is given by the relation

$$\Delta\rho/\rho_0 \propto H^{1.7}, \tag{9}$$

for $H$ either parallel or perpendicular to the trigonal axis. It is noted here that the magnetoresistance of bismuth single crystals[1] has a field dependence very similar to that given by Eq. (9).

Nothing definitive can be said about the temperature or field dependence of the oscillatory component of the magnetoresistance. Figure 7 shows that there is a strong temperature dependence for at least that particular orientation, but for other directions there seems to be little change over the range 1.5°–4.2°K. A more detailed study is needed before any firm conclusions are drawn. There is one more point, however, that is worthy of note. It concerns the fact that the amplitude of the oscillations in magnetoresistance as obtained from the Hall probes is considerably greater (relative to the total resistance) than that obtained from the resistance probes. Specifically for Sb IV at 25 kilogauss and 1.57°K the oscillatory component was 0.3 percent of the total resistance from the Hall probes and only 0.15 percent from the resistance probes. Aside from that difference the two magnetoresistance curves are very similar. They both exhibit maxima and minima at very nearly the same values of $H^{-1}$. This sort of behavior was also noted by Berlincourt and Steele[7] in their work on graphite. A possible explanation offered there was that the portion of the crystal between the Hall probes may have been purer (both from the single crystal and chemical points of view) than that between the resistance probes.

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# Energy Levels of a Crystal Modified by Alloying or by Pressure

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A perturbation method of calculating the energy levels of a crystal modified by alloying or by pressure is studied. Initially the calculation is developed by means of conventional first-order perturbation theory. It is then shown what is wrong with this approach and how the calculation can be improved by a modified form of perturbation theory. It is further shown that this modified form of perturbation theory is particularly appropriate to cases where the unperturbed wave functions are expanded in terms of orthogonalized plane waves.

## I. INTRODUCTION

We wish to calculate the electronic energy levels of a crystal modified in a certain fashion from a knowledge of the one-electron wave functions and energy levels of the original unmodified crystal. In particular, we consider the modifications of the crystal (a) under hydrostatic pressure and (b) containing a small mole-percentage of a foreign atom placed in the crystal at random. In the following sections we will work out the general theory for a binary disordered alloy containing a small percentage of one constituent. It will then be seen that the results can be applied as a special case to the problem of the pure crystal under pressure. In Sec. II we will develop the theory by means of conventional first-order perturbation theory. In Sec. III, we will discuss what is wrong with this approach and how our theory can be improved by using a modified form of perturbation theory. In Sec. IV, we show how the results of Sec. III can be written in a particularly simple form by expanding our unperturbed wave functions in terms of orthogonalized plane waves.[1] The special case of a crystal of the diamond structure is worked out in detail. This case is particularly appropriate since the three most important examples of this crystal structure, namely diamond,[2] silicon,[3] and germanium,[4] have all been studied by the orthogonalized plane wave method.

Insofar as it deals with disordered alloys, this paper is intended to supplement a general discussion of the problem in a previous publication by the author.[5] Unlike the previous publication, however, here we will study the formal mathematical aspects of a method suitable for numerical calculations of specific physical systems. In fact, the present study was undertaken with the purpose in mind of forming a basis for a program of detailed numerical calculations on the germanium-silicon alloy and on germanium under hydrostatic

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[1] C. Herring, Phys. Rev. **57**, 1169 (1940).

[2] F. Herman, Phys. Rev. **88**, 1210 (1952); **93**, 1214 (1954).

[3] T. O. Woodruff, dissertation, California Institute of Technology, 1955 (unpublished); Phys. Rev. **98**, 1741 (1955).

[4] F. Herman and J. Callaway, Phys. Rev. **89**, 518 (1953); F. Herman, Physica **20**, 801 (1954); Phys. Rev. (to be published).

[5] R. H. Parmenter, Phys. Rev. **97**, 587 (1955).

pressure. Both the alloy system[6] and the pressure system[7] have been studied experimentally recently, and both systems have been discussed from a theoretical standpoint.[8]

It should be emphasized that the methods developed in this paper for handling a disordered alloy are capable of determining how the energy levels of the original host crystal are modified by the introduction of an impurity. These methods cannot, however, determine the *new* energy levels associated with localized states that may occur in the vicinity of each impurity atom.[5] Such localized states will occur when the original host crystal is a semiconductor or insulator and the valence of the impurity atom differs from that of the host atom.

## II. CONVENTIONAL PERTURBATION THEORY

Consider the case of a host crystal composed of atoms of type $A$ containing at random lattice sites a small percentage of atoms of type $B$. Let $f$ be the fraction of lattice sites occupied by $B$ atoms, where $f \ll 1$. In the absence of $B$ atoms, we may express our one-electron crystal potential in the form

$$\sum_n V_a(\mathbf{r}-\mathbf{R}_n), \tag{1}$$

where $V_a(\mathbf{r})$ is an atomic-like potential characteristic of $A$ atoms and the vectors $\mathbf{R}_n$ denote the positions of the atoms of the crystal. In the case where $B$ atoms are present, we follow Nordheim[9] in assuming that the potential may be written as

$$\sum_n V_{a_n}(\mathbf{r}-\alpha\mathbf{R}_n), \tag{2}$$

where $a_n = a$ when $\alpha\mathbf{R}_n$ denotes an atomic site occupied by an $A$ atom, while $a_n = b$ when $\alpha\mathbf{R}_n$ denotes an atomic site occupied by a $B$ atom. $\alpha$ is the ratio of the new lattice constant to the old, and $V_b(\mathbf{r})$ is an atomic-like potential characteristic of $B$ atoms. Since $f$ is small, we may assume that $(\alpha-1)$ is proportional to $f$ (Vegard's law); i.e., we define $\epsilon$ and $\kappa$ such that

$$\epsilon \equiv \alpha - 1 \equiv \kappa f. \tag{3}$$

Since $f \ll 1$, then also $|\epsilon| \ll 1$. At this point we invoke Nordheim's virtual-crystal approximation[9]; i.e., we replace the alloy potential by that portion of it which gives rise to *coherent* electron scattering, namely,

$$\sum_n V(\mathbf{r}-\alpha\mathbf{R}_n), \tag{4}$$

where

$$V(\mathbf{r}) = [1-f]V_a(\mathbf{r}) + fV_b(\mathbf{r}). \tag{5}$$

As was shown by Muto,[10] the virtual-crystal approximation gives energy levels correctly to the order of conventional first-order perturbation theory.[11] (It is to be remembered that we are dealing with a completely disordered alloy, so that each type of atom is placed on the atom sites in a random fashion.) By the above approximation, we have reduced our problem to one having the periodicity of the lattice.

