

Solvable Three-Dimensional Lattice Models*

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A solvable three-dimensional model is developed for band-structure calculations in valence crystals. The local atomic potential at each lattice site is replaced by a simpler potential operator which in isolation gives a finite number of bound states. Furthermore, an algorithm is presented for constructing this operator such that the bound-state wave functions and energies exactly match those of any given local atomic potential. A sample calculation is carried out for a "Gaussian atom" set in a fcc lattice where the two parameters, range and strength, have been chosen to fit the atomic radius and the first ionization potential of a Ge atom.

INTRODUCTION

IN our studies of localized levels and propagation in disordered lattices we have found the following lattice model useful: The atomic potential at each site \mathbf{l} is replaced by a nonlocal potential operator

$$V_{\mathbf{l}}\psi(\mathbf{x}) \equiv -v(\mathbf{x}-\mathbf{l}) \int d^3x' v(\mathbf{x}'-\mathbf{l})\psi(\mathbf{x}'), \quad (1)$$

or, in other words, by a projective operator. It affords a simple, solvable three-dimensional model for the Bloch functions and the crystalline dispersion. It is the natural extension of the δ function or Kronig-Penny lattice of one dimension¹ which in three dimensions fails to scatter waves or bind them with a finite energy. Furthermore, its simplicity enables one to separate those topological features of the dispersion characteristic of the lattice geometry from those which manifest the peculiarities of individual potentials.

Mathematically speaking, the potential operator of Eq. (1) is a projective operator, in the sense that it maps all function space $\psi(\mathbf{x})$ into the one-dimensional space $v(\mathbf{x}-\mathbf{l})$. As such it is the simplest possible Hermitian operator, in contrast to a local potential, whose vector-space properties are more involved.

Moreover, the potential (1) may be generalized to a form which in isolation yields the first n bound-state wave functions of a given local potential (and the first n energy eigenvalues) *exactly*, and which in a lattice still leads to an exactly solvable Schrödinger equation. This forms the basis of a systematic approximation to band structure calculations. There is no theoretical limit to the numerical precision with which physical results may be obtained.

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¹ For example, see G. H. Wannier, *Elements of Solid State Theory* (Cambridge University Press, New York, 1959), Chap. V.

A discussion of such a model is the purpose of this paper. Results are derived for both a primitive lattice and one with basis.

GENERAL THEORY

In more detail then, we are investigating the Schrödinger equation, ($\hbar^2/2m=1$)

$$-\nabla^2\psi(\mathbf{x}) - \sum_{\mathbf{l}} v(\mathbf{x}-\mathbf{l}) \int d^3x' v(\mathbf{x}'-\mathbf{l})\psi(\mathbf{x}') = \mathcal{E}\psi(\mathbf{x}). \quad (2)$$

The sum extends over all lattice sites, \mathbf{l} . We begin with the analysis for a single atom.

A. The Single "Atom"

Specializing (1) to a single site, we have

$$-\nabla^2\psi(\mathbf{x}) - v(\mathbf{x}) \int d^3x' v(\mathbf{x}')\psi(\mathbf{x}') = \mathcal{E}\psi(\mathbf{x}). \quad (3)$$

Fourier transforming gives

$$q^2\tilde{\psi}(\mathbf{q}) - \tilde{v}(\mathbf{q})(2\pi)^{-3} \int d^3q' \tilde{v}^*(\mathbf{q}')\tilde{\psi}(\mathbf{q}') = \mathcal{E}\tilde{\psi}(\mathbf{q}),$$

where Parseval's theorem has been applied to the second term. The Fourier transform of a function, $f(\mathbf{x})$, has been denoted by $\tilde{f}(\mathbf{q})$. Solving for $\tilde{\psi}(\mathbf{q})$, we find

$$\tilde{\psi}(\mathbf{q}) = C\tilde{v}(\mathbf{q})/(q^2 - \mathcal{E}), \quad (4)$$

where

$$C \equiv (2\pi)^{-3} \int d^3q' \tilde{v}^*(\mathbf{q}')\tilde{\psi}(\mathbf{q}'), \quad \text{a const.}$$

Consistency requires [by multiplying both sides of (4) by $\tilde{v}^*(\mathbf{q})$ and integrating],

$$1 = (2\pi)^{-3} \int d^3q \frac{|\tilde{v}(\mathbf{q})|^2}{q^2 - \mathcal{E}} \equiv \phi(\mathcal{E}). \quad (5)$$

This relation determines the bound-state energy \mathcal{E} .

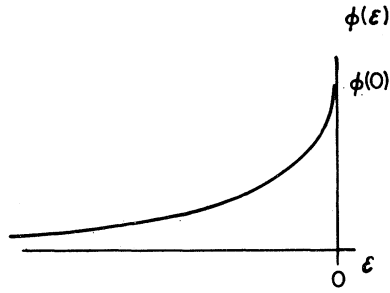


FIG. 1. Free-atom dispersion function, ϕ , versus energy, \mathcal{E} .

A few simple consequences of (5) show the general features of the system.

(1) The bound state clearly disappears when

$$\phi(0) \leq 1 \quad \text{or} \quad (2\pi)^{-3} \int (d^3q/q^2) |\bar{v}(\mathbf{q})|^2 \leq 1,$$

since the dispersion function, $\phi(\mathcal{E})$, decreases monotonically as $-\mathcal{E}$ increases (cf., Fig. 1). This sets a minimum value on the strength of a potential that will maintain a bound state.

