lating material. Frequently, however, the substance by itself has only poor fluorescent properties under high-energy radiation, and when it is put into an efficient fluorescent solution a considerable decrease in light output results because of quenching. Such behavior is often found when materials contain elements of medium or heavy atomic weights. By applying the results obtained with added naphthalene, solutions which exhibit considerable fluorescence have been made with such quenching molecules present.

A list of substances containing different elements is presented in Table I with which at least moderate high-energy fluorescence efficiencies can be obtained in organic liquid solutions. (The common elements in organic substances such as hydrogen, carbon, nitrogen, and oxygen are not included.) In most cases, as can be seen from the table, the addition of large amounts of naphthalene produces sizeable enhancement of the light output although considerable amounts of the quenching material may be present in the solution. The various fluorescent solutes shown in the table give comparable results, and in many cases α,α'-binaphthyl may also be used. p-terphenyl cannot be utilized because of the insufficient energy transfer found with naphthalene.[6] The heaviest element that has been successfully used to the present has been bismuth. The list which is presented represents the results of a preliminary search for successful substances. Finding substances with desirable properties presents certain problems. One of the major difficulties is the lack of solubility in suitable organic solvents. Once a soluble material is found, it must generally be such that it does not quench the solution too strongly. The naphthalene, as discussed above, acts as a "solvent" in which less quenching occurs and provides a medium to and from which more energy is transferred.

The investigation presented in this paper opens up the possibility of studying the influence of various atoms and molecules on other excited molecules not normally present in work with fluorescence.

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Energy Levels of a Disordered Alloy

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A study is made of the one-electron energy levels of a disordered alloy by means of perturbation theory, extending the results of Nordheim and Muto. To the accuracy of first-order perturbation theory, a disordered alloy is equivalent to a particular perfect crystal, the "virtual crystal," as was shown by Muto. For a certain rather general model, the effects of second-, third-, and fourth-order perturbation theory upon this "virtual-crystal" approximation are analyzed. The question of convergence of the perturbation approach is studied. A certain basic limitation of the perturbation approach is discussed, namely, the limitation to nonlocalized states. Accurate results obtained by Landauer and Helland for a hypothetical one-dimensional alloy are compared with results obtained by perturbation theory. It is pointed out that the same approach can be used with equal validity in discussing not only disordered alloys but also other types of imperfect crystals; e.g., imperfections resulting from dislocations. The most striking prediction of perturbation theory, i.e., the "tailing-off" of the density-of-states curve into a forbidden band, appears to have some experimental verification.

I. INTRODUCTION

In this paper we will discuss the one-electron energy levels of a completely disordered alloy. For hypothetical one-dimensional alloys, this problem has recently been solved with the aid of computing machines.[1,2] For the three-dimensional problem, however, there seems to be little hope of a reasonably exact solution. The great difficulty, over and above the problem of a perfect crystal, lies in the lack of spacial periodicity of the disordered alloy even though the atoms of the alloy may reasonably be assumed to lie on periodic lattice sites. For this reason, we will attempt to solve the problem by perturbation theory. Such an approach was used by Muto[3] in an attempt to justify Nordheim's "virtual-crystal" approximation.[4] This approximation consists of replacing the correct one-electron potential (appropriate to a given configuration of atoms of the alloy) by its average (the average to be taken over all possible random configurations). In order to gain some physical insight into the accuracy of the approximation, we will now rephrase Muto's discussion in terms of electron scattering in the alloy.

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[1] H. M. James and A. S. Ginzbarg, J. Phys. Chem. **57**, 840 (1953).

[2] R. Landauer and J. C. Helland, J. Chem. Phys. **22**, 1655 (1954).

[3] T. Muto, Sci. Papers Inst. Phys. Chem. Research (Tokyo) **34**, 377 (1938).

[4] L. Nordheim, Ann. Physik **9**, 607 and 641 (1931).

II. VIRTUAL-CRYSTAL APPROXIMATION

The straightforward way to obtain physical information about an alloy in the one-electron approximation would be to solve the one-electron Schrödinger equation appropriate to some particular configuration of atoms of the alloy. Results obtained for each configuration are then averaged over all possible configurations, weighting each configuration according to its probability of occurrence. In particular, the average of the wave function over all possible configurations, namely $\langle\Psi\rangle$, is known as the coherent-wave amplitude, and $\langle\Psi^*\rangle\langle\Psi\rangle$ as the coherent-wave intensity, while $\langle\Psi^*\Psi\rangle-\langle\Psi^*\rangle\langle\Psi\rangle$ is known as the incoherent-wave intensity. Thus $\langle\Psi^*\Psi\rangle$, the total intensity, is the sum of two parts, the coherent part and the incoherent part.

In atomic units, the one-electron Schrödinger equation for a particular configuration of atoms may be written

$$[-\nabla^2+\mathbf{V}(\mathbf{r},\mathbf{r}_n)]\Psi_q(\mathbf{r},t,\mathbf{r}_n)=E_q(\mathbf{r}_n)\Psi_q(\mathbf{r},t,\mathbf{r}_n),$$

where $\mathbf{r}$ is the electronic coordinate, while the N different $\mathbf{r}_n$, denoting the positions of the N atoms of the alloy for a given configuration, appear in $\mathbf{V}$, Ψ, and E parametrically. q is an index enumerating the solutions of the equation. Define

$$\mathbf{V}'(\mathbf{r},\mathbf{r}_n)=\mathbf{V}(\mathbf{r},\mathbf{r}_n)-\mathbf{V}_0(\mathbf{r}).$$

$\mathbf{V}_0(\mathbf{r})$, as yet unspecified, is independent of the $\mathbf{r}_n$ although it does depend upon the lattice structure of the alloy. Using the time-dependent Schrödinger equation, we may write

$$[-\nabla^2+\mathbf{V}_0(\mathbf{r})+\mathbf{V}'(\mathbf{r},\mathbf{r}_n)]\Psi_q(\mathbf{r},t,\mathbf{r}_n)=2i\frac{\partial}{\partial t}\Psi_q(\mathbf{r},t,\mathbf{r}_n).$$

Specify that at time $t=0$, Ψ be a particular solution to

$$\begin{aligned}[-\nabla^2+\mathbf{V}_0(\mathbf{r})]\Psi_q^0(\mathbf{r},t)&=2i\frac{\partial}{\partial t}\Psi_q^0(\mathbf{r},t)\\&=E_{0q}\Psi_q^0(\mathbf{r},t).\end{aligned}$$

Since $\mathbf{V}_0$ is independent of the $\mathbf{r}_n$, so also are Ψ_q^0 and E_{0q}. The development of Ψ with time can be determined by means of time-dependent perturbation theory. Thus we expand Ψ in terms of the Ψ^0's.

$$\Psi_q(\mathbf{r},t,\mathbf{r}_n)=\textstyle\sum_p a_{qp}(t,\mathbf{r}_n)\Psi_p^0(\mathbf{r},t),\quad a_{qp}(0,\mathbf{r}_n)=\delta_{qp}.$$

The time-dependent coefficients a depend upon the matrix elements of $\mathbf{V}'$ with respect to the unperturbed wave functions Ψ^0. Thus $\mathbf{V}'$ causes scattering of the electron. $a_{qq}\Psi_q^0$ represents the unscattered portion of the electron wave while $\Psi_q-a_{qq}\Psi_q^0$ represents the scattered portion.

Thus far we have not defined $\mathbf{V}_0$. We now choose $\mathbf{V}_0$ such that the scattered wave is completely *incoherent*. In the approximation of *first-order* time-dependent perturbation theory, this requirement can always be met by choosing $\mathbf{V}_0$ such that

$$\left\langle\int_\infty \Psi_p^{0*}(\mathbf{r},t)\mathbf{V}'(\mathbf{r},\mathbf{r}_n)\Psi_q^0(\mathbf{r},t)d\tau\right\rangle_{\mathbf{r}_n}=0.$$

The above integration is over all of the space occupied by the alloy, and the averaging is over all possible configurations of the atoms. Let us now place the array of atoms in a box and impose periodic boundary conditions on the electronic wave function. The wave functions Ψ_q^0 may therefore be expanded in terms of the complete set of plane waves satisfying the boundary conditions and *vice versa*. It follows that the above equation is equivalent to

$$\left\langle\int_\infty \mathbf{V}'(\mathbf{r},\mathbf{r}_n)e^{i\mathbf{k}\cdot\mathbf{r}}d\tau\right\rangle_{\mathbf{r}_n}=0,$$

where $\mathbf{k}$ is any of the set of k-vectors allowed by the periodic boundary conditions. It should be pointed out that this equation, in conjunction with the original definition of $\mathbf{V}_0$, serves to determine $\mathbf{V}_0$ uniquely.

