# $T$-Matrix Approach to Electron Distribution in Crystals*

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The wave functions for valence or conduction electrons are given in the form proposed by Phillips and Kleinman. The wave equation for the smooth part of the electron wave functions is rewritten as an integral equation which is solved by using the $t$-matrix formalism. The smooth part of the wave function is then given by a plane wave plus waves arising from electron scattering by the effective potential of the crystal which might contain point imperfections. Approximate expressions for the wave functions, density and energy of the valence electrons and the self-consistent crystal potential are given. Numerical results obtained for the Fourier coefficients of the valence electron charge density in diamond exhibit covalent bonding and are in good agreement with experimental results. The presented treatment of valence or conduction electrons is expected to be particularly useful in determining the electronic structure and the formation and migration energies of point defects in valence crystals.

## I. INTRODUCTION

RECENTLY, a great deal of progress has been made in the study of self-consistent valence or conduction electron distribution in metals and semiconductors.[1] Cohen and Phillips presented a simple method for determining self-consistently the screening of an effective crystal potential due to valence or conduction electrons.[2] By using first-order perturbation theory and the concept of dielectric screening these authors derived a simple expression for the self-consistent crystal potential. However, their simple method failed to describe covalent bonding in valence crystals. This failure arises essentially from the linearization of the valence electron response to the effective crystal potential. Kleinman and Phillips determined for diamond a valence electron distribution in good agreement with experiment by using valence electron wave functions in the form of symmetrized combinations of plane waves orthogonalized to closed-shell core electron eigenfunctions.[3] However, this approach to the valence electron wave functions is limited to symmetry points in reciprocal lattice space and, therefore, not very useful in determining self-consistent electron wave functions and, particularly, in determining the electron redistribution due to crystal imperfections.

These remarks upon previous work show that it is desirable to develop a simple method for a systematic determination of valence or conduction electron wave functions from a wave equation. Therefore, the aim of this paper is to determine systematically from a wave equation the Bloch wave functions in the form proposed by Phillips and Kleinman[4]—in a way which takes into account a nonlinear response of the electrons to the effective crystal potential and which can be readily applied to imperfect crystals. Assuming that the closed-

shell core electrons are dynamically independent from the valence or conduction electrons and their eigenfunctions are known, then the Bloch wave functions of the valence or conduction electrons are essentially determined by their smooth part which is called hereafter the effective wave function. The wave equation for the effective wave functions[4] is rewritten as an integral equation which is then solved by using the $t$-matrix formalism. The Hamiltonian of the wave equation for the effective wave function is split into $H' = H_0'$ $+\sum_l \Delta H_l'$, where $H_0'$ represents that part of $H'$ which has plane waves as eigenfunctions and $\Delta H_l'$ is the perturbing Hamiltonian associated with the lattice ion $l$. $l$ is summed over all atomic nuclei of the lattice. Introducing then the operator $t_l$ which describes the electron scattering by $\Delta H_l'$, the integral equation is solved in terms of $t_l$. The resulting effective wave function consists of a plane wave plus waves involving $t_l$ which arise from single, double, and higher multiple electron scattering by the $\Delta H_l'$. Assuming that the interatomic distances are large compared to the range of the $\Delta H_l'$, where the main electron scattering occurs, then the multiple electron scattering can be approximated by multiple forward and backward scattering between the scatterers and can be expressed in closed form.

The crystal might contain imperfections. Then, for example, a vacancy is described in $H'$ by $\Delta H_V' \equiv 0$, where $\Delta H_V'$ denotes the perturbing Hamiltonian associated in the perfect crystal with the lattice site $V$ of the vacancy. An interstitial is represented in $H'$ by a perturbing Hamiltonian $\Delta H_I'$ located at an interstitial lattice site. Approximate expressions for the Bloch wave functions, charge density and energy of the valence electrons, and for the electronic contribution to the formation energy of point defects and the self-consistent crystal potential are derived.

In Sec. II the wave equation for the effective wave functions is rewritten as an integral equation. In Sec. III the integral equation is solved by using the $t$-matrix formalism. An approximate expression for the effective wave function is given. In Secs. IV, V, and VI, approximate expressions for the $t$ matrix, the self-consistent

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[1] V. Heine, Proc. Roy. Soc. (London) A240, 340 (1957); L. Kleinman and J. C. Phillips, Phys. Rev. 116, 880 (1959); Phys. Rev. 117, 460 (1960); Phys. Rev. 118, 1153 (1960).

[2] M. H. Cohen and J. C. Phillips, Phys. Rev. 124, 1818 (1961).

[3] L. Kleinman and J. C. Phillips, Phys. Rev. 125, 819 (1962).

[4] J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287 (1959).

crystal potential, and, respectively, the energy of the valence electrons are derived. In Sec. VII the general method is applied to diamond. The Fourier coefficients $\rho_{111}$, $\rho_{220}$, $\rho_{311}$, $\rho_{222}$, and $\rho_{400}$ of the valence electron charge density are calculated. The obtained results are compared with experimental data and previous theoretical calculations.

The treatment of valence or conduction electrons proposed in this paper is discussed with respect to its limitations and applications in Sec. VIII.

## II. INTEGRAL EQUATION FOR THE EFFECTIVE WAVE FUNCTION

The Bloch wave functions for valence or conduction electrons are determined by

$$H\psi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\psi_{\mathbf{k}}(\mathbf{r}), \tag{II.1}$$

where the Hamiltonian $H$ is given by

$$H \equiv -(\hbar^2/2m)\nabla^2 + V_i(\mathbf{r}) + A_{iv}(\mathbf{r},E(\mathbf{k}))$$
$$+ C(\mathbf{r}) + A_{vv}(\mathbf{r},E(\mathbf{k})). \tag{II.2}$$

$V_i$ is the Coulomb potential of the lattice ions, e.g., atomic nuclei plus tightly bound core electrons. $A_{iv}$ describes the exchange and correlation interaction between the tightly bound core electrons and the valence or conduction electrons. $C$ is the Coulomb potential of the valence or conduction electrons. The operator $A_{vv}$ describes the exchange and residual correlation interaction among the valence electrons.[5]

Phillips and Kleinman[4] made for the Bloch wave functions $\psi_{\mathbf{k}}$ the ansatz

$$\psi_{\mathbf{k}}(\mathbf{r}) = C_{\mathbf{k}}\{\Phi_{\mathbf{k}}(\mathbf{r}) - \sum_{t,k'} b_{tk'}(\mathbf{k})\varphi_{t,\mathbf{k}'}(\mathbf{r})\}, \tag{II.3}$$

where the normalization constant $C_{\mathbf{k}}$ is given by

$$C_{\mathbf{k}} = (\langle \Phi_{\mathbf{k}} | \Phi_{\mathbf{k}}\rangle - \sum_{t,k'} |b_{tk'}(\mathbf{k})|^2)^{-1/2}. \tag{II.4}$$

$\Phi_{\mathbf{k}}$, the smooth part of the Bloch wave function, is called the effective wave function for the valence electrons. The $\varphi_{t,\mathbf{k}}$ are closed-shell crystal core electron eigenfunctions. $t$ is summed over all closed-shell core electron states. The $\varphi_{t,\mathbf{k}}$ are determined by

$$H\varphi_{t,\mathbf{k}}(\mathbf{r}) = E_t(\mathbf{k})\varphi_{t,\mathbf{k}}(\mathbf{r}). \tag{II.5}$$

In the tight-binding approximation (LCAO) the eigenfunctions $\varphi_{t,k}$ are given by

$$\varphi_{t,k}(\mathbf{r}) = \left(\frac{1}{N}\right)^{1/2} \sum_{l} U_{t,k}(\mathbf{r}_l)\varphi_t^l(\mathbf{r}-\mathbf{r}_l), \tag{II.6}$$

where $l$ is summed over all atomic nuclei of the lattice. The $\mathbf{r}_l$ give the positions of the $N$ atomic nuclei of the lattice. The functions $\varphi_t^l$ are atomic-like eigenfunctions associated with the $l$th atomic nucleus. The expansion coefficients $U_{t,k}(\mathbf{r}_l)$ are determined, in general, as shown in detail in Appendix C. In the case of a perfect

crystal the $U_{t,k}(\mathbf{r}_l)$ are given by $\exp(i\mathbf{k}\cdot\mathbf{r}_l)$. The requirement that $\psi_k$ is orthogonal to the eigenfunctions $\varphi_{t,\mathbf{k}}$ and

$$\langle\varphi_{s,\mathbf{k}} | \varphi_{t,\mathbf{k}}\rangle = \delta_{s,t} \tag{II.7}$$

lead to

$$b_{tk'}(\mathbf{k}) = \langle\varphi_{t,\mathbf{k}'} | \Phi_{\mathbf{k}}\rangle. \tag{II.8}$$

In the tight-binding approximation the condition (II.7) is fulfilled only if the overlapping of $\varphi_t^l$ and $\varphi_s^{l'}$ for which $l \neq l'$ is neglected. Combining now Eqs. (II.1), (II.3), and (II.5) one derives for $\Phi_{\mathbf{k}}$ the wave equation[4]

$$H'\Phi_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k})\Phi_{\mathbf{k}}(\mathbf{r}), \tag{II.9}$$

with the effective Hamiltonian

$$H' \equiv H + V_R. \tag{II.10}$$

The nonlocal potential $V_R(\mathbf{r},E(\mathbf{k}))$ is given by

$$V_R(\mathbf{r},E(\mathbf{k}))\Phi_{\mathbf{k}}(\mathbf{r})$$
$$= \sum_{t,k'}(E(\mathbf{k}) - E_t(\mathbf{k}'))b_{tk'}(\mathbf{k})\varphi_{t,\mathbf{k}'}(\mathbf{r}). \tag{II.11}$$

It may be noted that the indeterminacy of $\Phi_{\mathbf{k}}$ which can be seen from Eq. (II.3) allows one to impose an additional constraint on $\Phi_{\mathbf{k}}$ which can be used for simplifying $V_R$. The additional constraint on $\Phi_{\mathbf{k}}$ is usually applied in the form of a variational principle. In accordance with the varied quantity various expressions are obtained for $V_R$.[6-8]

Assuming that the tightly bound core electrons are dynamically independent from the system of valence or conduction electrons and the core states $\varphi_{t,\mathbf{k}}$ are known, the determination of the Bloch wave functions $\psi_{\mathbf{k}}$ is reduced to the determination of $\Phi_{\mathbf{k}}$ by the wave Eq. (II.9).

Equation (II.9) is now converted into an integral equation as follows. The Hamiltonian $H'$ is split into

$$H' = H_0' + \Delta H'. \tag{II.12}$$

$H_0'$, whose eigenfunctions are plane waves, is given by

$$H_0' \equiv -\frac{\hbar^2}{2m}\nabla^2 + V_i'(\mathbf{k},\mathbf{k};E(\mathbf{k})) + V_R(\mathbf{k},\mathbf{k};E(\mathbf{k})) + C_0$$
$$+ A_{vv}^0(\mathbf{r},E_0'(\mathbf{k})), \tag{II.13}$$

with

$$V_i'(\mathbf{k},\mathbf{k};E(\mathbf{k})) \equiv \Omega^{-1}\langle\mathbf{k} | V_i'(\mathbf{r},E(\mathbf{k})) | \mathbf{k}\rangle, \tag{II.14}$$

where $V_i'(\mathbf{r},E(\mathbf{k}))$ is defined as

$$V_i'(\mathbf{r},E(\mathbf{k})) \equiv V_i(\mathbf{r}) + A_{iv}(\mathbf{r},E(\mathbf{k})), \tag{II.15}$$

and with

$$V_R(\mathbf{k},\mathbf{k};E(\mathbf{k})) \equiv \Omega^{-1}\langle\mathbf{k} | V_R(\mathbf{r},E(\mathbf{k})) | \mathbf{k}\rangle. \tag{II.16}$$

Using Eq. (II.11) one gets

$$V_R(\mathbf{k},\mathbf{k};E(\mathbf{k}))$$
$$= \Omega^{-1}\sum_{t,k'}(E(\mathbf{k}) - E_t(\mathbf{k}'))|\langle\varphi_{t,\mathbf{k}'} | \mathbf{k}\rangle|^2. \tag{II.17}$$

[5] J. C. Phillips, Phys. Rev. **123**, 420 (1961).

[6] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).
[7] F. Bassani and V. Celli, Nuovo Cimento **11**, 805 (1959).
[8] W. A. Harrison, Phys. Rev. **126**, 497 (1962).

$\Omega$ denotes the volume of the crystal. If $V_i'(\mathbf{r},E(\mathbf{k}))$ and $V_R(\mathbf{r},E(\mathbf{k}))$ are local potentials, then $V_i'(\mathbf{k},\mathbf{k};E(\mathbf{k}))$ and $V_R(\mathbf{k},\mathbf{k};E(\mathbf{k}))$, respectively, are the space averages of these potentials. The perturbing Hamiltonian $\Delta H'$ is given by

$$\Delta H' \equiv \Delta V_i' + \Delta V_R + \Delta C + \Delta A_{vv} \qquad (\text{II.18})$$

with

$$\Delta V_i'(\mathbf{r},E(\mathbf{k})) \equiv V_i'(\mathbf{r},E(\mathbf{k})) - V_i'(\mathbf{k},\mathbf{k};E(\mathbf{k})),$$

$$\Delta V_R(\mathbf{r},E(\mathbf{k})) \equiv V_R(\mathbf{r},E(\mathbf{k})) - V_R(\mathbf{k},\mathbf{k};E(\mathbf{k})),$$

$$\Delta C(\mathbf{r}) \equiv C(\mathbf{r}) - C_0,$$

and

$$\Delta A_{vv}(\mathbf{r},E(\mathbf{k})) \equiv A_{vv}(\mathbf{r},E(\mathbf{k})) - A_{vv}{}^0(\mathbf{r},E_0'(\mathbf{k})). \qquad (\text{II.19})$$

$C_0$ and $A_{vv}{}^0$ result from $C$ and $A_{vv}$, respectively, for $\Delta H' \equiv 0$.