We wish to solve the Schrödinger equation

$$[-\nabla^2 + \sum_n V(\mathbf{r}-\alpha\mathbf{R}_n) - E_q'(\mathbf{k})]\Psi_q'(\mathbf{k},\mathbf{r}) = 0. \tag{6}$$

Here $q$ denotes the particular energy band under consideration, and $\mathbf{k}$ determines the translational properties of the wave function. We are using atomic units. Let $\mathbf{R}_n'$ denote the lattice positions of the Bravais lattice for the undilated lattice; thus $\alpha\mathbf{R}_n'$ will be the corresponding quantities for the dilated lattice. Define

$$\mathfrak{S}_q(\mathbf{k},\mathbf{r}) \equiv \Psi_q'(\alpha^{-1}\mathbf{k},\alpha\mathbf{r}). \tag{7}$$

Since

$$\Psi_q'(\mathbf{k},\, \mathbf{r}+\alpha\mathbf{R}_n') = e^{i\mathbf{k}\cdot\alpha\mathbf{R}_n'}\Psi_q'(\mathbf{k},\mathbf{r}), \tag{8}$$

it follows that

$$\mathfrak{S}_q(\mathbf{k},\, \mathbf{r}+\mathbf{R}_n') = e^{i\mathbf{k}\cdot\mathbf{R}_n'}\mathfrak{S}_q(\mathbf{k},\mathbf{r}), \tag{9}$$

so that $\mathfrak{S}_q$ has the correct periodicity properties for the undilated lattice containing only $A$ atoms. Equation (6) may be rewritten

$$[-\alpha^{-2}\nabla^2 + \sum_n V(\alpha[\mathbf{r}-\mathbf{R}_n]) - E_q'(\alpha^{-1}\mathbf{k})] \times \Psi_q'(\alpha^{-1}\mathbf{k},\alpha\mathbf{r}) = 0,$$

which, after multiplying by $\alpha^2$, is equivalent to

$$[-\nabla^2 + \sum_n \alpha^2 V(\alpha[\mathbf{r}-\mathbf{R}_n]) - \alpha^2 E_q'(\alpha^{-1}\mathbf{k})] \times \mathfrak{S}_q(\mathbf{k},\mathbf{r}) = 0. \tag{10}$$

Let us define

$$V_a'(\mathbf{r}) = [2 + r(\partial/\partial r)]V_a(\mathbf{r}), \tag{11}$$

$$V_{ba}(\mathbf{r}) = V_b(\mathbf{r}) - V_a(\mathbf{r}), \tag{12}$$

$$V'(\mathbf{r}) = V_a'(\mathbf{r}) + \kappa^{-1}V_{ba}(\mathbf{r}). \tag{13}$$

Expand $[\alpha^2 V(\alpha\mathbf{r}) - V_a(\mathbf{r})]$ in a power series in $\epsilon$, keeping only the leading term since $|\epsilon| \ll 1$. Thus

$$\alpha^2 V(\alpha\mathbf{r}) - V_a(\mathbf{r}) = \epsilon V'(\mathbf{r}). \tag{14}$$

Substituting (14) into (10), we get

$$[-\nabla^2 + \sum_n V_a(\mathbf{r}-\mathbf{R}_n) + \epsilon \sum_n V'(\mathbf{r}-\mathbf{R}_n)]\mathfrak{S}_q(\mathbf{k},\mathbf{r}) = \alpha^2 E_q'(\alpha^{-1}\mathbf{k})\mathfrak{S}_q(\mathbf{k},\mathbf{r}). \tag{15}$$

Let $\Psi_q(\mathbf{k},\mathbf{r})$ be a solution of the Schrödinger equation

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[6] E. R. Johnson and S. M. Christian, Phys. Rev. **95**, 560 (1954); Levitas, Wang, and Alexander, Phys. Rev. **95**, 846 (1954).

[7] W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954); Fan, Shepherd, and Spitzer, Atlantic City Conference on Photoconductivity, November, 1954 (John Wiley and Sons, Inc., New York, 1955); Warschauer, Paul, and Brooks, Phys. Rev. **98**, 1193(A) (1955), and following paper.

[8] One of the most interesting features of these systems is the fact that, as a function of composition or pressure respectively, there appears to be a point where the minimum of the conduction band shifts its position in $k$-space discontinuously. An explanation of this effect has been proposed by F. Herman, Phys. Rev. **95**, 847 (1954).

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

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

[11] For a discussion of the effect on the energy levels of higher orders of perturbation theory, see reference 5.

appropriate to the crystal containing only $A$ atoms,[12] i.e.,

$$[-\nabla^2+\textstyle\sum_n V_a(\mathbf{r}-\mathbf{R}_n)]\Psi_q(\mathbf{k},\mathbf{r})=E_q(\mathbf{k})\Psi_q(\mathbf{k},\mathbf{r}). \tag{16}$$

We see that we may solve Eq. (15) by means of first-order perturbation theory, taking the $\Psi$'s as our unperturbed wave functions. Since the perturbation potential

$$\textstyle\sum_n V'(\mathbf{r}-\mathbf{R}_n)$$

in no way affects the symmetry of the unperturbed host crystal, then we are justified in using *nondegenerate* perturbation theory, the perturbation potential being unable to remove any degeneracies associated with symmetry. Thus

$$\alpha^2 E_q'(\alpha^{-1}\mathbf{k})=E_q(\mathbf{k})+(\alpha-1)\mathbf{V}_q'(\mathbf{k}), \tag{17}$$

or

$$E_q'(\mathbf{k})=\alpha^{-2}[E_q(\alpha\mathbf{k})+(\alpha-1)\mathbf{V}_q'(\alpha\mathbf{k})], \tag{18}$$

where

$$\mathbf{V}_q'(\mathbf{k})=\frac{\int_\infty \Psi_q^*(\mathbf{k},\mathbf{r})\sum_n V'(\mathbf{r}-\mathbf{R}_n)\Psi_q(\mathbf{k},\mathbf{r})d\tau}{\int_\infty \Psi_q^*(\mathbf{k},\mathbf{r})\Psi_q(\mathbf{k},\mathbf{r})d\tau}. \tag{19}$$