Following Nordheim,[4] we assume that the crystal potential can be written as a spacial sum of atomic-like potentials; i.e.,

$$\mathbf{V}(\mathbf{r})=\textstyle\sum_n V_{s_n}(\mathbf{r}-\mathbf{R}_n),\tag{1}$$

where $\mathbf{R}_n$ denotes the position of the nth lattice site and the index s denotes the type of atom on the nth lattice site. $V_s(\mathbf{r})$ is an atomic-like potential associated with an atom of type s. Let f_s be the fraction of lattice sites occupied by atoms of type s.

$$\textstyle\sum_s f_s=1.\tag{2}$$

We have

$$\int_\infty \mathbf{V}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau=\sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n}\int_\infty V_{s_n}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau.$$

Thus

$$\left\langle\int_\infty \mathbf{V}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau\right\rangle=\sum_s f_s\int_\infty V_s(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau\sum_n e^{i\mathbf{k}\cdot\mathbf{R}_n}.$$

We now see that only by picking

$$\mathbf{V}_0(\mathbf{r})=\textstyle\sum_n V_0(\mathbf{r}-\mathbf{R}_n),\tag{3}$$

where

$$V_0(\mathbf{r})=\textstyle\sum_s f_sV_s(\mathbf{r}),\tag{4}$$

can we satisfy the requirement that

$$\left\langle\int_\infty \mathbf{V}'(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau\right\rangle=0,$$

so that $\mathbf{V}_0(\mathbf{r})$ is a potential having the periodicity of the lattice associated with the alloy. This periodicity results from the fact that the positions of the atoms in a disordered alloy are not completely random but must coincide with the lattice sites of the crystal. In an ideal liquid, on the other hand, where the positions of the atoms are random, $\mathbf{V}_0$ is a constant. The band gap observed experimentally[5] in a disordered alloy is a manifestation of the band structure resulting from the periodic nature of $\mathbf{V}_0$. The effect of $\mathbf{V}'$ is to scatter the electrons of the alloy incoherently. A disordered alloy is analogous to a perfect crystal at a finite temperature, where lattice vibrations have destroyed the perfect periodicity of the crystal potential. For this latter case also, the crystal potential can be written as a periodic $\mathbf{V}_0$ and a $\mathbf{V}'$ resulting from lattice vibrations which gives rise to incoherent scattering.

Why did we choose $\mathbf{V}_0$ such that $\mathbf{V}'$ would give rise only to incoherent scattering (in the approximation of first-order perturbation theory)? We wish to pick our initial wave function $\Psi_q{}^0(\mathbf{r},t)$ such that, aside from the phase factor, $\exp(-\frac{1}{2}iE_{0q}t)$, the change in Ψ_q with time is a minimum when averaged over all possible configurations of atoms. In other words, we wish to minimize the time-dependence of the "spacial part" of the wave function, since it is the perturbing potential $\mathbf{V}'$ which is giving rise to this time dependence of the "spacial part" of the wave function, and the success of any perturbation scheme depends upon the weakness of the perturbation. Mathematically, we wish to minimize

$$\left|\left\langle\frac{\partial}{\partial t}\Psi_q(\mathbf{r},t,\mathbf{r}_n)e^{\frac{1}{2}iE_{0q}t}\right\rangle_{\mathbf{r}_n}\right|;$$

but by picking $\mathbf{V}_0$, and thus $\Psi_q{}^0$, such that only incoherent scattering occurs, we insure that the above quantity vanishes (to the accuracy of first-order perturbation theory).

The problem of a disordered alloy has been resolved into two parts: (1) The determination of the wave functions and energy levels of an electron in the periodic potential $\mathbf{V}_0$. (2) The determination of the amount of incoherent scattering of the electron by $\mathbf{V}'$, this scattering giving rise to the "residual resistance" of a metallic alloy. The theory of the "residual resistance" has been worked out[4] and will not be discussed here.

In the following sections we will study the corrections, resulting from second- and higher-order perturbation theory, to the wave functions and energy levels associated with the periodic potential $\mathbf{V}_0$.

III. EFFECT OF SECOND-ORDER PERTURBATION THEORY

The effect of second-order perturbation theory on the unperturbed energy E_{0q} is to correct it by an amount

$$E_{2q}=\sum_p{}'|\mathbf{V}_{qp}{}'|^2(E_{0q}-E_{0p})^{-1}, \tag{5}$$

where

$$\mathbf{V}_{qp}{}'=\int_\infty \Psi_q{}^{0*}\mathbf{V}'\Psi_p{}^0 d\tau. \tag{6}$$

The prime on the summation sign denotes that the term for $p=q$ is not included. As was pointed out by Muto,[3] when E_{0q} lies in the middle of an energy band there will be roughly equal positive and negative contributions to the above sum so that E_{2q} might be expected to be small. When E_{0q} is near the bottom or the top of a band, however, the leading terms in the sum will be negative or positive, respectively. Thus the effect of E_{2q} will be to "smear" band edges out into the band gaps. Muto implied that E_{2q} vanishes in the limit as N, the number of atoms in the alloy, becomes infinite. Such is not the case. As will be shown presently, E_{2q} approaches a finite limit as N approaches infinity.

In order to study E_{2q} in detail, it will be convenient to restrict ourselves to a very specific model; namely the case where $\mathbf{V}_0$ is a constant. We refer to this as the "empty-lattice virtual-crystal" model. The practical advantage of working with this model lies in the fact that the unperturbed wave functions are particularly simple; namely plane waves. Without further loss of generality we can redefine the zero of energy such that $\mathbf{V}_0$ vanishes identically and only energies greater than zero are allowed to the accuracy of first-order perturbation theory. We now assume that the energy region in the neighborhood of zero corresponds qualitatively to the energy region in the neighborhood of the minimum of an allowed band associated with a more realistic, nonvanishing $\mathbf{V}_0$. The justification for this assumption lies in the well-known effective-mass approximation,[6] which states that in the energy region in the neighborhood of a minimum or a maximum of a nondegenerate allowed band, the equations of motion of an electron in a periodic potential are equivalent, for qualitative purposes, to the equations of motion of a free particle with a certain reciprocal effective-mass tensor. A positive mass corresponds to an electron in the bottom of a band while a negative mass corresponds to an electron in the top of a band. The empty-lattice virtual-crystal model is a specialization to the case where the effective mass equals the free-electron mass, but the generalization to arbitrary effective mass is trivial.

The Hamiltonian for the empty-lattice virtual-crystal model can be written

$$H=H_0+\mathbf{V}'(\mathbf{r}), \tag{7}$$

where

$$H_0=-\nabla^2, \tag{8}$$

$$\mathbf{V}'(\mathbf{r})=\sum_n V_{sn}{}'(\mathbf{r}-\mathbf{R}_n). \tag{9}$$

To conform with the results of the previous section, we must take

$$V_s{}'(\mathbf{r})=V_s(\mathbf{r})-\sum_t f_tV_t(\mathbf{r}), \tag{10}$$

where the various $V_s{}'$ must satisfy the relation

$$\sum_s f_sV_s{}'(\mathbf{r})=0 \tag{11}$$

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[5] E. R. Johnson and S. M. Christian, Phys. Rev. 95, 560 (1954). See also Levitas, Wang, and Alexander, Phys. Rev. 95, 846 (1954).

[6] J. C. Slater, Phys. Rev. 76, 1592 (1949).

for all values of **r**. The solution to the unperturbed Schrödinger equation

$$H_0\psi_0(\mathbf{k},\mathbf{r})=E_0(\mathbf{k})\psi_0(\mathbf{k},\mathbf{r})$$

is given by

$$\psi_0(\mathbf{k},\mathbf{r})=(N\Omega)^{-\frac{1}{2}}e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{12}$$

$$E_0(\mathbf{k})=k^2. \tag{13}$$

Here Ω is the volume per lattice site in the alloy, and N, as before, is the number of atoms in the alloy. The propagation vector **k** is any member of the set of k-vectors satisfying the periodic boundary conditions. As is shown in the Appendix, Eq. (5) becomes

$$E_2(\mathbf{k}_i)={\textstyle\sum_j}'|\mathbf{V}'(\mathbf{k}_j)|^2(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^{-1}, \tag{14}$$

where

$$\mathbf{V}'(\mathbf{k}_j)\equiv\mathbf{V}_{0j}'. \tag{15}$$

Now

$$\begin{aligned}\langle|\mathbf{V}'(\mathbf{k})|^2\rangle&=(N\Omega)^{-2}\left\langle\left|\int_\infty e^{i\mathbf{k}\cdot\mathbf{r}}\mathbf{V}'(\mathbf{r})d\tau\right|^2\right\rangle\\&=(N\Omega)^{-2}\left\langle\sum_{n,p}e^{i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_p)}\int_\infty V_{s_n}'(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau\right.\\&\qquad\left.\times\int_\infty V_{s_p}'(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}}d\tau\right\rangle\\&=(N\Omega)^{-2}\left\langle\sum_n\left|\int_\infty V_{s_n}'(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau\right|^2\right\rangle\\&=N^{-1}\Omega^{-2}{\textstyle\sum_s} f_s|\mathcal{V}_s'(\mathbf{k})|^2,\end{aligned} \tag{16}$$

where

$$\mathcal{V}_s'(\mathbf{k})=\int_\infty V_s'(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}d\tau. \tag{17}$$

Since there are N allowed states of a given spin in the first Brillouin zone, whose volume is $\Omega_k=(2\pi)^3/\Omega$, then the volume of k-space per allowed state of a given spin is given by

$$\Omega_k/N=(2\pi)^3/N\Omega.$$

In the limit as N becomes infinite, a summation over the allowed states of a given spin may be replaced by the corresponding integral over k-space, when the latter is divided by the volume of k-space per state, i.e.,

$$\textstyle\sum_{\mathbf{k}}=N\Omega(2\pi)^{-3}\displaystyle\int d\tau_k. \tag{18}$$

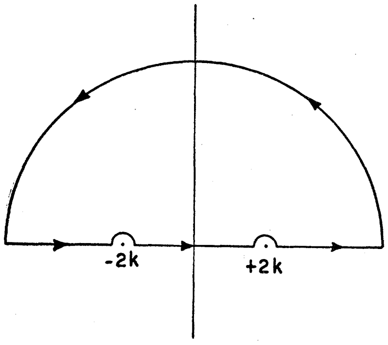

FIG. 1. Contour of integration in the σ-plane.

