General Treatment of the Conduction Electron Redistribution due to Point Defect Complexes and Lattice Distortion in Noble Metals*

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A general method is presented for determining the wave functions of the conduction electrons in noble metals containing point defect complexes consisting of interstitials, vacancies, and impurities. The wave functions are determined by an integral equation derived from the Hartree-Fock equation. An approximation scheme is developed for solving the integral equation taking into account the multiple scattering arising from the interacting point defects and the scattering by the lattice distortion associated with the point defects. The conduction electron density is derived in general form. The derived wave functions and the electron density can be used for a calculation of the interaction energy of point defects and the electric field resulting from the conduction electron redistribution.

I. INTRODUCTION

It is important in many studies of metals, in particular, nuclear magnetic resonance,[1] self-diffusion,[2] and annealing,[3] to know the redistribution of the conduction electrons due to impurities, interstitials, vacancies, and the lattice distortion associated with these point defects. The electron redistribution arises from the scattering of the conduction electrons by the point defects and the lattice distortion. The point defects and the displaced lattice ions represent an ensemble of scatterers which give rise to multiple scattering. In particular, the multiple scattering due to close lying point defects must be taken into account in determining the redistribution of the conduction electrons.

Knowing the redistribution of the conduction electrons, the electronic contribution to the interaction energy of point defects can be calculated. In the past the electronic interaction energy of a vacancy-impurity pair and two vacancies has been calculated.[2,4–7] However, in these previous calculations no attempt has been made to determine the conduction electron scattering by using a treatment as good as the Hartree-Fock approximation. All previous calculations used wave functions neglecting the effect of multiple scattering due to the interacting point defects and the scattering due to the displaced lattice ions. Therefore, the obtained results for the interaction energy of point defects, in particular, if these lie close together, cannot be regarded as being very accurate.

It is the aim of the present paper to develop, in general form, a method for determining the conduction electron redistribution due to an ensemble of interacting point defects in noble metals including multiple scattering by the point defects and the scattering by the lattice distortion associated with the point defects. The Hartree-Fock equation is used to determine the wave functions of the conduction electrons in the imperfect metal. Converting the Hartree-Fock equation into an integral equation and approximating the total perturbing potential by a superposition of perturbing potentials due to single scatterers a system of coupled integral equations is derived for determining the scattered waves due to the various single scatterers. A suitable approximation procedure is proposed for solving this system of coupled integral equations. The wave functions are determined in detailed form in first order in this approximation scheme. Thereby, the scattering potentials associated with the single point defects are approximated by spherically symmetric self-consistent potentials and in the integrals of the coupled system of integral equations the scattered waves are replaced by the scattered waves arising from single electron scattering by the noninteracting point defects and displaced lattice ions. Multiple electron scattering due to the displaced lattice ions is neglected. The scattering potentials act on conduction electron states which are approximated by normalized plane waves.

The conduction electron density resulting from these approximate wave functions is derived in general form suitable for numerical calculations.

II. CONDUCTION ELECTRON WAVE FUNCTIONS

The system of conduction electrons in the metal containing M point defects is described by the Hamiltonian

$$H^M=\sum_i \left\{-\frac{\hbar^2}{2m}\nabla_i{}^2+U^M(\mathbf{r}_i)\right\}+\tfrac{1}{2}\sum_{i,j(i\neq j)}\frac{e^2}{r_{ij}}, \quad (2.1)$$

where i and j are summed over all conduction electrons and m is the electron mass. U^M describes the interaction between the distorted lattice, including the M point defects, and the conduction electrons. The last term describes the Coulomb interaction among the electrons.

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The wave functions of the conduction electrons are determined by the Hartree-Fock equation[8]

$$(H_k{}^M)^{\mathrm{H-F}}\varphi_k{}^M=\epsilon_k\varphi_k{}^M, \tag{2.2}$$

where

$$(H_k{}^M)^{\mathrm{H-F}}=-\frac{\hbar^2}{2m}\nabla^2+U^M+C^M+A_k{}^M. \tag{2.3}$$

C^M is the Coulomb potential due to the conduction electrons and is given by

$$C^M(\mathbf{r}_1)=e^2\sum_k\left\langle\varphi_k{}^M(\mathbf{r}_2)\left|\frac{1}{r_{12}}\right|\varphi_k{}^M(\mathbf{r}_2)\right\rangle. \tag{2.4}$$

The exchange operator $A_k{}^M$ is defined by

$$A_k{}^M\varphi_k{}^M(\mathbf{r}_1)=-\frac{e^2}{2}\sum_{k'}\left\langle\varphi_{k'}{}^M(\mathbf{r}_2)\left|\frac{1}{r_{12}}\right|\varphi_k{}^M(\mathbf{r}_2)\right\rangle\varphi_{k'}{}^M(\mathbf{r}_1). \tag{2.5}$$

To obtain a local and eigenvalue-independent operator, $A_k{}^M$ is replaced by

$$A^M(\mathbf{r}_1)=-\frac{e^2}{2}\left[\int d^3r_2\,\rho^M(\mathbf{r}_1,\mathbf{r}_2)\rho^M(\mathbf{r}_2,\mathbf{r}_1)/r_{12}\right]\Big/\rho^M(\mathbf{r}_1,\mathbf{r}_1) \tag{2.6}$$

with

$$\rho^M(\mathbf{r}_\nu,\mathbf{r}_\mu)=\textstyle\sum_k\varphi_k{}^{M*}(\mathbf{r}_\nu)\varphi_k{}^M(\mathbf{r}_\mu)\quad(\nu,\mu=1,2). \tag{2.7}$$

A^M is obtained by averaging $A_k{}^M$ over k.[9] k and k' are summed over all conduction electrons. $(H^M)^{\mathrm{H-F}}$, obtained from $(H_k{}^M)^{\mathrm{H-F}}$ by replacing $A_k{}^M$ by A^M, is split into

$$(H^M)^{\mathrm{H-F}}=H^0+\Delta H^M. \tag{2.8}$$

H^0 is the Hartree-Fock operator for the perfect crystal and

$$\Delta H^M=\Delta U_1{}^M+\Delta U_2{}^M+\Delta C^M+\Delta A^M \tag{2.9}$$

represents the perturbing potential arising from the M point defects and the displaced lattice ions. $\Delta U_1{}^M$ is given by

$$\Delta U_1{}^M(\mathbf{r})=\sum_{s=1}^M\phi_s(\mathbf{r}-\mathbf{r}_s), \tag{2.10}$$

where $\phi_s(\mathbf{r}-\mathbf{r}_s)$ describes the change in the lattice potential due to the introduction of the point defect s at $\mathbf{r}_s$ in the perfect lattice neglecting the lattice distortion and electron redistribution associated with this point defect. The perturbing potential $\Delta U_2{}^M$ arises from the lattice distortion associated with the M point defects and is given by

$$\Delta U_2{}^M(\mathbf{r})=\sum_\mu\{\mathcal{V}(\mathbf{r}-\mathbf{r}_\mu{}^M)-\mathcal{V}(\mathbf{r}-\mathbf{r}_\mu{}^0)\}, \tag{2.11}$$

where the potential $\mathcal{V}$ describes the interaction between the ion μ and the conduction electrons. $\mathbf{r}_\mu{}^0$ and $\mathbf{r}_\mu{}^M$ denote the position of the ion μ in the perfect lattice and distorted lattice, respectively. The change in the Coulomb potential ΔC^M and the change in the exchange potential ΔA^M are defined by

$$\Delta C^M(\mathbf{r})=C^M-C^0 \tag{2.12}$$

and

$$\Delta A^M(\mathbf{r})=A^M-A^0, \tag{2.13}$$

where the potentials C^0 and A^0 are referred to the perfect crystal. Defining a Green's function G by

$$\{H^0-\epsilon_k\}G(\mathbf{r},\mathbf{r}',\mathbf{k})=-\delta(\mathbf{r}-\mathbf{r}'), \tag{2.14}$$

and the condition that G as a function of $\mathbf{r}$ has the same behavior for $r\rightarrow 0$ and $r\rightarrow\infty$ as the scattered wave due to the perturbing potential ΔH^M Eq. (2.2) is rewritten as

$$\varphi_k{}^M(\mathbf{r})=\varphi_k{}^0(\mathbf{r})+\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\Delta H^M(\mathbf{r}')\varphi_k{}^M(\mathbf{r}'). \tag{2.15}$$