The assumption that the tightly bound core electrons are dynamically decoupled from the system of valence electrons has the consequence that $A_{iv}$ is essentially unscreened. Therefore, in the following, $A_{iv}$ is approximated by $A_{iv}(\mathbf{r},0)$. Then, $V_i'(\mathbf{r},E(\mathbf{k}))$ and $V_i'(\mathbf{k},\mathbf{k};E(\mathbf{k}))$ are given by $V_i'(\mathbf{r},0)$ and $V_i'(\mathbf{k},\mathbf{k};0)$, respectively. Defining a Green's function $G_0'(\mathbf{r},\mathbf{r}',E_0'(\mathbf{k}))$ by

$$\{H_0' - E_0'(\mathbf{k})\}G_0'(\mathbf{r},\mathbf{r}',E_0'(\mathbf{k})) = -\delta(\mathbf{r}-\mathbf{r}') \qquad (\text{II.20})$$

and the requirement that $G_0'(\mathbf{r},\mathbf{r}',E_0'(\mathbf{k}))$ as a function of $\mathbf{r}$ has the same behavior for $r \to 0$ and $r \to \infty$ as the scattered wave arising from $\Delta H'$, Eq. (II.9) can be rewritten as the integral equation

$$\Phi_\mathbf{k}(\mathbf{r}) = \Phi_\mathbf{k}{}^0(\mathbf{r}) + \int d^3r' G_0'(\mathbf{r},\mathbf{r}',E_0'(\mathbf{k}))$$
$$\times \{\Delta H' - \Delta E\}\Phi_\mathbf{k}(\mathbf{r}'). \qquad (\text{II.21})$$

The eigenfunctions $\Phi_\mathbf{k}{}^0$ of $H_0'$ are given by

$$\Phi_\mathbf{k}{}^0(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r}). \qquad (\text{II.22})$$

$\Delta E$ is defined by

$$\Delta E \equiv E - E_0', \qquad (\text{II.23})$$

with

$$E_0'(\mathbf{k}) = \Omega^{-1}\langle \Phi_\mathbf{k}{}^0 | H_0' | \Phi_\mathbf{k}{}^0 \rangle. \qquad (\text{II.24})$$

$$\Delta\Phi_\mathbf{k}(\mathbf{r}) = \int d^3r' G_0'(\mathbf{r},\mathbf{r}',E_0'(\mathbf{k}))\{\Delta H' - \Delta E\}\Phi_\mathbf{k}(\mathbf{r}') \qquad (\text{II.25})$$

is the scattered wave resulting from the scattering of the free electron in state $\Phi_\mathbf{k}{}^0$ by $\Delta H'$. Denoting by $g_\mathbf{k}$ the integral operator with kernel $G_0'(\mathbf{r},\mathbf{r}',E_0'(\mathbf{k}))$, Eq. (II.21) can be rewritten as

$$\Phi_\mathbf{k} = | \mathbf{k}\rangle + g_\mathbf{k}(\Delta H' - \Delta E)\Phi_\mathbf{k}, \qquad (\text{II.26})$$

where the state vector $| \mathbf{k}\rangle$ represents $\Phi_\mathbf{k}{}^0$.

### III. THE SOLUTION OF THE INTEGRAL EQUATION

The integral Eq. (II.26) can be formally solved by

$$\Phi_\mathbf{k} = [1 - g_\mathbf{k}(\Delta H' - \Delta E)]^{-1} | \mathbf{k}\rangle. \qquad (\text{III.1})$$

The scattered wave $\Delta\Phi_\mathbf{k}$ is then given by

$$\Delta\Phi_\mathbf{k} = g_\mathbf{k}(\Delta H' - \Delta E)[1 - g_\mathbf{k}(\Delta H' - \Delta E)]^{-1} | \mathbf{k}\rangle. \qquad (\text{III.2})$$

As shown in detail in Appendix A, $\Delta H'$ can be split into

$$\Delta H'(\mathbf{r},E(\mathbf{k})) = \sum_l \Delta H_l'(\mathbf{r} - \mathbf{r}_l, E(\mathbf{k})), \qquad (\text{III.3})$$

where $l$ is summed over all atomic nuclei of the lattice. The perturbing Hamiltonian $\Delta H_l'$ is associated with the atomic nucleus $l$ located at $\mathbf{r}_l$ in the lattice. In accordance with Eq. (III.3), one gets

$$\Delta E = \sum_l \Delta E_l. \qquad (\text{III.4})$$

Equation (III.2) can now be rewritten as

$$\Delta\Phi_\mathbf{k} = \sum_l \Delta\Phi_\mathbf{k}{}^l, \qquad (\text{III.5})$$

with

$$\Delta\Phi_\mathbf{k}{}^l = g_\mathbf{k}(\Delta H_l' - \Delta E_l)$$
$$\times [1 - \sum_{l'} g_\mathbf{k}(\Delta H_{l'}' - \Delta E_{l'})]^{-1} | \mathbf{k}\rangle. \qquad (\text{III.6})$$

$\Delta\Phi_\mathbf{k}{}^l$ is the scattered wave arising from $\Delta H_l'$. Expanding the expression $[1 - \sum_{l'} g_\mathbf{k}(\Delta H_{l'}' - \Delta E_{l'})]^{-1}$ in a series, introducing the operator

$$t_l = (\Delta H_l' - \Delta E_l)[1 - g_\mathbf{k}(\Delta H_l' - \Delta E_l)]^{-1}, \qquad (\text{III.7})$$

which describes the electron scattering by $\Delta H_l'$, and using the operator identities $[1 - g_\mathbf{k}(\Delta H_l' - \Delta E_l)]^{-1} = 1 + g_\mathbf{k}t_l$ and

$$(\Delta H_l' - \Delta E_l)[1 - g_\mathbf{k}(\Delta H_l' - \Delta E_l)]^{-1}$$
$$= [1 - (\Delta H_l' - \Delta E_l)g_\mathbf{k}]^{-1}(\Delta H_l' - \Delta E_l),$$

the scattered wave $\Delta\Phi_\mathbf{k}{}^l$ is expanded as

$$\Delta\Phi_\mathbf{k}{}^l = (g_\mathbf{k}t_l + \sum_{\substack{l' \\ (l' \neq l)}} g_\mathbf{k}t_l g_\mathbf{k}t_{l'}$$
$$+ \sum_{\substack{l', l'' \\ (l' \neq l, l' \neq l'')}} g_\mathbf{k}t_l g_\mathbf{k}t_{l'} g_\mathbf{k}t_{l''} + \cdots) | \mathbf{k}\rangle, \qquad (\text{III.8})$$

where always successive indices are different. The various terms in Eq. (III.8) are interpreted as arising from single, double, and higher multiple electron scattering. For example, $g_\mathbf{k}t_l | \mathbf{k}\rangle$ represents the scattered wave due to scattering of an electron in state $| \mathbf{k}\rangle$ by $\Delta H_l'$ and the scattered wave $\sum_{l'} g_\mathbf{k}t_l g_\mathbf{k}t_{l'} | \mathbf{k}\rangle$ results from the subsequent scattering of the various scattered waves $g_\mathbf{k}t_{l'} | \mathbf{k}\rangle$ by $\Delta H_l'$.

The main contributions to $\Delta\Phi_\mathbf{k}{}^l$ will arise from single electron scattering by $\Delta H_l'$ and from multiple scattering involving beside $\Delta H_l'$ such perturbing Hamiltonians $\Delta H_{l'}'$ which are associated with atomic nuclei $l'$ in the next neighborhood of the atomic nucleus $l$. Therefore, $\Delta\Phi_\mathbf{k}{}^l$ is approximately given by

$$\Delta\Phi_\mathbf{k}{}^l = g_\mathbf{k}t_l | \mathbf{k}\rangle + \sum_{\substack{l' \\ (l' \neq l)}} \Delta\Phi_\mathbf{k}{}^{l'l} + \cdots, \qquad (\text{III.9})$$

with

$$\Delta\Phi_\mathbf{k}{}^{ll'} \equiv (g_\mathbf{k}t_l g_\mathbf{k}t_{l'} + g_\mathbf{k}t_l g_\mathbf{k}t_{l'} g_\mathbf{k}t_l$$
$$+ g_\mathbf{k}t_l g_\mathbf{k}t_{l'} g_\mathbf{k}t_l g_\mathbf{k}t_{l'} + \cdots) | \mathbf{k}\rangle. \qquad (\text{III.10})$$
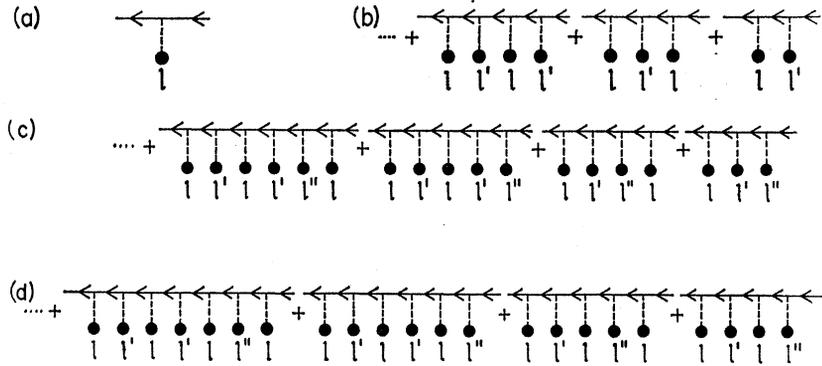
(a) 

(b) 

(c) 

FIG. 1. Graphical representation of (a) $g_{kl}|\mathbf{k}\rangle$, (b) Eq. (III.10); (c) $\Delta\phi_1{}^{ll'l''}(\mathbf{k})$, and (d) $\Delta\phi_2{}^{ll'l''}(\mathbf{k})$.

(d) 

The physical significance of this term is illuminated by the graphical representation given in Fig. 1. If necessary, all higher-order terms in Eq. (III.9) can readily be written down in explicit form using their graphical representation. For example, the two next higher-order terms in Eq. (III.9) denoted by

$$\Delta\Phi_1{}^{ll'l''}(\mathbf{k})$$

and

$$\Delta\Phi_2{}^{ll'l''}(\mathbf{k})$$

are pictorially given in Fig. 1.

For a further evaluation of Eq. (III.8) the Green's function $G_0'(\mathbf{r},\mathbf{r}',E_0'(\mathbf{k}))$ need be determined. Fourier transforming Eq. (II.20) one obtains

$$G_0'(\mathbf{r},\mathbf{r}',E_0'(\mathbf{k})) = -\frac{2m}{\hbar^2}\int\frac{d^3q}{(2\pi)^3}G_0'[q,E_0'(\mathbf{k})]\exp[i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')], \tag{III.11}$$

with

$$G_0'[\mathbf{q},E_0'(\mathbf{k})] = -\frac{\hbar^2}{2m}\left(E_0'(\mathbf{k})-\frac{\hbar^2}{2m}q^2-V_i'(\mathbf{k},\mathbf{k};0)-V_R(\mathbf{k},\mathbf{k};E(\mathbf{k}))-C_0-A_{vv}{}^0(\mathbf{q},\mathbf{q};E_0'(\mathbf{k}))+i\epsilon\right)^{-1}, \tag{III.12}$$

$$\epsilon > 0.$$

The limit $\epsilon \to 0$ is taken after the $q$ integration is performed. The irreducible self-energy $A_{vv}{}^0(\mathbf{q},\mathbf{q};E_0'(\mathbf{k}))$ is given by

$$A_{vv}{}^0(\mathbf{q},\mathbf{q};E_0'(\mathbf{k})) \equiv \Omega^{-1}\langle\mathbf{q}|A_{vv}{}^0(\mathbf{r},E_0'(\mathbf{k})|\mathbf{q}\rangle. \tag{III.13}$$

Approximating $A_{vv}{}^0(\mathbf{r},E_0'(\mathbf{k}))$ by[9]

$$A_{vv}{}^0(\mathbf{r},E_0'(\mathbf{k}))\exp(i\mathbf{q}\cdot\mathbf{r})$$

$$= i\int\int d^3r'\frac{dp_0}{2\pi}V_s{}^0(\mathbf{r}-\mathbf{r}', E_0'(\mathbf{k})-p_0)$$

$$\times G_0''(\mathbf{r},\mathbf{r}',p_0)\exp(i\mathbf{q}\cdot\mathbf{r}'), \tag{III.14}$$

where the Fourier transform $G_0''(p_1p_0)$ of the Green's function $G_0''$ is given by Eq. (III.12) with $\epsilon > 0$ for

$p > k_F$ and $\epsilon < 0$ for $p < k_F$, $k_F$ being the Fermi wave number, and where $V_s{}^0(r-r', E_0'(\mathbf{k})-p_0)$ denotes the screened electron-electron interaction in a uniform electron gas, one derives

$$A_{vv}{}^0(\mathbf{q},\mathbf{q};E_0'(\mathbf{k}))$$

$$= i\int\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}V_s{}^0(\mathbf{q}-\mathbf{p}, E_0'(\mathbf{k})-p_0)$$

$$\times G_0''(\mathbf{p},p_0). \tag{III.15}$$

It follows from Eqs. (II.24) and (II.13) that $E_0'(\mathbf{k})$ is given by

$$E_0'(\mathbf{k}) = (\hbar^2/2m)k^2+V_i'(\mathbf{k},\mathbf{k};0)+V_R(\mathbf{k},\mathbf{k};E(\mathbf{k}))$$
$$+C_0+A_{vv}{}^0(\mathbf{k},\mathbf{k};E_0'(\mathbf{k})). \tag{III.16}$$

Thus, Eq. (III.12) can be rewritten as

$$G_0'(\mathbf{q},E_0'(\mathbf{k})) = \frac{(\hbar^2/2m)}{(\hbar^2/2m)(q^2-k^2)+A_{vv}{}^0(\mathbf{q},\mathbf{q};E_0'(\mathbf{k}))-A_{vv}{}^0(\mathbf{k},\mathbf{k};E_0'(\mathbf{k}))-i\epsilon}. \tag{III.17}$$

[9] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

Performing the angular integrations in Eq. (III.11), one gets

$$G_0'(\mathbf{r},\mathbf{r}';E_0'(\mathbf{k})) = -\frac{2m}{4\pi^2\hbar^2}\frac{1}{i|\mathbf{r}-\mathbf{r}'|}\left\{\int_{-\infty}^{\infty}dq\,q\,G_0'(q,E_0'(\mathbf{k}))\exp(iq|\mathbf{r}-\mathbf{r}'|)\right.$$

$$\left.+\int_0^{\infty}dq\,q\exp(iq|\mathbf{r}-\mathbf{r}'|)[G_0'(-q,E_0'(\mathbf{k}))-G_0'(q,E_0'(\mathbf{k}))]\right\},\quad\text{(III.18)}$$

where it has been assumed that $A_{vv}^0(\mathbf{q},\mathbf{q};E_0'(\mathbf{k}))$ is not angular-dependent with respect to $\mathbf{q}$.