($\int_\infty d\tau$ denotes an integration over the entire volume of the crystal.) Expanding Eq. (18) in a power series in $\epsilon$, keeping only the constant and linear terms, we get

$$E_q'(\mathbf{k})=E_q(\mathbf{k})+\kappa[2\mathbf{k}\cdot\mathbf{v}_q(\mathbf{k})-2E_q(\mathbf{k})+\mathbf{V}_q'(\mathbf{k})]f, \tag{20}$$

where the velocity $\mathbf{v}_q(\mathbf{k})$ is given by

$$\mathbf{v}_q(\mathbf{k})=\tfrac{1}{2}\nabla_k E_q(\mathbf{k}). \tag{21}$$

In Eq. (13), the definition of $V'(\mathbf{r})$, the term $\kappa^{-1}V_{ba}$ arises from the presence of type $B$ atoms in the lattice. The term $V_a'$, however, arises solely from the change in lattice spacing. Similarly, in Eq. (18) the term $\alpha^{-2}E_q(\alpha\mathbf{k})$ arises solely from the change in lattice spacing. Thus by specializing to the case where $\kappa^{-1}=0$ and $f=0$ such that $\epsilon$ remains finite (i.e., by removing the term $\kappa^{-1}V_{ba}$), we obtain the effect of dilation or compression on the energy levels of a perfect crystal. An amusing example of the effect (or lack of effect) of dilation is the case of the empty lattice where all potentials vanish. The solution to the Schrödinger equation is a plane wave, while

$$E_q(\mathbf{k})=k^2.$$

Clearly the energy levels must be independent of any hypothetical dilation, on physical grounds. To see this mathematically, we note that

$$E_q'(\mathbf{k})=\alpha^{-2}E_q(\alpha\mathbf{k})=k^2=E_q(\mathbf{k}).$$

### III. MODIFIED PERTURBATION THEORY

In essence, the procedure carried out in the previous section is equivalent to that of *scaling* the wave function appropriate to the undilated host crystal, this scaling to be done in both $r$- and $k$-space, and then taking the expectation value of the Hamiltonian appropriate to the alloy with respect to this scaled wave function. There are two objections to this procedure. The first objection is that we have effectively assumed that the square of the wave function appropriate to the alloy has the periodicity of the Bravais lattice, an assumption which is certainly not true.[13] It would be desirable to construct some approximate wave function appropriate to the disordered alloy which correctly expresses the fact that the electronic charge density in the neighborhood of a $B$ atom is different from that in the neighborhood of an $A$ atom. The second objection has to do with the fact that when the lattice constant of a crystal is changed, the change in the wave function cannot be represented by scaling alone. In fact, in the immediate vicinity of a particular ion core of the crystal, the wave function, rather than being scaled, probably remains unchanged (aside from a phase factor) since as a first approximation the crystal potential remains unchanged (aside from an additive constant). If we had assumed that the crystal potential is scaled upon changing the lattice constant, then Eq. (2) would have been replaced by

$$\textstyle\sum_n V_{a_n}(\alpha^{-1}[\mathbf{r}-\alpha\mathbf{R}_n]). \tag{22}$$

It is felt by the writer, however, that Eq. (2) is a better approximation to the crystal potential for the alloy than in Eq. (22).

Both of the above objections can be overcome by modifying the perturbation procedure in the following fashion. First we consider the undilated host crystal containing only $A$ atoms. We designate by $\Phi_s(\mathbf{k},\mathbf{r})$ an ion-core Bloch wave function appropriate to this case, and by $\Psi_q(\mathbf{k},\mathbf{r})$ any of the other Bloch wave functions appropriate to this case. Since the $\Psi$'s and $\Phi$'s are solutions to the same Schrödinger equation, the $\Psi$'s must be orthogonal to the $\Phi$'s. In analogy with Herring's method of defining an orthogonalized plane wave,[1] we consider a function $\Gamma_q(\mathbf{k},\mathbf{r})$ such that

$$\Psi_q(\mathbf{k},\mathbf{r})=\Gamma_q(\mathbf{k},\mathbf{r})-\textstyle\sum_s \Phi_s(\mathbf{k},\mathbf{r}) \times\int \Phi_s^*(\mathbf{k},\mathbf{r})\Gamma_q(\mathbf{k},\mathbf{r})d\tau. \tag{23}$$

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[12] With regard to notation, throughout this paper we will prime wave functions appropriate to the disordered alloy and leave unprimed wave functions appropriate to the unperturbed crystal containing only $A$ atoms. Also we will use Greek and German symbols to denote exact and approximate wave functions respectively, appropriate to either the unperturbed or the perturbed crystal; e.g., $\mathfrak{S}$ is an approximate solution of Eq. (16) appropriate to the unperturbed cystal.

[13] It is this incorrect assumption which leads to the complete inability of conventional perturbation theory to correctly predict the ion-core energy levels of a disordered alloy, a difficulty discussed in reference 5.

Assuming the orthonormality of the Φ's,

$$\int_{\infty} \Phi_s^*(\mathbf{k},\mathbf{r})\Phi_t(\mathbf{k},\mathbf{r})d\tau=\delta_{s,\,t}, \tag{24}$$

we see that Eq. (23) merely expresses the fact that the Ψ's are orthogonal to the Φ's, i.e.,

$$\int_{\infty} \Phi_s^*(\mathbf{k},\mathbf{r})\Psi_q(\mathbf{k},\mathbf{r})d\tau=0. \tag{25}$$

In a case of a monatomic host crystal where there is more than one atom per unit cell of the crystal, the index $s$ appearing in the last three equations really stands for two indices, $s$ and $\sigma$, where $s$ denotes the type of atomic orbital from which the Bloch function is composed, while $\sigma$ denotes with which atom in the unit cell the Bloch function is associated; i.e.,

$$\Phi_{s,\,\sigma}(\mathbf{k},\mathbf{r})=N^{-\frac{1}{2}}\textstyle\sum_n \exp[i\mathbf{k}\cdot(\mathbf{R}_n'+\mathfrak{R}_\sigma)] \times\varphi_s(\mathbf{r}-\mathbf{R}_n'-\mathfrak{R}_\sigma). \tag{26}$$