The electron states $\varphi_k{}^0$ on which the perturbation potential ΔH^M acts are determined by

$$(H^0-\epsilon_k)\varphi_k{}^0=0. \tag{2.16}$$

The integral in Eq. (2.15) describes the scattering of the conduction electrons by the perturbing potential ΔH^M. It is required that the scattered wave

$$\Delta\varphi_k{}^M=\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\Delta H^M(\mathbf{r}')\varphi_k{}^M(\mathbf{r}') \tag{2.17}$$

has the behavior

$$\lim_{r\rightarrow 0}\Delta\varphi_k{}^M(\mathbf{r})\quad\text{finite} \tag{2.18}$$

and

$$\lim_{r\rightarrow\infty}\Delta\varphi_k{}^M(\mathbf{r})\sim\frac{e^{ikr}}{r}. \tag{2.19}$$

To solve the integral equation (2.15) the perturbing potential ΔH^M is expanded as

$$\Delta H^M=\Delta H_1{}^M+(\Delta H_2{}^M-\Delta H_1{}^M)+\cdots+(\Delta H_n{}^M-\Delta H_{n-1}{}^M)+(\Delta H^M-\Delta H_n{}^M), \tag{2.20}$$

where the potential $\Delta H_1{}^M$ represents a close approximation of ΔH^M and the potentials $\Delta H_2{}^M,\cdots,\Delta H_n{}^M$ are constructed from the wave functions $\varphi_k{}^M$ obtained from Eq. (2.15) approximating ΔH^M by $\Delta H_1{}^M$, $\Delta H_2{}^M$, etc. The corrections $(\Delta H_2{}^M-\Delta H_1{}^M)$, etc., to $\Delta H_1{}^M$ involve only changes in the Coulomb and exchange potential.

[8] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).
[9] F. C. Slater, Phys. Rev. **81**, 385 (1951).

In order to get a rapid convergence of the expansion (2.20) $\Delta H_1{}^M$ must closely approximate ΔH^M. It is assumed that ΔH^M is closely approximated by

$$\Delta H_1{}^M(\mathbf{r})=\sum_{s=1}^{M}\Delta H^s(\mathbf{r}-\mathbf{r}_s)+\sum_{\mu}\Delta(H^M(\mathbf{r}-\mathbf{r}_\mu{}^0))^\mu, \quad (2.21)$$

where ΔH^s is the self-consistent perturbing potential due to the single point defect s and $\Delta(H^M)^\mu$ is the self-consistent perturbing potential due to the displaced lattice ion μ. $\Delta(H^M)^\mu$ arises from the displacement of the ion μ which results from the M point defects. ΔH^s is given by

$$\Delta H^s(\mathbf{r}-\mathbf{r}_s)=\phi_s(\mathbf{r}-\mathbf{r}_s)+\Delta C^s(\mathbf{r}-\mathbf{r}_s)+\Delta A^s(\mathbf{r}-\mathbf{r}_s). \quad (2.22)$$

ΔC^s and ΔA^s are the changes in the Coulomb potential and exchange potential due to the point defect s. $\Delta(H^M)^\mu$ is given by

$$\Delta(H^M)^\mu=\mathcal{V}(\mathbf{r}-\mathbf{r}_\mu{}^M)-\mathcal{V}(\mathbf{r}-\mathbf{r}_\mu{}^0)+\Delta(C^M(\mathbf{r}-\mathbf{r}_\mu{}^0))^\mu+\Delta(A^M(\mathbf{r}-\mathbf{r}_\mu{}^0))^\mu. \quad (2.23)$$

$\Delta(C^M)^\mu$ and $\Delta(A^M)^\mu$ are the changes in the Coulomb potential and exchange potential of the conduction electrons due to displacing the lattice ion μ by $\mathbf{v}_\mu\equiv\mathbf{r}_\mu{}^M-\mathbf{r}_\mu{}^0$ from its regular lattice position. If the expansion (2.20) converges rapidly, the term $(\Delta H^M-\Delta H_n{}^M)$ can be neglected for $n>n_0(M)$, where n_0 is a small positive integer depending on M. Then using Eqs. (2.20) and (2.21) the integral equation (2.15) can be rewritten as

$$\varphi_k{}^M(\mathbf{r})=\varphi_k{}^0(\mathbf{r})+\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\left\{\sum_{s=1}^{M}\Delta H^s+\sum_{\mu}\Delta(H^M)^\mu+\cdots+(\Delta H_{n_0}{}^M-\Delta H_{n_0-1}{}^M)\right\}\varphi_k{}^M(\mathbf{r}'). \quad (2.24)$$

Regarding $\Delta H_1{}^M$ as a good approximation for ΔH^M the integral equation is approximately solved by substituting for $\varphi_k{}^M$ into the integral the wave function resulting from approximating ΔH^M by $\Delta H_1{}^M$. The wave function resulting from Eq. (2.24) by neglecting all corrections to the potentials ΔH^s and $\Delta(H^M)^\mu$ can be written in the form

$$\varphi_k{}^M(\mathbf{r})=\varphi_k{}^0(\mathbf{r})+\sum_{s=1}^{M}\Delta(\varphi_k{}^M)^s+\sum_{\mu}\Delta(\psi^M)^\mu, \quad (2.25)$$

with

$$\Delta(\varphi_k{}^M)^s=\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\Delta H^s(\mathbf{r}')\{\varphi_k{}^0(\mathbf{r}')+\sum_{t=1}^{M}\Delta(\varphi_k{}^M)^t+\sum_{\mu}\Delta(\psi_k{}^M)^\mu\}\quad(s=1,\cdots,M), \quad (2.26)$$

and

$$\Delta(\psi_k{}^M)^\mu=\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\Delta(H^M)^\mu\{\varphi_k{}^0(\mathbf{r}')+\sum_{t=1}^{M}\Delta(\varphi_k{}^M)^t+\sum_{\sigma}\Delta(\psi_k{}^M)^\sigma\}\quad(\mu=1,2,\cdots). \quad (2.27)$$

Equations (2.26) and (2.27) represent a system of coupled integral equations for the scattered waves $\Delta(\varphi_k{}^M)^1,\cdots,\Delta(\varphi_k{}^M)^M$, $\Delta(\psi_k{}^M)^1$, etc., arising from the various potentials ΔH^s and $\Delta(H^M)^\mu$. The first term on the right in Eqs. (2.26) and (2.27) gives the contribution to the scattered wave $\Delta(\varphi_k{}^M)^s$ and $\Delta(\psi_k{}^M)^\mu$ as resulting from the Born approximation. The additional terms arise from the subsequent scattering of the scattered waves $\Delta(\varphi_k{}^M)^t$ and $\Delta(\psi_k{}^M)^\sigma$ by ΔH^s and $\Delta(H^M)^\mu$.