Then, neglecting the second integral and evaluating the first integral by using the Cauchy theorem, one obtains

$$G_0'(\mathbf{r},\mathbf{r}';E_0'(\mathbf{k})) = -\frac{2m}{2\pi\hbar^2}\frac{1}{|\mathbf{r}-\mathbf{r}'|}\quad\text{(III.19)}$$

$$\times\sum_j\text{Res.}(q\exp(iq|\mathbf{r}-\mathbf{r}'|)G_0'(q,E_0'(\mathbf{k})))_{q=q_j}.$$

$j$ is summed over all poles of $G_0'(q,E_0'(\mathbf{k}))$. The $q_j$ are determined by

$$(G_0'(q,E_0'(\mathbf{k})))^{-1}=0.\quad\text{(III.20)}$$

It follows from Eq. (III.17) that in first-order approximation, $G_0'(\mathbf{r},\mathbf{r}';E_0'(\mathbf{k}))$ is given by

$$G_0'(\mathbf{r},\mathbf{r}';E_0'(k))\simeq -\frac{2m}{4\pi\hbar^2}\frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|},\quad\text{(III.21)}$$

which is the free-particle Green's function. The corrections to this approximation arise from many-body effects. Approximating $E_0'(\mathbf{k})$ by $E_0'(k)$, and assuming that the major contribution to the sum in Eq. (III.19)

is given by the residuum associated with the pole at $q=k$, one gets

$$G_0'(\mathbf{r},\mathbf{r}';E_0'(k))$$

$$=-\frac{2m}{2\pi\hbar^2}a_{-1}(k,|\mathbf{r}-\mathbf{r}'|)\frac{\exp(ik|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|},\quad\text{(III.22)}$$

with

$$a_{-1}(k,|\mathbf{r}-\mathbf{r}'|)\equiv 2\,\text{Res.}\{qe^{i(q-k)|\mathbf{r}-\mathbf{r}'|}G_0'(q,E_0'(k))\}_{q=k}.$$

$$\text{(III.23)}$$

$a_{-1}$ takes into account effects due to the interaction of the electron, described by the propagator $G_0'(\mathbf{r},\mathbf{r}';E_0'(k))$, with the other electrons of the system.

Using the relations

$$\int d^3\lambda\,|\lambda\rangle\langle\lambda| = (2\pi)^3\delta(\mathbf{r}-\mathbf{r}')\quad\text{(III.24)}$$

and

$$\langle\gamma|g_k|\lambda\rangle = -(2m/\hbar^2)(2\pi)^3$$
$$\times G_0'(\lambda,E_0'(k))\delta(\gamma-\lambda),\quad\text{(III.25)}$$

one gets

$$g_k t_l|\mathbf{k}\rangle = \frac{1}{2\pi^2}\int d^3q\,\exp(i\mathbf{q}\cdot\mathbf{r})G_0'(q,E_0'(k))t_l(\mathbf{q},\mathbf{k};E(\mathbf{k}))\quad\text{(III.26)}$$

and

$$\Delta\Phi_{\mathbf{k}}^{ll'} = \int d^3q\,\exp(i\mathbf{q}\cdot\mathbf{r})\left\{(1/2\pi^2)^2\int d^3\gamma\,G_0'(q,E_0'(k))t_l(\mathbf{q},\gamma;E(\mathbf{k}))G_0'(\gamma,E_0'(k))t_{l'}(\gamma,\mathbf{k};E(\mathbf{k}))\right.$$

$$+(1/2\pi^2)^3\int\int d^3\gamma\,d^3\lambda\,G_0'(q,E_0'(k))t_l(\mathbf{q},\gamma;E(\mathbf{k}))G_0'(\gamma,E_0'(k))t_{l'}(\gamma,\lambda;E(\mathbf{k}))G_0'(\lambda,E_0'(k))t_l(\lambda,\mathbf{k};E(\mathbf{k}))$$

$$\left.+\cdots\right\}.\quad\text{(III.27)}$$

The $t$ matrices $t_l(\mathbf{q},\mathbf{k};E(\mathbf{k}))$ are defined as

$$t_l(\mathbf{q},\mathbf{k};E(\mathbf{k}))\equiv -(2m/4\pi\hbar^2)\langle\mathbf{q}|t_l|\mathbf{k}\rangle.\quad\text{(III.28)}$$

$t_l$ is the $t$ matrix describing the electron scattering by $\Delta H_l'$ centered at $\mathbf{r}=\mathbf{r}_l$. $t_l$ is related to $t_l^0$ which is the $t$ matrix for scattering by $\Delta H_l'$ when centered at $\mathbf{r}=0$ by

$$t_l(\mathbf{q},\mathbf{k};E(\mathbf{k}))=\exp[i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_l]t_l^0(\mathbf{q},\mathbf{k};E(\mathbf{k})).\quad\text{(III.29)}$$

The terms $\Delta\Phi_1^{ll'l''}(\mathbf{k})$ and $\Delta\Phi_2^{ll'l''}(\mathbf{k})$ are similarly

evaluated from their graphical representation using the rules for Feynman graphs.

For a further evaluation of the expression for the scattered wave $\Delta\Phi_{\mathbf{k}}^{ll'}(\mathbf{r})$, integrals of the type

$$I(\mathbf{r}_{ll'},\sigma,\gamma,\mathbf{k})$$

$$=\int d^3\lambda\,t_l^0(\sigma,\lambda;E(\mathbf{k}))t_{l'}^0(\lambda,\gamma;E(\mathbf{k}))$$

$$\times G_0'(\lambda,E_0'(k))\exp(i\lambda\cdot\mathbf{r}_{ll'})\quad\text{(III.30)}$$

need be evaluated. Assuming that the angular dependence of the integrand with respect to $\lambda$ is essentially determined by $\exp(i\lambda \cdot \mathbf{r}_{ll'})$, the angular integrations in Eq. (III.30) are performed by putting $\lambda$ in the $t$ matrices equal to $\lambda \mathbf{r}_{ll'}/r_{ll'}$. The result is

$$I(\mathbf{r}_{ll'},\sigma,\gamma,\mathbf{k}) = \frac{4\pi}{r_{ll'}} \int_0^\infty d\lambda \lambda t_l^0\left(\sigma,\lambda\frac{\mathbf{r}_{ll'}}{r_{ll'}}; E(\mathbf{k})\right)$$

$$\times t_{l'}^0\left(\lambda\frac{\mathbf{r}_{ll'}}{r_{ll'}},\gamma; E(\mathbf{k})\right)$$

$$\times G_0'(\lambda,E_0'(k))\sin\lambda r_{ll'}. \quad \text{(III.31)}$$

Again, assuming that $\sin\lambda r_{ll'}$ varies more rapidly as a function of $\lambda$ than the $t$ matrices, the $t$ matrices can be taken out of the integral and evaluated at $\lambda$ equal to $k$.

Then, the remaining integral can be easily performed. Using the same approximation as in deriving Eq. (III.22) one gets

$$I(\mathbf{r}_{ll'},\sigma,\gamma,\mathbf{k}) = 2\pi^2 a_{-1}(k,r_{ll'})t_l^0\left(\sigma,k\frac{\mathbf{r}_{ll'}}{r_{ll'}}; E(\mathbf{k})\right)$$

$$\times t_{l'}^0\left(k\frac{\mathbf{r}_{ll'}}{r_{ll'}},\gamma; E(\mathbf{k})\right)\frac{\exp(ikr_{ll'})}{r_{ll'}}. \quad \text{(III.32)}$$

Then, making use of $t_l^0(\lambda,\gamma; E(\mathbf{k})) = t_l^0(-\gamma, -\lambda; E(\mathbf{k}))$, all multiple scattering terms in Eq. (III.27) can be summed up and one obtains:

$$\Delta\Phi_{\mathbf{k}}^{ll'}(\mathbf{R}_l) = \exp(i\mathbf{k}\cdot\mathbf{r}_l)A_{\mathbf{k}}^{ll'}F_l(\mathbf{R}_l,\mathbf{n}_{ll'},\mathbf{k}), \quad \text{(III.33)}$$

with

$$A_{\mathbf{k}}^{ll'} \equiv \frac{a_{-1}(k,r_{ll'})[\exp(ikr_{ll'})/r_{ll'}]}{1 - t_{l'}^0(k\mathbf{n}_{ll'}, -k\mathbf{n}_{ll'}; E(\mathbf{k}))t_l^0(-k\mathbf{n}_{ll'}, k\mathbf{n}_{ll'}; E(\mathbf{k}))[\exp(ikr_{ll'})/r_{ll'}]^2(a_{-1}(k,r_{ll'}))^2}$$

$$\times \{a_{-1}(k,r_{ll'})[\exp(ikr_{ll'})/r_{ll'}]t_l^0(-k\mathbf{n}_{ll'}, \mathbf{k}; E(\mathbf{k}))t_{l'}^0(k\mathbf{n}_{ll'}, -k\mathbf{n}_{ll'}; E(\mathbf{k}))$$

$$+ \exp(i\mathbf{k}\cdot\mathbf{r}_{l'l})t_{l'}^0(k\mathbf{n}_{ll'},\mathbf{k}; E(\mathbf{k}))\}, \quad \text{(III.34)}$$

where

$$\mathbf{n}_{ll'} \equiv \mathbf{r}_{ll'}/r_{ll'}, \quad \mathbf{r}_{ll'} \equiv \mathbf{r}_l - \mathbf{r}_{l'}, \quad \text{(III.35)}$$

and

$$F_l(\mathbf{R}_l,\mathbf{n}_{ll'},\mathbf{k}) \equiv \frac{1}{2\eta^2}\int d^3q \exp(i\mathbf{q}\cdot\mathbf{R}_l)G_0'(q,E_0'(k))$$

$$\times t_l^0(\mathbf{q},k\mathbf{n}_{ll'}; E(\mathbf{k})), \quad \text{(III.36)}$$

where

$$\mathbf{R}_l \equiv \mathbf{r} - \mathbf{r}_l. \quad \text{(III.37)}$$

It may be noted that if all the perturbing Hamiltonians $\Delta H_{l'}$ are equal, as in the case of a monoatomic perfect crystal, then all $t_{l'}^0(\mathbf{p},\mathbf{q}; E(\mathbf{k}))$ in Eq. (III.34) can be replaced by $t_l^0(\mathbf{p},\mathbf{q}; E(\mathbf{k}))$. The scattered wave $\Delta\Phi_{\mathbf{k}}^l$ can now be rewritten in the form

$$\Delta\Phi_{\mathbf{k}}^l = \exp(i\mathbf{k}\cdot\mathbf{r}_l)\{F_l(\mathbf{R}_l,(\mathbf{k}/k),\mathbf{k})$$

$$+ \sum_{\substack{l'\\(l'\neq l)}} (A_{\mathbf{k}}^{ll'}+\cdots)F_l(\mathbf{R}_l,\mathbf{n}_{ll'},\mathbf{k})\}. \quad \text{(III.38)}$$

Using the same argument as in evaluating I, Eq. (III.30), for large $R_l$ $t_l^0(\mathbf{q},k\mathbf{n}_{ll'}; E(\mathbf{k}))$ can be taken out of the integral in Eq. (III.36) and be evaluated at $\mathbf{q} = k\mathbf{R}_l/R_l$. One gets then

$$F_l\left(R_l\to\infty, \frac{\mathbf{k}}{k}, \mathbf{k}\right)$$

$$\approx a_{-1}(kR_l)t_l^0\left(k\frac{\mathbf{R}_l}{R_l},\mathbf{k}; E(\mathbf{k})\right)\frac{\exp(ikR_l)}{R_l}. \quad \text{(III.39)}$$

In the case of a perfect crystal the scattered wave

$\Delta\Phi_{\mathbf{k}}$ can be expanded in a Fourier series as

$$\Delta\Phi_{\mathbf{k}} = \sum_{\mathbf{K}\neq 0} \alpha_{\mathbf{K}}(\mathbf{k}) \exp[i(\mathbf{k}+\mathbf{K})\cdot\mathbf{r}], \quad \text{(III.40)}$$

where $\mathbf{K}$ is a reciprocal lattice vector. Using Eqs. (III.5) and (III.38) one gets

$$\alpha_{\mathbf{K}}(\mathbf{k}) = \frac{S_{\mathbf{K}}}{\Omega_0}\{T_{\mathbf{K}}(\mathbf{k}) + \sum_{\substack{l'\\(l'\neq l_0)}} (A_{\mathbf{k}}^{l_0l'}+\cdots)T_{\mathbf{K}}(k\mathbf{n}_{l_0l'})\},$$

$$\text{(III.41)}$$

with

$$T_{\mathbf{K}}(\mathbf{p}) = \int d^3R_{l_0} \exp[-i(\mathbf{k}+\mathbf{K})\cdot\mathbf{R}_{l_0}]F_l(\mathbf{R}_{l_0},(\mathbf{p}/p),\mathbf{p}),$$

$$(\mathbf{p}=\mathbf{k}, k\mathbf{n}_{l_0l'}). \quad \text{(III.42)}$$

$\Omega_0$ denotes the volume of a unit lattice cell and $l_0$ denotes any one of the lattice ions. $S_{\mathbf{K}}$ is called the structure factor and is given by

$$S_{\mathbf{K}} = \sum_j \exp(-i\mathbf{K}\cdot\mathbf{d}_j), \quad \text{(III.43)}$$

where the $\mathbf{d}_j$ are the position vectors of the lattice ions $j$ within the unit lattice cell. $j$ is summed over all ions within the unit lattice cell. Using Eq. (III.36), Eq. (III.42) can be rewritten as

$$T_{\mathbf{K}}(\mathbf{p}) = 4\pi G_0'(|\mathbf{k}+\mathbf{K}|, E_0'(p))$$

$$\times t_{l_0}^0(\mathbf{k}+\mathbf{K}, \mathbf{p}; E(\mathbf{k})). \quad \text{(III.44)}$$

In order to get self-consistent wave functions $\psi_{\mathbf{k}}$, the $t$ matrices $t_l^0(\mathbf{q},\mathbf{k}; E(\mathbf{k}))$ need be determined self-consistently. This requires a self-consistent determination of $\Delta H_l'$. In the next two sections we discuss the

self-consistent determination of the scattering amplitude $t_l^0(\mathbf{q},\mathbf{k};E(\mathbf{k}))$ and the crystal potential $\Delta H_l'$.