Substituting (16) and (18) in (14), we find that E_2, suitably averaged over all possible configurations, is given by

$$E_2(\mathbf{k})=(2\pi)^{-3}\Omega^{-1}\sum_s f_s\int_\infty|\mathcal{V}_s'(\boldsymbol{\sigma})|^2(2\mathbf{k}\cdot\boldsymbol{\sigma}-\sigma^2)^{-1}d\tau_\sigma. \tag{19}$$

If we assume that $V_s'(\mathbf{r})$ is independent of the orientation of **r** then $\mathcal{V}_s'(\boldsymbol{\sigma})$ will be independent of the orientation of $\boldsymbol{\sigma}$ and the angular integrations in the above integral can be performed immediately.

$$\begin{aligned}E_2(\mathbf{k})&=(2\pi)^{-2}\Omega^{-1}\sum_s f_s\int_0^\infty d\sigma\sigma^2|\mathcal{V}_s'(\sigma)|^2\\&\quad\times\int_0^\pi d\theta\sin\theta(2k\sigma\cos\theta-\sigma^2)^{-1}\\&=(8\pi^2\Omega k)^{-1}\sum_s f_s\int_0^\infty|\mathcal{V}_s'(\sigma)|^2\\&\qquad\times\ln[(\sigma-2k)/(\sigma+2k)]\sigma d\sigma.\end{aligned}$$

We may define $\mathcal{V}_s'(\sigma)$ to be a real even function of σ, so that the complete integrand will be an even function of σ, and we may write

$$\begin{aligned}E_2(\mathbf{k})&=(4\pi)^{-2}(\Omega k)^{-1}\sum_s f_s\int_{-\infty}^\infty[\mathcal{V}_s'(\sigma)]^2\\&\qquad\times\ln[(\sigma-2k)/(\sigma+2k)]\sigma d\sigma.\end{aligned} \tag{20}$$

Letting σ range over the entire complex plane, we will finally assume that $\mathcal{V}_s'(\sigma)$ is analytic except at a finite number of singular points. We assume that none of these singular points lie on the real axis and that $\mathcal{V}_s'(\sigma)$ approaches zero at least as fast as σ^{-1} as σ approaches infinity in the complex plane. It is now possible to evaluate the above integral by integration around the contour illustrated in Fig. 1. Define

$$F_s(\sigma)=[\mathcal{V}_s'(\sigma)]^2\sigma\ln[(\sigma-2k)/(\sigma+2k)]. \tag{21}$$

$F_s(\sigma)$ has branch points at $\sigma=\pm 2k$ with branch lines extending to infinity is the lower half plane. Denote by R_1 the radius of the semicircular contours about the branch points, and denote by R_2 the radius of the large semicircular contour about the origin. The integral of $F_s(\sigma)$ over the latter contour, in the limit as $R_2\rightarrow\infty$, is

$$8kR_2[\mathcal{V}_s'(R_2)]^2=0.$$

The integral of $F_s(\sigma)$ over the contour at $\sigma=+2k$, in the limit as $R_1\rightarrow 0$, is

$$4k[\mathcal{V}_s'(2k)]^2R_1\ln R_1=0.$$

Similarly, the integral of $F_s(\sigma)$ over the contour at $\sigma=-2k$ vanishes in the limit as $R_1\rightarrow 0$. By the residue theorem, we now have

$$\int_{-\infty}^{\infty} F_s(\sigma)d\sigma = 2\pi i \sum{}' \,\mathrm{Res}F_s(\sigma); \tag{22}$$

i.e., the integral equals $2\pi i$ times the sum of the residues of $F_s(\sigma)$ in the *upper* half plane (excluding the real axis). The fact that the integrand diverges at $\sigma=\pm 2k$ results from the fact that second-order perturbation theory is invalid in the neighborhoods of these two points. Since, however, the total contribution to the integral in Eq. (22) comes from the residues of poles none of which lie in the neighborhoods of the points $\sigma=\pm 2k$, and since we may assume that perturbation theory correctly predicts the integrand in the neighborhood of these poles, then there appears to be some justification for using perturbation theory as we have done here.

We now take the specific example where

$$V_s'(\mathbf{r}) = r^{-1}A_s e^{-ar}. \tag{23}$$

From Eq. (11) it follows that

$$\sum\nolimits_s f_s A_s = 0. \tag{24}$$

$\mathcal{V}_s'(\boldsymbol{\sigma})$ is given by

$$\begin{aligned}\mathcal{V}_s'(\boldsymbol{\sigma}) &= \int_\infty V_s'(\mathbf{r}) \exp(i\boldsymbol{\sigma}\cdot\mathbf{r})d\tau \\ &= 4\pi A_s \sigma^{-1} \int_0^\infty \sin(\sigma r) e^{-ar} dr \\ &= 4\pi A_s (a^2+\sigma^2)^{-1}.\end{aligned} \tag{25}$$

Note that $\mathcal{V}_s'(\sigma)$ has all the properties previously assumed in evaluating the integral. $F_s(\sigma)$ will have second-order poles at $\sigma=\pm ia$. We are interested in the pole at $\sigma=+ia$. The residue at this pole is

$$\mathrm{Res}F_s(ia) = (4\pi A_s)^2 ika^{-1}(a^2+4k^2)^{-1},$$

so that

$$E_2(k) = -(2\pi/a\Omega)(\sum\nolimits_s f_s A_s^2)(a^2+4k^2)^{-1}. \tag{26}$$

Taking

$$E(k) = E_0(k) + E_2(k), \tag{27}$$

and solving for k in terms of E, we get

$$\begin{aligned}2k^2 = {} & [E-(\tfrac{1}{2}a)^2] \\ & + \{[E+(\tfrac{1}{2}a)^2]^2 + (2\pi/a\Omega)\sum\nolimits_s f_s A_s^2\}^{\frac{1}{2}}.\end{aligned} \tag{28}$$

Define n as the total number of states (of a given spin) per unit volume of the crystal having an energy less than $E(k)$.

$$\begin{aligned} n &= (1/N\Omega)(4\pi k^3/3\Omega_k)N = (k^3/6\pi^2), \\ dn/dE &= (dn/dk)(dk/dE) \\ &= 2^{\frac{1}{2}}(4\pi)^{-2}\{[E-(\tfrac{1}{2}a)^2] + ([E+(\tfrac{1}{2}a)^2]^2 \\ &\quad + (2\pi/a\Omega)\sum\nolimits_s f_s A_s^2)^{\frac{1}{2}}\}^{\frac{1}{2}} \\ &\quad \times\{1+[E+(\tfrac{1}{2}a)^2]([E+(\tfrac{1}{2}a)^2]^2 \\ &\quad + (2\pi/a\Omega)\sum\nolimits_s f_s A_s^2)^{-\frac{1}{2}}\}.\end{aligned} \tag{29}$$

In order to study the shape of the density-of-states curve, we introduce the following variables.

$$\left.\begin{aligned}\epsilon(k) &= (2/a)^2 E(k), \\ \epsilon_0 &= (8\pi/a^5\Omega)\sum\nolimits_s f_s A_s^2, \\ \eta &= (2\pi)^2(2/a)^3 n.\end{aligned}\right\} \tag{30}$$

Thus

$$\epsilon(k) = (2k/a)^2 - \epsilon_0[1+(2k/a)^2]^{-1}, \tag{31}$$

so that

$$\epsilon(0) = -\epsilon_0. \tag{32}$$

Also

$$\begin{aligned}d\eta/d\epsilon = {} & \tfrac{1}{4}\sqrt{2}\{1+(\epsilon+1)[(\epsilon+1)^2+4\epsilon_0]^{-\frac{1}{2}}\} \\ & \times\{(\epsilon-1)+[(\epsilon+1)^2+4\epsilon_0]^{\frac{1}{2}}\}^{\frac{1}{2}}.\end{aligned} \tag{33}$$

As $\epsilon\rightarrow\infty$,

$$d\eta/d\epsilon \rightarrow \sqrt{\epsilon}.$$

Also, for $\epsilon_0=0$,

$$d\eta/d\epsilon = \sqrt{\epsilon}.$$

As can be seen from Fig. 2, the shape of the $d\eta/d\epsilon$ curve depends upon ϵ_0. For large values of ϵ_0, the low-energy tail of the curve becomes very sharp. This represents that portion of the density-of-states curve which has penetrated into the forbidden band. Let us examine this tail in more detail. Consider the case where ϵ is negative and

$$2\sqrt{\epsilon_0} \leqslant |\epsilon+1| \leqslant \epsilon_0.$$

By picking $\epsilon_0 \gg 4$, we can insure that there will be a large range of values of ϵ for which the above conditions hold. To see this, we note that the ratio of the upper to the lower limit is given by

$$(\epsilon_0/2\sqrt{\epsilon_0}) = \tfrac{1}{2}\sqrt{\epsilon_0} \gg 1,$$

since $\epsilon_0 \gg 4$. Since

$$\begin{aligned}(\epsilon-1)+[(\epsilon+1)^2+4\epsilon_0]^{\frac{1}{2}} &\cong 2(\epsilon_0-|\epsilon|)|\epsilon|^{-1}, \\ 1+(\epsilon+1)[(\epsilon+1)^2+4\epsilon_0]^{-\frac{1}{2}} &\cong 2\epsilon_0|\epsilon|^{-2},\end{aligned}$$

then

$$d\eta/d\epsilon \cong \epsilon_0|\epsilon|^{-5/2}(\epsilon_0-|\epsilon|)^{\frac{1}{2}}, \tag{34}$$

for ϵ negative such that

$$2\sqrt{\epsilon_0} \leqslant |\epsilon| \leqslant \epsilon_0 \gg 4.$$

Equation (34) shows that for large ϵ_0 the density-of-states curve drops off very rapidly as it penetrates the forbidden band. For small ϵ_0, on the other hand, the shape of the curve is hardly affected, as can be seen in Fig. 2, the apparent band edge merely being shifted down in energy. The case of small ϵ_0 corresponds qualitatively to the effect of thermal vibrations on the energy levels of a perfect crystal.[7]

IV. CONDUCTIVITY

If

$$E = E_0 + E_2$$

represents the energy to the accuracy of second-order perturbation theory, and if

$$\mathbf{v} = \mathbf{v}_0 + \mathbf{v}_2$$

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[7] H. Y. Fan, Phys. Rev. 82, 900 (1951).