The system of coupled integral equations for the scattered waves is solved approximating $\Delta(\varphi_k{}^M)^t$ and $\Delta(\psi_k{}^M)^\sigma$ by

$$\Delta(\varphi_k{}^M)^t=\Delta\varphi_k{}^t+\sum_{t'(t'\neq t)}^{M}\Delta(\Delta\varphi_k{}^{t'})^t+\sum_{\mu}\Delta(\Delta\psi_k{}^\mu)^t+\cdots, \quad (2.28)$$

and

$$\Delta(\psi_k{}^M)^\sigma=\Delta\psi_k{}^\sigma+\sum_{\mu(\mu\neq\sigma)}\Delta(\Delta\psi_k{}^\mu)^\sigma+\sum_{t'}\Delta(\Delta\varphi_k{}^{t'})^\sigma+\cdots. \quad (2.29)$$

The scattered waves $\Delta\varphi_k{}^t$ and $\Delta\psi_k{}^\sigma$ are defined by

$$\Delta\varphi_k{}^t=\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\Delta H^t(\mathbf{r}')\{\varphi_k{}^0(\mathbf{r}')+\Delta\varphi_k{}^t(\mathbf{r}')\}, \quad (2.30)$$

and

$$\Delta\psi_k{}^\mu=\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\Delta(H^M(\mathbf{r}'))^\sigma\{\varphi_k{}^0(\mathbf{r}')+\Delta\psi_k{}^\sigma(\mathbf{r}')\}. \quad (2.31)$$

$\Delta(\Delta\varphi_k^{t'})$ and $\Delta(\Delta\psi_k^{\mu})^t$ arise from the subsequent scattering of $\Delta\varphi_k^{t'}$ and $\Delta\psi_k^{\mu}$ by ΔH^t and are determined by

$$\Delta(\Delta\varphi_k^{t'})^t=\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\Delta H^t(\mathbf{r}')\Delta\varphi_k^{t'}(\mathbf{r}') \qquad (2.32)$$

and

$$\Delta(\Delta\psi_k^{\mu})^t=\int d^3r'\,G(\mathbf{r},\mathbf{r}',\mathbf{k})\Delta H^t(\mathbf{r}')\Delta\psi_k^{\mu}(\mathbf{r}'). \qquad (2.33)$$

$\Delta(\Delta\varphi_k^{t'})^{\sigma}$ and $\Delta(\Delta\psi_k^{\mu})^{\sigma}$ arise from the subsequent scattering of $\Delta\varphi_k^{t'}$ and $\Delta\psi_k^{\mu}$ by $\Delta(H^M)^{\sigma}$ and are obtained from Eqs. (2.32) and (2.33), respectively, by replacing ΔH^t by $\Delta(H^M)^{\sigma}$. The higher terms in the expansions (2.28) and (2.29) arise from higher multiple scattering of the conduction electrons by the perturbing potentials. The number of terms which have to be taken into account in these expansions depends mainly on the separations among the point defects and decrease with increasing separations.

With the help of the expansions (2.28) and (2.29) the system of coupled integral equations (2.26) and (2.27) can be reduced to the set of uncoupled equations

$$\Delta(\varphi_k^M)^s=\Delta\varphi_k^s+\sum_{t(t\neq s)}^{M}\Delta(\Delta\varphi_k^t)^s +\sum_{\mu}\Delta(\Delta\psi_k^{\mu})^s+\cdots,\quad (s=1,\cdots,M), \qquad (2.34)$$

and

$$\Delta(\psi_k^M)^{\mu}=\Delta\psi_k^{\mu}+\sum_{\sigma(\sigma\neq\mu)}\Delta(\Delta\psi_k^{\sigma})^{\mu} +\sum_{t=1}^{M}\Delta(\Delta\varphi_k^t)^{\mu}+\cdots,\quad (\mu=1,2,\cdots). \qquad (2.35)$$

In order to get explicit expressions for the scattered waves $\Delta\varphi_k^s$, $\Delta\psi_k^{\mu}$, etc., the Green's function G defined by Eq. (2.14) need be determined.

Approximating in H^0 the lattice potential by the potential resulting from an uniform distribution of the ion charges; e.g., neglecting in H^0 the structure of the lattice potential, Eq. (2.14) is reduced to

$$(\nabla^2+k^2)G(\mathbf{r},\mathbf{r}',\mathbf{k})=\frac{2m}{\hbar^2}\delta(\mathbf{r}-\mathbf{r}'), \qquad (2.36)$$

and then solved by[10]

$$G(\mathbf{r},\mathbf{r}',\mathbf{k})=-\frac{m}{2\pi\hbar^2}\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}, \qquad (2.37)$$

which yields the required behavior of the scattered wave $\Delta\varphi_k^M$ for $r\to 0$ and $r\to\infty$.

In the following, explicit expressions are derived for the scattered waves $\Delta\varphi_k^s$, $\Delta(\Delta\varphi_k^t)^s$, and $\Delta\psi_k^{\mu}$. Assuming spherically symmetric potentials ΔH^s and approximating φ_k^0 by a normalized plane wave, one obtains, as shown in detail in Appendixes A and B,

$$\Delta\varphi_k^s(R_s)=\frac{4\pi}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}_s}\sum_{l=0}^{\infty}i^l\left(\frac{2l+1}{4\pi}\right)^{1/2}Y_{l0}(\vartheta_{\mathbf{k},\mathbf{R}_s},0)\Omega_l^s(k,R_s), \qquad (2.38)$$

and

$$\Delta(\Delta\varphi_k^t(\mathbf{R}_s))^s=\frac{4\pi}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}_t}\sum_{l,h}\sum_{m}i^l\alpha_{hlm}\times Y_{lm}^*(\vartheta_{\mathbf{k},\mathbf{r}_{ts}},\varphi_{\mathbf{k},\mathbf{r}_{ts}})Y_{hm}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})H_{hlm}^s(r_{ts},k,R_s). \qquad (2.39)$$

V is the volume of the crystal. Y_{l0}, Y_{lm}, and Y_{hm} are spherical harmonics. $\vartheta_{\mathbf{k},\mathbf{r}_{ts}}$ and $\varphi_{\mathbf{k},\mathbf{r}_{ts}}$ are defined by

$$\vartheta_{\mathbf{k},\mathbf{r}_{ts}}=\vartheta_{\mathbf{k}}-\vartheta_{\mathbf{r}_{ts}},\quad \varphi_{\mathbf{k},\mathbf{r}_{ts}}=\varphi_{\mathbf{k}}-\varphi_{\mathbf{r}_{ts}}, \qquad (2.40)$$

where the polar angles $\vartheta_{\mathbf{k}}$ and $\vartheta_{\mathbf{r}_{ts}}$ and the azimuthal angles $\varphi_{\mathbf{k}}$ and $\varphi_{\mathbf{r}_{ts}}$ are defined by

$$\mathbf{k}=(k,\vartheta_{\mathbf{k}},\varphi_{\mathbf{k}})\quad\text{and}\quad \mathbf{r}_{ts}=(r_{ts},\vartheta_{\mathbf{r}_{ts}},\varphi_{\mathbf{r}_{ts}}).$$

Correspondingly, the angles $\vartheta_{\mathbf{k},\mathbf{R}_s}$, $\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}}$, and $\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}}$ are given. R_s and r_{ts} are defined by

$$R_s=|\mathbf{r}-\mathbf{r}_s|,\quad r_{ts}=|\mathbf{r}_t-\mathbf{r}_s|. \qquad (2.41)$$