The vector $\mathfrak{R}_\sigma$ denotes the position of the $\sigma$th atom of the unit cell with respect to the center of the unit cell. As in the previous section, the Bravais lattice vectors $\mathbf{R}_n'$ denote the positions of the centers of the unit cells, while the atomic positions, previously denoted by $\mathbf{R}_n$, can be written as $\mathbf{R}_n'+\mathfrak{R}_\sigma$. $N$ denotes the number of unit cells in the complete crystal. Let us take the ion-core atomic orbitals on a given atomic site to be orthonormal and assume that the atomic orbitals on neighboring atomic sites do not overlap; i.e.,

$$\int_{\infty} \varphi_s^*(\mathbf{r}-\mathbf{R}_m'-\mathfrak{R}_\sigma)\varphi_t(\mathbf{r}-\mathbf{R}_n'-\mathfrak{R}_\tau)d\tau =\delta_{s,\,t}\delta_{m,\,n}\delta_{\sigma,\,\tau}. \tag{27}$$

We see that Eq. (24) is consistent with Eqs. (26) and (27). Using the fact that

$$\Gamma_q(\mathbf{k},\,\mathbf{r}+\mathbf{R}_n')=e^{i\mathbf{k}\cdot\mathbf{R}_n'}\Gamma_q(\mathbf{k},\mathbf{r}), \tag{28}$$

we see that Eq. (23) can be rewritten

$$\Psi_q(\mathbf{k},\mathbf{r})=\Gamma_q(\mathbf{k},\mathbf{r})-\sum_{s,n}\varphi_s(\mathbf{r}-\mathbf{R}_n) \times\int_{\infty}\varphi_s^*(\mathbf{r}-\mathbf{R}_n)\Gamma_q(\mathbf{k},\mathbf{r})d\tau. \tag{29}$$

Equation (29) expresses the fact that the Ψ's are orthogonal to the φ's, i.e.,

$$\int_{\infty}\varphi_s^*(\mathbf{r}-\mathbf{R}_n)\Psi_q(\mathbf{k},\mathbf{r})d\tau=0. \tag{30}$$

This is consistent with the fact that the φ's, rather than the Φ's, may be considered to be the ion-core solutions to the Schrödinger equation for the undilated host crystal. Although such a point of view is not particularly advantageous for a perfect crystal, it will be very advantageous when we consider the disordered alloy. By means of Eq. (29), we have broken up the wave function $\Psi_q(\mathbf{k},\mathbf{r})$ into two parts, one part

$$-\sum_{s,n}\varphi_s(\mathbf{r}-\mathbf{R}_n)\int_{\infty}\varphi_s^*(\mathbf{r}-\mathbf{R}_n)\Gamma_q(\mathbf{k},\mathbf{r})d\tau \tag{31}$$

being appreciable only in the immediate vicinity of each ion core of the crystal and representing the rapid variations of the wave function in these regions, while the other part $\Gamma_q(\mathbf{k},\mathbf{r})$ is more smoothly varying and is of importance throughout all regions of the crystal.

Turning now to the disordered alloy, we define the function

$$\mathfrak{S}_q'(\mathbf{k},\mathbf{r})\equiv\mathfrak{G}_q'(\mathbf{k},\mathbf{r})-\sum_{s,n}\varphi_{s,a_n}(\mathbf{r}-\alpha\mathbf{R}_n) \times\int_{\infty}\varphi_{s,a_n}^*(\mathbf{r}-\alpha\mathbf{R}_n)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau, \tag{32}$$

where

$$\mathfrak{G}_q'(\mathbf{k},\mathbf{r})\equiv\Gamma_q(\alpha\mathbf{k},\alpha^{-1}\mathbf{r}). \tag{33}$$

As in the previous section, the index $a_n$ appearing in Eq. (32) designates the type of atom appearing on the $n$th atomic site. In analogy with Eq. (28), we have

$$\mathfrak{G}_q'(\mathbf{k},\,\mathbf{r}+\alpha\mathfrak{R}_n')=e^{i\mathbf{k}\cdot\alpha\mathbf{R}_n'}\mathfrak{G}_q'(\mathbf{k},\mathbf{r}), \tag{34}$$

so that this portion of the wave function $\mathfrak{S}_q'(\mathbf{k},\mathbf{r})$ has been scaled from the corresponding portion of the wave function $\Psi_q$ appropriate to the undilated host crystal. The remaining portion of the wave function $\mathfrak{S}_q'$, namely

$$-\sum_{s,n}\varphi_{s,a_n}(\mathbf{r}-\alpha\mathbf{R}_n)\int_{\infty}\varphi_{s,a_n}^*(\mathbf{r}-\alpha\mathbf{R}_n)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau, \tag{35}$$

has not been obtained by scaling (31), however, but by replacing (31) by linear combinations of the ion-core wave functions appropriate to the modified crystal, their coefficients being chosen such that the $\mathfrak{S}_q'$'s so obtained are orthogonal to these latter ion-core wave functions,[14] i.e.,

$$\int_{\infty}\varphi_{s,a_n}^*(\mathbf{r}-\alpha\mathbf{R}_n)\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau=0. \tag{36}$$

Equation (36) is the analogy for the modified crystal to Eq. (30), which holds for the unmodified crystal. We wish to approximate the wave function appropriate to the disordered alloy by $\mathfrak{S}_q'(\mathbf{k},\mathbf{r})$. It is apparent that such a procedure in large measure removes the two basic defects of the conventional perturbation procedure

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[14] The writer is indebted to F. Herman for pointing out the importance of working with approximate alloy wave functions which are orthogonal to the ion-core states of the alloy.

which were discussed at the beginning of this section. It should be mentioned that $\mathbf{k}$ is no longer a good quantum number, since unlike Eq. (8)

$$\mathfrak{S}_q'(\mathbf{k}, \mathbf{r}+\alpha\mathbf{R}_n')=e^{i\mathbf{k}\cdot\alpha\mathbf{R}_n'}\mathfrak{S}_q'(\mathbf{k},\mathbf{r}) \tag{37}$$

does not hold in general. It does hold, however, in regions outside of the ion cores of the alloy where (35) vanishes. The method expounded in this section therefore treats $\mathbf{k}$ as a certain approximation to a good quantum number. That such should be the case is, of course, suggested by the results of conventional perturbation theory given in Sec. II.