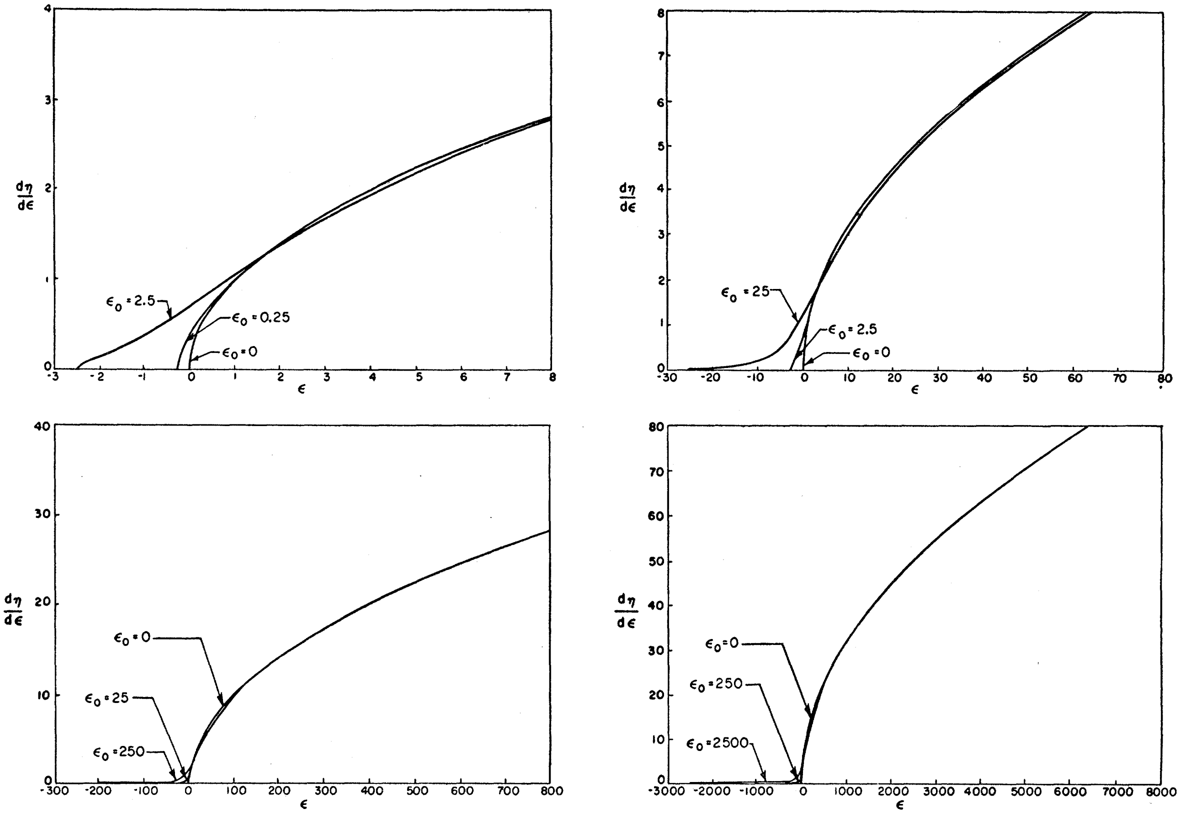

FIG. 2. $d\eta/d\epsilon$ *versus* ϵ for various values of ϵ_0.

represents the expectation value of velocity to the same approximation, then it can be shown (see Appendix) that for the empty-lattice virtual-crystal model

$$\mathbf{v}_n(\mathbf{k})=\tfrac{1}{2}\nabla_k E_n(\mathbf{k}),\quad n=0,1,2. \tag{35}$$

(It is also true for $n=3$ in the case of third-order perturbation theory.) Note that Eq. (35) is identical with the usual relationship between $\mathbf{v}$ and E in the conventional theory of energy bands. Define

$$A=\pi(2a\Omega)^{-1}\textstyle\sum_s f_sA_s^2. \tag{36}$$

Thus

$$\begin{aligned}E(\mathbf{k})&=k^2-A[(\tfrac{1}{2}a)^2+k^2]^{-1},\\ \mathbf{v}(\mathbf{k})&=\mathbf{k}\{1+A[(\tfrac{1}{2}a)^2+k^2]^{-2}\}.\end{aligned} \tag{37}$$

In particular,

$$E(0)\equiv-E_0=-(2/a)^2A. \tag{38}$$

If E_0 stays finite but a becomes very small, then there will be very large values of $\mathbf{v}$ (diverging as a^{-2}) in the low-energy tail. We wish to show that these very large values of $\mathbf{v}$ make a negligible contribution to the total electronic current in the allowed band in the limit as $a\rightarrow0$ (E_0 remaining finite). This results from the vanishing of dn/dE in the same limit.

We assume that all electrons in the conduction band have a mean life τ between collisions. According to the elementary theory of electric conductivity, in the presence of an electric field $\mathcal{E}$ the distribution of electrons in momentum space is shifted by an amount $\mathbf{K}$, where

$$\mathbf{K}=e\mathcal{E}\tau. \tag{39}$$

We will assume that the Fermi level E_F lies far enough below $E(0)$ so that we may use Boltzmann statistics. In the presence of an electric field in the z-direction, we have

$$\langle v_z\rangle=\frac{\int_\infty v_z(\mathbf{k})e^{-[E(\mathbf{k}-\mathbf{K})-E_F]/\kappa T}d\tau_k}{\int_\infty e^{-[E(\mathbf{k}-\mathbf{K})-E_F]/\kappa T}d\tau_k},$$

$$n=2(2\pi)^{-3}\int_\infty e^{-[E(\mathbf{k}-\mathbf{K})-E_F]/\kappa T}d\tau_k,$$

$$J=n\langle v_z\rangle.$$

$\langle v_z\rangle$ is the mean value of velocity in the field direction, J is the electronic current density, κ is Boltzmann's constant, and n, in this section, refers to the number of electrons (of both spins) per unit volume. J and n may be written in the forms

$$J=2(2\pi)^{-3}e^{E_F/\kappa T}\int_{\infty} v_z(\mathbf{k}+\mathbf{K})e^{-E(\mathbf{k})/\kappa T}d\tau_k, \tag{40}$$

$$n=2(2\pi)^{-3}e^{E_F/\kappa T}\int_{\infty} e^{-E(\mathbf{k})/\kappa T}d\tau_k. \tag{41}$$

For all reasonable values of $\mathcal{E}$, $\mathbf{K}$ will be very small, so that

$$\begin{aligned}v_z(\mathbf{k}+\mathbf{K})&\cong v_z(\mathbf{k})+K\frac{\partial}{\partial k_z}v_z(\mathbf{k})\\&=(k\mu+K)[1+A(\tfrac{1}{4}a^2+k^2)^{-2}]\\&\qquad-4Kk^2\mu^2A(\tfrac{1}{4}a^2+k^2)^{-3}\end{aligned}$$

where μ is the cosine of the angle between $\mathbf{k}$ and $\mathbf{K}$. Thus

$$\begin{aligned}\int_{\infty} v_z(\mathbf{k}+\mathbf{K})e^{-E(\mathbf{k})/\kappa T}d\tau_k&\\=(4/3)\pi K\int_0^\infty k^2[3-A(\tfrac{1}{4}a^2+k^2)^{-2}&\\+a^2A(\tfrac{1}{4}a^2+k^2)^{-3}]e^{-E(k)/\kappa T}dk.&\end{aligned}$$

Define

$$t=A^{-\frac{1}{2}}(\tfrac{1}{4}a^2+k^2),\quad B=\tfrac{1}{4}aA^{-\frac{1}{2}}.$$

We now see that

$$\begin{aligned}E_0&=(2B)^{-2},\\E(k)&=(a/4B)(t-t^{-1})-\tfrac{1}{4}a^2,\\k^2dk&=\tfrac{1}{2}(a/4B)^{\frac{3}{2}}(t-aB)^{\frac{1}{2}}dt.\end{aligned}$$

Thus

$$\begin{aligned}J=(K/6\pi^2)(a/4B)^{\frac{3}{2}}\exp[(E_F+\tfrac{1}{4}a^2)/\kappa T]&\\\times\int_{aB}^\infty[3-t^{-2}+4aBt^{-3}](t-aB)^{\frac{1}{2}}&\\\times\exp[-(t-t^{-1})(a/4B\kappa T)]dt.&\end{aligned}$$