## IV. SELF-CONSISTENT DETERMINATION OF THE $T$ MATRIX $t_l^0(\mathbf{q},\mathbf{k};E(\mathbf{k}))$

It is useful for determining self-consistently the $t$ matrices $t_l^0$ to derive an integral equation for $t^0(\mathbf{q},\mathbf{k};E(\mathbf{k}))$. Because of

$$t_l|\mathbf{k}\rangle = (\Delta H_l' - \Delta E_l)|\mathbf{k}\rangle + (\Delta H_l' - \Delta E_l)g_k(\Delta H_l' - \Delta E_l)$$
$$\times (1 - g_k(\Delta H_{l'} - \Delta E_l))^{-1}|\mathbf{k}\rangle, \quad \text{(IV.1)}$$

one gets

$$t_l^0(\mathbf{q},\mathbf{k};E(\mathbf{k})) = -\frac{2m}{4\pi\hbar^2}\langle\mathbf{q}|\Delta H_l' - \Delta E_l|\mathbf{k}\rangle$$

$$-\frac{2m}{4\pi\hbar^2}\langle\mathbf{q}|(\Delta H_{l'} - \Delta E_l)g_k t_l|\mathbf{k}\rangle. \quad \text{(IV.2)}$$

Neglecting $\Delta E_l$ and evaluating the second term in Eq. (IV.2) by using the relations (III.24), (III.25), and (III.28) one gets for $t_l^0$ the integral equation

$$t_l^0(\mathbf{q},\mathbf{k};E(\mathbf{k})) = -(2m/4\pi\hbar^2)(\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k}))^0$$

$$-\frac{2m}{(2\pi)^3\hbar^2}\int d^3p(\Delta H_l'(\mathbf{q},\mathbf{p};E(\mathbf{k}))^0$$

$$\times G_0'(p,E_0'(k))t_l^0(\mathbf{p},\mathbf{k};E(\mathbf{k})). \quad \text{(IV.3)}$$

The matrix element $(\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k}))^0$ is defined as

$$(\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k})))^0 \equiv \int d^3R_l \exp(-i\mathbf{q}\cdot\mathbf{R}_l)$$

$$\times \Delta H_l'(\mathbf{R}_l,E(\mathbf{k})) \exp(i\mathbf{k}\cdot\mathbf{R}_l). \quad \text{(IV.4)}$$

$\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k}))$ is defined as

$$\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k})) = \exp[i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_l]$$
$$\times (\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k})))^0. \quad \text{(IV.5)}$$

The integral Eq. (IV.3) can be solved by iteration. Since $(\Delta H_l')^0$ involves $t_l^0$, the self-consistent determination of $t_l^0$ is performed as indicated by

$$(\Delta H_l')^0 \rightleftharpoons t_l^0. \quad \text{(IV.6)}$$

To obtain a self-consistent expression for

$$\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k})) \equiv (\Delta V_i^l(\mathbf{q},\mathbf{k};0)' + \Delta V_R^l(\mathbf{q},\mathbf{k};E(\mathbf{k}))$$
$$+\Delta C_l(\mathbf{q},\mathbf{k})+\Delta A_{vv}^l(\mathbf{q},\mathbf{k};E(\mathbf{k})), \quad \text{(IV.7)}$$

the matrix elements $\Delta C_l$ and $\Delta A_{vv}^l$ need be determined self-consistently. The potential $\Delta C_l$ arises from the polarization of the valence electron Fermi sea induced by $\Delta H_l$ which results from $\Delta H_l'$ for $\Delta V_R^l \equiv 0$. This amounts to an effective, e.g., screened one-body potential

$$(\Delta V_i^l)_s' \equiv (\Delta V_i^l)' + \Delta C_l. \quad \text{(IV.8)}$$

$(\Delta V_i^l)_s'$ and $\Delta A_{vv}^l$ are determined in detail in the next section.

If $\Delta H_l'(\mathbf{R}_l,E(\mathbf{k}))$ is a smooth potential, then Eq. (IV.3) is solved by

$$t_l^0(\mathbf{q},\mathbf{k};E(\mathbf{k})) = -\frac{2m}{4\pi\hbar^2}\frac{(\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k})))^0}{1+\dfrac{2m}{(2\pi)^3\hbar^2}\displaystyle\int d^3p G_0'(p,E_0'(k))(\Delta H_l'(\mathbf{q},\mathbf{p};E(\mathbf{k})))^0}. \quad \text{(IV.9)}$$

## V. SELF-CONSISTENT DETERMINATION OF $\Delta H_l'(\mathbf{q},\lambda;E(\mathbf{k}))$

Assuming that the eigenfunctions $\varphi_{l,k}$ are self-consistent, then the self-consistent determination of $\Delta H_l'$ is reduced to the self-consistent determination of $\Delta H_l$. To determine self-consistently $\Delta H_l(\mathbf{q},\lambda;E(\mathbf{k}))$, the dependence of the potential $\Delta C_l(\mathbf{r})$ and the operator $\Delta A_{vv}^l(\mathbf{r},E(\mathbf{k}))$ on $\Delta H_l(\mathbf{r},E(\mathbf{k}))$ need be evaluated explicitly. First, $\Delta C(\mathbf{r})$ is given by[9]

$$\Delta C(\mathbf{r}) = -2i\int\int d^3r'\frac{dp_0}{2\pi}V|\mathbf{r}-\mathbf{r}'|$$

$$\times\{G(\mathbf{r}',\mathbf{r}',p_0) - G_0(\mathbf{r}',\mathbf{r}',p_0)\}, \quad \text{(V.1)}$$

with

$$V(|\mathbf{r}-\mathbf{r}'|) = e^2/|\mathbf{r}-\mathbf{r}'|. \quad \text{(V.2)}$$

The exact one-electron Green's function $G(\mathbf{r},\mathbf{r}',p_0)$ is defined by

$$\{H-p_0\}G(\mathbf{r},\mathbf{r}',p_0) = -\delta(\mathbf{r}-\mathbf{r}') \quad \text{(V.3)}$$

and the same boundary conditions as imposed on the Green's function $G_0''$. The Green's function $G_0(\mathbf{r},\mathbf{r}',p_0)$ is defined by Eq. (V.3), replacing the Hamiltonian $H$ by $\{H_0' - V_R(\mathbf{k},\mathbf{k};E(\mathbf{k}))\}$. Converting Eq. (V.3) into an integral equation one gets

$$G(\mathbf{r},\mathbf{r}',p_0) = G_0(\mathbf{r},\mathbf{r}',p_0)$$

$$+ \int d^3r'' G_0(\mathbf{r},\mathbf{r}'',p_0)\Delta H(\mathbf{r}'',p_0)$$

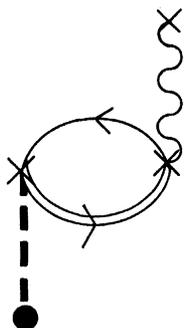$$\times G(\mathbf{r}'',\mathbf{r}',p_0). \quad \text{(V.4)}$$

Equation (V.1) can then be rewritten as

$$\Delta C(\mathbf{r}) = \sum_l \Delta C_l(\mathbf{r}), \quad \text{(V.5)}$$

with

$$\Delta C_l(\mathbf{r}) = -2i\int\int\int d^3r' d^3r''\frac{dp_0}{2\pi}V(|\mathbf{r}-\mathbf{r}'|)$$

$$\times G_0(\mathbf{r}',\mathbf{r}'',p_0)\Delta H_l(\mathbf{r}'',p_0)G(\mathbf{r}'',\mathbf{r}',p_0), \quad \text{(V.6)}$$

which is pictorially represented in Fig. 2. The wavy and striped line represent the electron-electron interaction

Fig. 2. Determination of $\Delta C_l$.

and the interaction due to $\Delta H_l$, respectively. The upper and lower half-circle represent the Green's function $G_0$ and $G$, respectively. Expressing $G$ in terms of the wave functions $\psi_p$ as

$$G(\mathbf{r},\mathbf{r}',p_0)=\Omega \int \frac{d^3p}{(2\pi)^3}G(\mathbf{p},p_0)\psi_p(\mathbf{r})\psi_p{}^*(\mathbf{r}'), \quad (V.7)$$

with

$$G(p,p_0)=[E(\mathbf{p})-p_0-i\epsilon]^{-1}, \quad (V.8)$$

where $\epsilon$ is defined as in $G_0''$, Fourier transforming the potential $V$ and $G_0$, then the matrix element $\Delta C_l(\mathbf{q},\lambda)$ is given by

$$\Delta C_l(\mathbf{q},\lambda)=-2i\Omega \int \int \int \frac{dp_0}{2\pi}\frac{d^3p}{(2\pi)^3}\frac{d^3p'}{(2\pi)^3}V(|\mathbf{q}-\lambda|)$$

$$\times G_0(p',p_0)G(\mathbf{p},p_0)\langle\psi_p|\mathbf{p}'+\lambda-\mathbf{q}\rangle$$

$$\times \langle \mathbf{p}'|\Delta H_l|\psi_p\rangle, \quad (V.9)$$

with

$$V(|\mathbf{q}-\lambda|)=4\pi e^2/|\mathbf{q}-\lambda|^2. \quad (V.10)$$

Approximating $G$ by $G_0$ yields the random phase approximation.[9] Assuming momentum conservation one obtains $\mathbf{p}=\mathbf{p}'+\lambda-\mathbf{q}$. This result would follow automatically from the evaluation of the matrix element $\langle\psi_p|\mathbf{p}'+\lambda-\mathbf{q}\rangle$ in the case of a uniform electron gas and in the case of a perfect crystal when momentum exchange between lattice and electrons is neglected.[10] The integration over $p_0$ in Eq. (V.9) yields the factor $f_p(1-f_{p+q-\lambda})$, where $f_p$ and $f_{p+q-\lambda}$ denote the Fermi distribution function. This implies that the matrix element $\langle\psi_p|\mathbf{p}\rangle$ can be taken out of the integral in Eq. (V.9) and can be replaced by $\langle\psi_p|\mathbf{p}\rangle_{av}$, which is averaged over values of $\mathbf{p}$ within the Fermi sea.[10] It follows then for $\Delta C_l$ the approximate expression

$$\Delta C_l(\mathbf{q},\lambda)=-2i\Omega V(|\mathbf{q}-\lambda|)$$

$$\times\langle\psi_p|\mathbf{p}\rangle_{av}\int\int\frac{dp_0}{2\pi}\frac{d^3p}{(2\pi)^3}G_0(|\mathbf{p}+\mathbf{q}-\lambda|,p_0)$$

$$\times G(\mathbf{p},p_0)\langle\mathbf{p}+\mathbf{q}-\lambda|\Delta H_l|\psi_p\rangle. \quad (V.11)$$

[10] F. Bassani, J. Robinson, B. Goodman, and J. R. Schrieffer, Phys. Rev. **127**, 1969 (1962).

Using formula (III.24), Eq. (V.11) can be rewritten as

$$\Delta C_l(\mathbf{q},\lambda)=-2i\Omega V(|\mathbf{q}-\lambda|)$$

$$\times\langle\psi_p|\mathbf{p}\rangle_{av}\int\frac{d^3\sigma}{(2\eta)^3}\langle\sigma|\psi_p\rangle_{av}$$

$$\times\int\int\frac{dp_0}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}G_0(|\mathbf{p}+\mathbf{q}-\lambda|,p_0)$$

$$\times G(\mathbf{p},p_0)\Delta H_l(\mathbf{p}+\mathbf{q}-\lambda,\sigma;p_0), \quad (V.12)$$

where $\langle\sigma|\psi_p\rangle_{av}$ is averaged over all values of $\mathbf{p}$ within the Fermi sea.

The sum of the potentials $(\Delta V_i{}^l)'$ and $\Delta C_l$ yields an effective, e.g., screened, one-body potential denoted by $(\Delta V_i{}^l)_s{}'$. The screening of the one-body potential $(\Delta V_i{}^l)'$ arises from the polarization of the valence electron Fermi sea induced by $(\Delta V_i{}^l)'$ itself. As was shown by Ehrenreich and Cohen,[11] this screened potential is, to first order in the external potential $(\Delta V_i{}^l)'$, equivalent to $\Delta H_l$ obtained within the Hartree approximation.

The dependence of $\Delta A_{vv}{}^l(\mathbf{q},\lambda;E(\mathbf{k}))$ on $\Delta H_l$ is evaluated as follows. The operator $\Delta A_{vv}(\mathbf{r},E(\mathbf{k}))$ is defined as

$$\Delta A_{vv}(\mathbf{r},E(\mathbf{k}))\exp(i\lambda\cdot\mathbf{r})$$

$$=\int d^3r'\{\Sigma(\mathbf{r},\mathbf{r}';E(\mathbf{k}))-\Sigma_0(\mathbf{r},\mathbf{r}',E_0(\mathbf{k}))\}$$

$$\times\exp(i\lambda\cdot\mathbf{r}'), \quad (V.13)$$

where $\Sigma$ and $\Sigma_0$ denote that part of the irreducible valence electron self-energy which is not taken into account in the Hartree approximation. $\Sigma$ results from the Hamiltonian $H$ and $\Sigma_0$ from $H_0$ which is obtained from $H_0'$ for $V_R(\mathbf{k},\mathbf{k};E(\mathbf{k}))\equiv0$. The self-energies are determined according to the diagram given in Fig. 3. The wavy line represents a screened electron-electron interaction and the straight double line represents the exact one-electron Green's function $G$. One gets[9]

$$\Sigma(\mathbf{r},\mathbf{r}';E(\mathbf{k}))$$

$$=i\int\frac{dp_0}{2\pi}V_s(\mathbf{r},\mathbf{r}',p_0)G(\mathbf{r},\mathbf{r}',E(\mathbf{k})-p_0), \quad (V.14)$$

where $V_s$ denotes the screened electron-electron interaction which is determined in detail later on in this section. $\Sigma_0(\mathbf{r},\mathbf{r}';E_0(\mathbf{k}))$ is obtained from Eq. (V.14) replacing $V_s$ by $V_s{}^0$, which refers to the case
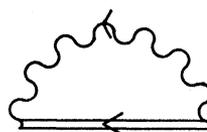


Fig. 3. Diagram for the self-energy $\Sigma$.