The functions Ω_l^s and H_{hlm}^s and the coefficients α_{hlm} are given by Eqs. (A8) and (B6) and (B4). Assuming that $\Delta H^s(R_s')$ tends rapidly to zero with increasing R_s', it follows from Eq. (A4) that for large R_s the scattered waves $\Delta\varphi_k^s$ and $\Delta(\Delta\varphi_k^t)^s$ can be written in the form

$$\Delta\varphi_k^s(\mathbf{R}_s)\underset{R_s\to\infty}{=}\frac{e^{i\mathbf{k}\cdot\mathbf{r}_s}}{V^{1/2}}f_1^s(k)\frac{e^{ikR_s}}{R_s}, \qquad (2.42)$$

and

$$\Delta(\Delta\varphi_k^t(\mathbf{R}_s))^s\underset{R_s\to\infty}{=}\frac{e^{i\mathbf{k}\cdot\mathbf{r}_t}}{V^{1/2}}f^{ts}\left(\mathbf{k},\frac{\mathbf{R}_s}{R_s}\right)\frac{e^{ikR_s}}{R_s}, \qquad (2.43)$$

[10] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955).

where the scattering amplitudes $f_1{}^s$ and f^{ts} are given by

$$f_1{}^s(k)=-\frac{8\pi m}{\hbar^2}\sum_{l=0}^{\infty}\left(\frac{2l+1}{4\pi}\right)^{1/2}Y_{l0}(\vartheta_{\mathbf{k},\mathbf{R}_s},0)\omega_l{}^s(k), \tag{2.44}$$

with

$$\omega_l{}^s(k)=\int_0^\infty dR_s'\,R_s'^2 j_l(kR_s')\Delta H^s(R_s')F_l{}^s(k,R_s'), \tag{2.45}$$

and

$$f^{ts}\left(\mathbf{k},\frac{\mathbf{R}_s}{R_s}\right)=-\frac{8\pi m}{\hbar^2}\sum_{l,h}^{\infty}\sum_{m}\alpha_{hlm}Y_{lm}{}^*(\vartheta_{\mathbf{k},\mathbf{r}_{ts}},\varphi_{\mathbf{k},\mathbf{r}_{ts}})Y_{hm}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})\beta_h{}^s(k,r_{ts}), \tag{2.46}$$

with

$$\beta_h{}^s(k,r_{ts})=\int_0^\infty dR_s'^2 R_s' j_h(kR_s')\Delta H^s(R_s')a_{hlm}{}^t(r_{ts},k,R_s'). \tag{2.47}$$

$F_l{}^s$ and $a_{hlm}{}^t$ are given by the Eqs. (A6) and (B3).

As shown in detail in Appendix C, the scattered wave $\Delta\psi_k{}^\mu$ arising from the displaced lattice ion μ is given by

$$\Delta\psi_k{}^\mu(\mathbf{R}_\mu)=\frac{4\pi}{V^{1/2}}e^{i\mathbf{k}\cdot\mathbf{r}_\mu}\sum_{t,n}^{\infty}\sum_{g,m}Y_{tg}(\vartheta_{\mathbf{R}\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}\mu,\mathbf{v}_\mu})Y_{nm}{}^*(\vartheta_{\mathbf{k},\mathbf{v}_\mu},\varphi_{\mathbf{k},\mathbf{v}_\mu})K_{tgnm}{}^\mu(v_\mu,k,R_\mu), \tag{2.48}$$

where the function $K_{tgnm}{}^\mu$ is given by Eq. (C8). $\mathbf{R}_\mu$ and the displacement $\mathbf{v}_\mu$ are defined by

$$\mathbf{R}_\mu=\mathbf{r}-\mathbf{r}_\mu{}^0,\quad \mathbf{v}_\mu=\mathbf{r}_\mu{}^M-\mathbf{r}_\mu{}^0. \tag{2.49}$$

Assuming that with increasing R_μ' $\Delta(H^M(\mathbf{R}_\mu'))^\mu$ tends rapidly to zero $\Delta\psi_k{}^\mu$ can be written for large R_μ in the form

$$\Delta\psi_k{}^\mu(\mathbf{R}_\mu)\underset{\mathbf{R}_\mu\to\infty}{=}\frac{e^{i\mathbf{k}\cdot\mathbf{r}_\mu}}{V^{1/2}}f_2{}^\mu\left(v_\mu,\mathbf{k},\frac{\mathbf{R}_\mu}{R_\mu}\right)\frac{e^{ik\mathbf{R}_\mu}}{R_\mu}, \tag{2.50}$$

where the scattering amplitude is given by

$$f_2{}^\mu\left(v_\mu,\mathbf{k},\frac{\mathbf{R}_\mu}{R_\mu}\right)=-\frac{8\pi m}{\hbar^2}\sum_{t,n}\sum_{g,m}Y_{tg}{}^*(\vartheta_{\mathbf{k},\mathbf{v}_\mu},\varphi_{\mathbf{k},\mathbf{v}_\mu})Y_{nm}(\vartheta_{\mathbf{R}\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}\mu,\mathbf{v}_\mu})\gamma_{tgnm}{}^\mu(v_\mu,k). \tag{2.51}$$

$\gamma_{tgnm}{}^\mu$ is defined by

$$\gamma_{tgnm}{}^\mu(v_\mu,k)=\sum_{l,p}i^{l-t}(4\pi)^{1/2}(2p+1)^{1/2}\sigma(plt;\,(g-m)mg)\int_0^\infty dR_\mu'\,R_\mu'^2U_{p(g-m)}{}^\mu(v_\mu,R_\mu')F_{lnm}{}^\mu(k,v_\mu,R_\mu')j_t(kR_\mu'). \tag{2.52}$$

$\sigma(plt;\,(g-m)mg)$, $U_{p(g-m)}{}^\mu$, and $F_{lnm}{}^\mu$ are defined by Eqs. (E3), (C5), and (C9), respectively.

The scattered waves $\Delta(\Delta\psi^\mu)^s$, $\Delta(\Delta(\Delta\varphi_k{}^t)^j)^s$, etc., can in principle be determined using the same mathematical treatment as for the evaluation of $\Delta\varphi_k{}^s$, $\Delta(\Delta\varphi_k{}^t)^s$, and $\Delta\psi_k{}^\mu$.

III. THE DENSITY OF THE CONDUCTION ELECTRONS

The density of the conduction electrons in the distorted metal containing M point defects is given by

$$\rho^M(\mathbf{r})=\textstyle\sum_k \varphi_k{}^{M*}\varphi_k{}^M, \tag{3.1}$$

where k is summed over all conduction electrons. Approximating $\varphi_k{}^M$ by

$$\varphi_k{}^M=\varphi_k{}^0+\sum_{s=1}^{M}\Delta\varphi_k{}^s+\sum_{s,t(s\neq t)}\Delta(\Delta\varphi_k{}^t)^s+\sum_{\mu}\Delta\psi_k{}^\mu \tag{3.2}$$

ρ^M can be rewritten as

$$\rho^M(\mathbf{r})=\rho^0+\Delta\rho^{\text{s.s.}}+\Delta\rho^{\text{m.s.}}. \tag{3.3}$$