Define

$$w=\tfrac{1}{2}a(t-t^{-1}),$$

so that

$$at=w+(w^2+a^2)^{\frac{1}{2}}.$$

Thus

$$\begin{aligned}J=(K/6\pi^2)\exp[(E_F+\tfrac{1}{4}a^2)/\kappa T](4B)^{-\frac{3}{2}}&\\\times\int_{-(1-a^2B^2)(2B)^{-1}}^\infty\left[3-\frac{a^2}{[w+(w^2+a^2)^{\frac{1}{2}}]^2}\right.&\\\left.+\frac{4a^4B}{[w+(w^2+a^2)^{\frac{1}{2}}]^3}\right]\left[1+\frac{w}{(w^2+a^2)^{\frac{1}{2}}}\right]&\\\times[w-a^2B+(w^2+a^2)^{\frac{1}{2}}]^{\frac{1}{2}}e^{-(w/2B\kappa T)}dw.&\end{aligned}$$

In the limit as $a\rightarrow 0$,

$$\begin{aligned}J&=K\pi^{-2}(4B)^{-\frac{3}{2}}e^{E_F/\kappa T}\int_0^\infty(2w)^{\frac{1}{2}}e^{-(w/2B\kappa T)}dw\\&=\tfrac{1}{4}K(\kappa T/\pi)^{\frac{3}{2}}e^{E_F/\kappa T}.\end{aligned}\tag{42}$$

Also,

$$\begin{aligned}n&=2(2\pi)^{-3}e^{E_F/\kappa T}\int_{\infty} e^{-E(\mathbf{k})/\kappa T}d\tau_k\\&=\pi^{-2}e^{E_F/\kappa T}\int_0^\infty k^2e^{-E(k)/\kappa T}dk\\&=\tfrac{1}{2}\pi^{-2}(a/4B)^{\frac{3}{2}}\exp[(E_F+\tfrac{1}{4}a^2)/\kappa T]\\&\quad\times\int_{aB}^\infty(t-aB)^{\frac{1}{2}}\exp[-(t-t^{-1})(a/4B\kappa T)]dt\\&=\tfrac{1}{2}\pi^{-2}(4B)^{-\frac{3}{2}}\exp[(E_F+\tfrac{1}{4}a^2)/\kappa T]\\&\quad\times\int_{-(1-a^2B^2)(2B)^{-1}}^\infty[1+w(w^2+a^2)^{-\frac{1}{2}}]\\&\qquad\times[w-a^2B+(w^2+a^2)^{\frac{1}{2}}]^{\frac{1}{2}}e^{-(w/2B\kappa T)}dw.\end{aligned}$$

In the limit as $a\rightarrow 0$,

$$\begin{aligned}n&=\pi^{-2}(4B)^{-\frac{3}{2}}e^{E_F/\kappa T}\int_0^\infty(2w)^{\frac{1}{2}}e^{-(w/2B\kappa T)}dw\\&=\tfrac{1}{4}(\kappa T/\pi)^{\frac{3}{2}}e^{E_F/\kappa T}.\end{aligned}\tag{43}$$

We can show that Eqs. (42) and (43) are identical with the equations appropriate for J and n in the case where there is no low-energy tail (i.e., $A=0$). Applying the condition $A=0$ to the general equations obtained previously, we get

$$\begin{aligned}\int_{\infty} v_z(\mathbf{k}+\mathbf{K})e^{-E(\mathbf{k})/\kappa T}dT_k&=4\pi K\int_0^\infty k^2e^{-E(k)/\kappa T}dk\\&=2\pi K(\kappa T)^{\frac{3}{2}}\int_0^\infty x^{\frac{1}{2}}e^{-x}dx=K(\pi\kappa T)^{\frac{3}{2}},\end{aligned}$$

so that

$$\begin{aligned}J&=2(2\pi)^{-3}e^{E_F/\kappa T}\int_{\infty} v_z(\mathbf{k}+\mathbf{K})e^{-E(\mathbf{k})/\kappa T}d\tau_k\\&=\tfrac{1}{4}K(\kappa T/\pi)^{\frac{3}{2}}e^{E_F/\kappa T}.\end{aligned}\tag{44}$$

Likewise,

$$\begin{aligned}n&=\pi^{-2}e^{E_F/\kappa T}\int_0^\infty k^2e^{-E(k)/\kappa T}dk\\&=\tfrac{1}{2}\pi^{-2}(\kappa T)^{\frac{3}{2}}e^{E_F/\kappa T}\int_0^\infty x^{\frac{1}{2}}e^{-x}dx\\&=\tfrac{1}{4}(\kappa T/\pi)^{\frac{3}{2}}e^{E_F/\kappa T}.\end{aligned}\tag{45}$$

The significance of the above results lies in the fact that the vanishing of the density of states in the tail overrides the divergence of the velocity. It should be pointed out, however, that for finite A and a there can be an appreciable contribution to the current from the electrons in the tail, in particular for temperatures low enough such that κT is much smaller than the width of the tail in energy.

V. EFFECT OF THIRD-ORDER PERTURBATION THEORY

As is shown in the Appendix, the third-order contribution to the energy for the empty-lattice virtual-crystal model is

$$E_3(\mathbf{k}_i)=\sum_{j,p}{}' \mathbf{V}'(-\mathbf{k}_j)\mathbf{V}'(\mathbf{k}_j-\mathbf{k}_p)\mathbf{V}'(\mathbf{k}_p) \times(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^{-1}(2\mathbf{k}_i\cdot\mathbf{k}_p-k_p^2)^{-1}. \quad (46)$$

(Here we have made use of the fact that $\mathbf{V}'(\mathbf{k})$ vanishes for $\mathbf{k}=0$.) Now

$$\langle \mathbf{V}'(\mathbf{k}_1)\mathbf{V}'(\mathbf{k}_2)\mathbf{V}'(\mathbf{k}_3)\rangle =(N\Omega)^{-3}\langle \sum_{n_1n_2n_3} \exp[i(\mathbf{k}_1\cdot\mathbf{R}_{n_1}+\mathbf{k}_2\cdot\mathbf{R}_{n_2} +\mathbf{k}_3\cdot\mathbf{R}_{n_3})]\mathcal{V}_{sn_1}'(\mathbf{k}_1)\mathcal{V}_{sn_2}'(\mathbf{k}_2)\mathcal{V}_{sn_3}'(\mathbf{k}_3)\rangle,$$

where the averaging is to be taken over all possible configurations of atoms in the alloy. The total contribution to the average comes from the terms where

$$\mathbf{R}_{n_1}=\mathbf{R}_{n_2}=\mathbf{R}_{n_3}.$$

We are interested only in the case

$$\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3=0,$$

so that

$$\langle \mathbf{V}'(\mathbf{k}_1)V'(\mathbf{k}_2)V'(\mathbf{k}_3)\rangle =N^{-2}\Omega^{-3}\textstyle\sum_s f_s\mathcal{V}_s'(\mathbf{k}_1)\mathcal{V}_s'(\mathbf{k}_2)\mathcal{V}_s'(\mathbf{k}_3). \quad (47)$$

Applying Eq. (18), we have, in the limit as $N\rightarrow\infty$,

$$E_3(\mathbf{k})=\frac{1}{(2\pi)^6\Omega}\sum_s f_s \times\int_\infty\int_\infty \frac{\mathcal{V}_s'(-\boldsymbol{\kappa})\mathcal{V}_s'(\boldsymbol{\kappa}-\boldsymbol{\sigma})\mathcal{V}_s'(\boldsymbol{\sigma})}{(2\mathbf{k}\cdot\boldsymbol{\kappa}-\kappa^2)(2\mathbf{k}\cdot\boldsymbol{\sigma}-\sigma^2)}d\tau_\kappa d\tau_\sigma, \quad (48)$$

where E_3 is understood to be suitably averaged over all configurations of atoms. Returning to the special case denoted by Eqs. (23) and (25), we get

$$E_3(\mathbf{k})=\pi^{-3}\Omega^{-1}\sum_s f_sA_s^3\int_\infty\int_\infty \{(a^2+\kappa^2)[a^2+(\boldsymbol{\kappa}-\boldsymbol{\sigma})^2] \times(a^2+\sigma^2)(2\mathbf{k}\cdot\boldsymbol{\kappa}-\kappa^2)(2\mathbf{k}\cdot\boldsymbol{\sigma}-\sigma^2)\}^{-1}d\tau_\kappa d\tau_\sigma. \quad (49)$$

It does not appear that this integral can be evaluated exactly. Therefore we will make the following approximation:

$$[a^2+(\boldsymbol{\kappa}-\boldsymbol{\sigma})^2]^{-1}\cong a^2(a^2+\kappa^2)^{-1}(a^2+\sigma^2)^{-1}. \quad (50)$$

To this approximation, we have

$$E_3(\mathbf{k})=(a^2/\pi^3\Omega)\sum_s f_sA_s^3\left[\int_\infty (a^2+\sigma^2)^{-2}(2\mathbf{k}\cdot\boldsymbol{\sigma}-\sigma^2)^{-1}d\tau_\sigma\right]^2.$$

The above integral is identical with that evaluated in Sec. III, so that finally

$$E_3(k)=(\pi/\Omega)(\textstyle\sum_s f_sA_s^3)(a^2+4k^2)^{-2}. \quad (51)$$

As a check on the approximation used in evaluating E_3, we will find the exact value for $k=0$ where

$$E_3(0)=(\pi^3\Omega)^{-1}\sum_s f_sA_s^3\int_\infty\int_\infty \{\kappa^2(a^2+\kappa^2)\sigma^2(a^2+\sigma^2) \times[a^2+(\boldsymbol{\kappa}-\boldsymbol{\sigma})^2]\}^{-1}d\tau_\kappa d\tau_\sigma.$$