[11] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

of a uniform electron gas, and $G(\mathbf{r}, \mathbf{r}', E(\mathbf{k}) - p_0)$ by $G_0(\mathbf{r}, \mathbf{r}', E_0(\mathbf{k}) - p_0)$. Using then Eqs. (V.4) and (V.7), approximating the term $V_s G_0$ by $V_s^0 G_0$, Fourier transforming $V_s$ and $G_0$, and using formula (III.24), one obtains

$$\Delta A_{vv}{}^l(\mathbf{q}, \boldsymbol{\lambda}; E(\mathbf{k}))$$

$$= i\Omega \int\int\int\int \frac{dp_0}{2\pi} \frac{d^3p}{(2\pi)^3} \frac{d^3p'}{(2\pi)^3} \frac{d^3\sigma}{(2\pi)^3} V_s(\mathbf{p}, p_0)$$

$$\times G_0(|\mathbf{q} - \mathbf{p}|, E_0(k) - p_0) G(\mathbf{p}', E(\mathbf{k}) - p_0) \langle \sigma | \psi_{\mathbf{p}'} \rangle$$

$$\times \langle \psi_{\mathbf{p}'} | \boldsymbol{\lambda} - \mathbf{p} \rangle \Delta H_l(\mathbf{q} - \mathbf{p}, \sigma; E(\mathbf{k}) - p_0). \quad (V.15)$$

Assuming momentum conservation, one gets $\mathbf{q} = \boldsymbol{\lambda} = \mathbf{p} + \mathbf{p}'$. Then Eq. (V.15) can approximately be rewritten as

$$\Delta A_{vv}{}^l(\mathbf{q}, \boldsymbol{\lambda}; E(\mathbf{k}))$$

$$= i\Omega(2\pi)^3 \delta(\mathbf{q} - \boldsymbol{\lambda}) \langle \psi_{\mathbf{q}-\mathbf{p}} | \mathbf{q} - \mathbf{p} \rangle_{\mathrm{av}} \int \frac{d^3\sigma}{(2\pi)^3} \langle \sigma | \psi_{\mathbf{q}-\mathbf{p}} \rangle$$

$$\times \int\int \frac{dp_0}{2\pi} \frac{d^3p}{(2\pi)^3} V_s(\mathbf{p}, p_0) G_0(|\mathbf{q} - \mathbf{p}|, E_0(k) - p_0)$$

$$\times G(\mathbf{q} - \mathbf{p}, E(\mathbf{k}) - p_0) \Delta H_l(\mathbf{q} - \mathbf{p}, \sigma; E(\mathbf{k}) - p_0), \quad (V.16)$$

where the matrix elements are averaged over values of $\mathbf{p}$ within the Fermi sea. In a further approximation the Green's function $G(\mathbf{q} - \mathbf{p}, E(\mathbf{k}) - p_0)$ can be approached by $G_0(|\mathbf{q} - \mathbf{p}|, E_0(k) - p_0)$.

The wave functions $\psi_{\mathbf{p}}$ in the matrix elements involved in the formulas for $\Delta C_l(\mathbf{q}, \boldsymbol{\lambda})$ and $\Delta A_{vv}{}^l(\mathbf{q}, \boldsymbol{\lambda}; E(\mathbf{k}))$ can be approximated by the wave functions $\psi_{\mathbf{p}}$ which result from approximating $\Delta H_l$ by $(\Delta V_i{}^l)'$.

It follows from Eqs. (V.11) and (V.15) that $\Delta H_l(\mathbf{q}, \boldsymbol{\lambda}; E(\mathbf{k}))$ is self-consistently determined by

$$\Delta H_l(\mathbf{q}, \boldsymbol{\lambda}; E(\mathbf{k}))$$

$$= (\Delta V_i{}^l(\mathbf{q}, \boldsymbol{\lambda}; 0))' + \int\int\int \frac{dp_0}{2\pi} \frac{d^3p}{(2\pi)^3} \frac{d^3\sigma}{(2\pi)^3}$$

$$\times \{ \Theta(\mathbf{q}, \boldsymbol{\lambda}, p_0, \mathbf{p}, \sigma) \Delta H_l(\mathbf{p} + \mathbf{q} - \boldsymbol{\lambda}, \sigma; p_0)$$

$$+ \Gamma(\mathbf{q}, \boldsymbol{\lambda}, E(\mathbf{k}) - p_0, \mathbf{p}, \sigma) \Delta H_l(\mathbf{q} - \mathbf{p}, \sigma; E(\mathbf{k}) - p_0) \}, \quad (V.17)$$

with

$$\Theta(\mathbf{q}, \boldsymbol{\lambda}, p_0 \mathbf{p}, \sigma) \equiv -2i\Omega V(|\mathbf{q} - \boldsymbol{\lambda}|)$$

$$\times \langle \psi_{\mathbf{p}} | \mathbf{p} \rangle_{\mathrm{av}} G_0(|\mathbf{p} + \mathbf{q} - \boldsymbol{\lambda}|, p_0) G(\mathbf{p}, p_0) \langle \sigma | \psi_{\mathbf{p}} \rangle \quad (V.18)$$

and

$$\Gamma(\mathbf{q}, \boldsymbol{\lambda}, E(\mathbf{k}) - p_0, \mathbf{p}, \sigma)$$

$$\equiv i\Omega(2\pi)^3 \delta(\mathbf{q} - \boldsymbol{\lambda}) V_s(\mathbf{p}, p_0) G_0(|\mathbf{q} - \mathbf{p}|, E_0(k) - p_0)$$

$$\times G(\mathbf{q} - \mathbf{p}, E(\mathbf{k}) - p_0) \langle \sigma | \psi_{\mathbf{q}-\mathbf{p}} \rangle \langle \psi_{\mathbf{q}-\mathbf{p}} | \mathbf{q} - \mathbf{p} \rangle. \quad (V.19)$$
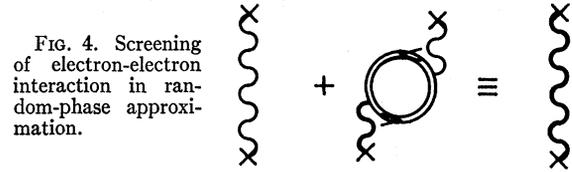


FIG. 4. Screening of electron-electron interaction in random-phase approximation.

The local part of $\Delta H_l$, denoted as $(\Delta V_i{}^l)_s'$, is then approximately given by

$$(\Delta V_i{}^l(\mathbf{q} - \boldsymbol{\lambda}; 0))_s' = \frac{(\Delta V_i{}^l(\mathbf{q} - \boldsymbol{\lambda}; 0))'}{\kappa(\mathbf{q} - \boldsymbol{\lambda}; 0)}, \quad (V.20)$$

with

$$\kappa(\mathbf{q} - \boldsymbol{\lambda}; 0) \equiv 1 - \int\int\int \frac{d^3p}{(2\pi)^3} \frac{d^3\sigma}{(2\pi)^3} \frac{dp_0}{2\pi}$$

$$\times \Theta(\mathbf{q}, \boldsymbol{\lambda}, p_0, \mathbf{p}, \sigma). \quad (V.21)$$

$\kappa(\mathbf{q} - \boldsymbol{\lambda}; 0)$ can approximately be rewritten as

$$\kappa(\mathbf{q} - \boldsymbol{\lambda}; 0) = 1 + i\Omega V(|\mathbf{q} - \boldsymbol{\lambda}|)$$

$$\times \int \frac{d^3\sigma}{(2\pi)^3} \langle \psi_{\mathbf{p}} | \mathbf{p} \rangle_{\mathrm{av}} \langle \sigma | \psi_{\mathbf{p}} \rangle_{\mathrm{av}} P_0(\mathbf{q} - \boldsymbol{\lambda}; 0), \quad (V.22)$$

where $P_0(\mathbf{q} - \boldsymbol{\lambda}; 0)$ is given by

$$P_0(\mathbf{q} - \boldsymbol{\lambda}; 0) \equiv 2 \int\int \frac{dp_0}{2\pi} \frac{d^3p}{(2\pi)^3}$$

$$\times G_0(|\mathbf{p} + \mathbf{q} - \boldsymbol{\lambda}|, p_0) G(\mathbf{p}, p_0). \quad (V.23)$$

If the Green's function $G$ is approximated by $G_0$ then $P_0$ is the polarization propagator in the random-phase approximation for a uniform electron gas. An explicit expression for this polarization propagator is given by Lindhard.[12]

In the general case, where the potential $\Delta H_l$ is not local, $\Delta H_l(\mathbf{q}, \boldsymbol{\lambda}; E(\mathbf{k}))$ can be determined approximately by substituting on the right-hand side in Eq. (V.17) for $\Delta H_l$ the expression for $(\Delta V_i{}^l)_s'$. In the limit $p \to 0$, see Eq. (V.17), $\Delta H_l$ is given by $(\Delta V_i{}^l)_s'$.

The screened interaction $V_s$ among the valence electrons is determined as indicated by the diagram in Fig. 4. In Fig. 4 the wavy light lines represent unscreened electron-electron interaction and the wavy heavy lines represent screened electron-electron interaction. Using Eq. (V.7) and assuming momentum conservation one gets

$$V_s(\mathbf{q}, q_0) = V(q) / \epsilon(\mathbf{q}, q_0), \quad (V.24)$$

where the dielectric function $\epsilon(\mathbf{q}, q_0)$ is given by

$$\epsilon(\mathbf{q}, q_0) \equiv 1 + iV(q) P(\mathbf{q}, q_0). \quad (V.25)$$

[12] J. Lindhard, Kgl. Danske Videnskab, Selskab, Mat.-Fys. Medd. 28, 8 (1954).

The polarization propagator $P(\mathbf{q},q_0)$ is determined by

$$P(\mathbf{q},q_0) \equiv 2 \int \int \frac{d^3p}{(2\pi)^3} \frac{dp_0}{2\pi} G(\mathbf{p},p_0) G(\mathbf{p}+\mathbf{q},\, p_0+q_0)$$

$$\times \langle \psi_\mathbf{p} | \exp(-i\mathbf{q}\cdot\mathbf{r}) | \psi_{\mathbf{p}+\mathbf{q}} \rangle$$

$$\times \langle \psi_{\mathbf{p}+\mathbf{q}} | \exp(i\mathbf{q}\cdot\mathbf{r}) | \psi_\mathbf{p} \rangle. \quad (\text{V.26})$$

Since the integration over $p_0$ yields the factor $f_\mathbf{p} \times (1-f_{\mathbf{p}+\mathbf{q}})$, one gets for $P(\mathbf{q},p_0)$ the approximate expression

$$P(\mathbf{q},q_0) = 2\langle \psi_\mathbf{p} | \exp(-i\mathbf{q}\cdot\mathbf{r}) | \psi_{\mathbf{p}+\mathbf{q}} \rangle_{\text{av}}$$

$$\times \langle \psi_{\mathbf{p}+\mathbf{q}} | \exp(i\mathbf{q}\cdot\mathbf{r}) | \psi_\mathbf{p} \rangle_{\text{av}}$$

$$\times \int \frac{d^3p}{(2\pi)^3} \frac{dp_0}{2\pi} G(\mathbf{p},p_0) G(\mathbf{p}+\mathbf{q},\, p_0+q_0). \quad (\text{V.27})$$

The matrix elements are averaged over values of $\mathbf{p}$ within the Fermi sea. Approximating the Green's functions $G$ in Eq. (V.27) by the Green's functions $G_0$,

then $P(\mathbf{q},q_0)$ is given by

$$P(\mathbf{q},q_0) = \langle \psi_\mathbf{p} | \exp(-i\mathbf{q}\cdot\mathbf{r}) | \psi_{\mathbf{p}+\mathbf{q}} \rangle_{\text{av}}$$

$$\times \langle \psi_{\mathbf{p}+\mathbf{q}} | \exp(i\mathbf{q}\cdot\mathbf{r}) | \psi_\mathbf{p} \rangle_{\text{av}} P_{00}(q,q_0), \quad (\text{V.28})$$

where $P_{00}$ is given by Eq. (V.23) putting $G=G_0$.

## VI. ELECTRON ENERGIES

The energy of a valence or conduction electron with momentum $\mathbf{k}$ is given by $\text{Re}E(\mathbf{k})$ where it follows from the wave Eq. (II.9) that $E(\mathbf{k})$ is determined by

$$E(\mathbf{k}) = \langle \Phi_\mathbf{k} | H' | \Phi_\mathbf{k} \rangle / \langle \Phi_\mathbf{k} | \Phi_\mathbf{k} \rangle. \quad (\text{VI.1})$$

Then, using Eqs. (II.12), (III.3), (III.24), (IV.4), and (IV.5), one obtains

$$E(\mathbf{k}) = E_0'(\mathbf{k}) + \sum_l (\Delta E(\mathbf{k}))_l, \quad (\text{VI.2})$$

where $\langle \mathbf{k} | H_0' | \mathbf{k} \rangle / \langle \Phi_\mathbf{k} | \Phi_\mathbf{k} \rangle$ has been approximated by

$$E_0'(\mathbf{k}) = \Omega^{-1} \langle \mathbf{k} | H_0' | \mathbf{k} \rangle, \quad (\text{VI.3})$$

and where $(\Delta E(\mathbf{k}))_l$ is given by

$$(\Delta E(\mathbf{k}))_l = \frac{1}{\langle \Phi_\mathbf{k} | \Phi_\mathbf{k} \rangle} \left\{ \frac{\hbar^2 k^2}{2m} (\langle \Delta \Phi_\mathbf{k}^l | \mathbf{k} \rangle + \text{c.c.}) + \frac{\hbar^2}{2m} \int \frac{d^3p}{(2\pi)^3} p^2 \langle \Delta \Phi_\mathbf{k}^l | \mathbf{p} \rangle \langle \mathbf{p} | \Delta \Phi_\mathbf{k} \rangle \right.$$

$$+ \int \frac{d^3p}{(2\pi)^3} \left[ \langle \Delta \Phi_\mathbf{k}^l | \mathbf{p} \rangle A_{vv}^0(\mathbf{p},\mathbf{k};\, E_0'(\mathbf{k})) + \langle \mathbf{p} | \Delta \Phi_\mathbf{k}^l \rangle A_{vv}^0(\mathbf{k},\mathbf{p};\, E_0'(\mathbf{k})) \right.$$

$$\left. + \int \frac{d^3q}{(2\pi)^3} \langle \Delta \Phi_\mathbf{k}^l | \mathbf{p} \rangle \langle \mathbf{q} | \Delta \Phi_\mathbf{k} \rangle A_{vv}^0(\mathbf{p},\mathbf{q};\, E_0'(\mathbf{k})) \right] + \int \int \frac{d^3p}{(2\pi)^3} \frac{d^3q}{(2\pi)^3} \langle \Phi_\mathbf{k} | \mathbf{q} \rangle \langle \mathbf{p} | \Phi_\mathbf{k} \rangle \Delta H_l'(\mathbf{q},\mathbf{p};\, E(\mathbf{k})) \right\}. \quad (\text{VI.4})$$