We shall approximate the energy for the disordered alloy by

$$E_q'(\mathbf{k})=\frac{\int_\infty \mathfrak{S}_q'^*(\mathbf{k},\mathbf{r})H'\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau}{\int_\infty \mathfrak{S}_q'^*(\mathbf{k},\mathbf{r})\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau}, \tag{38}$$

the expectation value of $H'$ with respect to the approximate wave function $\mathfrak{S}_q'$. As we shall see presently, $E_q'(\mathbf{k})$ is the same for all random configurations of atoms in the alloy consistent with the specified composition. The Hamiltonian $H'$ is given by

$$H'=-\nabla^2+\textstyle\sum_n V_{a_n}(\mathbf{r}-\alpha\mathbf{R}_n)-\mathbf{V}_0'. \tag{39}$$

The additive constant

$$\mathbf{V}_0'\equiv\textstyle\sum_n' V(\alpha\mathbf{R}_n-\alpha\mathbf{R}_m) \tag{40}$$

has been incorporated into the Hamiltonian for convenience in the calculation. $V(\mathbf{r})$ is the potential defined by Eq. (5), and the prime over the summation in Eq. (40) indicates that the term for $\mathbf{R}_n=\mathbf{R}_m$ is omitted. (We shall restrict ourselves to crystals having sufficient symmetry for $\mathbf{V}_0'$ to be independent of the index $m$.) Aside from the constant $\mathbf{V}_0'$, the crystal potential in $H'$ is that given by Eq. (2). Since in the immediate neighborhood of the $n$th atomic site of the crystal, the crystal potential may be closely approximate (aside from an additive constant) by the atomic-like potential centered on that site, we shall define the $\varphi$'s such that

$$[-\nabla^2+V_a(\mathbf{r})]\varphi_{s,a}(\mathbf{r})=E_{s,a}\varphi_{s,a}(\mathbf{r}), \tag{41}$$

and similarly for $\varphi_{s,b}$.[15] Thus, to a good approximation,

$$\begin{aligned}H'\varphi_{s,a_n}(\mathbf{r}-\alpha\mathbf{R}_n)=\{E_{s,a_n}-\mathbf{V}_0'\\ +\textstyle\sum_m' V_{a_m}(\alpha[\mathbf{R}_m-\mathbf{R}_n])\}\times\varphi_{s,a_n}(\mathbf{r}-\alpha\mathbf{R}_n)\end{aligned} \tag{42}$$

(the prime over the summation indicating that the term for $m=n$ is omitted). We now find

$$\begin{aligned}\int_\infty \mathfrak{S}_p'^*(\mathbf{k},\mathbf{r})H'\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau\\ =\int_\infty \mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})H_0'\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau\\ -N\sum_{s,\sigma}(1-f)E_{s,a}\int_\infty \varphi_{s,a}(\mathbf{r}-\alpha\mathfrak{R}_\sigma)\mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})d\tau\\ \times\int_\infty \varphi_{s,a}^*(\mathbf{r}-\alpha\mathfrak{R}_\sigma)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau\\ -N\sum_{s,\sigma} fE_{s,b}\int_\infty \varphi_{s,b}(\mathbf{r}-\alpha\mathfrak{R}_\sigma)\mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})d\tau\\ \times\int_\infty \varphi_{s,b}^*(\mathbf{r}-\alpha\mathfrak{R}_\sigma)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau,\end{aligned} \tag{43}$$

where $H_0'$ is defined as

$$H_0'=-\nabla^2+\textstyle\sum_n V(\mathbf{r}-\alpha\mathbf{R}_n)-\mathbf{V}_0'. \tag{44}$$

Similarly

$$\begin{aligned}\int_\infty \mathfrak{S}_p'^*(\mathbf{k},\mathbf{r})\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau\\ =\int_\infty \mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau\\ -N\sum_{s,\sigma}(1-f)\int_\infty \varphi_{s,a}(\mathbf{r}-\alpha\mathfrak{R}_\sigma)\mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})d\tau\\ \times\int_\infty \varphi_{s,a}^*(\mathbf{r}-\alpha\mathfrak{R}_\sigma)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau\\ -N\sum_{s,\sigma} f\int_\infty \varphi_{s,b}(\mathbf{r}-\alpha\mathfrak{R}_\sigma)\mathfrak{G}_p'^*(\mathbf{k},\mathbf{r})d\tau\\ \times\int_\infty \varphi_{s,b}^*(\mathbf{r}-\alpha\mathfrak{R}_\sigma)\mathfrak{G}_q'(\mathbf{k},\mathbf{r})d\tau.\end{aligned} \tag{45}$$

For the special case where the band indices $p$ and $q$ are the same, Eqs. (43), (44), and (45) prove the statement made previously that $E_q'(\mathbf{k})$ is independent of the configuration of atoms of the alloy. Let $\Psi_p(\alpha\mathbf{k},\alpha^{-1}\mathbf{r})$ and and $\Psi_q(\alpha\mathbf{k},\alpha^{-1}\mathbf{r})$ be two degenerate wave functions associated with the undilated host crystal, with $\alpha\mathbf{k}$ being a symmetry point in $k$-space, $\Psi_p$ and $\Psi_q$ having different point symmetries in real space. If $\mathfrak{S}_p'(\mathbf{k},\mathbf{r})$ and $\mathfrak{S}_q'(\mathbf{k},\mathbf{r})$ are the corresponding wave functions for the alloy, then by applying symmetry considerations to Eqs. (43), (44), and (45), we find that

$$\int_\infty \mathfrak{S}_p'^*(\mathbf{k},\mathbf{r})H'\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau=0, \tag{46}$$

and

$$\int \mathfrak{S}_p'^*(\mathbf{k},\mathbf{r})\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau=0. \tag{47}$$

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[15] We shall assume that the atomic-like potentials $V_a$ and $V_b$ may be approximated by the corresponding isolated-atom potentials. Thus the $\varphi_s$'s and the $E_s$'s are those for the isolated atoms.

It is for this reason that we are justified in using a modified form of *nondegenerate* first-order perturbation theory.