(2) $\bar{v}(\mathbf{q})$ must drop off sufficiently fast in order that $\phi(\mathcal{E})$ exist for $\mathcal{E} < 0$. E.g., if $v(\mathbf{x})$ is spherically symmetric, the integral fails to converge unless $|\bar{v}|^2$ goes to zero faster than $1/q$. This precludes the three-dimensional δ function potential.

In general, an analytic expression for $\phi(\mathcal{E})$ is not available but asymptotic values are readily derived. The asymptotic behavior of $\phi(\mathcal{E})$ as $\mathcal{E} \rightarrow \infty$ is

$$\phi(\mathcal{E}) \sim \frac{1}{(2\pi)^3} \frac{1}{\mathcal{E}} \int d^3q |\bar{v}(\mathbf{q})|^2,$$

provided that the integral converge. This is a stronger condition than implied above, but we restrict our models to these. Also we find for $\mathcal{E} \rightarrow 0$,

$$\phi(\mathcal{E}) \sim \phi(0) - (1/4\pi)(\mathcal{E})^{1/2} |\bar{v}(0)|^2,$$

which follows from the scaling properties of the integral.

There are two observations to make: First, in the strong-coupling limit, the ground-state energy, \mathcal{E} , approaches the limit,

$$\mathcal{E} \rightarrow -\frac{1}{2\pi^2} \int_{\alpha} q \langle q^2 |\bar{v}(\mathbf{q})|^2 \rangle.$$

(The bracket indicates an average over 4π sr.) And second, $\phi(\mathcal{E})$ has a branch singularity at the origin of the complex \mathcal{E} plane.

Finally, a generalization of the potential (1) may be used to imitate a local potential to any desired accuracy. If the Schrödinger equation

$$-\nabla^2 \psi_{\mu}(\mathbf{x}) + V(\mathbf{x}) \psi_{\mu}(\mathbf{x}) = \mathcal{E}_{\mu} \psi_{\mu}(\mathbf{x})$$

has n -specified solutions ($\mu=1, \dots, n$), the same n eigenfunctions and eigenvalues will be the n -bound solutions to the equation

$$-\nabla^2 \psi(\mathbf{x}) + \sum_{\nu, \lambda} \alpha_{\nu\lambda} v_{\nu}(\mathbf{x}) \int d^3x' v_{\lambda}^*(\mathbf{x}') \psi(\mathbf{x}') = \mathcal{E} \psi(\mathbf{x}), \quad (6)$$

where $v_{\nu}(\mathbf{x}) = V(\mathbf{x}) \psi_{\nu}(\mathbf{x})$, and $\alpha_{\nu\lambda}$ is the matrix reciprocal to

$$V_{\lambda\mu} = \int d^3x' \psi_{\lambda}^*(\mathbf{x}') V(\mathbf{x}') \psi_{\mu}(\mathbf{x}'), \quad (7)$$

in the sense that

$$\sum_{\lambda} \alpha_{\nu\lambda} V_{\lambda\mu} = \delta_{\nu\mu}.$$

The proof is immediate, by substitution. The potential (1) is evidently the simplest case, where $n=1$.

For example, let us consider a theory with only p waves. The appropriate wave equation is

$$-\nabla^2 \psi(\mathbf{x}) - \sum_{j'} v_{j'}(\mathbf{x}) \int d^3x' v_{j'}(\mathbf{x}') \psi(\mathbf{x}') = \mathcal{E} \psi(\mathbf{x}); \quad (8)$$

here $v_j(\mathbf{x}) = f(|\mathbf{x}|) x_j$; $j=1, 2, 3$ and $f(|\mathbf{x}|)$ is a spherically symmetric function. Solving by the techniques already discussed we find,

$$\tilde{\psi}(\mathbf{q}) = \frac{1}{q^2 - \mathcal{E}} \sum_{j'} \tilde{v}_{j'}(\mathbf{q}) C_{j'}$$

where

$$C_j \equiv \frac{1}{(2\pi)^3} \int d^3q' \tilde{v}_j^*(\mathbf{q}') \tilde{\psi}(\mathbf{q}'),$$

and, therefore,

$$C_j = \sum_{j'} M_{jj'}(\mathcal{E}) C_{j'}, \quad (9a)$$

where

$$M_{jj'}(\mathcal{E}) = \frac{1}{(2\pi)^3} \int d^3q \frac{\tilde{v}_j^*(\mathbf{q}) \tilde{v}_{j'}(\mathbf{q})}{q^2 - \mathcal{E}}. \quad (9b)$$

By symmetry, only the diagonal terms of this 3×3 matrix are nonzero, and they are all identical; i.e.,

$$M_{jj'}(\mathcal{E}) = \frac{1}{(2\pi)^3} \int d^3q \frac{|\tilde{v}_j(\mathbf{q})|^2}{q^2 - \mathcal{E}}, \quad j=j'$$

$$= 0, \quad j \neq j'$$

so that this p -wave potential puts in three degenerate states. Of course the nonlocal potential could be generalized and constructed from a combination of s and p in which case one state splits off from the other three, and so on.

B. Lattices

Primitive Lattice

Here we have specifically chosen atoms with a single bound state. The equation of concern is

$$-\nabla^2\psi(\mathbf{x}) - \sum_{\mathbf{l}} v(\mathbf{x}-\mathbf{l}) \int d^3x' v(\mathbf{x}'-\mathbf{l})\psi(\mathbf{x}') = \mathcal{E}\psi(\mathbf{x}). \quad (10)$$

We are looking for solutions of the Bloch form,

$$\psi_{\mathbf{k}}(\mathbf{x}) = \exp(i\mathbf{k}\cdot\mathbf{x}) \sum_{\mathbf{b}} C_{\mathbf{b}} \exp(i\mathbf{b}\cdot\mathbf{x}), \quad (11)$$

where \mathbf{k} lies in the first Brillouin zone and the \mathbf{b} are the vectors of the reciprocal lattice.