Due to $\Delta H_l'(\mathbf{q},\mathbf{p};\, E(\mathbf{k}))$, the energy $E(\mathbf{k})$ is given by Eq. (VI.2) implicitly. Equation (VI.2) can be solved by iteration.[13] In first-order approximation $E(\mathbf{k})$ can be approximated in $\Delta H_l'$ by $E_0'(\mathbf{k})$. Equation (VI.2) can be rewritten in the form

$$E(\mathbf{k}) = E_0'(\mathbf{k}) + \frac{1}{\langle \Phi_\mathbf{k} | \Phi_\mathbf{k} \rangle} \sum_{\mathbf{K},\mathbf{K}'} \left\{ \alpha_\mathbf{K}^*(\mathbf{k}) \alpha_{\mathbf{K}'}(\mathbf{k}) \left[ \Omega \frac{\hbar^2}{2m} (\mathbf{k}+\mathbf{K})^2 \delta_{\mathbf{K},\mathbf{K}'} + A_{vv}^0(\mathbf{k}+\mathbf{K},\, \mathbf{k}+\mathbf{K}';\, E_0'(\mathbf{k})) \right] \right.$$

$$\left. + \frac{N}{s} S_{\mathbf{K}-\mathbf{K}'} (\delta_{\mathbf{K},0} + \alpha_\mathbf{K}^*(\mathbf{k}))(\delta_{\mathbf{K}',0} + \alpha_{\mathbf{K}'}(\mathbf{k}))(\Delta H_{l_0}'(\mathbf{k}+\mathbf{K},\, \mathbf{k}+\mathbf{K}';\, E(\mathbf{k})))^0 \right\} + E_F(\mathbf{k}), \quad (\text{VI.5})$$

where $s$ denotes the number of atoms per unit lattice cell and where $E_F(\mathbf{k})$, denoting the change in energy of the perfect crystal due to crystal imperfections, is defined as

$$E_F(\mathbf{k}) \equiv \sum_{l'} (\Delta E(\mathbf{k}))_{l'} - \sum_l (\Delta E(\mathbf{k}))_l^{(0)}. \quad (\text{VI.6})$$

$(\Delta E(\mathbf{k}))_l^{(0)}$ refers to the perfect crystal, e.g., $(\Delta E(\mathbf{k}))_l$ in the case of a perfect crystal. $l'$ and $l$ are summed over all atomic nuclei in the imperfect and perfect crystal, respectively. For example, in the case of a vacancy at a lattice site $l=V$ it is $(\Delta E(\mathbf{k}))_{l'=V} \equiv 0$. However, the vacancy at the lattice site $l=V$ is created by bringing the lattice atom which occupies in the perfect crystal this lattice site $l$ to the surface and, of course, the term $(\Delta E(\mathbf{k}))_{l'}$ associated with the surface atom appears in the sum over $l'$. An interstitial is created by bringing a surface atom into an interstitial position in the interior of the crystal. Thus, the term $(\Delta E(\mathbf{k}))_l^{(0)}$ associated with this surface atom is omitted in the sum over $l'$ and instead of it the term due to the interstitial appears. In first-order approximation

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[13] P. O. Löwdin, Suppl. J. Appl. Phys. 33, 251 (1962).

$(\Delta E(\mathbf{k}))_l$ is given by

$$(\Delta E(\mathbf{k}))_l = \frac{1}{\langle \Phi_{\mathbf{k}}|\Phi_{\mathbf{k}}\rangle}\left\{ \frac{\hbar^2 k^2}{2m}\langle \Delta \Phi_{\mathbf{k}}{}^l|\mathbf{k}\rangle + \text{c.c.} + \sum_{\mathbf{K}\neq 0}\alpha_{\mathbf{k}}(\mathbf{k})\frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K})^2\langle \Delta\Phi_{\mathbf{k}}{}^l|\mathbf{k}+\mathbf{K}\rangle + \int \frac{d^3p}{(2\pi)^3} \right.$$

$$\times [\langle \Delta\Phi_{\mathbf{k}}{}^l|\mathbf{p}\rangle A_{vv}{}^0(\mathbf{p},\mathbf{k};E_0'(\mathbf{k})) + \langle \mathbf{p}|\Delta\Phi_{\mathbf{k}}{}^l\rangle A_{vv}{}^0(\mathbf{k},\mathbf{p};E_0'(\mathbf{k})) + \sum_{\mathbf{K}\neq 0}\alpha_{\mathbf{K}}(\mathbf{k})\langle \Delta\Phi_{\mathbf{k}}{}^l|\mathbf{p}\rangle A_{vv}{}^0(\mathbf{p},\mathbf{k}+\mathbf{K};E_0'(\mathbf{k}))]$$

$$\left. + \sum_{\mathbf{K},\mathbf{K}'}(\delta_{\mathbf{K},0}+\alpha_{\mathbf{K}}{}^*(\mathbf{k}))(\delta_{\mathbf{K}',0}+\alpha_{\mathbf{K}'}(\mathbf{k}))\exp[-i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}_l](\Delta H_l'(\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{K}';E(\mathbf{k})))^0 \right\}. \quad (VI.7)$$

If multiple electron scattering is neglected, then $(\Delta H_l')^0$ becomes independent of $\mathbf{r}_l$. The redistribution of the electronic energy levels due to the imperfections is determined by $E_F(\mathbf{k})$. This is of importance in determining the optical properties of imperfections. The single-electron energy $E(\mathbf{k})$ given by Eq. (VI.2) includes correlation among the valence electrons. $E(\mathbf{k})$ is in general complex. The imaginary part of $E(\mathbf{k})$ determines the lifetime of the electron state $\Phi_{\mathbf{k}}$.

The total energy of the system of valence or conduction electrons is given by

$$E = \sum_{\mathbf{k}}\{E_0'(\mathbf{k}) - \tfrac{1}{2}[C_0 + A_{vv}{}^0(\mathbf{k},\mathbf{k};E_0'(\mathbf{k}))]\} + \sum_l \Delta E_l, \quad (VI.8)$$

with

$$\Delta E_l = \sum_{\mathbf{k}}\frac{1}{\langle\Phi_{\mathbf{k}}|\Phi_{\mathbf{k}}\rangle}\left\{ \frac{\hbar^2 k^2}{2m}\langle\Delta\Phi_{\mathbf{k}}{}^l|\mathbf{k}\rangle + \text{c.c.} + \frac{\hbar^2}{2m}\int\frac{d^3p}{(2\pi)^3}p^2\langle\Delta\Phi_{\mathbf{k}}{}^l|\mathbf{p}\rangle\langle\mathbf{p}|\Delta\Phi_{\mathbf{k}}\rangle + \frac{1}{2}\int\frac{d^3p}{(2\pi)^3} \right.$$

$$\times\left[ \langle\Delta\Phi_{\mathbf{k}}{}^l|\mathbf{p}\rangle A_{vv}{}^0(\mathbf{p},\mathbf{k};E_0'(\mathbf{k})) + \langle\mathbf{p}|\Delta\Phi_{\mathbf{k}}{}^l\rangle A_{vv}{}^0(\mathbf{k},\mathbf{p};E_0'(\mathbf{k})) + \int\frac{d^3q}{(2\pi)^3}\langle\Delta\Phi_{\mathbf{k}}{}^l|\mathbf{p}\rangle\langle\mathbf{q}|\Delta\Phi_{\mathbf{k}}\rangle A_{vv}{}^0(\mathbf{p},\mathbf{q};E_0'(\mathbf{k})) \right]$$

$$\left. + \int\int\frac{d^3p}{(2\pi)^3}\frac{d^3q}{(2\pi)^3}\langle\Phi_{\mathbf{k}}|\mathbf{q}\rangle\langle\mathbf{p}|\Phi_{\mathbf{k}}\rangle[(\Delta V_i{}^l(\mathbf{q},\mathbf{p};0))' + \Delta V_R{}^l(\mathbf{q},\mathbf{p};E(\mathbf{k})) + \tfrac{1}{2}(\Delta C_l(\mathbf{q},\mathbf{p}) + \Delta A_{vv}{}^l(\mathbf{q},\mathbf{p};E(\mathbf{k})))] \right\}.$$
$$(VI.9)$$

The summation over $\mathbf{k}$ includes spin summation. Equation (VI.8) can be rewritten as

$$E = \sum_{\mathbf{k}}\left\{ E_0'(\mathbf{k}) - \tfrac{1}{2}(C_0 + A_{vv}{}^0(\mathbf{k},\mathbf{k};E_0'(\mathbf{k}))) + \sum_{\mathbf{K}}\frac{\Omega}{\langle\Phi_{\mathbf{k}}|\Phi_{\mathbf{k}}\rangle}\left[ |\alpha_{\mathbf{K}}(\mathbf{k})|^2\left(\frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{K})^2 + \tfrac{1}{2}A_{vv}{}^0(\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{K};E_0'(\mathbf{k}))\right)\right.\right.$$

$$+ \sum_{\mathbf{K}'}\frac{S_{\mathbf{K}-\mathbf{K}'}}{\Omega_0}(\delta_{\mathbf{K},0}+\alpha_{\mathbf{K}}{}^*(\mathbf{k}))(\delta_{\mathbf{K}',0}+\alpha_{\mathbf{K}'}(\mathbf{k}))\exp[i(\mathbf{K}-\mathbf{K}')\cdot\mathbf{r}_{l_0}]\{(\Delta V_i{}^{l_0}(\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{K}';0))'$$

$$\left.\left. + \Delta V_R{}^{l_0}(\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{K}';E(\mathbf{k})) + \tfrac{1}{2}[\Delta C_{l_0}(\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{K}') + \Delta A_{vv}{}^{l_0}(\mathbf{k}+\mathbf{K},\mathbf{k}+\mathbf{K}';E(\mathbf{k}))]\} \right]\right\} + E_F, \quad (VI.10)$$

where $E_F$ denotes the formation energy of imperfections. In first-order approximation $\Delta E_l$ is given by Eq. (VI.9), putting all $\Delta\Phi_{\mathbf{k}}{}^{l'}$ due to interstitials equal to zero and using for $\Delta\Phi_{\mathbf{k}}{}^{l'}$ and $\Delta\Phi_{\mathbf{k}}$ the expressions obtained for a perfect crystal.

## VII. VALENCE ELECTRON CHARGE DENSITY WITH APPLICATION TO DIAMOND

The charge density of the valence electrons is given by

$$\rho(\mathbf{r}) = 2\Omega\int\int\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}G(\mathbf{p},p_0)\psi_{\mathbf{p}}(\mathbf{r})\psi_{\mathbf{p}}{}^*(\mathbf{r}). \quad (VII.1)$$

Performing the integration over $p_0$ one gets

$$\rho(\mathbf{r}) = 2\Omega\int\frac{d^3p}{(2\pi)^3}f_{\mathbf{p}}\psi_{\mathbf{p}}(\mathbf{r})\psi_{\mathbf{p}}{}^*(\mathbf{r}). \quad (VII.2)$$

If one expands $\rho(\mathbf{r})$ in a Fourier series, one obtains

$$\rho(\mathbf{r}) = \sum_{\mathbf{K}} \rho_{\mathbf{K}} \exp(i\mathbf{K}\cdot\mathbf{r}), \tag{VII.3}$$

with

$$\rho_{\mathbf{K}} = \frac{1}{\Omega}\int d^3r \rho(\mathbf{r}) \exp(-i\mathbf{K}\cdot\mathbf{r}). \tag{VII.4}$$

Using Eq. (VII.2) and writing $\psi_{\mathbf{p}}$ as

$$\psi_{\mathbf{p}}(\mathbf{r}) = C_{\mathbf{p}} \sum_{\mathbf{K}} \tau_{\mathbf{K}}(\mathbf{p}) \exp[i(\mathbf{p}+\mathbf{K})\cdot\mathbf{r}], \tag{VII.5}$$

with

$$\tau_{\mathbf{K}}(\mathbf{p}) = \delta_{\mathbf{K},0} + \alpha_{\mathbf{K}}(\mathbf{p}) + \beta_{\mathbf{K}}(\mathbf{p}), \tag{VII.6}$$

where $\alpha_{\mathbf{K}}(\mathbf{p})$ is given by Eq. (III.41) and $\beta_{\mathbf{K}}(\mathbf{p})$ is given by

$$\beta_K(\mathbf{p}) = -\frac{1}{\Omega}\sum_{t,p'} b_{tp'}(\mathbf{p})\int d^3r \varphi_{t,p'}(\mathbf{r}) \exp[-i(\mathbf{p}+\mathbf{K})\cdot\mathbf{r}], \tag{VII.7}$$

one gets

$$\rho_{\mathbf{K}} = 2\Omega \sum_{\mathbf{K}'} \int \frac{d^3p}{(2\pi)^3} f_{\mathbf{p}} |C_{\mathbf{p}}|^2 \tau_{\mathbf{K}'}{}^*(\mathbf{p})\tau_{\mathbf{K}'+\mathbf{K}}(\mathbf{p}). \tag{VII.8}$$

Using Eq. (VII.6) one obtains

$$\rho_{\mathbf{K}} = 2\Omega \int \frac{d^3p}{(2\pi)^3} f_p |C_{\mathbf{p}}|^2 \{\delta_{\mathbf{K},0} + \alpha_{\mathbf{K}}(\mathbf{p}) + \alpha_{-\mathbf{K}}{}^*(\mathbf{p}) + \beta_{\mathbf{K}}(\mathbf{p}) + \beta_{-\mathbf{K}}{}^*(\mathbf{p}) + \sum_{\mathbf{K}'} [\alpha_{\mathbf{K}'}{}^*(\mathbf{p})\beta_{\mathbf{K}'+\mathbf{K}}(\mathbf{p}) + \beta_{\mathbf{K}'}{}^*(\mathbf{p})\alpha_{\mathbf{K}'+\mathbf{K}}(\mathbf{p})$$
$$+ \beta_{\mathbf{K}'}{}^*(\mathbf{p})\beta_{\mathbf{K}'+\mathbf{K}}(\mathbf{p}) + \alpha_{\mathbf{K}'}{}^*(\mathbf{p})\alpha_{\mathbf{K}'+\mathbf{K}}(\mathbf{p})]\}. \tag{VII.9}$$

The normalization factor $|C_{\mathbf{p}}|^2$ is expressed in terms of $\alpha_{\mathbf{K}}(\mathbf{p})$ by

$$|C_{\mathbf{p}}|^2 = \frac{1}{\Omega}\left(1 + \sum_{\mathbf{K}\neq 0} |\alpha_{\mathbf{K}}(\mathbf{p})|^2 - \frac{1}{\Omega}\sum_{t,p'} |b_{tp'}(\mathbf{p})|^2\right)^{-1}. \tag{VII.10}$$

