is evident from Eqs. (13) that localized impurity states can occur for

$$-\tfrac{1}{4}<\beta=1/\lambda<\tfrac{1}{12}\,,$$

whereas convergence of Eq. (30) is limited to the range

$$-\tfrac{1}{12}\leqslant\beta\leqslant\tfrac{1}{12}.$$

A solution with more favorable convergence properties can be obtained by making an appropriate nonzero choice of c and α. This corresponds to a change in the origin from which λ is measured. In seeking an iterative solution of Eq. (23), Eqs. (27) must be replaced by more general equations

$$\begin{aligned}G_n(\mathbf{R}_i;\,\mathbf{R}_p)&=\alpha G_{n-1}(\mathbf{R}_i;\,\mathbf{R}_p)\\&\quad+\beta\sum_{\mathbf{d}i}G_{n-1}(\mathbf{R}_i+\mathbf{d}_i;\,\mathbf{R}_p)\,,\quad \mathbf{R}_i\neq\mathbf{R}_p\\G_n(\mathbf{R}_p;\,\mathbf{R}_p)&=\alpha G_{n-1}(\mathbf{R}_p;\,\mathbf{R}_p)\\&\quad+\beta\sum_{\mathbf{d}_p}G_{n-1}(\mathbf{R}_p+\mathbf{d}_p;\,\mathbf{R}_p)+1.\end{aligned} \tag{34}$$

We interpret these equations again in terms of weight distributions. The weight at $\mathbf{R}_i$ at any given iteration will, on the next iteration, add β to the weight at any site $\mathbf{R}_j$ reached from $\mathbf{R}_i$ by a single nonzero step, and a weight α at any point reached by a step of zero length; after τ interations it will contribute to the weight at $\mathbf{R}_j$ an amount $\alpha^m\beta^{\tau-m}$ for each walk of τ steps of which m are of zero length. Let $P_{\tau,m}(\mathbf{R}_i;\,\mathbf{R}_p)$ be the total number of walks from $\mathbf{R}_p$ to $\mathbf{R}_i$ in τ steps, of which m are of zero length. Unit weight added at $\mathbf{R}_p$ will, after τ iterations, contribute to the weight at $\mathbf{R}_i$ an amount

$$\sum_{m=0}^{\tau}\alpha^m\beta^{\tau-m}P_{\tau,m}(\mathbf{R}_i;\,\mathbf{R}_p).$$

Summing such contributions from unit weights added at $\mathbf{R}_p$ in an infinite number of iterations, one finds

$$G(\mathbf{R}_i;\,\mathbf{R}_p)=\sum_{\tau=0}^{\infty}\sum_{m=0}^{\tau}\alpha^m\beta^{\tau-m}P_{\tau,m}(\mathbf{R}_i;\,\mathbf{R}_p). \tag{35}$$

Noting that

$$P_{\tau,m}(\mathbf{R}_i;\,\mathbf{R}_p)=\frac{\tau!}{m!(\tau-m)!}P_{\tau-m}(\mathbf{R}_i;\,\mathbf{R}_p)\,, \tag{36}$$

and changing the index of summation, one obtains

$$G(\mathbf{R}_i;\,\mathbf{R}_p)=\sum_{\tau=0}^{\infty}\alpha^\tau Q_\tau(\mathbf{R}_i;\,\mathbf{R}_p)\,, \tag{37}$$

where

$$Q_\tau(\mathbf{R}_i;\,\mathbf{R}_p)=\sum_{s=0}^{\tau}\frac{\tau!}{s!(\tau-s)!}\left(\frac{\beta}{\alpha}\right)^s P_s(\mathbf{R}_i;\,\mathbf{R}_p). \tag{38}$$

Discussion of the convergence of this expansion of $G(\mathbf{R}_i;\,\mathbf{R}_p)$ will be limited to cases in which $P_n(\mathbf{R}_i;\,\mathbf{R}_i)$ is the same for all i. This includes a wide variety of periodic lattices, and all close-packed lattices. It will be shown that by appropriate choice of the arbitrary constant c one can assure the convergence of the expansion of $G(\mathbf{R}_p;\,\mathbf{R}_p)$ for all energies (frequencies) outside the unperturbed band—that is, for all cases in which localized states exist. For this choice of c the condition [Eq. (26)] that determines the energy (frequency) of localized states due to a single impurity will always be meaningful. Further, since $P_s(\mathbf{R}_p;\,\mathbf{R}_p)$ and $G(\mathbf{R}_p;\,\mathbf{R}_p)$ are the same for all close-packed lattices, with any choice of $\mathbf{R}_p$, it follows that the energy of a localized state due to a single impurity will be the same for all close-packed lattices and all impurity sites.