Substituting this form of the wave function into (1) and looking at the $(\mathbf{k}+\mathbf{b})$ th Fourier component of the equation, one finds,

$$\begin{aligned} \{(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}\} C_{\mathbf{b}} - \frac{1}{N\Omega} \sum_{\mathbf{l}} \sum_{\mathbf{b}'} \exp[i(\mathbf{k}+\mathbf{b}')\cdot\mathbf{l}] \\ \times \tilde{v}(\mathbf{k}+\mathbf{b}') C_{\mathbf{b}'} \int d^3x v(\mathbf{x}-\mathbf{l}) \exp[-i(\mathbf{k}+\mathbf{b}')\cdot\mathbf{x}] = 0. \end{aligned}$$

Here Ω is the volume of the unit cell and N is the number in the crystal such that $N\Omega$ is the volume.

Now the last term can be simplified and is

$$\begin{aligned} &= -\frac{\tilde{v}(-\mathbf{k}-\mathbf{b})}{N\Omega} \sum_{\mathbf{b}'} \sum_{\mathbf{l}} \exp[i(\mathbf{b}'-\mathbf{b})\cdot\mathbf{l}] \tilde{v}(\mathbf{k}+\mathbf{b}') C_{\mathbf{b}'}, \\ &= -\frac{\tilde{v}(-\mathbf{k}-\mathbf{b})}{\Omega} \sum_{\mathbf{b}'} \tilde{v}(\mathbf{k}+\mathbf{b}') C_{\mathbf{b}'}, \end{aligned}$$

since each term in the internal sum is one.

Solving for the wave function,

$$C_{\mathbf{b}}(\mathbf{k}) = \frac{1}{\Omega} \frac{\tilde{v}(-\mathbf{k}-\mathbf{b}) D(\mathbf{k})}{(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}}, \quad (12)$$

where

$$D(\mathbf{k}) \equiv \sum_{\mathbf{b}'} \tilde{v}(\mathbf{k}+\mathbf{b}') C_{\mathbf{b}'}(\mathbf{k}).$$

Consistency requires that

$$1 = -\frac{1}{\Omega} \sum_{\mathbf{b}} \frac{\tilde{v}(-\mathbf{k}-\mathbf{b}) \tilde{v}(\mathbf{k}+\mathbf{b})}{(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}} \equiv \Phi(\mathcal{E}), \quad (13)$$

which is the desired dispersion relation. This along with the analogous relation for a lattice with basis, Eq. (18), is the central equation of this paper. Solutions of this equation, \mathcal{E}_n , for a given \mathbf{k} yield the energy bands $\mathcal{E}_n(\mathbf{k})$.

For complex \mathbf{k} it is important to leave numerators in the form

$$\tilde{v}(-\mathbf{k}-\mathbf{b}) \tilde{v}(\mathbf{k}+\mathbf{b}).$$

Only for real \mathbf{k} they are equivalent to $|\tilde{v}(\mathbf{k}+\mathbf{b})|^2$.

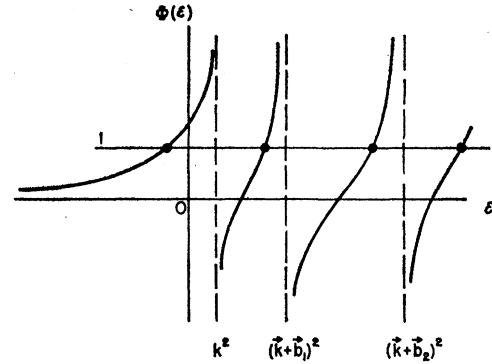


FIG. 2. Dispersion function for a primitive lattice, ϕ , versus energy, \mathcal{E} .

Some further comments on mathematical structure are in order. The periodic potential of Eq. (10) has the evident property that, working on a function of the form

$$\exp(i\mathbf{k}\cdot\mathbf{x}) u_{\mathbf{k}}(\mathbf{x}), \quad (u_{\mathbf{k}} \text{ periodic});$$

it will give another function of the same form. It does not mix subspaces of $\psi(\mathbf{x})$ belonging to different \mathbf{k} . This means that it mixes among themselves only the *discrete* set of Fourier components belonging to $\mathbf{k}+\mathbf{b}$. Moreover, for a given \mathbf{k} the function the potential yields is *independent* of $u(\mathbf{x})$ (except for a numerical coefficient). On each \mathbf{k} subspace the potential is merely a projective operator, leading to easy solvability of the eigenvalue problem.

The solution is analogous to Eq. (5), but since now only a discrete subset of states are involved, the former integral is replaced by a discrete sum. The branch line for all positive \mathcal{E} is replaced by a set of discrete poles, and instead of Fig. 1, we get Fig. 2 below. There is one solution to the dispersion relation falling below the free-particle energy for each band; hence, the band structure of \mathcal{E} as a function of \mathbf{k} has been obtained.

There are three points of further interest.

(1) Additional solutions: In solving the original wave equation we made the assumption that the potential term was not zero, but if $\psi(\mathbf{x})$ is such that

$$\int d^3x' v(\mathbf{x}'-\mathbf{l})\psi(\mathbf{x}') = 0,$$

then the equation reduces to

$$-\nabla^2\psi(\mathbf{x}) = \mathcal{E}\psi(\mathbf{x}).$$

For ψ satisfying both of these relations, there are additional free-particle eigenvalues besides the solutions to $\Phi(\mathcal{E})=1$. These free particle states are orthogonal to the potential; i.e., for a s wave potential they are not invariant under $G_{\mathbf{k}}$, the group of symmetry operators leaving both the lattice and \mathbf{k} unchanged. Therefore,

we expect to find these "free" states along points, lines and planes of high symmetry.