To perform the angular integrations in Eq. (VII.9) the quantities $C_{\mathbf{K}}$, $\alpha_{\mathbf{K}}$, and $\beta_{\mathbf{K}}$ are expanded into spherical harmonics. One gets then

$$\rho_{\mathbf{K}} = 2\Omega \int_0^{\infty} dp\, p^2 f_p \{\delta_{\mathbf{K},0} N_{00}(p) + \sum_{g,m} N_{gm}(p)[(\alpha_{-\mathbf{K}}(p))_{gm}{}^* + (-1)^m (\alpha_{\mathbf{K}}(p))_{gm} + (\beta_{-\mathbf{K}}(p)_{gm}{}^* + (-1)^m (\beta_{\mathbf{K}}(p))_{gm}]$$

$$+ \sum_{\mathbf{K}'} \sum_{\substack{g,m \\ g',m' \\ g''}} \sigma(g'g''g, m'(m-m')m) N_{g''(m-m')}(p)[(\alpha_{\mathbf{K}'}(p))_{gm}{}^* (\beta_{\mathbf{K}'+\mathbf{K}}(p))_{g'm'} + (\beta_{\mathbf{K}'}(p))_{gm}{}^* (\alpha_{\mathbf{K}'+\mathbf{K}}(p))_{g'm'}$$

$$+ (\beta_{\mathbf{K}'}(p))_{gm}{}^* (\beta_{\mathbf{K}'+\mathbf{K}}(p))_{g'm'} + (\alpha_{\mathbf{K}'}(p))_{gm}{}^* (\alpha_{\mathbf{K}'+\mathbf{K}}(p))_{g'm'}]\}, \tag{VII.11}$$

with

$$N_{gm}(p) = \int d\Omega |C_{\mathbf{p}}|^2 Y_{gm}{}^*(\theta_p, \varphi_p), \tag{VII.12}$$

$$(\alpha_{\mathbf{K}}(p))_{gm} = \int d\Omega \alpha_{\mathbf{K}}(\mathbf{p}) Y_{gm}{}^*(\theta_p, \varphi_p), \tag{VII.13}$$

$$(\beta_{\mathbf{K}}(p))_{gm} = \int d\Omega \beta_{\mathbf{K}}(\mathbf{p}) Y_{gm}{}^*(\theta_p, \varphi_p), \tag{VII.14}$$

where always $\theta_p$ and $\varphi_p$ refer to the same coordinate system, and

$$\sigma(g'g''g,m'(m-m')m) = \left(\frac{(2g'+1)(2q''+1)}{4\pi(2g+1)}\right)^{1/2} C(g'g''g,m'(m-m')m)C(g'g''g,000).$$ (VII.15)

The $C$'s are usual Clebsch-Gordan coefficients.[14] The remaining integration over $p$ in Eq. (VII.11) has in general to be performed numerically. $(\alpha_K(p))_{gm}$ and $(\beta_K(p))_{gm}$ are evaluated in more detail in Appendix B.

To demonstrate the usefulness of the above results, some Fourier coefficients of the valence electron charge density in diamond are calculated. The scattering amplitude $t_l^0(\mathbf{q},\mathbf{k};E(k))$ is determined by Eq. (IV.9). $(\Delta H_l'(\mathbf{q},\mathbf{k};E(\mathbf{k})))$ is approximated by the sum of $\Delta V_i^l(|\mathbf{q}-\mathbf{k}|;0)/\epsilon^{(0)}(|\mathbf{q}-\mathbf{k}|;0)$ and $\Delta V_R^l(\mathbf{q},\mathbf{k};E(k))$. $\epsilon^{(0)}$ denotes the free-electron gas dielectric constant.[12] $\Delta V_i^l$ and $\Delta V_R^l$ are determined using earlier results obtained by Herman[15] and Kleinman and Phillips.[1] It is now $t_l^0(\mathbf{K},E(k)) \equiv t_l^0(K,E(k))$ and $t_l^0(\mathbf{k}+\mathbf{K},k\mathbf{n}_{ll'};E(k))$ is approximated by the first terms in the expansion (B1) with $g=0$ and $g=1$. $(\Delta H_l'(k,\mathbf{K},\mathbf{n}_{ll'};E(k)))_{gm}^0$ is given by

$$(\Delta H_l'(k,\mathbf{K},\mathbf{n}_{ll'};E(k)))_{gm}^0 = (\Delta H_l'(k,|k\mathbf{n}_{ll'}-\mathbf{K}|;E(k)))_g^0 Y_{gm}*(\theta_{\mathbf{K},\mathbf{n}_{ll'}-\mathbf{K}},\varphi_{\mathbf{K},\mathbf{n}_{ll'}-\mathbf{K}}),$$ (VII.16)

with

$$(\Delta H_l'(k,|k\mathbf{n}_{ll'}-\mathbf{K}|;E(k)))_g^0 = \int d\Omega \Delta H_l'(\mathbf{k}+\mathbf{K},k\mathbf{n}_{ll'};E(k))P_g(\cos\theta_{\mathbf{k},\mathbf{n}_{ll'}-\mathbf{K}}).$$ (VII.17)

$P_g$ are Legendre polynomials. $(\beta_K(k))_{gm}$ is approximated by the first term in the curly brackets of Eq. (B12). $f_k$ is approximated by

$$f_k = 1, \quad \text{for} \quad k \leq k_{max}$$
$$= 0, \quad \text{for} \quad k > k_{max},$$

with $k_{max} = 1.31$ in atomic units. $a_{-1}$ is approximated in the formulas by 1.

The obtained numerical results are given in Table I

TABLE I. Fourier coefficients $\rho_K$ of valence electron charge density in diamond given in units of electrons per atom. Column 2 presents the results of the calculations of the present paper. Column 3 presents the results obtained by Kleinman and Phillips (Ref. 3) and column 4 presents the experimental results obtained by Göttlicher and Wölfel (Ref. 16).

| $(a/2\pi)\mathbf{K}$ | $\rho_K$ | $\rho_K$ | $\rho_K$ |
|---|---|---|---|
| $\langle 111 \rangle$ | 0.91 | 0.88 | 0.98 |
| $\langle 220 \rangle$ | 0.12 | 0.01 | 0.18 |
| $\langle 311 \rangle$ | −0.10 | −0.14 | −0.04 |
| $\langle 222 \rangle$ | −0.13 | −0.15 | ±0.15[a] |
| $\langle 400 \rangle$ | −0.11 | −0.13 | −0.14 |

[a] Measured by Renninger [M. Renninger, Z. Krist. 97, 107 (1937); M. Renninger, Acta Cryst. 8, 606 (1955)].

and are compared with theoretical ones obtained by Kleinman and Phillips[3] from a plane-wave calculation, and with experimental results obtained by Göttlicher and Wölfel[16] from x-ray scattering due to diamond powder. Our results are generally in good agreement

[14] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).
[15] F. Herman, Phys. Rev. 93, 1214 (1954).
[16] S. Göttlicher and E. Wölfel, Z. Elektrochem. 63, 891 (1959).

TABLE II. Fourier coefficients $\rho_K$ of valence electron charge density in diamond given in units of electrons per atom. Column 2 presents the results following from the approximation $t = \Sigma_l \Delta H_l$. Column 3 gives the results obtained by using the approximation $t = \Sigma_l t_l$. Column 4 gives the results following from the exact $t$-matrix, see column 2 of Table I.

| $(a/2\pi)\mathbf{K}$ | $\rho_K$ | $\rho_K$ | $\rho_K$ |
|---|---|---|---|
| $\langle 111 \rangle$ | 0.78 | 0.86 | 0.91 |
| $\langle 220 \rangle$ | 0.26 | 0.27 | 0.12 |
| $\langle 311 \rangle$ | 0.07 | 0.07 | −0.10 |
| $\langle 222 \rangle$ | 0 | 0 | −0.13 |
| $\langle 400 \rangle$ | 0.02 | 0.02 | −0.11 |

with the earlier ones listed in Table I. Note, however, that for $\rho_{220}$ the various results disagree.

To demonstrate the significance of the $t$-matrix approach in Table II the Fourier coefficients resulting from the approximations $t = \sum_l \Delta H_l'$ and $t = \sum_l t_l$, respectively, are compared with the results obtained in Table I. The covalent bonding is demonstrated by the difference between the corresponding $\rho_k$ listed in columns 3 and 4.

## VIII. LIMITATIONS AND APPLICATIONS

A general method is presented for a systematic determination of the effective valence or conduction electron wave function in static crystals of arbitrary structure. The tightly bound core electrons are treated as dynamically independent of the valence electrons. The neglect of correlation between core and valence electrons is valid if electron transitions between tightly bound core-electron states and valence-electron states are negligible and if the excitation energies of tightly bound core electrons are large compared to excitation energies of

the valence electrons, for example, the plasma energy. Under these two conditions the core-valence electron interactions are essentially unscreened and thus can be treated within the Hartree-Fock approximation. This is the case, for example, for small ion cores. Correlation among the valence electrons is taken into account. A major advantage of the $t$-matrix approach is its ease of physical interpretation which is very useful in finding good approximations for the wave functions, self-consistent crystal potential, and electron energies. Further, with respect to previous work, the present treatment of valence electrons offers the advantage that the determination of the wave function is not limited to symmetry points of the lattice. This, consequently, permits a more systematic determination of a self-consistent valence electron density. The determination of the valence-electron response to the effective crystal potential includes nonlinear screening, e.g., local field corrections. Therefore, it is expected that this treatment of the valence electrons will be useful particularly for describing the electronic structure of a variety of crystals, for example, covalent bonding. Actually, the performed determination of the valence-electron charge density in diamond yields covalent bonding.

The scattering of the valence electrons by the crystal potential is treated by taking into account the atomic configuration of the lattice. Thus, the proposed method is adopted to imperfect crystals and can be used for determining the electronic structure, for example, of interstitials, vacancies, and color centers. The special electronic structure of a crystal is manifested by the interference of the scattered waves due to the lattice atoms. This aspect is of importance in studying the validity of various approximations applied to valence electrons, for example, orthogonalized plane wave method, tight-binding approximation, etc.

The main assumption made in deriving explicit expressions for the $t$ matrix and the valence-electron wave function, which are the basic quantities in the present treatment of valence electrons, requires that the perturbing Hamiltonian $\Delta H_l'$ scatter the valence electrons mainly in the core region and that the $\Delta H_l'$ do not overlap appreciably. Then, the multiple electron scattering is essentially given by multiple forward and backward scattering between lattice ions. In some crystals the above basic assumption may not be valid for those $\Delta H_l'$ associated with next-neighbored lattice ions. Then, a more careful analysis of the corresponding multiple electron scattering need be performed.

It will be interesting, in particular, with respect to imperfect crystals, to extend the present method by taking into account electron-phonon interaction.[17]

The presented method will be used in a continuing paper to calculate the formation and migration energies of vacancies and interstitials in valence crystals.

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[17] J. W. Wilkins, thesis, University of Illinois, 1963 (unpublished).

## APPENDIX A. THE PERTURBING HAMILTONIAN $\Delta H_l'$

In this Appendix, it is shown how the perturbing Hamiltonian $\Delta H'$ given by Eq. (II.18) can be split into

$$\Delta H' = \sum_l \Delta H_l'. \tag{A1}$$

First, the potential $V_i$ can be written as

$$V_i(\mathbf{r}) = \sum_l V_i{}^l(\mathbf{r} - \mathbf{r}_l), \tag{A2}$$

where $V_i{}^l$ is the Coulomb potential due to the ion core $l$ centered at $\mathbf{r}_l$ in the lattice. Using for the eigenfunctions $\varphi_{l,k}$ the expression given by Eq. (II.6), then $A_{iv}$ is given by

$$A_{iv}(\mathbf{r}, E(\mathbf{k})) = \sum_l A_{iv}{}^l(\mathbf{r}, E(\mathbf{k})), \tag{A3}$$

with

$$A_{iv}{}^l(\mathbf{r}, E(\mathbf{k})) \Phi_{\mathbf{k}}(\mathbf{r})$$

$$= \left(\frac{1}{N}\right)^{1/2} \sum_{t,\mathbf{k}'} U_{t,\mathbf{k}'}(\mathbf{r}_l) \int d^3r' V_S'(\mathbf{r} - \mathbf{r}', E(\mathbf{k})) \varphi_t{}^l(\mathbf{r} - \mathbf{r}_l)$$

$$\times \varphi_{t,\mathbf{k}'}{}^*(\mathbf{r}') \Phi_{\mathbf{k}}(\mathbf{r}'), \tag{A4}$$

where $V_S'$ denotes the screened interaction between core and valence electrons. Thus, $\Delta V_i'(\mathbf{r}, E(\mathbf{k}))$ can be written as

$$\Delta V_i'(\mathbf{r}, E(\mathbf{k})) = \sum_l (\Delta V_i{}^l(\mathbf{r}, E(\mathbf{k})))', \tag{A5}$$

with

$$(\Delta V_i{}^l(\mathbf{r}, E(\mathbf{k})))' \equiv V_i{}^l(\mathbf{r}) - \Omega^{-1}\langle \mathbf{k} | V_i{}^l | \mathbf{k} \rangle$$
$$+ A_{iv}{}^l(\mathbf{r}, E(\mathbf{k})) - \Omega^{-1}\langle \mathbf{k} | A_{iv}{}^l | \mathbf{k} \rangle. \tag{A6}$$

Using again Eq. (II.6) one gets for $\Delta V_R$

$$\Delta V_R(\mathbf{r}, E(\mathbf{k})) = \sum_l \Delta V_R{}^l(\mathbf{r}, E(\mathbf{k})), \tag{A7}$$

with

$$\Delta V_R{}^l(\mathbf{r}, E(\mathbf{k})) \equiv V_R{}^l(\mathbf{r}, E(\mathbf{k})) - \Omega^{-1}\langle \mathbf{k} | V_R{}^l | \mathbf{k} \rangle, \tag{A8}$$

where $V_R{}^l$ is defined as

$$V_R{}^l(\mathbf{r}, E(\mathbf{k})) \Phi_{\mathbf{k}}(\mathbf{r}) = \left(\frac{1}{N}\right)^{1/2} \sum_{t,\mathbf{k}'} U_{t,\mathbf{k}'}(\mathbf{r}_l)(E(\mathbf{k}) - E_t(\mathbf{k}'))$$
$$\times b_{t\mathbf{k}'}(\mathbf{k}) \varphi_t{}^l(\mathbf{r} - \mathbf{r}_l). \tag{A9}$$

$\Delta C$ and $\Delta A_{vv}$ can in general be expanded as

$$\Delta C = \Delta C^{(1)} + (\Delta C^{(2)} - \Delta C^{(1)}) + \cdots \tag{A10}$$

and

$$\Delta A_{vv} = \Delta A_{vv}{}^{(1)} + (\Delta A_{vv}{}^{(2)} - \Delta A_{vv}{}^{(1)}) + \cdots. \tag{A11}$$