The values of λ in the unperturbed band will be distinguished by a subscript k, which may, but need not, correspond to a value of a propagation vector $\mathbf{k}$. The extent of the unperturbed band is expressed in the condition

$$\lambda_m\leqslant\lambda_k\leqslant\lambda_M. \tag{39}$$

(It has already been noted that for any close-packed lattice $\lambda_m=-4$, $\lambda_M=12$.) The value of λ for a localized

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[12] An equivalent form has been obtained by M. Toda, T. Kotera, and K. Kogure [J. Phys. Soc. Japan **17**, 426 (1962)] in considering the vibrations of simple cubic lattices with a single impurity. See also T. Kotera, Progr. Theoret. Phys. (Kyoto), Suppl. No. **23**, 141 (1962).

impurity level, λ_i, must lie outside this range. By the moment theorem, Eq. (22), one has

$$P_s(\mathbf{R}_\rho;\mathbf{R}_\rho)=\langle\lambda_k{}^s\rangle. \tag{40}$$

By Eq. (38),

$$Q_\tau(\mathbf{R}_\rho;\mathbf{R}_\rho)=\langle(1+\beta\lambda_k/\alpha)^\tau\rangle. \tag{41}$$

The successive terms in Eq. (37) with $\mathbf{R}_i=\mathbf{R}_\rho$ can thus be expressed as $\langle(\alpha+\beta\lambda_k)^\tau\rangle$. For large τ, these will vary nearly as the τth power of the extreme value in the spectrum of $\alpha+\beta\lambda_k$. The expansion of $G(\mathbf{R}_\rho;\mathbf{R}_\rho)$ will converge if both $|\alpha+\beta\lambda_m|$ and $|\alpha+\beta\lambda_M|$ are less than 1. Best convergence is attained by choosing c so as to make the larger of these as small as possible. It is easily seen that this occurs when

$$\begin{gathered}\alpha+\beta\lambda_m=-(\alpha+\beta\lambda_M),\\ \alpha/\beta=-c=-\frac{\lambda_M+\lambda_m}{2}.\end{gathered} \tag{42}$$

The expansion of $G(\mathbf{R}_\rho;\mathbf{R}_\rho)$ then converges nearly like a sum of powers of

$$\alpha+\beta\lambda_M=\tfrac{1}{2}(\lambda_M-\lambda_m)/[\lambda_i-\tfrac{1}{2}(\lambda_M+\lambda_m)]. \tag{43}$$

This has magnitude less than 1, and the expansion of $G(\mathbf{R}_\rho;\mathbf{R}_\rho)$ converges, if λ_i lies outside the band of values of λ_k. Q.E.D.

This argument can be carried farther, to determine the behavior of $G(0;0)$ as λ_i approaches the band edge. One has

$$\begin{aligned}G(0;0)&=\sum_\tau\langle(\alpha+\beta\lambda_k)^\tau\rangle\\ &=\sum_\tau\left\langle\left[\frac{\lambda_k-\frac{1}{2}(\lambda_M+\lambda_m)}{\lambda_i-\frac{1}{2}(\lambda_M+\lambda_m)}\right]^\tau\right\rangle,\end{aligned} \tag{44}$$

when Eq. (42) is satisfied. For all λ_i outside the band, the series converges to

$$G(0;0)=[\lambda_i-\tfrac{1}{2}(\lambda_M+\lambda_m)]\left\langle\frac{1}{\lambda_i-\lambda_k}\right\rangle. \tag{45}$$

If λ_i approaches any band edge at which the density of λ_k values vanishes like a power of the distance from the band edge, the last average will remain finite, as will $G(0;0)$. By Eqs. (26) and (11) this merging of the impurity level into the unperturbed band, and the vanishing of the localized impurity state, will occur for finite γ and for nonzero perturbation by the impurity. On the other hand, if the density of λ_k values does not approach zero at the band edge the average in Eq. (45) will diverge as λ_i approaches the band edge: the discrete impurity level will vanish only as γ and the impurity perturbation go to zero.

IV. CONCLUSION

Equation (37) has been used by James and Van Kranendonk[6] in making detailed calculations of the energy and of some properties of $U(\mathbf{R}_i;\mathbf{R}_\rho)$ for localized impurity states due to isolated impurity species in H_2. The simpler Eq. (30) was also applied, and found to provide satisfactory convergence in the case at hand, in treating a model that involved a regular lattice of interacting impurities. Such calculations are so simple that a desk calculator, while convenient, could have been dispensed with. It appears that the walk-counting method may be a more useful computational resource than has previously been realized.

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