ρ^0 is the conduction electron density in the perfect metal. $\Delta\rho^{\text{s.s.}}$ arises from the single electron scattering by the point defects and the displaced lattice ions. $\Delta\rho^{\text{m.s.}}$ arises from the multiple electron scattering by the point defects. $\Delta\rho^{\text{s.s.}}$ is split into

$$\Delta\rho^{\text{s.s.}}=\Delta\rho_1{}^{\text{s.s.}}+\Delta\rho_2{}^{\text{s.s.}}+\Delta\rho_3{}^{\text{s.s.}}+\Delta\rho_4{}^{\text{s.s.}}+\Delta\rho_5{}^{\text{s.s.}}, \tag{3.4}$$

with

$$\Delta\rho_1{}^{\mathrm{s.s.}}=\sum_{s=1}^{M}\sum_{k}\{\varphi_k{}^{0*}\Delta\varphi_k{}^s+\mathrm{c.c.}+\Delta\varphi_k{}^{s*}\Delta\varphi_k{}^s\},\tag{3.5}$$

$$\Delta\rho_2{}^{\mathrm{s.s.}}=\sum_{\mu}\sum_{k}\{\varphi_k{}^{0*}\Delta\psi_k{}^\mu+\mathrm{c.c.}+\Delta\psi_k{}^{\mu*}\Delta\psi_k{}^\mu\},\tag{3.6}$$

$$\Delta\rho_3{}^{\mathrm{s.s.}}=\sum_{s,t(s\neq t)}\sum_{k}\Delta\varphi_k{}^{s*}\Delta\varphi_k{}^t,\tag{3.7}$$

$$\Delta\rho_4{}^{\mathrm{s.s.}}=\sum_{\mu,\nu(\mu\neq\nu)}\sum_{k}\Delta\psi_k{}^{\mu*}\Delta\psi_k{}^\nu,\tag{3.8}$$

and

$$\Delta\rho_5{}^{\mathrm{s.s.}}=\sum_{s,\mu}\sum_{k}\{\Delta\varphi_k{}^{s*}\Delta\psi_k{}^\mu+\mathrm{c.c.}\}.\tag{3.9}$$

$\Delta\rho_1{}^{\mathrm{s.s.}}$ represents the sum of the density changes $\Delta\rho^s$ due to the point defects. $\Delta\rho_2{}^{\mathrm{s.s.}}$ represents the sum of the density changes $\Delta\rho^\mu$ due to the displaced lattice ions μ. $\Delta\rho_3{}^{\mathrm{s.s.}}$, $\Delta\rho_4{}^{\mathrm{s.s.}}$, and $\Delta\rho_5{}^{\mathrm{s.s.}}$ arise from the interference of the different scattered waves. $\Delta\rho^{\mathrm{m.s.}}$ is split into

$$\Delta\rho^{\mathrm{m.s.}}=\Delta\rho_1{}^{\mathrm{m.s.}}+\Delta\rho_2{}^{\mathrm{m.s.}}+\Delta\rho_3{}^{\mathrm{m.s.}}+\Delta\rho_4{}^{\mathrm{m.s.}},\tag{3.10}$$

with

$$\Delta\rho_1{}^{\mathrm{m.s.}}=\sum_{s,t(s\neq t)}\sum_{k}\{\varphi_k{}^{0*}\Delta(\Delta\varphi_k{}^t)^s+\mathrm{c.c.}\},\tag{3.11}$$

$$\Delta\rho_2{}^{\mathrm{m.s.}}=\sum_{s,s',t(t\neq s)}\sum_{k}\{\Delta\varphi_k{}^{s'*}\Delta(\Delta\varphi_k{}^t)^s+\mathrm{c.c.}\},\tag{3.12}$$

$$\Delta\rho_3{}^{\mathrm{m.s.}}=\sum_{\mu,s,t(t\neq s)}\sum_{k}\{\Delta\psi_k{}^{\mu*}\Delta(\Delta\varphi_k{}^t)^s+\mathrm{c.c.}\},\tag{3.13}$$

and

$$\Delta\rho_4{}^{\mathrm{m.s.}}=\sum_{s,t,s',t'(t\neq s,t'\neq s')}\sum_{k}\Delta(\Delta\varphi_k{}^t)^{s*}\Delta(\Delta\varphi_k{}^{t'})^{s'}.\tag{3.14}$$

The various terms into which ρ^M is split are now evaluated by replacing the summation over $\mathbf{k}$ by an integration. Using Eqs. (2.38), (2.39), (2.48), and (E8) the following results are obtained:

$$\Delta\rho_1{}^{\mathrm{s.s.}}=\frac{4}{\pi}\sum_{s=1}^{M}\sum_{l=0}^{\infty}\frac{2l+1}{4\pi}\int_0^{k_F}dk\,k^2\{j_l(kR_s)\Omega_l{}^s(k,R_s)+\mathrm{c.c.}+\Omega_l{}^{s*}(k,R_s)\Omega_l{}^s(k,R_s)\},\tag{3.15}$$

$$\begin{aligned}\Delta\rho_2{}^{\mathrm{s.s.}}=\frac{4}{\pi}\sum_{\mu}\sum_{l,g,n,m,q}(-1)^g\sigma(nlq;m(-g)(m-g))\Big\{i^nY_{q(m-g)}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu\mathbf{v}_\mu})\int_0^{k_F}dk\,k^2j_n(kR_\mu)K_{lgnm}{}^{\mu*}(v_\mu,k,R_\mu)\\+\mathrm{c.c.}+Y_{q(m-g)}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu})\sum_{l',g'}\int_0^{k_F}dk\,k^2K_{lgl'g'}{}^{\mu*}(v_\mu,k,R_\mu)K_{nml'g'}{}^{\mu}(v_\mu,k,R_\mu)\Big\},\end{aligned}\tag{3.16}$$

$$\begin{aligned}\Delta\rho_3{}^{\mathrm{s.s.}}=\sum_{s,t(s\neq t)}\sum_{l,l',\alpha,m}16(-1)^li^{l+l'+\alpha}\left(\frac{2\alpha+1}{4\pi}\right)^{1/2}\sigma(ll'\alpha;m(-m)0)Y_{lm}{}^*(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s{}',\mathbf{r}_{ts}})\\\times Y_{l'(-m)}(\vartheta_{\mathbf{R}_t,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_t,\mathbf{r}_{ts}})\int_0^{k_F}dk\,k^2\Omega_l{}^{s*}(k,R_s)\Omega_{l'}{}^t(k,R_t)j_\alpha(kr_{ts}),\end{aligned}\tag{3.17}$$

$$\begin{aligned}\Delta\rho_4{}^{\mathrm{s.s.}}=\sum_{\mu,\nu(\mu\neq\nu)}\sum_{l,g,n,m,l',g',n',\alpha,\beta,\gamma}16i^\beta\sigma(n\beta n';\alpha\gamma(\alpha+\gamma))D_{\alpha m}{}^n(\varphi_{\mathbf{v}_\mu,\mathbf{v}_\nu},\vartheta_{\mathbf{v}_\mu,\mathbf{v}_\nu})Y_{\beta\gamma}{}^*(\vartheta_{\mathbf{r}_{\nu\mu},\mathbf{v}_\nu},\varphi_{\mathbf{r}_{\nu\mu},\mathbf{v}_\nu})\\\times Y_{lg}{}^*(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu})Y_{l'g'}(\vartheta_{\mathbf{R}_\nu,\mathbf{v}_\nu},\varphi_{\mathbf{R}_\nu,\mathbf{v}_\nu})\int_0^{k_F}dk\,k^2K_{lgnm}{}^{\mu*}(v_\mu,k,R_\mu)K_{l'g'n'(\alpha+\gamma)}{}^\nu(v_\nu,k,R_\nu)j_\beta(kr_{\nu\mu}),\end{aligned}\tag{3.18}$$

and

$$\begin{aligned}\Delta\rho_5{}^{\mathrm{s.s.}}=\sum_{s,\mu}\Bigg(\sum_{l,t,g,n,\alpha,\beta,\gamma}16(-1)^li^{l+\beta}\sigma(\beta ln;\gamma\alpha(\gamma+\alpha))Y_{\beta\gamma}{}^*(\vartheta_{\mathbf{r}_{\mu s},\mathbf{v}_\mu},\varphi_{\mathbf{r}_{\mu s},\mathbf{v}_\mu})Y_{tg}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu})\\\times Y_{l\alpha}{}^*(\vartheta_{\mathbf{R}_s,\mathbf{v}_\mu},\varphi_{\mathbf{R}_s,\mathbf{v}_\mu})\int_0^{k_F}dk\,k^2\Omega_l{}^{s*}(k,R_s)K_{tgn(\alpha+\gamma)}{}^\mu(v_\mu,k,R_\mu)j_\beta(kr_{\mu s})+\mathrm{c.c.}\Bigg).\end{aligned}\tag{3.19}$$