For the Hamiltonian of the undilated host crystal we take

$$H=-\nabla^2+\sum\nolimits_n V_a(\mathbf{r}-\mathbf{R}_n)-\mathrm{V}_0, \tag{48}$$

where

$$\mathrm{V}_0\equiv\sum\nolimits_n{}' V_a(\mathbf{R}_n-\mathbf{R}_m). \tag{49}$$

The corresponding energy is

$$E_q(\mathbf{k})=[I_q(\mathbf{k})]^{-1}\int_\infty \Psi_q^*(\mathbf{k},\mathbf{r})H\Psi_q(\mathbf{k},\mathbf{r})d\tau, \tag{50}$$

where

$$I_q(\mathbf{k})\equiv\int_\infty \Psi_q^*(\mathbf{k},\mathbf{r})\Psi_q(\mathbf{k},\mathbf{r})d\tau=\int_\infty |\Gamma_q(\mathbf{k},\mathbf{r})|^2 d\tau \\ -N\sum_{s,\sigma}\left|\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2, \tag{51}$$

and

$$\int_\infty \Psi_q^*(\mathbf{k},\mathbf{r})H\Psi_q(\mathbf{k},\mathbf{r})d\tau \\ =\int_\infty \Gamma_q^*(\mathbf{k},\mathbf{r})H\Gamma_q(\mathbf{k},\mathbf{r})d\tau \\ -N\sum_{s,\sigma}E_{s,a}\left|\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2. \tag{52}$$

We now define

$$\varphi_{s,a}'(\mathbf{r})\equiv r\frac{\partial}{\partial r}\varphi_{s,a}(\mathbf{r}). \tag{53}$$

Making use of Eqs. (33), (45), (51), and (53), and keeping only terms linear in $\epsilon=\alpha-1$, we get

$$\alpha^{-3}\int_\infty \mathfrak{S}_q'^*(\mathbf{k},\mathbf{r})\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau \\ -\int_\infty \Psi_q^*(\alpha\mathbf{k},\mathbf{r})\Psi_q(\alpha\mathbf{k},\mathbf{r})d\tau \\ =-\epsilon N\sum_{s,\sigma}\left\{3\left|\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2\right. \\ +\kappa^{-1}\left|\int_\infty \varphi_{s,b}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2 \\ -\kappa^{-1}\left|\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2 \\ +2\,\mathrm{Re}\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau \\ \left.\times\int_\infty \varphi_{s,a}'(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q^*(\mathbf{k},\mathbf{r})d\tau\right\}, \tag{54}$$

where Re means "real part of." In a similar fashion, we have

$$\alpha^{-3}\int_\infty \mathfrak{S}_q'^*(\mathbf{k},\mathbf{r})H'\mathfrak{S}_q'(\mathbf{k},\mathbf{r})d\tau \\ -\alpha^{-2}\int_\infty \Psi_q^*(\alpha\mathbf{k},\mathbf{r})H\Psi_q(\alpha\mathbf{k},\mathbf{r})d\tau \\ =\epsilon\int_\infty |\Gamma_q(\mathbf{k},\mathbf{r})|^2[\sum_n V'(\mathbf{r}-\mathbf{R}_n)-\sum_n{}' V'(\mathbf{R}_n-\mathbf{R}_m)]d\tau \\ -\epsilon N\sum_{s,\sigma}\left\{5E_{s,a}\left|\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2\right. \\ +\kappa^{-1}E_{s,b}\left|\int_\infty \varphi_{s,b}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2 \\ -\kappa^{-1}E_{s,a}\left|\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2 \\ +2E_{s,a}\,\mathrm{Re}\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathbf{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau \\ \left.\times\int_\infty \varphi_{s,a}'(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q^*(\mathbf{k},\mathbf{r})d\tau\right\}. \tag{55}$$

Substituting Eqs. (50), (51), (54), and (55) into Eq. (38), we get

$$E_q'(\mathbf{k})-\alpha^{-2}E_q(\alpha\mathbf{k})=\epsilon[I_q(\mathbf{k})]^{-1}\{[A_{1q}(\mathbf{k})+A_{2q}(\mathbf{k})] \\ +\kappa^{-1}[B_{1q}(\mathbf{k})+B_{2q}(\mathbf{k})]\}, \tag{56}$$

where

$$A_{1q}(\mathbf{k})\equiv\int_\infty |\Gamma_q(\mathbf{k},\mathbf{r})|^2[\sum_n V_a'(\mathbf{r}-\mathbf{R}_n) \\ -\sum_n{}' V_a'(\mathbf{R}_n-\mathbf{R}_m)]d\tau, \tag{57}$$

$$A_{2q}(\mathbf{k})\equiv N\sum_{s,\sigma}\left\{[3E_q(\mathbf{k})-5E_{s,a}]\right. \\ \times\left|\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2 \\ +2[E_q(\mathbf{k})-E_{s,a}]\,\mathrm{Re}\int_\infty \varphi_{s,a}^*(\mathbf{r}-\mathfrak{R}_\sigma) \\ \left.\times\Gamma_q(\mathbf{k},\mathbf{r})d\tau\int_\infty \varphi_{s,a}'(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q^*(\mathbf{k},\mathbf{r})d\tau\right\}, \tag{58}$$

$$B_{1q}(\mathbf{k})\equiv\int_\infty |\Gamma_q(\mathbf{k},\mathbf{r})|^2[\sum_n V_{ba}(\mathbf{r}-\mathbf{R}_n) \\ -\sum_n{}' V_{ba}(\mathbf{R}_m-\mathbf{R}_m)]d\tau, \tag{59}$$

$$B_{2q}(\mathbf{k})\equiv N\sum_{s,\sigma}\left\{[E_q(\mathbf{k})-E_{s,b}]\left|\int_\infty \varphi_{s,b}{}^*(\mathbf{r}-\mathfrak{R}_\sigma)\times\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2-[E_q(\mathbf{k})-E_{s,a}]\times\left|\int_\infty \varphi_{s,a}{}^*(\mathbf{r}-\mathfrak{R}_\sigma)\Gamma_q(\mathbf{k},\mathbf{r})d\tau\right|^2\right\}. \quad (60)$$

Making use of Eqs. (3) and (21), and defining

$$A_{3q}(\mathbf{k})\equiv 2[\mathbf{k}\cdot\mathbf{v}_q(\mathbf{k})-E_q(\mathbf{k})]I_q(\mathbf{k}), \quad (61)$$

we finally obtain

$$E_q{}'(\mathbf{k})-E_q(\mathbf{k})=\kappa[I_q(\mathbf{k})]^{-1}[A_{1q}(\mathbf{k})+A_{2q}(\mathbf{k})+A_{3q}(\mathbf{k})]f+[I_q(\mathbf{k})]^{-1}[B_{1q}(\mathbf{k})+B_{2q}(\mathbf{k})]f. \quad (62)$$

It is clear that the effect of a dilation upon a perfect crystal may be studied with the aid of Eq. (62) simply by removing the $B$ terms.