$\Delta C^{(1)}$ and $\Delta A_{vv}{}^{(1)}$ are determined using the wave function $\psi_k$ resulting from approximating $\Delta H'$ by the sum of $\Delta V_i'$ and $\Delta V_R$. $\Delta C^{(2)}$ and $\Delta A_{vv}{}^{(2)}$ are determined using the wave function $\psi_k$ resulting from approximating $\Delta H'$ by the sum of $\Delta V_i'$, $\Delta V_R$, $\Delta C^{(1)}$, and $\Delta A_{vv}{}^{(1)}$. The higher terms in the expansions (A10) and (A11) are determined in this manner. This implies then, that $\Delta C$ and $\Delta A_{vv}$ can be written as

$$\Delta C = \sum_l \Delta C_l \qquad \text{(A12)}$$

and

$$\Delta A_{vv} = \sum_l \Delta A_{vv}{}^l. \qquad \text{(A13)}$$

Hence, Eq. (A1) is shown to be valid. In summary, it is

$$\Delta H_l' = (\Delta V_i{}^i)' + \Delta V_R{}^l + \Delta C_l + \Delta A_{vv}{}^l. \qquad \text{(A14)}$$

## APPENDIX B. DETERMINATION OF $(\alpha_K(k))_{gm}$ AND $(\beta_K(k))_{gm}$

To perform the integration in Eq. (VII.13) $\alpha_K(k)$ need be expressed in terms of $\theta_k$ and $\varphi_k$. It follows from approximating $E(k)$ by $E(k)$ and Eqs. (IV.3) that $t_l{}^0(k+K, k; E(k)) = t_l{}^0(K, E(k))$. For $t_l{}^0(k+K, k n_{ll'}; E(k))$ one gets

$$t_l{}^0(k+K, k n_{ll'}; E(k)) = \sum_{g,m} (-i)^g Y_{gm}(\theta_k, \varphi_k)$$

$$\times (t_l{}^0(k, K, n_{ll'}; E(k))_{gm}, \qquad \text{(B1)}$$

where $(t_l{}^0(k, K, n_{ll'}; E(k)))_{gm}$ is approximately given by

$$(t_l{}^0(k, K, n_{ll'}; E(k)))_{gm} = -\frac{2m}{4\pi\hbar^2} \frac{(\Delta H_l'(k, K, n_{ll'}; E(k)))_{gm}{}^0}{1 + \frac{2m}{(2\pi)^3\hbar^2} \int d^3 p \, G_0'(p, E_0'(k)(\Delta H_l'(k, p; E(k)))^0}, \qquad \text{(B2)}$$

with

$$(\Delta H_l(k, K, n_{ll'}; E(k)))_{gm}{}^0 = 4\pi \int d^3 R \, Y_{gm}(\theta_R, \varphi_R) j_g(kR) \exp(-iK \cdot R) \Delta H_l'(R; E(k)) \exp(ik n_{ll'} \cdot R). \qquad \text{(B3)}$$

Using these results and Eqs. (III.41), (III.44), (III.34), one obtains

$$(\alpha_K(k))_{gm} = (S_K/\Omega_0)\{4\pi t_{l_0}{}^0(K, E(k))(G_0'(k, K; E_0'(k)))_g \delta_{m,0} + H_{gm}(k, K) + \cdots\}. \qquad \text{(B4)}$$

$(G_0')_g$ is given by

$$(G_0'(k, K; E_0'(k)))_g = \int d\Omega \, G_0'(|k+K|, E_0'(k)) Y_{g0}*(\theta_{k,K}, 0). \qquad \text{(B5)}$$

$H_{gm}(k, K)$ is given by

$$H_{gm}(k, K) = \sum_{\substack{l' \\ (l' \neq l_0)}} \sum_{\substack{s,t,r \\ \mu,\nu,f,\delta}} a_{l_0 l'}(k) \Lambda_{str}(k, K, n_{l_0 l'})(-i)^{\mu+s} \Gamma_{gm,\mu\nu,st,f\delta}$$

$$\times \{\delta_{f,r} \delta_{\delta,0} t_{l'}{}^0(k n_{l_0 l'}, -k n_{l_0 l'}; E(k))(t_{l_0}{}^0(k, K=0, k n_{l_0 l'}; E(k)))_{\mu\nu} a_{-1} \frac{e^{ikr_{ll'}}}{r_{ll'}}$$

$$+ 4\pi \sum_\gamma i^\gamma \sigma(r\gamma f, 0\delta\delta) j_\gamma(kr_{l_0 l'})(t_{l'}{}^0(k, K=0, -k n_{l_0 l'}; E(k)))_{\mu\nu} Y_{\gamma\delta}*(\theta_{K,n_{l_0 l'}}, \varphi_{K,n_{l_0 l'}})\}, \qquad \text{(B6)}$$

with

$$a_{l_0 l'}(k) \equiv a_{-1} \frac{\exp(ikr_{l_0 l'})}{r_{l_0 l'}} \left[1 - t_{l'}{}^0(k n_{l_0 l'}, -k n_{l_0 l'}; E(k)) t_{l_0}'(-k n_{l_0 l'}, k n_{l_0 l'}; E(k)) \left(\frac{\exp(ikr_{l_0 l'})}{r_{l_0 l'}}\right)^2 (a_{-1})^2\right]^{-1}, \qquad \text{(B7)}$$

$$\Lambda_{str}(k, K, n_{l_0 l'}) \equiv (t_{l_0}{}^0(k, K, k n_{l_0 l'}; E(k)))_{st} G_0'(k, K, E_0'(k))_r, \qquad \text{(B8)}$$

$$\Gamma_{gm,\mu\nu,st,f\delta} \equiv \sum_\eta \sigma(sf\eta, t\delta(t+\delta)) \sigma(\mu\eta g, \nu(t+\delta)m), \qquad \text{(B9)}$$

and

$$\sigma(sf\eta, t\delta(t+\delta)) \equiv \left(\frac{(2S+1)(2f+1)}{4\pi(2\eta+1)}\right)^{1/2} C(sf\eta, t\delta(t+\delta)) C(sf\eta, 000). \qquad \text{(B10)}$$

$j_\gamma$ is the $\gamma$th spherical Bessel function. The quantity $H_{gm}(k,K)$ represents local-field corrections to the valence electron-charge density and reflects the crystal structure. It describes, for example, in covalent crystals the hybridization.

It follows from Eqs. (VII.7) and (II.6) and writing

$$\varphi_t{}^l(\mathbf{R}_l) = \sum_\lambda \frac{P_{t\lambda}{}^l(R_l)}{R_l} Y_{t\lambda}(\theta_{\mathbf{R}_l}, \varphi_{\mathbf{R}_l}) \tag{B11}$$

that $(\beta_\mathbf{K}(k))_{gm}$ is given by

$$(\beta_\mathbf{K}(k))_{gm} = -\frac{S_\mathbf{K}}{\Omega_0} \sum_{t,\mu} \{ I_{tm\mu g}(k,K) b_1(k) + \sum_{\mathbf{K}'} \sum_{\substack{\lambda,\nu,\lambda',\nu' \\ \mu',g',m',\eta}} (-1)^{\lambda'} \sigma(\nu'g'\eta, -\lambda'm'(m'-\lambda)) \sigma(\nu\eta g, \lambda(m-\lambda)m)$$

$$\times D_{m'-\lambda',m-\lambda}{}^\eta(\alpha_{\mathbf{K}',\mathbf{K}},\beta_{\mathbf{K}',\mathbf{K}},0)(\alpha_{\mathbf{K}'}(k))_{g'm'} S_{-\mathbf{K}'} I_{t\lambda\mu\nu}(k,K) I_{t\lambda'\mu'\nu'}{}^*(k,K') \}. \tag{B12}$$

The function $I_{tm\mu g}(k,K)$ is defined as

$$I_{tm\mu g}(k,K) \equiv (-i)^{\mu+g}(4\pi)^2 \left(\frac{2\mu+1}{4\pi N}\right)^{1/2} \sigma(t\mu g, m0m) \int_0^\infty dR\, R\, P_{tm}{}^{l_0}(R) j_\mu(KR) j_g(kR). \tag{B13}$$

$b_1(k)$ is given by

$$b_1(k) \equiv \int d^3r\, \varphi_{t,k}{}^*(\mathbf{r}) \Phi_k{}^0(\mathbf{r}). \tag{B14}$$

The function $D_{m'-\lambda',m-\lambda}{}^\eta(\alpha_{\mathbf{K}',\mathbf{K}},\beta_{\mathbf{K}',\mathbf{K}},0)$ results from using the formula

$$Y_{lm}(\theta,\varphi) = \sum_{m'} D_{mm'}{}^l(\alpha,\beta,0) Y_{lm'}(\theta',\varphi'), \tag{B15}$$

which describes the transformation of spherical harmonics under the rotation of the axis of the polar coordinate system. $\alpha$ is the azimuthal angle and $\beta$ the polar angle of the new polar axis, to which $\theta'$ refers, with respect to the original axis. The matrix $D_{mm'}{}^l$ is given by[14]

$$D_{mm'}{}^l(\alpha,\beta,0) = e^{-im'\alpha} d_{m'm}{}^l(\beta), \tag{B16}$$

with

$$d_{m'm}{}^l(\beta) = ((l+m)!(l-m)!(l+m')!(l-m')!)^{1/2} \left( \sum_q \frac{(-1)^q [\cos(\beta/2)]^{2l+m-m'-2q}[-\sin(\beta/2)]^{m'-m+2q}}{(l-m'-q)!(l+m-q)!(q+m'-m)!q!} \right), \tag{B17}$$

where the sum is over the values of the integer $q$ for which the factorial arguments are greater or equal to zero.

In first-order approximation $(\beta_\mathbf{K}(k))_{gm}$ is given by the first term in the curly brackets of Eq. (B12). The corrections are typically of the order of 10%.

## APPENDIX C. DETERMINATION OF THE EXPANSION COEFFICIENT $U_{t,\mathbf{k}}(\mathbf{r}_l)$

Writing

$$H = H^0 + \sum_l (\delta H)_l, \tag{C1}$$

where $H^0$ denotes that part of the Hamiltonian $H$ which is associated with the perfect crystal, it follows from Eqs. (II.5) and (II.6) for $U_{t,\mathbf{k}}(\mathbf{r}_l)$ the set of equations[18]

$$\sum_l F_t(\mathbf{r}_s,\mathbf{r}_l) U_{t,\mathbf{k}}(\mathbf{r}_l) - E_t(\mathbf{k}) U_{t,\mathbf{k}}(\mathbf{r}_s)$$
$$= \sum_l M_t(\mathbf{r}_s,\mathbf{r}_l) U_{t,\mathbf{k}}(\mathbf{r}_l). \tag{C2}$$

[18] G. F. Koster, Phys. Rev. 95, 1436 (1954).

$F_t(\mathbf{r}_s,\mathbf{r}_l)$ and $M_t(\mathbf{r}_s,\mathbf{r}_l)$ are defined by

$$F_t(\mathbf{r}_s,\mathbf{r}_l) \equiv \langle \varphi_t{}^s | H^0 | \varphi_t{}^l \rangle \tag{C3}$$

and

$$M_t(\mathbf{r}_s,\mathbf{r}_l) \equiv -\sum_{l'} \langle \varphi_t{}^s | (\delta H)_{l'} | \varphi_t{}^l \rangle. \tag{C4}$$

Defining then $U_{t,\mathbf{k}}{}^0(\mathbf{r}_l)$ by

$$\sum_l F_t(\mathbf{r}_s,\mathbf{r}_l) U_{t,\mathbf{k}}{}^0(\mathbf{r}_l) - E_t(\mathbf{k}) U_{t,\mathbf{k}}{}^0(\mathbf{r}_s) = 0 \tag{C5}$$

and a Green's function $G(\mathbf{r}_l,\mathbf{r}_{l'},E_t(\mathbf{k}))$ by

$$\sum_l \{ F_t(\mathbf{r}_s,\mathbf{r}_l) - E_t(\mathbf{k}) \delta_{\mathbf{r}_s,\mathbf{r}_l} \} G(\mathbf{r}_l,\mathbf{r}_{l'},E_t(\mathbf{k})) = \delta_{\mathbf{r}_s,\mathbf{r}_{l'}}, \tag{C6}$$

one obtains

$$U_{t,\mathbf{k}}(\mathbf{r}_j) = U_{t,\mathbf{k}}{}^0(\mathbf{r}_j) + \sum_l T_{t,\mathbf{k}}(\mathbf{r}_l) G(\mathbf{r}_j,\mathbf{r}_l,E_t(\mathbf{k})), \quad (C7)$$

where the $T_{t,\mathbf{k}}(\mathbf{r}_l)$ are determined by the set of linear inhomogeneous equations

$$\sum_{l'} \{ \delta_{\mathbf{r}_s,\mathbf{r}_{l'}} - \sum_l M_t(\mathbf{r}_s,\mathbf{r}_l) G(\mathbf{r}_l,\mathbf{r}_{l'},E_t(\mathbf{k})) \}$$
$$\times T_{t,\mathbf{k}}(\mathbf{r}_{l'}) = \sum_l M_t(\mathbf{r}_s,\mathbf{r}_l) U_{t,\mathbf{k}}{}^0(\mathbf{r}_l). \quad (C8)$$

For a vacancy $U_{t,k}(\mathbf{r}_V) \equiv 0$. It follows that in the case of a perfect crystal the $U_{t,\mathbf{k}}{}^0(\mathbf{r}_l)$ are given by $\exp(i\mathbf{k}\cdot\mathbf{r}_l)$.

Assuming that the $(\delta H)_t$ are well localized, then the matrix elements $M_t(\mathbf{r}_s,\mathbf{r}_l)$ can be approximated by $M_t(\mathbf{r}_s,\mathbf{r}_s)\delta_{\mathbf{r}_s,\mathbf{r}_l}$. Then, in first-order approximation, which neglects coupling between different $T_{t,\mathbf{k}}(\mathbf{r}_l)$, one gets

$$T_{t,\mathbf{k}}(\mathbf{r}_s) = \frac{M_t(\mathbf{r}_s,\mathbf{r}_s) U_{t,\mathbf{k}}{}^0(\mathbf{r}_s)}{1 - M_t(\mathbf{r}_s,\mathbf{r}_s) G(\mathbf{r}_s,\mathbf{r}_s,E_t(\mathbf{k}))}. \quad (C9)$$

$G(\mathbf{r}_s,\mathbf{r}_l,E_t(\mathbf{k}))$ can be determined similarly as $U_{t,\mathbf{k}}(\mathbf{r}_l)$ using the Green's function

$$G^0(\mathbf{r}_s,\mathbf{r}_l,E_t(\mathbf{k}))$$
$$= \sum_\mathbf{p} \exp[i\mathbf{p}\cdot(\mathbf{r}_s-\mathbf{r}_l)] G^0(\mathbf{p},E_t(\mathbf{k})), \quad (C10)$$

to which the Green's function $G(\mathbf{r}_s,\mathbf{r}_l,E_t(\mathbf{k}))$ reduces in the case of a perfect crystal.