(2) The effective mass tensor: The dispersion relation reads,

$$1 = \Phi(\mathcal{E}, \mathbf{k}),$$

such that,

$$0 = \left(\frac{\partial \Phi}{\partial \mathcal{E}} \right) \nabla_{\mathbf{k}} \mathcal{E} + \nabla_{\mathbf{k}} \Phi,$$

or

$$0 = \left(\frac{\partial}{\partial \mathcal{E}} \nabla_{\mathbf{k}} \Phi \right) \nabla_{\mathbf{k}} \mathcal{E} + \left(\frac{\partial \Phi}{\partial \mathcal{E}} \right) \nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \mathcal{E} + \nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \Phi,$$

but at the center of the zone, assuming nondegenerate bands,

$$\nabla_{\mathbf{k}} \mathcal{E} = 0;$$

consequently,

$$\nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \mathcal{E} = - \frac{\nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \Phi}{(\partial \Phi / \partial \mathcal{E})}. \quad (14)$$

The components of this tensor are simply proportional to the reciprocal effective-mass components. Φ is, of course, a known function of \mathbf{k} , so that the components may be written out explicitly, if desired.

(3) An asymptotic solution: A weak binding approximation exists within the theory. As the potential strength $\rightarrow 0$, each eigenvalue is found in the neighborhood of a free-electron value. This follows because each term in the sum is of the type $A/(B - \mathcal{E})$. As $A_i \rightarrow 0$, the i th term contributes only for $\mathcal{E} \approx B_i$. If there are no other nearby resonances then all the other terms in the sum are approximately stationary while the behavior of the i th term dominates. Simple algebra shows that

$$\mathcal{E}_i \approx B_i - A_i / \left(1 - \sum_{i \neq j} \frac{A_j}{B_j - B_i} \right),$$

which approaches free-wave propagation as $A_i \rightarrow 0$.

If plane waves differing by reciprocal lattice vectors are nearly degenerate they are strongly mixed by the potential. These terms must be treated exactly, while the remainder of the sum is approximated as above.

Lattice with a Basis

In this case the potential term becomes,

$$-\sum_{1,j} v(\mathbf{x} - \boldsymbol{\tau}_{1,j}) \int d^3x' v(\mathbf{x}' - \boldsymbol{\tau}_{1,j}) \psi(\mathbf{x}'), \quad (15)$$

$$j = 0, 1, \dots, r.$$

For $j \neq 0$, the $\boldsymbol{\tau}_{1,j}$ are nonprimitive translations. Assuming again wave functions of the Bloch form and looking at the $(\mathbf{k} + \mathbf{b})$ th Fourier component of the above expression, we find

$$-\frac{1}{\Omega} \bar{v}(-\mathbf{k} - \mathbf{b}) \sum_j \sum_{\mathbf{b}'} \exp[-i(\mathbf{b} - \mathbf{b}') \cdot \boldsymbol{\tau}_{1,j}] \bar{v}(\mathbf{k} + \mathbf{b}') C_{\mathbf{b}'}(\mathbf{k})$$

by the same devices used previously. Therefore, the Schrödinger equation reads

$$C_{\mathbf{b}}(\mathbf{k}) = \frac{1}{\Omega} \frac{\bar{v}(-\mathbf{k} - \mathbf{b})}{(\mathbf{k} + \mathbf{b})^2 - \mathcal{E}} \sum_j \exp(i\mathbf{b} \cdot \boldsymbol{\tau}_{1,j}) \times \sum_{\mathbf{b}'} \exp(i\mathbf{b}' \cdot \boldsymbol{\tau}_{1,j}) \bar{v}(\mathbf{k} + \mathbf{b}') C_{\mathbf{b}'}(\mathbf{k}).$$

Defining a set of r functions,

$$D_j(\mathbf{k}) \equiv \sum_{\mathbf{b}} \exp(i\mathbf{b}' \cdot \boldsymbol{\tau}_{1,j}) \bar{v}(\mathbf{k} + \mathbf{b}') C_{\mathbf{b}'}(\mathbf{k}),$$

the above equation implies

$$D_j(\mathbf{k}) = \sum_{j'} \Phi_{jj'}(\mathcal{E}, \mathbf{k}) D_{j'}(\mathbf{k}), \quad (16)$$

where the elements of the dispersion matrix are

$$\Phi_{jj'}(\mathcal{E}, \mathbf{k}) = \frac{1}{\Omega} \sum_{\mathbf{b}} \frac{\bar{v}(\mathbf{k} + \mathbf{b}) \bar{v}(-\mathbf{k} - \mathbf{b})}{(\mathbf{k} + \mathbf{b})^2 - \mathcal{E}} \times \exp[i\mathbf{b} \cdot (\boldsymbol{\tau}_{1,j} - \boldsymbol{\tau}_{1,j'})]. \quad (17)$$

In general, there are $\frac{1}{2}r(r-1) + 1$ independent matrix elements for \mathbf{k} real, and we note that the diagonal elements are independent of j . The secular equation determining the energy eigenvalues is

$$\det(\Phi_{jj'} - \delta_{jj'}) = \Phi. \quad (18)$$

We have, therefore, a determinantal dispersion relation.