Now if

$$g(\mathbf{r})=(4\pi r)^{-1}e^{-ar},$$

then

$$G(\mathbf{k})\equiv\int_\infty e^{i\mathbf{k}\cdot\mathbf{r}}g(\mathbf{r})d\tau=(a^2+k^2)^{-1}.$$

Similarly if

$$h(\mathbf{r})=(4\pi a^2r)^{-1}[1-e^{-ar}],$$

then it follows that

$$H(\mathbf{k})=a^{-2}[k^{-2}-(a^2+k^2)^{-1}]=[k^2(a^2+k^2)]^{-1}.$$

We may write

$$E_3(0)=(\pi^3\Omega)^{-1}\sum_s f_sA_s^3\int_\infty\int_\infty H^*(\boldsymbol{\kappa})G(\boldsymbol{\kappa}-\boldsymbol{\sigma})H(\boldsymbol{\sigma})d\tau_\kappa d\tau_\sigma.$$

From the following form of Parseval's theorem,[8]

$$\int_\infty f^*(\mathbf{r})g^*(\mathbf{r})h(\mathbf{r})d\tau =(2\pi)^{-6}\int_\infty\int_\infty F^*(\boldsymbol{\kappa})G(\boldsymbol{\kappa}-\boldsymbol{\sigma})H(\boldsymbol{\sigma})d\tau_\kappa d\tau_\sigma,$$

it follows that

$$E_3(0)=(4\pi)^3\Omega^{-1}\sum_s f_sA_s^3\int_\infty h^*(\mathbf{r})g^*(\mathbf{r})h(\mathbf{r})d\tau =(4\pi/a^4\Omega)\sum_s f_sA_s^3\int_0^\infty (1-e^{-ar})^2e^{-ar}r^{-1}dr.$$

The above integral can be evaluated by the following trick.

$$\int_0^\infty (1-e^{-ar})^2e^{-ar}r^{-1}dr =\int_a^\infty db\int_0^\infty (1-e^{-ar})^2e^{-br}dr=\ln(4/3).$$

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[8] See, for example, I. N. Sneddon, *Fourier Transforms* (McGraw-Hill Book Company, Inc., New York, 1951), p. 26.

Thus the exact value of $E_3(0)$ is

$$(\pi/a^4\Omega)(\textstyle\sum_s f_s A_s^3)[4\ln(4/3)],$$

while the previously obtained approximate value was

$$(\pi/a^4\Omega)(\textstyle\sum_s f_s A_s^3).$$

Since $4\ln(4/3)\cong 1.151$, we see that the exact value is about 15 percent larger than the approximate value.

A rough measure of the rapidity of convergence of perturbation theory is the smallness of the ratio

$$E_3(0)/E_2(0)=2a^{-1}\ln(4/3)(\textstyle\sum_s f_s A_s^3)/(\sum_s f_s A_s^2). \quad (52)$$

In many cases, a single term in each sum over s predominates so that

$$E_3(0)/E_2(0)\cong 4\ln(4/3)(A_{s\,\max}/2a). \quad (53)$$

Equation (53) shows that for perturbation theory to be valid the maximum value of A_s must be smaller than $2a$.

The effect of third-order perturbation theory is similar to second-order in that only energies near the bottom or the top of a band are shifted appreciably; however, third-order differs from second-order in that the former shifts both ends of an allowed band in the same direction, this direction depending upon whether the perturbative potential is predominantly attractive or repulsive.

VI. EFFECT OF FOURTH-ORDER PERTURBATION THEORY

As is shown in the Appendix, the fourth-order contribution to the energy for the empty-lattice virtual-crystal model is

$$E_4(\mathbf{k}_i)=\sum_{j,p,q}{}' \frac{\mathbf{V}'(-\mathbf{k}_j)\mathbf{V}'(\mathbf{k}_j-\mathbf{k}_p)\mathbf{V}'(\mathbf{k}_p-\mathbf{k}_q)\mathbf{V}'(\mathbf{k}_q)}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)(2\mathbf{k}_i\cdot\mathbf{k}_p-k_p^2)(2\mathbf{k}_i\cdot\mathbf{k}_q-k_q^2)} -\left[\sum_i{}'\frac{|\mathbf{V}'(\mathbf{k}_j)|^2}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)}\right]\left[\sum_i{}'\frac{|\mathbf{V}'(\mathbf{k}_j)|^2}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^2}\right]. \quad (54)$$

(Here we have made use of the fact that $\mathbf{V}'(\mathbf{k})$ vanishes for $\mathbf{k}=0$.) Now

$$\langle\mathbf{V}'(\mathbf{k}_1)\mathbf{V}'(\mathbf{k}_2)\mathbf{V}'(\mathbf{k}_3)\mathbf{V}'(\mathbf{k}_4)\rangle =(N\Omega)^{-4}\Big\langle\sum_{n_1n_2n_3n_4}\exp[i(\mathbf{k}_1\cdot\mathbf{R}_{n1}+\mathbf{k}_2\cdot\mathbf{R}_{n2} +\mathbf{k}_3\cdot\mathbf{R}_{n3}+\mathbf{k}_4\cdot\mathbf{R}_{n4})] \times\mathcal{V}_{sn_1}'(\mathbf{k}_1)\mathcal{V}_{sn_2}'(\mathbf{k}_2)\mathcal{V}_{sn_3}'(\mathbf{k}_3)\mathcal{V}_{sn_4}'(\mathbf{k}_4)\Big\rangle, \quad (55)$$

The only nonvanishing terms occur if all four running indices in the quadruple sum coincide or if the running indices coincide in pairs; i.e.,

$$n_1=n_2=n_3=n_4,$$

or

$$n_i=n_j,\quad n_k=n_l,\quad i,j,k,l=1,2,3,4.$$

Furthermore, these terms fail to vanish only if the sum of the k-vectors associated with a set of coincident running indices is equal to a vector of the reciprocal lattice, $\mathbf{K}_i$. Since we are interested in the case where

$$\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0,$$

we have

$$\begin{aligned}\langle\mathbf{V}'(\mathbf{k}_1)\mathbf{V}'(\mathbf{k}_2)\mathbf{V}'(\mathbf{k}_3)\mathbf{V}'(\mathbf{k}_4)\rangle &=N^{-3}\Omega^{-4}\textstyle\sum_s f_s\mathcal{V}_s'(\mathbf{k}_1)\mathcal{V}_s'(\mathbf{k}_2)\mathcal{V}_s'(\mathbf{k}_3)\mathcal{V}_s'(\mathbf{k}_4)\\ &\quad+N^{-2}\Omega^{-4}[\textstyle\sum_s f_s\mathcal{V}_s'(\mathbf{k}_1)\mathcal{V}_s'(\mathbf{k}_2)]\\ &\quad\times[\textstyle\sum_s f_s\mathcal{V}_s'(\mathbf{k}_3)\mathcal{V}_s'(\mathbf{k}_4)]\\ &\quad\times\delta(\mathbf{k}_1+\mathbf{k}_2,\mathbf{K}_i)\delta(\mathbf{k}_3+\mathbf{k}_4,-\mathbf{K}_i)\\ &\quad+N^{-2}\Omega^{-4}[\textstyle\sum_s f_s\mathcal{V}_s'(\mathbf{k}_1)\mathcal{V}_s'(\mathbf{k}_3)]\\ &\quad\times[\textstyle\sum_s f_s\mathcal{V}_s'(\mathbf{k}_2)\mathcal{V}_s'(\mathbf{k}_4)]\\ &\quad\times\delta(\mathbf{k}_1+\mathbf{k}_3,\mathbf{K}_i)\delta(\mathbf{k}_2+\mathbf{k}_4,-\mathbf{K}_i)\\ &\quad+N^{-2}\Omega^{-4}[\textstyle\sum_s f_s\mathcal{V}_s'(\mathbf{k}_1)\mathcal{V}_s'(\mathbf{k}_4)]\\ &\quad\times[\textstyle\sum_s f_s\mathcal{V}_s'(\mathbf{k}_2)\mathcal{V}_s'(\mathbf{k}_3)]\\ &\quad\times\delta(\mathbf{k}_1+\mathbf{k}_4,\mathbf{K}_i)\delta(\mathbf{k}_2+\mathbf{k}_3,-\mathbf{K}_i).\end{aligned}$$

Since

$$\textstyle\sum_{\mathbf{k}}\rightarrow N\Omega(2\pi)^{-3}\displaystyle\int d\tau_k,$$

we have for the fourth-order contribution to the energy $E_4(\mathbf{k})$, in the limit as $N\rightarrow\infty$, a large number of terms, including terms of the following type:

$$(2\pi)^{-6}\Omega^{-2}\textstyle\sum_i(2\mathbf{k}\cdot\mathbf{K}_i-K_i^2)^{-1}\left|\sum_s f_s\displaystyle\int_\infty\mathcal{V}_s'(\mathbf{K}_i-\boldsymbol{\sigma}) \times\mathcal{V}_s'(\boldsymbol{\sigma})[2\mathbf{k}\cdot\boldsymbol{\sigma}-\sigma^2]^{-1}d\tau_\sigma\right|^2. \quad (56)$$

It is clear that, because of the factor $(2\mathbf{k}\cdot\mathbf{K}_i-K_i^2)^{-1}$, the above expression diverges as $\mathbf{k}$ approaches the face of a Brillouin zone. This behavior results from our use of *nondegenerate* perturbation theory. If we had used degenerate perturbation theory however, there would be no divergences, but energy discontinuities would be introduced at the faces of the Brillouin zones. It is interesting that in the case of the empty-lattice virtual-crystal model, the presence of lattice periodicity asserts itself in fourth-order perturbation theory. Of course, in a more realistic model where the average potential does not vanish, then the presence of the lattice is felt in all orders of perturbation theory.