The terms arising from multiple scattering are given by

$$\Delta\rho_1^{\text{m.s.}}=\sum_{s,t(s\neq t)}\bigg(\sum_{l,m,h,n,\alpha,q}16(-1)^{n+m}i^{l+n+\alpha}\bigg(\frac{2\alpha+1}{4\pi}\bigg)^{1/2}\alpha_{hlm}\sigma(n\alpha l;m0m)\sigma(hnq;m(-m)0)$$
$$\times Y_{q0}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},0)\int_0^{kF}dk\,k^2H_{hlm}{}^s(r_{ts},k,R_s)j_n(kR_s)j_\alpha(kr_{ts})+\text{c.c.}\bigg),\quad(3.20)$$

$$\Delta\rho_2^{\text{m.s.}}=\sum_{s,t,s'(s\neq t)}\bigg(\sum_{l,m,h,n,\alpha,\beta}16(-1)^n i^{l+n+\alpha}\alpha_{hlm}\sigma(n\alpha l;(m-\beta)\beta m)Y_{\alpha\beta}{}^*(\vartheta_{\mathbf{r}_{ts'},\mathbf{r}_{ts}},\varphi_{\mathbf{r}_{ts'},\mathbf{r}_{ts}})$$
$$\times Y_{n(m-\beta)}{}^*(\vartheta_{\mathbf{R}_{s'},\mathbf{r}_{ts}},\varphi_{\mathbf{R}_{s'},\mathbf{r}_{ts}})Y_{hm}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})\int_0^{kF}dk\,k^2H_{hlm}{}^s(r_{ts},k,R_s)\Omega_n{}^{s'*}(k,R_{s'})j_\alpha(kr_{ts'})+\text{c.c.}\bigg),\quad(3.21)$$

$$\Delta\rho_3^{\text{m.s.}}=\sum_{\mu,s,t(s\neq t)}\bigg(\sum_{l,g,n,m,f,h,\alpha,\beta,\gamma}16i^{f+\beta}\alpha_{hf(\gamma+\alpha)}\sigma(\beta nf;\gamma\alpha(\gamma+\alpha))D_{\alpha m}{}^n(\varphi_{\mathbf{V}_\mu,\mathbf{r}_{ts}},\vartheta_{\mathbf{V}_\mu,\mathbf{r}_{ts}},0)$$
$$\times Y_{\beta\gamma}{}^*(\vartheta_{\mathbf{r}_{t\mu},\mathbf{r}_{ts}},\varphi_{\mathbf{r}_{t\mu},\mathbf{r}_{ts}})Y_{lg}{}^*(\vartheta_{\mathbf{R}_\mu,\mathbf{V}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{V}_\mu})Y_{h(\gamma+\alpha)}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})$$
$$\times\int_0^{kF}dk\,k^2H_{hf(\gamma+\alpha)}{}^s(r_{ts},k,R_s)K_{lgnm}{}^{\mu*}(v_\mu,k,R_\mu)j_\beta(kr_{t\mu})+\text{c.c.}\bigg),\quad(3.22)$$

and finally

$$\Delta\rho_4^{\text{m.s.}}=\sum_{s,t,s',t'(s\neq t,s'\neq t')}\bigg(\sum_{l,m,h,l',m',h',\alpha,\beta}16(-1)^l i^{l+l'+\beta}\alpha_{hlm}\alpha_{h'l'm'}\sigma(\beta ll';(\alpha-m)m\alpha)D_{\alpha m'}{}^{l'*}(\varphi_{\mathbf{r}_{t's'},\mathbf{r}_{ts}},\vartheta_{\mathbf{r}_{t's'},\mathbf{r}_{ts}},0)$$
$$\times Y_{\beta(\alpha-m)}{}^*(\vartheta_{\mathbf{r}_{t't},\mathbf{r}_{ts}},\varphi_{\mathbf{r}_{t't},\mathbf{r}_{ts}})\cdot Y_{hm}{}^*(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})Y_{h'm'}(\vartheta_{\mathbf{R}_{s'},\mathbf{r}_{t's'}},\varphi_{\mathbf{R}_{s'},\mathbf{r}_{t's'}})$$
$$\times\int_0^{kF}dk\,k^2H_{hlm}{}^{s*}(r_{ts},k,R_s)H_{h'l'm'}{}^{s'}(r_{t's'},k,R_{s'})j_\beta(kr_{t't})+\text{c.c.}\bigg).\quad(3.23)$$

To determine the interaction energy of point defects and the electric field resulting from the conduction electron redistribution, it is necessary to rewrite in ρ^m all expressions involving two coordinate systems in a form referring only to one coordinate system. This can be achieved with the help of the transformations (D2) and (E4). The obtained expressions are given in Appendix F.

IV. THE CONDUCTION ELECTRON DENSITY AT LARGE DISTANCES FROM THE SCATTERERS

The integrations over k in the formulas of the previous section need, in general, to be performed by numerical methods. However, at large distances from the scatterers, e.g., the point defects and the displaced lattice ions, all integrals over k can be evaluated analytically as follows. It follows from Eqs. (2.42), (2.43), and (2.50) that the wave function $\varphi_k{}^M$ which is given by Eq. (3.2) can be written at large distances from the scatters in the form

$$\varphi_k{}^M(\mathbf{R}_\sigma)\underset{R_\sigma\to\infty}{=}\frac{1}{V^{1/2}}\bigg(e^{i\mathbf{k}\cdot\mathbf{R}_\sigma}+f^M\frac{e^{ikR_\sigma}}{R_\sigma}\bigg),\quad(4.1)$$

where the scattering amplitude f^m is given by

$$f^M=\sum_s\sum_n i^{-n}(4\pi)^{1/2}(2n+1)^{1/2}Y_{n0}(\vartheta_{\mathbf{k}_\sigma,\mathbf{r}_\sigma},0)j_n(kr_{s\sigma})e^{i\mathbf{k}\cdot\mathbf{r}_{s\sigma}}\{f_1{}^s+f_2{}^s+\sum_{t(t\neq s)}e^{i\mathbf{k}\cdot\mathbf{r}_{ts}}f^{ts}\}.\quad(4.2)$$

Equation (4.1) yields the conduction electron density

$$\rho^M(\mathbf{R}_\sigma)\underset{R_\sigma\to\infty}{=}\rho^0+\frac{1}{4\pi^3}\int_{\mathbf{k}<\mathbf{k}_F}d^3k\bigg\{f^M\frac{\exp[-ikR_\sigma(\cos\vartheta_{\mathbf{k},\mathbf{R}_\sigma}-1)]}{R_\sigma}+\text{c.c.}+\frac{|f^M|^2}{R_\sigma{}^2}\bigg\}.\quad(4.3)$$