As an example, we chose the diamond lattice. There are two atoms per unit cell; the nonprimitive translation vector is $\boldsymbol{\tau} = \frac{1}{4}a(1,1,1)$. For real \mathbf{k} there are two independent matrix elements since

$$\Phi_{11} = \Phi_{22} \equiv \Phi,$$

$$\Phi_{12} = \Phi_{21}^*, \quad \mathbf{k} \text{ real.}$$

Consequently,

$$(\Phi - 1)^2 - |\Phi_{12}|^2 = 0$$

or

$$1 = \Phi(\mathcal{E}) \pm |\Phi_{12}(\mathcal{E})| \quad (19)$$

in this case. The branch going with the positive sign refers to the bonding orbitals whereas the other refers to the antibonding.

CALCULATION FOR A GAUSSIAN POTENTIAL

In this section we report on calculations of a nonlocal Gaussian potential set in a fcc lattice; our intention here is to illustrate the technique. The two free parameters in the potential, strength and range, will be chosen in order to match a bound-state energy and the atomic radius of a specific atom. Indeed, in view of the implications of Eqs. (6) and (7) we could have constructed a more detailed model with knowledge of the free-atom Hartree-Fock potential and the corresponding wave functions for the states of interest.

A plot of \mathcal{E}_n versus \mathbf{k} along the $[100]$ symmetry axis is presented (cf., Fig. 5).

We begin by examining the isolated "Gaussian atom." In the sense of Eq. (3), the potential is

$$v(\mathbf{x}) = \lambda e^{-|\mathbf{x}|^2/x_0^2} \quad (20)$$

(where λ and x_0 are the two forementioned parameters). Its transform is

$$\tilde{v}(\mathbf{q}) = \lambda \pi^{3/2} x_0^3 e^{-\frac{1}{4} q^2 x_0^2}.$$

This potential binds at most one state and the wave function must be spherically symmetric. If A is an unspecified normalization constant, then

$$\psi_{b.s.}(\mathbf{x}) = \frac{A}{|\mathbf{x}|} \int_0^\infty q dq \frac{e^{-\frac{1}{4} q^2 x_0^2}}{q^2 - \mathcal{E}_{b.s.}} \sin(q|\mathbf{x}|)$$

whereas the dispersion function is

$$\phi(\mathcal{E}) = \lambda^2 x_0^6 \frac{\pi}{2} \int_0^\infty \frac{dq q^2 e^{-\frac{1}{4} q^2 x_0^2}}{q^2 - \mathcal{E}}.$$

Assuming $|\mathcal{E}| \gg 1/x_0^2$, then the major contribution to each of these integrals comes from $q \approx 1/x_0$. This means that the extent of the wave function $\approx x_0$ and

$$\phi(\mathcal{E}) \approx \frac{\lambda^2 x_0^3}{(-\mathcal{E})} \left(\frac{1}{2}\pi\right)^{3/2}$$

or

$$\lambda^2 \approx \left(\frac{2}{\pi}\right)^{3/2} \frac{|\mathcal{E}_{b.s.}|}{x_0^3}, \quad (21)$$

which relates the coupling constant and the spread of the well to the bound-state energy and the extent of the wave function. The "ansatz" above is well satisfied for the valence states of most atomic systems.

We now wish to embed these "atoms" in a fcc Bravais lattice. (It should be emphasized that the crystalline descendants of the free atom scattering states as well as the bound states are organized by the crystal into allowed and forbidden bands.)

Equation (18), the dispersion relation for Bloch waves, becomes

$$1 = \frac{\lambda^2 \pi^3 x_0^6}{\Omega} \sum_{\mathbf{b}} \frac{\exp[-\frac{1}{2} x_0^2 (\mathbf{k} + \mathbf{b})^2]}{(\mathbf{k} + \mathbf{b})^2 - \mathcal{E}},$$

where the sum extends over the bcc lattice which is reciprocal to the fcc. The three primitive vectors in this reciprocal lattice are the three permutations of $(2\pi/l)(1, -1, -1)$; l is the length of the cube edge in the real lattice, and therefore, the volume of the unit cell is

$$\Omega = \frac{1}{4} l^3.$$

At this point in the calculation it is worthwhile finding the characteristic dimensionless parameters of

the problem. If lengths are measured in units of l , so that

$$\mathbf{k}' \equiv l\mathbf{k}, \\ \mathcal{E}' \equiv l^2 \mathcal{E},$$

the dispersion relation becomes

$$1 = \lambda^2 \pi^3 x_0^6 \frac{4}{l} \sum_{\mathbf{b}'} \frac{\exp[-\frac{1}{2} (x_0/l)^2 (\mathbf{k}' + \mathbf{b}')^2]}{(\mathbf{k}' + \mathbf{b}')^2 - \mathcal{E}'}$$

Therefore, we are dealing with a two-parameter system. These are

(i) a dimensionless coupling strength, g , where

$$g \equiv \lambda^2 \pi^3 x_0^6 (4/l), \quad (22)$$

or, in view of the result of Eq. (21),

$$g = |\mathcal{E}_{b.s.}| (x_0^3/l) 4\pi^3 (2/\pi)^{3/2};$$

and (ii) a parameter, s , where s^3 is the fractional filled volume,

$$s \equiv x_0/l. \quad (23)$$

The dispersion relation, therefore, simplifies to

$$\frac{1}{g} = \sum_{\mathbf{b}'} \frac{\exp[-\frac{1}{2} s^2 (\mathbf{k}' + \mathbf{b}')^2]}{(\mathbf{k}' + \mathbf{b}')^2 - \mathcal{E}'}. \quad (24)$$

For the numerical example we have chosen, we have

$$s = 1/(\sqrt{2}\pi). \quad (25)$$

The reason for this value is that it falls within 5% of the nearest-neighbor hard-sphere contact distance, $\sqrt{3}/8$, in a diamond configuration (for which this calculation is a precursor); and furthermore, this value is numerically convenient. The value of g necessary to give the experimental bound state energy $\mathcal{E}_{b.s.}$ is now

$$g = |\mathcal{E}_{b.s.}| x_0^2 2^3 \pi^{1/2}. \quad (26)$$

Specifying g is the last step in the calculation. Once the right-hand side of Eq. (24) has been computed as a function of \mathcal{E} , the eigenvalues may be found with ease for any coupling strength.