## IV. APPLICATION TO THE DIAMOND STRUCTURE

The procedure developed in the preceding section is particularly suited to an unmodified crystal for which wave functions and energy levels have been calculated by the orthogonalized plane wave (OPW) method.[1] In this method the wave function is expanded in terms of orthogonalized pane waves $X(\mathbf{k}_i,\mathbf{r})$, $\mathbf{k}_i$ being defined as

$$\mathbf{k}_i\equiv\mathbf{k}+\mathbf{K}_i, \quad (63)$$

$\mathbf{K}_i$ being a vector of the reciprocal lattice such that

$$e^{i\mathbf{K}_i\cdot\mathbf{R}_n{}'}=1, \quad (64)$$

for all $i$ and $n$. $X(\mathbf{k}_i,\mathbf{r})$ is defined as

$$X(\mathbf{k}_i,\mathbf{r})\equiv(N\Omega)^{-\frac{1}{2}}e^{i\mathbf{k}_i\cdot\mathbf{r}}-\Omega^{-\frac{1}{2}}\sum_{s,\sigma}\exp(i\mathbf{K}_i\cdot\mathfrak{R}_\sigma)\times\mu_{s,a}(\mathbf{k}_i)\Phi_{s,\sigma,a}(\mathbf{k},\mathbf{r}), \quad (65)$$

where

$$\mu_{s,a}(\mathbf{k}_i)=N^{-\frac{1}{2}}\exp(-i\mathbf{K}_i\cdot\mathfrak{R}_\sigma)\times\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\Phi_{s,\sigma,a}{}^*(\mathbf{k},\mathbf{r})d\tau=\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\varphi_{s,a}{}^*(\mathbf{r})d\tau, \quad (66)$$

and where $\Omega$ is the volume of the unit cell of the unmodified crystal. We see now that

$$\int_\infty \Phi_{s,\sigma,a}{}^*(\mathbf{k},\mathbf{r})X(\mathbf{k}_i,\mathbf{r})d\tau=0. \quad (67)$$

Expanding $\Psi_q(\mathbf{k},\mathbf{r})$ in terms of the $X$'s, we have

$$\Psi_q(\mathbf{k},\mathbf{r})=\textstyle\sum_i \mathcal{A}_q(\mathbf{k}_i)X(\mathbf{k}_i,\mathbf{r}). \quad (68)$$

Hence it follows that $\Gamma_q(\mathbf{k},\mathbf{r})$, as defined by Eq. (23), can be written as

$$\Gamma_q(\mathbf{k},\mathbf{r})=(N\Omega)^{-\frac{1}{2}}\textstyle\sum_i \mathcal{A}_q(\mathbf{k}_i)e^{i\mathbf{k}_i\cdot\mathbf{r}}. \quad (69)$$

It is because of the simplicity of Eq. (69) that the orthogonalized plane wave method is particularly adapted to the results of Sec. III.

We shall now specialize to the case where the unmodified crystal has the diamond structure, this being a case of great practical importance. There are now two atoms per unit cell such that $\mathfrak{R}_\sigma=\pm\mathfrak{R}$, where $\mathfrak{R}$ points in the (111) direction, and $2\mathfrak{R}$ is the nearest-neighbor distance. Thus

$$\int_\infty X^*(\mathbf{k}_i,\mathbf{r})X(\mathbf{k}_j,\mathbf{r})d\tau=\cos(\mathbf{K}_j-\mathbf{K}_i)\cdot\mathfrak{R}\left[\delta_{ij}-\frac{2}{\Omega}\sum_s \mu_{s,a}{}^*(\mathbf{k}_i)\mu_{s,a}(\mathbf{k}_j)\right]. \quad (70)$$

Defining

$$\mathcal{B}_{ij}{}^q(\mathbf{k})\equiv\mathcal{A}_q{}^*(\mathbf{k}_i)\mathcal{A}_q(\mathbf{k}_j)\cos(\mathbf{K}_j-\mathbf{K}_i)\cdot\mathfrak{R}, \quad (71)$$

we have

$$I_q(\mathbf{k})=\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\left[\delta_{ij}-\frac{2}{\Omega}\sum_s \mu_{s,a}{}^*(\mathbf{k}_i)\mu_{s,a}(\mathbf{k}_j)\right]. \quad (72)$$

We may write

$$\sum_n V_a{}'(\mathbf{r}-\mathbf{R}_n)-\sum_n{}' V_a{}'(\mathbf{R}_n-\mathbf{R}_m)=\sum_i \cos\mathbf{K}_i\cdot\mathfrak{R}\,\mathcal{V}_a{}'(\mathbf{K}_i)e^{-i\mathbf{K}_i\cdot\mathbf{r}}, \quad (73)$$

where

$$\mathcal{V}_a{}'(\mathbf{K}_i)\equiv\frac{2}{\Omega}\int_\infty e^{i\mathbf{K}_i\cdot\mathbf{r}}V_a{}'(\mathbf{r})d\tau-\delta_{i0}\sum_n{}' V_a{}'(\mathbf{R}_n-\mathbf{R}_m). \quad (74)$$

Thus

$$A_{1q}(\mathbf{k})=\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\mathcal{V}_a{}'(\mathbf{K}_j-\mathbf{K}_i). \quad (75)$$

Similarly, if we define

$$\mathcal{V}_{ba}(\mathbf{K}_i)\equiv\frac{2}{\Omega}\int_\infty e^{i\mathbf{K}_i\cdot\mathbf{r}}V_{ba}(\mathbf{r})d\tau-\delta_{i0}\sum_n{}' V_{ba}(\mathbf{R}_n-\mathbf{R}_m), \quad (76)$$

then

$$B_{1q}(\mathbf{k})=\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\mathcal{V}_{ba}(\mathbf{K}_j-\mathbf{K}_i). \quad (77)$$

$B_2$ is given by

$$B_{2q}(\mathbf{k})=\frac{2}{\Omega}\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\sum_s\{[E_q(\mathbf{k})-E_{s,b}]\mu_{s,b}{}^*(\mathbf{k}_i)\mu_{s,b}(\mathbf{k}_j)-[E_q(\mathbf{k})-E_{s,a}]\mu_{s,q}{}^*(\mathbf{k}_i)\mu_{s,a}(\mathbf{k}_j)\}, \quad (78)$$

where $\mu_{s,b}$ is defined in a manner analogous to Eq. (66).