Now for large R_σ the first term in the integral contributes essentially only for $\cos\vartheta_{\mathbf{k},\mathbf{R}_\sigma}\approx1$, e.g., $\mathbf{k}/k\approx\mathbf{R}_\sigma/R_\sigma$. One gets, therefore,

$$\rho^M(\mathbf{R}_\sigma) \underset{R_\sigma\to\infty}{=} \rho^0+\frac{1}{2\pi^2R_\sigma^2}\int_0^{k_F} dk\, k(f^M)_{\mathbf{k}/k=\mathbf{R}_\sigma/R_\sigma}e^{2ikR_\sigma}+\text{c.c.}-\frac{1}{\pi^2R_\sigma^2}\int_0^{k_F} dk\, k\, \text{Im}(f^M)_{\mathbf{k}/k=\mathbf{R}_\sigma/R_\sigma} +\frac{1}{4\pi^3R_\sigma^2}\int_{k<k_F} d^3k\, |f^M|^2. \quad (4.4)$$

Using the well-known optical theorem,

$$\int d\Omega\, |f^M|^2=\frac{4\pi}{k}\,\text{Im}(f^M)_{\mathbf{k}/k=\mathbf{R}_\sigma/R_\sigma}, \quad (4.5)$$

one obtains

$$\rho^M(\mathbf{R}_\sigma) \underset{R_\sigma\to\infty}{=} \rho^0+\frac{1}{2\pi^2R_\sigma^2}\int_0^{k_F} dk\, k(f^M)_{\mathbf{k}/k=\mathbf{R}_\sigma/R_\sigma}e^{2ikR_\sigma}+\text{c.c.} \quad (4.6)$$

Again, for large R_σ, e^{2ikR_σ} varies quite more rapidly than $(f^m)_{\mathbf{k}/k=\mathbf{R}_\sigma/R_\sigma}$. Therefore, the integral can be readily evaluated. The result is

$$\rho^M(\mathbf{R}_\sigma) \underset{R_\sigma\to\infty}{=} \rho^0-\frac{1}{4\pi^2R_\sigma^3}\{(f^M(k=k_F))_{\mathbf{k}/k=\mathbf{R}_\sigma/R_\sigma}e^{2ik_FR_\sigma}+\text{c.c.}\}, \quad (4.7)$$

with

$$(f^M(k=k_F))_{\mathbf{k}/k=\mathbf{R}_\sigma/R_\sigma}=-\frac{32\pi^2m}{\hbar^2}\sum_s\sum_{n,q,q'} i^{q-n}(2n+1)^{1/2}(2q+1)^{1/2}\sigma(nqq';000)j_n(k_Fr_{s\sigma})j_q(k_Fr_{s\sigma})Y_{q'0}(\vartheta_{\mathbf{R}_\sigma,\mathbf{r}_{s\sigma}},0)$$
$$\times\left\{\sum_{l=0}^{\infty}\left(\frac{2l+1}{4\pi}\right)^{1/2}\omega_l^s(k_F)Y_{l0}(\vartheta_{\mathbf{R}_\sigma,\mathbf{R}_s},0)+\sum_{t,g,n,m}\gamma_{tgnm}^s(v_s,k_F)Y_{tg}^*(\vartheta_{\mathbf{R}_\sigma,\mathbf{V}_s},\varphi_{\mathbf{R}_\sigma,\mathbf{V}_s})\right.$$
$$\times Y_{nm}(\vartheta_{\mathbf{R}_s,\mathbf{V}_s},\varphi_{\mathbf{R}_s,\mathbf{V}_s})+\sum_{t(t\neq s)}\sum_{l,h,m,p,p'} i^p(4\pi)^{1/2}(2p+1)^{1/2}\alpha_{hlm}\sigma(lpp';(-m)0(-m))$$
$$\left.\times\beta_h^s(k_F,r_{ts})j_p(k_Fr_{ts})Y_{p'm}^*(\vartheta_{\mathbf{R}_\sigma,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_\sigma,\mathbf{r}_{ts}})Y_{hm}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})\right\}. \quad (4.8)$$

For $R_\sigma \gg r_{s\sigma}$ this expression can be simplified by putting $R_s=R_\sigma$.

V. CONCLUDING REMARKS

The scattering of the conduction electrons due to point defect complexes in noble metals has been treated in general form by using the Hartree-Fock approximation. The scattering potentials act on electron states approximated by plane waves. The electron scattering due to the lattice distortion associated with the point defects is taken into account in determining the wave functions of the conduction electrons. The multiple electron scattering due to the point defects is determined in first order. However, using the same mathematical treatment multiple electron scattering can be determined in higher order. To what extent multiple scattering need be taken into account in determining the electron wave functions depends on the strength of the scattering potentials and on the separations between the interacting scatterers. If the scattering potentials overlap or lie very close together, multiple scattering will play an important role. Also, for example, multiple scattering has to be taken into account in determining the conduction electron redistribution resulting from a split interstitial when regarded as an extended defect consisting of a vacancy and two interstitials lying symmetrically with respect to the vacancy.

In the past it was thought that only the lattice distortion associated with interstitials must be taken into account in determining the electron redistribution due to point defects. However, there exists now some experimental evidence[13] that the relaxation of the lattice around vacancies is much stronger than expected and, therefore, will have some effect on the electron redistribution.

The perturbing potentials due to the point defects have been assumed to be spherically symmetric. This is no main limitation of the outlined method. It has been shown in the case of scattering due to the lattice distortion how the scattering by arbitrarily shaped potentials can be treated.

The essential limitation of the expressions derived in this paper arises from the neglection of correlation among the conduction electrons and from the neglection of the lattice potential in H^0, e.g., from using plane

[11] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Parts I and II.

[12] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

[13] Suggested by Professor D. Lazarus by means of recent experimental results obtained by his collaborators at the University of Illinois.

waves instead of Bloch waves for the unperturbed electron wave functions.

It is possible to include in φ^M or ρ^m, respectively, the effect of electron correlation by using many body techniques. Also, it seems that the proposed treatment of the electron scattering can be extended to Bloch electrons. The scattering of plane waves can be regarded as a good approximation if the scattering potentials cover essentially lattice regions where the Bloch waves can be fairly well approximated by plane waves.

The wave functions and electron density which have been derived in this paper will be used in a continuing paper to calculate the interaction energy of point defects.

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APPENDIX A: DERIVATION OF $\Delta\varphi_k^s$

The scattered wave $\Delta\varphi_k^s$ arising from the single scattering of the conduction electrons by the potential ΔH^s is given by

$$\Delta\varphi_k^s(\mathbf{R}_s)=\int d^3R_s'\, G(\mathbf{R}_s,\mathbf{R}_s',\mathbf{k})\Delta H^s(\mathbf{R}_s')\varphi_k^s(\mathbf{R}_s') \tag{A1}$$

with

$$\varphi_k^s=\varphi_k^0+\Delta\varphi_k^s. \tag{A2}$$

Equation (A1) is derived in the same way as Eq. (2.17). The Green's function G is determined by Eq. (2.14). It is now assumed that ΔH^s is spherically symmetric. To perform the angular integrations in Eq. (A1) G, as given by Eq. (2.37), and φ_k^s are expanded as

$$G(\mathbf{R}_s,\mathbf{R}_s',\mathbf{k})=\sum_{n=0}^{\infty}\left(\frac{2n+1}{4\pi}\right)^{1/2}Y_{n0}(\vartheta_{\mathbf{R}_s,\mathbf{R}_s'},0)G_n(R_s,R_s',k), \tag{A3}$$

with

$$G_n(R_s,R_s',k)=-\frac{2imk}{\hbar^2}\times\begin{cases} j_n(kR_s)h_n^{(1)}(kR_s'), & R_s<R_s' \\ j_n(kR_s')h_n^{(1)}(kR_s), & R_s>R_s' \end{cases} \tag{A4}$$

and

$$\varphi_k^s(\mathbf{R}_s)=4\pi\frac{e^{i\mathbf{k}\cdot\mathbf{r}_s}}{V^{1/2}}\sum_{l=0}^{\infty}i^l\left(\frac{2l+1}{4\pi}\right)^{1/2}Y_{l0}(\vartheta_{\mathbf{k},\mathbf{R}_s},0)F_l^s(k,R_s). \tag{A5}$$