The reciprocal lattice sum has been evaluated

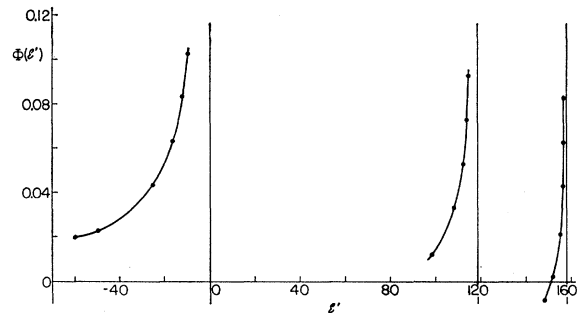


FIG. 3. The dispersion function for a "Gaussian atom" set in a fcc crystal versus \mathcal{E}' (energy in units of $\hbar^2/2ml^2$) at the Γ point.

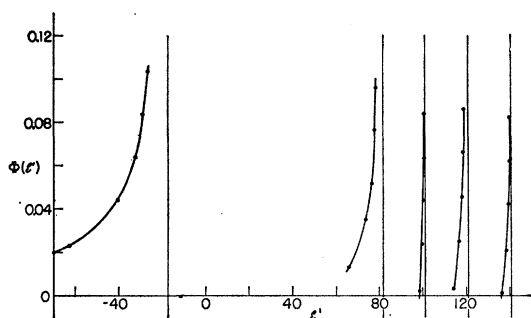


FIG. 4. The dispersion function for a "Gaussian atom" versus \mathcal{E}' at the point, $\mathbf{k} = (\pi/2l)(1,0,0)$.

numerically with a slide rule; this is a simple task requiring no more than an afternoon's labor. The sum has been plotted as a function of \mathcal{E} for \mathbf{k} along the Δ or $[100]$ axis. We recall that the wave vector appears parametrically so that for five sample points in the first Brillouin zone

$$\mathbf{k}' = 2\pi(m/4)(1,0,0), \quad m=0, 1, 2, 3, 4$$

(i.e., the Γ and X along with three interior points) we have obtained five graphs. Two representative plots, for the Γ and $m=1$ points, are included to illustrate this discussion (Figs. 3 and 4). As noted before, poles exist in the dispersion function at the free electron energies, $\mathcal{E} = (\mathbf{k} + \mathbf{b})^2$. Since it has already been assumed that $|\mathcal{E}_{b,s}|x_0^2 \gg 1$, only values falling between 0.0 and 0.1 are important.

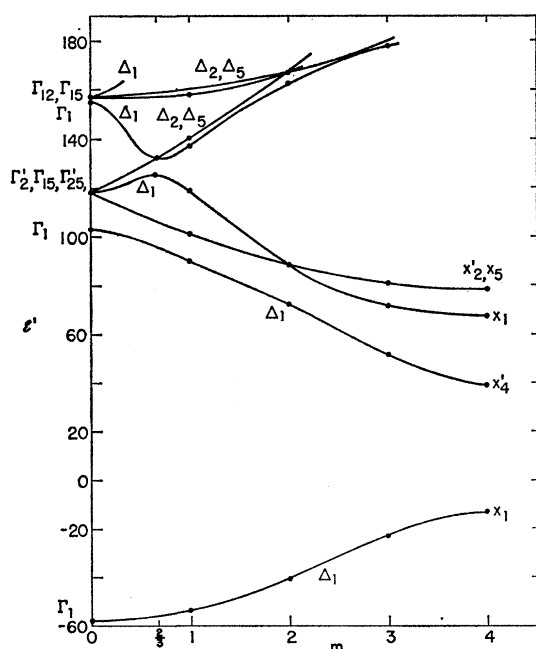


FIG. 5. Energy bands along the Δ axis for Ge fitted to a "Gaussian atom" and set in a fcc lattice. \mathcal{E}' is energy in units of $\hbar^2/2ml^2$ and $\mathbf{k} = (m\pi/2l)(1,0,0)$.

The exponential form of the numerators guarantees rapid convergence of the sum. Consequently, the sum has been truncated for reciprocal lattice sites such that

$$(\mathbf{k}' + \mathbf{b}'/2\pi)^2 \geq 5. \quad (27)$$

These terms have a negligible influence on the energy of the remaining states and the modes cut off describe nearly free electrons. For our choice of s and with \mathbf{k} along the Δ symmetry axis, there are no more than five distinct terms in the truncated sum.

To determine the energy bands we set $g = \text{const.}$, and read the intersections from each graph of the lattice sum for \mathbf{k} fixed; and subsequently vary \mathbf{k} . This has been

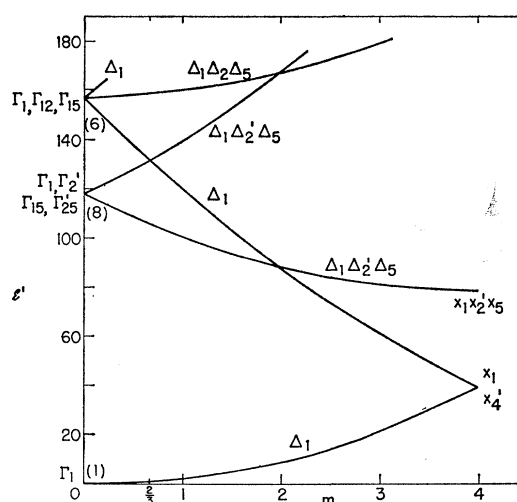


FIG. 6. Free electron energy bands for a fcc lattice along the Δ axis.

done and Fig. 5 is the result for $g = 0.5 \times 10^2$. This value of g corresponds to a free atom ionization energy of about 8 eV, and an atomic radius of about 1.2 Å, which is representative of Ge. For comparison a separate graph (Fig. 6) of the free electron dispersion is included.²

Several features deserve attention.