VII. ONE-DIMENSIONAL ALLOYS

It is instructive to apply the perturbation approach to the hypothetical one-dimensional alloys[1,2] for which reasonably exact solutions are available. In particular, we consider the problem solved by Landauer and Helland,[2] which consists of two types of square-well potentials occurring with equal probability on a one-dimensional lattice of lattice-constant 2π. Each well is centered on its lattice-site and has a width of π. The top of each well is at the zero of energy. One type of well has a depth of 2.5, the other a depth of 4. (These numbers are expressed in atomic units.) In the virtual-crystal approximation, each well would be replaced by a well of depth 3.25. The band edges appropriate to this virtual-crystal problem can be obtained immediately by reading numbers off a graph in a paper by Allen.[9] The "effective band edges" obtained by Landauer and Helland in their accurate solution to the true problem are shown in Fig. 3(a) and should be compared with the band edges given by the virtual-crystal approximation which are shown in Fig. 3(b). For energies greater than +1, there is a one-to-one correspondence between the two sets of band gaps. The gaps given by the virtual-crystal approximation occur at about the right mean energy but are too wide. This discrepancy would probably be removed by second-order perturbation theory, since, as we have already seen, the effect of second-order perturbation theory is to push band edges out into the forbidden bands, thus effectively narrowing the latter. This probably also explains the fact that Landauer and Helland see no band gap at 0.9 whereas the virtual-crystal approximation gives a very narrow one. Thus for positive energies the perturbation approach appears to be satisfactory. For negative energies, however, this is certainly not the case. The negative energy levels are associated with wave functions localized in a given well, so that these levels are characteristic of the separate constituents composing the alloy. Obviously the virtual-crystal approximation is unsatisfactory here. These negative energy levels correspond to the localized ion-core states in a real alloy. Another type of localized state are the impurity levels of a semiconductor. As James and Ginzbarg[1] have emphasized, it would be impossible to obtain these levels from the virtual-crystal approximation. This points up the major limitation of the perturbation approach; namely that it cannot predict the localized states which may occur in a given problem. This limitation, however, does not negate the method's usefulness in studying nonlocalized states, in particular those lying near a "band edge."

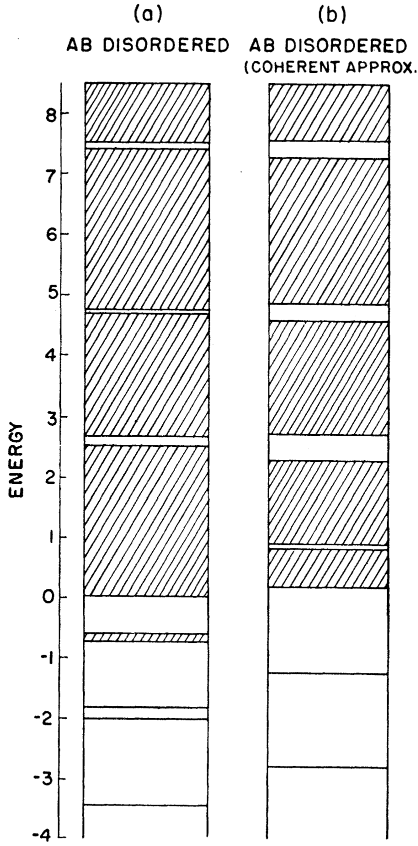

Fig. 3. "Allowed bands" of a one-dimensional alloy (a) exact, (b) virtual-crystal approximation.

VIII. DISCUSSION

Although this paper is concerned primarily with disordered alloys, it is clear that the perturbation approach may be used with equal validity in determining energy levels in a number of other problems concerned with imperfections in crystals. The conventional treatment of thermal vibrations in a crystal follows this approach. The problem already mentioned of a semiconductor doped with impurities is really the alloy problem. The problem of vacancies in a crystal is a special case of a binary alloy where one of the constituents is a missing atom. Likewise, other types of dislocations in crystals will probably give rise to qualitatively similar changes in the energy-band structure appropriate to the associated perfect crystal. The most striking aspect of these changes, namely the "tailing-off" of the density-of-states curve into a forbidden band, appears to have some experimental verification. One example is the low-energy tail appearing in the soft x-ray emission spectra of metals,[10] an experimental effect which has never been satisfactorily explained. Experimental results on a variety of photoconductors also suggest a tailing-off of the density-of-states curve into a forbidden band.[11] The fact that a rather large electronic velocity (see Sec. IV) may be associated with the states in this tail could explain the unexpectedly large "dark currents" sometimes seen in photoconductors.

The writer is indebted to D. O. North, F. Herman, and L. P. Smith for many stimulating discussions. The writer is also indebted to Rolf Landauer for a copy of his paper prior to publication.

APPENDIX

We wish to obtain expressions for the expectation values of the energy and of the velocity by means of

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[9] G. Allen, Phys. Rev. **91**, 531 (1953).

[10] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 436.

[11] A. Rose, R.C.A. Rev. **12**, 362 (1951).

time-independent nondegenerate perturbation theory. The Hamiltonian is

$$H=H_0+\lambda H'. \tag{1a}$$

The wave function and the expectation values will be written as power series in λ. Thus

$$\psi_i=\psi_{0i}+\sum_{n=1}^{\infty}\lambda^n\psi_{ni}, \tag{2a}$$

where

$$\psi_{ni}=\sum\nolimits_p{}'\ {}_na_{ip}\psi_{0p};\quad n\geqslant 1, \tag{3a}$$

the prime denoting that $p\neq i$ in the sum.

$$E_i=E_{0i}+\sum_{n=1}^{\infty}\lambda^nE_{ni}. \tag{4a}$$

Substituting these expressions into Schrödinger's equation, we get

$$\begin{aligned}
&H\psi_i-E\,\psi_i=0\\
&\quad=H_0\psi_i+\lambda H'\psi_i-E_i\psi_i\\
&\quad=E_{0i}\psi_{0i}+\sum_{n=1}^{\infty}\lambda^n\sum_p{}'\ {}_na_{ip}E_{0p}\psi_{0p}+\lambda H'\psi_{0i}\\
&\qquad+\sum_{n=1}^{\infty}\lambda^{n+1}\sum_p{}'\ {}_na_{ip}H'\psi_{0p}\\
&\qquad-\left(E_{0i}+\sum_{n=1}^{\infty}\lambda^nE_{ni}\right)\left(\psi_{0i}+\sum_{n=1}^{\infty}\lambda^n\sum_p{}'\ {}_na_{ip}\psi_{0p}\right)\\
&\quad=\lambda\Big[\sum_p{}'\ {}_1a_{ip}(E_{0p}-E_{0i})\psi_{0p}+(H'-E_{1i})\psi_{0i}\Big]\\
&\qquad+\sum_{n=2}^{\infty}\lambda^n\Bigg[\sum_p{}'\ {}_na_{ip}(E_{0p}-E_{0i})\psi_{0p}+\sum_p{}'\ {}_{n-1}a_{ip}H'\psi_{0p}\\
&\qquad\qquad-E_{ni}\psi_{0i}-\sum_{n'=1}^{n-1}\sum_p{}'\ {}_{n'}a_{ip}E_{n-n',\,i}\,\psi_{0p}\Bigg].
\end{aligned}$$

Here we have taken

$$(H_0-E_{0i})\psi_{0i}=0. \tag{5a}$$

Multiplying on the left by ψ_{0j}^* and integrating, we get

$$\begin{aligned}
&\lambda[(E_{0j}-E_{0i})\ {}_1a_{ij}+H_{ji}'-E_{1i}\delta_{ij}]\\
&\qquad+\sum_{n=2}^{\infty}\lambda^n\Bigg[(E_{0j}-E_{0i})\ {}_na_{ij}+\sum_p{}'\ {}_{n-1}a_{ip}H_{jp}'\\
&\qquad\qquad-E_{ni}\delta_{ij}-\sum_{n'=1}^{n-1}{}_{n'}a_{ij}E_{n-n',\,i}(1-\delta_{ij})\Bigg]=0,
\end{aligned}$$

where

$$H_{ji}'\equiv\int_\infty\psi_{0j}^*H'\psi_{0i}d\tau. \tag{6a}$$

Equating to zero the coefficients of each power of λ, we get for $n=1$

$$E_{1i}=H_{ii}', \tag{7a}$$

$${}_1a_{ij}=H_{ji}'(E_{0i}-E_{0j})^{-1},\quad i\neq j, \tag{8a}$$

while for $n\geqslant 2$

$$E_{ni}=\sum\nolimits_j{}'\ {}_{n-1}a_{ij}H_{ij}', \tag{9a}$$

$$\begin{aligned}
{}_na_{ij}=(E_{0i}-E_{0j})^{-1}\Bigg[&\sum_p{}'\ {}_{n-1}a_{ip}H_{jp}'\\
&-\sum_{n'=1}^{n-1}{}_{n'}a_{ij}E_{n-n',\,i}\Bigg].
\end{aligned}\tag{10a}$$