In order to determine $A_2$ we must define

$$\mu_{s,a}'(\mathbf{k}_i)\equiv\int_\infty e^{i\mathbf{k}_i\cdot\mathbf{r}}\varphi_{s,a}'^*(\mathbf{k})d\tau. \quad (79)$$

Thus

$$A_{2q}(\mathbf{k})=\frac{2}{\Omega}\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\sum_s\{[3E_q(\mathbf{k})-5E_{s,a}]\times\mu_{s,a}^*(\mathbf{k}_i)\mu_{s,a}(\mathbf{k}_j)+[E_q(\mathbf{k})-E_{s,a}]\times[\mu_{s,a}^*(\mathbf{k}_i)\mu_{s,a}'(\mathbf{k}_j)+\mu_{s,a}'^*(\mathbf{k}_i)\mu_{s,a}(\mathbf{k}_j)]\}. \quad (80)$$

The divergence theorem of vector analysis tells us that

$$\int_\infty \nabla\cdot[\mathbf{r}e^{i\mathbf{k}_i\cdot\mathbf{r}}\varphi_{s,a}^*(\mathbf{r})]d\tau=0,$$

so that

$$\mu_{s,a}'(\mathbf{k}_i)=-[3+\mathbf{k}_i\cdot\nabla_{ki}]\mu_{s,a}(\mathbf{k}_i), \quad (81)$$

and therefore

$$A_{2q}(\mathbf{k})=-\frac{2}{\Omega}\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\sum_s\{2E_q(\mathbf{k})+[E_q(\mathbf{k})-E_{s,a}]\times[\mathbf{k}_i\cdot\nabla_{ki}+\mathbf{k}_j\cdot\nabla_{kj}+1]\}\mu_{s,a}^*(\mathbf{k}_i)\mu_{s,a}(\mathbf{k}_j). \quad (82)$$

Consistent with Eq. (27), we may define the *real* quantity $Q_{n,l}(r)$ such that

$$\varphi_{nlm}(\mathbf{r})=i^l r^{-1}Q_{nl}(r)\mathcal{Y}_l{}^m(\theta,\varphi), \quad (83)$$

where

$$\int_0^\infty Q_{nl}(r)Q_{n'l}(r)dr=\delta_{nn'}, \quad (84)$$

and

$$\int\mathcal{Y}_l{}^m(\theta,\varphi)^*\mathcal{Y}_{l'}{}^{m'}(\theta,\varphi)d\omega=\delta_{ll'}\delta_{mm'}. \quad (85)$$

(Here $\int d\omega$ denotes a surface integral over the unit sphere.) $\mathcal{Y}_l{}^m$ is defined as

$$\mathcal{Y}_l{}^m(\theta,\varphi)=\left[\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}P_l{}^{|m|}(\cos\theta)e^{im\varphi}. \quad (86)$$

Since

$$e^{i\mathbf{k}_i\cdot\mathbf{r}}=4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{+l}i^l j_l(k_ir)\mathcal{Y}_l{}^m(\theta,\varphi)\mathcal{Y}_l{}^m(\theta_i,\varphi_i)^*, \quad (87)$$

(where $\theta_i$ and $\varphi_i$ give the orientation of $\mathbf{k}_i$), we have

$$\mu_{nlm}(\mathbf{k}_i)=4\pi g_{nl}(k_i)\mathcal{Y}_l{}^m(\theta_i,\varphi_i)^*, \quad (88)$$

where

$$g_{nl}(k_i)\equiv\int_0^\infty rQ_{nl}(r)j_l(k_ir)dr. \quad (89)$$

($j_l$ is the spherical Bessel function of order $l$.) Let $\theta_{ij}$ be the angle between $\mathbf{k}_i$ and $\mathbf{k}_j$. Unsöld's addition theorem states that

$$\sum_{m=-l}^{+l}\mathcal{Y}_l{}^m(\theta_i,\varphi_i)\mathcal{Y}_l{}^m(\theta_j,\varphi_j)^*=(4\pi)^{-1}(2l+1)P_l(\cos\theta_{ij}). \quad (90)$$

Thus we obtain finally

$$I_q(\mathbf{k})=\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\left[\delta_{ij}-\frac{8\pi}{\Omega}\sum_l(2l+1)P_l(\cos\theta_{ij})\times\sum_n g_{nla}(k_i)g_{nla}(k_j)\right], \quad (91)$$

$$A_{2q}(\mathbf{k})=-\frac{8\pi}{\Omega}\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\sum_{nl}(2l+1)P_l(\cos\theta_{ij})\times\left\{2E_q(\mathbf{k})+[E_q(\mathbf{k})-E_{nla}]\times\left[k_i\frac{\partial}{\partial k_i}+k_j\frac{\partial}{\partial k_j}+1\right]\right\}g_{nla}(k_i)g_{nla}(k_j), \quad (92)$$

$$B_{2q}(\mathbf{k})=\frac{8\pi}{\Omega}\sum_{ij}\mathcal{B}_{ij}{}^q(\mathbf{k})\sum_{nl}(2l+1)P_l(\cos\theta_{ij})\times\{[E_q(\mathbf{k})-E_{nlb}]g_{nlb}(k_i)g_{nlb}(k_j)-[E_q(\mathbf{k})-E_{nla}]g_{nla}(k_i)g_{nla}(k_j)\}. \quad (93)$$

In a specific application, Eqs. (75), (77), (91), (92), and (93) are what need to be evaluated numerically. These equations look considerably more formidable than they really are. Actually they are particularly suitable for numerical computation. The $g_{nl}$'s which are needed in these equations can be obtained through Eq. (89) from the radial ion-core wave functions $r^{-1}Q_{nl}$ appropriate to isolated atoms in question. These $Q_{nl}$'s are available in the literature for many atoms, as are the corresponding $E_{nl}$'s. As can be seen from Eq. (41), these $E_{nl}$'s are the ion-core energy levels appropriate to the *isolated* atoms in question. ($E_{nl}$ and $Q_{nl}$ for the ion-core levels are approximately independent of the assumed degree of ionization of the isolated atom.) For $V_a$ and $V_b$, needed in calculating $\mathcal{V}_a'$ and $\mathcal{V}_{ba}$, it is probably satisfactory to use the spherically symmetrical atomic potentials appropriate to the two isolated atoms.

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