(1) *The consequences of symmetry.* With $v(\mathbf{x})$ chosen spherically symmetric, the potential (1) affects only those combinations of plane wave which are invariant under $G_{\mathbf{k}}$. For a general \mathbf{k} all waves are influenced, but along lines of symmetry some are untouched. This means that at points Γ and X and along the line Δ our dispersion relation refers, respectively, to the Γ_1 , X_1 , and Δ_1 irreducible representations. Modes with other transformation properties propagate as free plane waves. At point Γ , fifteen plane waves satisfy the criterion Eq. (27), and we find three Γ_1 , one Γ_2 , one Γ_{12} , two Γ_{15} , and one Γ_{25} representations among this set. Along line

² H. Jones, *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960), Chap. III.

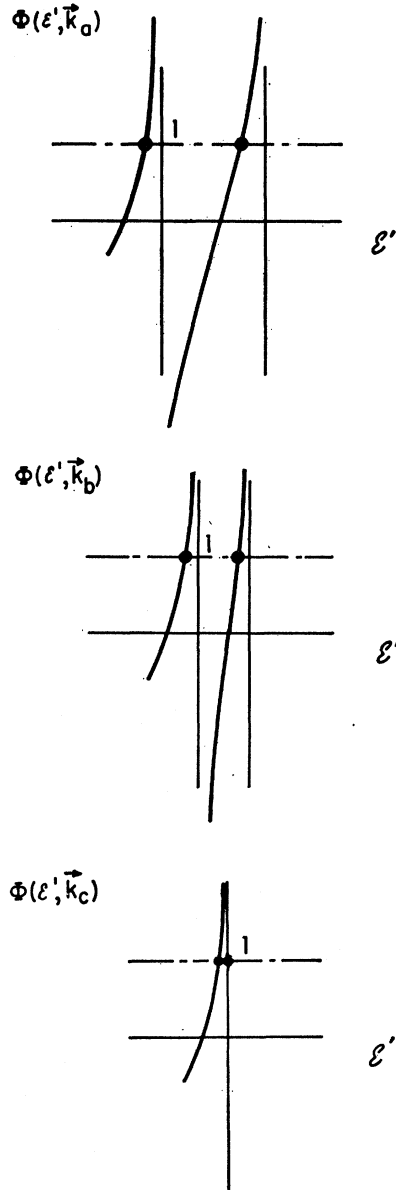


FIG. 7. Dispersion function versus energy for a sequence of wave vectors converging on \mathbf{k}_c , a point of free-particle degeneracy.

Δ they split into six Δ_1 , two Δ_2 , one Δ_2 and three Δ_5 types. $\Gamma_1-\Delta_1-X_1$ bands have lower energies than the corresponding free particle bands since the potential is attractive.

On the other hand, if the isolated "atom" were constructed out of both s and p waves, energy bands characterized by $\Gamma_{15}-(\Delta_5 \text{ or } \Delta_1)-(X_5, X_5', X_1, \text{ or } X_4)$ would appear in the dispersion relation and so on.

(2) *The splitting of degeneracies.* Crossings of the free-electron energy surfaces for general \mathbf{k} and with Δ_1 or Λ_1 symmetry are split by the interaction (1). For example, such intersections occur in Fig. 6 at $\mathbf{k}' = \frac{1}{3}\pi$, π , and 2π . The reason for the splitting is easily seen. Consider a sequence of \mathbf{k}' s converging on \mathbf{k}_0 , the point

of intersection. The relevant part of the dispersion function has the behavior shown in Fig. 7. At the point of free-particle degeneracy in the crystal, one state has precisely the free-particle energy eigenvalue while the other falls below. This happens because in the degenerate subspace it is always possible to form a linear combination of free-particle states orthogonal to the potential (1). The resulting feature of energy extrema in the interior of the Brillouin zone is an intrinsically three-dimensional result.

SUMMARY

We have developed a simple analytic approach to band structure calculations. The theory, with a Gaussian potential, was used to build Bloch waves in a fcc lattice.

We are presently engaged in constructing a few parameter model for valence crystals of the diamond type. Of particular interest will be the dependence of the band minima on lattice constant. And, finally, analytic continuation into the forbidden band will be used to investigate the properties of deep impurity states.