Thus

$$\begin{aligned}
{}_2a_{ij}&=(E_{0i}-E_{0j})^{-1}\sum_p{}'\ H_{jp}'H_{pi}'(E_{0i}-E_{0p})^{-1}\\
&\qquad-H_{ii}'H_{ji}'(E_{0i}-E_{0j})^{-2},\\
{}_3a_{ij}&=(E_{0i}-E_{0j})^{-1}[\sum_{p,\,q}{}'\ H_{jp}'H_{pq}'H_{qi}'(E_{0i}-E_{0p})^{-1}\\
&\qquad\times(E_{0i}-E_{0q})^{-1}-{}_1a_{ij}E_{2i}-{}_2a_{ij}E_{1i}],
\end{aligned}$$

$$E_{2i}=\sum_j{}'|H_{ij}'|^2(E_{0i}-E_{0j})^{-1}, \tag{11a}$$

$$\begin{aligned}
E_{3i}=&\sum_{j,\,p}{}'\ H_{ij}'H_{jp}'H_{pi}'(E_{0i}-E_{0j})^{-1}(E_{0i}-E_{0p})^{-1}\\
&-H_{ii}'\sum_j{}'|H_{ij}'|^2(E_{0i}-E_{0j})^{-2},
\end{aligned}\tag{12a}$$

$$\begin{aligned}
E_{4i}=&\sum_{j,\,p,\,q}{}'\ H_{ij}'H_{jp}'H_{pq}'H_{qi}'(E_{0i}-E_{0j})^{-1}\\
&\times(E_{0i}-E_{0p})^{-1}(E_{0i}-E_{0q})^{-1}\\
&-[\sum_j{}'|H_{ij}'|^2(E_{0i}-E_{0j})^{-1}]\\
&\times[\sum_j{}'|H_{ij}'|^2(E_{0i}-E_{0j})^{-2}]\\
&-H_{ii}'\sum_{j,\,p}{}'\ H_{ij}'H_{jp}'H_{pi}'\\
&\times(E_{0i}-E_{0j})^{-2}(E_{0i}-E_{0p})^{-1}.
\end{aligned}\tag{13a}$$

The expectation value of velocity is given by

$$\begin{aligned}
\mathbf{v}_i&=\int_\infty\psi_i^*(-i\boldsymbol{\nabla})\psi_id\tau\Big/\int_\infty\psi_i^*\psi_id\tau\\
&=\mathbf{v}_{0i}+\sum_{n=1}^{\infty}\lambda^n\mathbf{v}_{ni},
\end{aligned}\tag{14a}$$

where

$$\mathbf{v}_{0i}=\int_\infty\psi_{0i}^*(-i\boldsymbol{\nabla})\psi_{0i}d\tau. \tag{15a}$$

We will assume that

$$\int_\infty\psi_{0j}^*(-i\boldsymbol{\nabla})\psi_{0i}d\tau=0,\quad i\neq j. \tag{16a}$$

This assumption is true for the case studied in detail in this paper where the unperturbed wave functions are plane waves. For the more general energy-band problem it is true for two different wave functions belonging to the same energy band. We now obtain

$$\mathbf{v}_i\int_\infty \psi_i^*\psi_i d\tau-\int_\infty \psi_i^*(-i\boldsymbol{\nabla})\psi_i d\tau=0$$

$$=\lambda\mathbf{v}_{1i}+\lambda^2\Big[\mathbf{v}_{2i}+\sum_p{}'\ {}_1a_{ip}^*\ {}_1a_{ip}\ (\mathbf{v}_{0i}-\mathbf{v}_{0p})\Big]$$

$$+\sum_{n=3}^{\infty}\lambda^n\Bigg[\mathbf{v}_{ni}+\sum_{n'=1}^{n-1}\sum_p{}'\ {}_{n-n'}a_{ip}^*\ {}_{n'}a_{ip}\ (\mathbf{v}_{0i}-\mathbf{v}_{0p})$$

$$+\sum_{n''=2}^{n-1}\ \sum_{n'=1}^{n''-1}\sum_p{}'\ {}_{n''-n'}a_{ip}^*\ {}_{n'}a_{ip}\ \mathbf{v}_{n-n'',i}\Bigg].$$

Equating to zero the coefficients of each power of λ, we get for $n=1$,

$$\mathbf{v}_{1i}=0, \tag{17a}$$

for $n=2$

$$\mathbf{v}_{2i}=\textstyle\sum_j{}'|H_{ij}'|^2(E_{0i}-E_{0j})^{-2}(\mathbf{v}_{0j}-\mathbf{v}_{0i}), \tag{18a}$$

while for $n\geqslant 3$

$$\mathbf{v}_{ni}=\sum_{n'=1}^{n-1}\sum_p{}'\ {}_{n-n'}a_{ip}^*\ {}_{n'}a_{ip}\ (\mathbf{v}_{0p}-\mathbf{v}_{0i})$$

$$-\sum_{n''=2}^{n-1}\ \sum_{n'=1}^{n''-1}\sum_p{}'\ {}_{n''-n'}a_{ip}^*\ {}_{n'}a_{ip}\ \mathbf{v}_{n-n'',i}. \tag{19a}$$

Thus

$$\mathbf{v}_{3i}=\sum_{j,p}{}'\frac{H_{ij}'H_{jp}'H_{pi}'}{(E_{0i}-E_{0j})(E_{0i}-E_{0p})}\times\left\{\left(\frac{\mathbf{v}_{0j}-\mathbf{v}_{0i}}{E_{0i}-E_{0j}}\right)+\left(\frac{\mathbf{v}_{0p}-\mathbf{v}_{0i}}{E_{0i}-E_{0p}}\right)\right\}$$

$$-2H_{ii}'\sum_j{}'|H_{ij}'|^2(E_{0i}-E_{0j})^{-3}(\mathbf{v}_{0j}-\mathbf{v}_{0i}). \tag{20a}$$

We now consider the special case where

$$\psi_{0i}=(N\Omega)^{-\frac{1}{2}}e^{i\mathbf{k}_i\cdot\mathbf{r}}, \tag{21a}$$

the plane wave being normalized over the volume $N\Omega$, and the propagation vector $\mathbf{k}_i$ satisfying the periodic boundary conditions associated with this volume. We write

$$H_{ji}'\equiv H'(\mathbf{k}_i-\mathbf{k}_j). \tag{22a}$$

We have

$$E_{0i}=k_i^2,\qquad \mathbf{v}_{0i}=\mathbf{k}_i,$$
$$E_{1i}=H'(0),\quad \mathbf{v}_{1i}=0, \tag{23a}$$

so that

$$E_{2i}=\textstyle\sum_j{}'|H'(\mathbf{k}_j)|^2(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^{-1}, \tag{24a}$$

$$\mathbf{v}_{2i}=-\textstyle\sum_j{}'|H'(\mathbf{k}_j)|^2\mathbf{k}_j(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^{-2}. \tag{25a}$$

In obtaining the last two equations, we have replaced $\mathbf{k}_j$ by $(\mathbf{k}_i-\mathbf{k}_j)$ as a dummy index. The primes on the summation signs now mean that $\mathbf{k}_j\neq 0$. In a similar fashion we get

$$E_{3i}=\sum_{j,p}{}'H'(-\mathbf{k}_j)H'(\mathbf{k}_j-\mathbf{k}_p)H'(\mathbf{k}_p)\times[2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2]^{-1}[2\mathbf{k}_i\cdot\mathbf{k}_p-k_p^2]^{-1}$$

$$-H'(0)\sum_j{}'|H'(\mathbf{k}_j)|^2(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^{-2}, \tag{26a}$$

$$\mathbf{v}_{3i}=-\sum_{j,p}{}'\frac{H'(-\mathbf{k}_j)H'(\mathbf{k}_j-\mathbf{k}_p)H'(\mathbf{k}_p)}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)(2\mathbf{k}_i\cdot\mathbf{k}_p-k_p^2)}\times\left\{\frac{\mathbf{k}_j}{2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2}+\frac{\mathbf{k}_p}{2\mathbf{k}_i\cdot\mathbf{k}_p-k_p^2}\right\}$$

$$+2H'(0)\sum_j{}'\frac{|H'(\mathbf{k}_j)|^2\mathbf{k}_j}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^3}. \tag{27a}$$

It is now seen that

$$\mathbf{v}_{ni}=\tfrac{1}{2}\boldsymbol{\nabla}_{ki}E_{ni},\quad n=0,1,2,3, \tag{28a}$$

so that, through third-order perturbation theory at least, the standard energy-band relation holds between $\mathbf{v}$ and E for the special case denoted by Eq. (21a). It can be seen that Eq. (28a) follows as a result of the fact that the matrix elements of H' can be written in the form given in Eq. (22a). The expression for E_{4i} is given by

$$E_{4i}=\sum_{j,p,q}{}'\frac{H'(-\mathbf{k}_j)H'(\mathbf{k}_j-\mathbf{k}_p)H'(\mathbf{k}_p-\mathbf{k}_q)H'(\mathbf{k}_q)}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)(2\mathbf{k}_i\cdot\mathbf{k}_p-k_p^2)(2\mathbf{k}_i\cdot\mathbf{k}_q-k_q^2)}$$

$$-\left[\sum_j{}'\frac{|H'(\mathbf{k}_j)|^2}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)}\right]\left[\sum_j{}'\frac{|H'(\mathbf{k}_j)|^2}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^2}\right]$$

$$-H'(0)\sum_{j,p}{}'\frac{H'(-\mathbf{k}_j)H'(\mathbf{k}_j-\mathbf{k}_p)H'(\mathbf{k}_p)}{(2\mathbf{k}_i\cdot\mathbf{k}_j-k_j^2)^2(2\mathbf{k}_i\cdot\mathbf{k}_p-k_p^2)}. \tag{29a}$$