APPENDIX: ORTHOGONALITY OF THE WAVE FUNCTIONS, \mathbf{k} REAL

(1) Primitive lattice:

$$C_{nb}(\mathbf{k}) = \frac{1}{\Omega} \frac{\tilde{v}(-\mathbf{k}-\mathbf{b})D(\mathbf{k})}{(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}_n}.$$

States where $\mathbf{k} \neq \mathbf{k}'$ are manifestly orthogonal. For $\mathbf{k} = \mathbf{k}'$, forming the inner product (\mathbf{k} real), we have

$$\langle \psi_{n\mathbf{k}} | \psi_{m\mathbf{k}} \rangle \propto \sum_{\mathbf{b}} \frac{\tilde{v}(-\mathbf{k}-\mathbf{b})\tilde{v}(\mathbf{k}+\mathbf{b})}{[(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}_n][(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}_m]}, \quad (\text{A1})$$

where unessential factors have been dropped. Assuming that the bands do not touch and expanding the denominators by partial fractions, we obtain

$$\frac{1}{[(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}_n][(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}_m]} = \frac{1}{\mathcal{E}_m - \mathcal{E}_n} \left\{ \frac{1}{(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}_n} - \frac{1}{(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}_m} \right\}$$

which when substituted in the right-hand side of Eq. (A1) yields

$$\frac{1}{\mathcal{E}_m - \mathcal{E}_n} \{ \Phi(\mathcal{E}_n) - \Phi(\mathcal{E}_m) \} = 0$$

since both \mathcal{E}_n and \mathcal{E}_m are solutions of the equation

$$\Phi(\mathcal{E}) = 1.$$

(2) Lattice with a basis:

$$C_{nb}(\mathbf{k}) = \frac{1}{\Omega} \frac{\tilde{v}(-\mathbf{k}-\mathbf{b})}{(\mathbf{k}+\mathbf{b})^2 - \mathcal{E}_n} \sum_i \exp(-i\mathbf{b} \cdot \boldsymbol{\tau}_{ij}) D_j(\mathbf{k}).$$

The inner product (I.P.) between two Bloch function ($\mathbf{k}=\mathbf{k}'$) is

$$\begin{aligned} \text{I.P.} &\propto \sum_{\mathbf{b}} C_{n\mathbf{b}} C_{m\mathbf{b}}^* \\ &\propto \sum_{\mathbf{b}} \frac{\bar{v}(-\mathbf{k}-\mathbf{b})\bar{v}(\mathbf{k}+\mathbf{b})}{[(\mathbf{k}+\mathbf{b})^2-\mathcal{E}_n][(\mathbf{k}+\mathbf{b})^2-\mathcal{E}_m]} \\ &\quad \times \sum_{jj'} \exp[-i\mathbf{b}\cdot(\boldsymbol{\tau}_{1j}-\boldsymbol{\tau}_{1j'})] D_j D_{j'}^*. \quad (\text{A2}) \end{aligned}$$

Again decomposing into partial fractions, we obtain

$$\text{I.P.} \propto \frac{1}{(\mathcal{E}_m-\mathcal{E}_n)} \sum_{ii'} D_j D_{j'}^* \{\Phi_{jj'}(\mathcal{E}_m) - \Phi_{jj'}(\mathcal{E}_n)\},$$

which clearly vanishes, since the D_j are components of an eigenvector of the Φ matrix.

Magnetization and Electrical Resistivity of Gadolinium Single Crystals*

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The magnetic moment of single-crystal Gd has been measured in fields from 0 to 18 kOe along the $\langle 001 \rangle$, $\langle 10\bar{1}0 \rangle$, and $\langle 11\bar{2}0 \rangle$ directions at temperatures from 1.4 to 900°K. Small anisotropy was observed below the Curie temperature and the easy direction of magnetization was found to be a function of temperature. The absolute saturation magnetic moment was found to be 7.55 Bohr magnetons/atom. The saturation magnetization was observed to follow the $T^{3/2}$ law from 200 to 50°K with a deviation from this law observed below 50°K. A ferromagnetic Curie temperature of 293.2°K is reported. The effective Bohr magneton number in the paramagnetic region is 7.98 and the paramagnetic Curie temperature is 317°K. Electrical resistivity measurements were made from 4.2 to 380°K on the b -axis and c -axis crystals. For the b axis, the resistivity changes slope at 293.2°K. The c axis exhibits a small maximum at 292°K and a shallow minimum at 340°K.

INTRODUCTION

GADOLINIUM was the fourth ferromagnetic element to be discovered.¹ Trombe² and Elliott *et al.*³ found a Curie temperature of 289°K and an absolute saturation magnetization of 7.12 Bohr magnetons/atom. Henry⁴ found a saturation magnetization of 7.05 Bohr magnetons/atom at 1.3°K and 60 000G. Gaskell and Motz⁵ report magnetic moments at 80 000G which are about 15% higher than those for infinite fields as extrapolated by Elliott *et al.*

Arajs and Colvin⁶ reported a paramagnetic Curie temperature of 310°K and an effective Bohr magneton number of 8.07. They observed a small anomaly, which could be enhanced by small additions of Mo and Ta, at about 750°K.

Belov *et al.*⁷ found a peak in the magnetic moment

at 210°K in magnetic fields of less than 1.12 Oe from measurements on a toroidal sample. The isofields below 112 Oe also showed anomalous behavior at low temperatures. In addition, they reported small kinks in the magnetization curves above 210°K. Their conclusion was that a spiral spin structure exists in Gd between 210 and 290°K.

More recently, the magnetocrystalline anisotropy of Gd has been measured by Graham⁸ and by Corner *et al.*⁹ They both found that above 240 to 245°K the c axis is the easy direction of magnetization. Graham reports an easy cone of magnetization between 225 and 245°K, and below about 165°K. Between 165 and 225°K he found that the easy direction of magnetization is in the basal plane. Corner *et al.* report an easy cone of magnetization from 240 to 37.5°K, the lowest temperature used. Corner found that the easy direction reaches a maximum angle of 70° with respect to the c axis at 220°K. In addition, Graham observed that low field magnetization curves were in qualitative agreement with those calculated from the anisotropy constants.

The temperature dependence of the lattice parameters of single crystal Gd has been measured recently by Darnell.¹⁰ He reports a Curie temperature of 298°K.

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