The functions j_n and $h_n^{(1)}$ are the nth spherical Bessel function and the nth spherical Hankel function of the first kind, respectively. $\mathbf{r}_s$ gives the lattice position of the point defect s. V is the volume of the crystal. The function F_l^s is determined by

$$F_l^s(k,R_s)=j_l(kR_s)+\int_0^{\infty}dR_s'\,R_s'^2G_l(R_s,R_s',k)\Delta H^s(R_s')F_l^s(k,R_s') \tag{A6}$$

which results from Eq. (A2) by using Eqs. (A1) and (A5) and expanding φ_k^0, approximated by a normalized plane wave, into spherical harmonics. It follows from Eq. (A1) using the expansions (A3) and (A5) and Eq. (A6)

$$\Delta\varphi_k^s(\mathbf{R}_s)=4\pi\frac{e^{i\mathbf{k}\cdot\mathbf{r}_s}}{V^{1/2}}\sum_{l=0}^{\infty}i^l\left(\frac{2l+1}{4\pi}\right)^{1/2}Y_{l0}(\vartheta_{\mathbf{k},\mathbf{R}_s},0)\Omega_l^s(k,R_s) \tag{A7}$$

with

$$\Omega_l^s(k,R_s)=F_l^s(k,R_s)-j_l(kR_s). \tag{A8}$$

To determine F_l^s, the Coulomb potential

$$\Delta C^s(\mathbf{R}_s)=e^2\int d^3R_s'\frac{\rho^s(\mathbf{R}_s')-\rho^0(\mathbf{R}_s')}{|\mathbf{R}_s-\mathbf{R}_s'|}, \tag{A9}$$

and the exchange potential

$$\Delta A^s(\mathbf{R}_s)=-\frac{e^2}{2}\left\{\int d^3R_s'\frac{|\rho^s(\mathbf{R}_s,\mathbf{R}_s')|^2}{|\mathbf{R}_s-\mathbf{R}_s'|}\Big/\rho^s(\mathbf{R}_s,\mathbf{R}_s)-\int d^3R_s'\frac{|\rho^0(\mathbf{R}_s,\mathbf{R}_s')|^2}{|\mathbf{R}_s-\mathbf{R}_s'|}\Big/\rho^0(\mathbf{R}_s,\mathbf{R}_s)\right\} \tag{A10}$$

need be evaluated by using Eq. (A5). The density matrix $\rho^s(\mathbf{R}_s,\mathbf{R}_s')$ is given by Eq. (27) replacing φ_k^M by φ_k^s.

$\rho^s(\mathbf{R}_s')$ is given by $\rho^s(\mathbf{R}_s',\mathbf{R}_s')$. Using

$$\rho^s(\mathbf{R}_s,\mathbf{R}_s')=\frac{1}{\pi^2}\sum_{l=0}^{\infty}(2l+1)p_l(\cos\vartheta_{\mathbf{R}_s,\mathbf{R}_s'})\rho_l(R_s,R_s'), \tag{A11}$$

with

$$\rho_l(R_s,R_s')=\int_0^{k_F}dk\,k^2\{j_l(kR_s)j_l(kR_s')+j_l(kR_s)\Omega_l^s(k,R_s')+\Omega_l^{s*}(k,R_s)j_l(kR_s')+\Omega_l^{s*}(k,R_s)\Omega_l^s(k,R_s')\}, \tag{A12}$$

and expanding $|\mathbf{R}_s-\mathbf{R}_s'|^{-1}$ in Legendre polynomials, one obtains

$$\Delta C^s(\mathbf{R}_s)=\frac{4e^2}{\pi}\sum_{l=0}^{\infty}(2l+1)\int_0^{k_F}dk\,k^2\int_0^{\infty}dR_s'\,R_s'^2\gamma_0(R_s,R_s')\{j_l(kR_s')\Omega_l^s(k,R_s')+\text{c.c.}+\Omega_l^{s*}(k,R_s')\Omega_l^s(k,R_s)\}, \tag{A13}$$

and

$$\Delta A^s(R_s)=-\frac{2e^2}{\pi}\sum_{l,l',l''}(2l'+1)c^2(l'l''l;000)\left\{\int^{\infty}dR_s'R_s'^2\gamma_{l''}(R_s,R_s')\rho_l^*(R_s,R_s')\rho_{l'}(R_s,R_s')\Big/\sum_{t=0}^{\infty}(2t+1)\rho_t(R_s,R_s)\right.$$

$$\left.-\int_0^{\infty}dR_s'R_s'^2\gamma_{l''}(R_s,R_s')\rho_l^{0*}(R_s,R_s')\rho_{l'}^0(R_s,R_s')\Big/\sum_{t=0}^{\infty}(2t+1)\rho_t^0(R_s,R_s)\right\}. \tag{A14}$$

The function $\gamma_{l''}$ is given by

$$\gamma_{l''}(R_s,R_s')=\frac{1}{R_s'}\left(\frac{R_s}{R_s'}\right)^{l''},\quad R_s<R_s',$$

$$=\frac{1}{R_s}\left(\frac{R_s'}{R_s}\right)^{l''},\quad R_s>R_s'. \tag{A15}$$

k_f is the Fermi wave number. The $c(l'l''l;000)$ are Clebsch-Gordan coefficients.[12] $\rho_l^0(R_s,R_s')$ is obtained from Eq. (A12) putting $\Omega_l^s=0$.

F_l^s can now be determined self-consistently by expanding ΔC^s and ΔA^s as

$$\Delta C^s=\Delta C_1^s+(\Delta C_2^s-\Delta C_1^s)+\cdots, \tag{A16}$$

and

$$\Delta A^s=\Delta A_1^s+(\Delta A_2^s-\Delta A_1^s)+\cdots. \tag{A17}$$

ΔC_1^s and ΔA_1^s are determined from Eqs. (A13) and (A14) by using a wave function approximating φ_k^s closely. ΔC_2^s and ΔA_2^s are determined from Eqs. (A13) and (A14), using for φ_k^s the wave function resulting from approximating ΔC^s and ΔA^s by ΔC_1^s and ΔA_1^s. By continuing this process the higher terms in Eqs. (A16) and (A17) are determined.

APPENDIX B: DERIVATION OF $\Delta(\Delta\varphi_k^t)^s$

The scattered wave $\Delta(\Delta\varphi_k^t)^s$ is defined by Eq. (2.32) as

$$\Delta(\Delta\varphi_k^t)^s=\int d^3R_s'\,G(\mathbf{R}_s,\mathbf{R}_s',\mathbf{k})\Delta H^s(R_s')\Delta\varphi_k^t. \tag{B1}$$

To perform the integration the scattered wave $\Delta\varphi_k^t$ need be expressed in terms of R_s. Using the addition theorem for spherical harmonics and the transformation formula (D2) $\Delta\varphi_k^t$ is expressed in the coordinate system $(R_s',\vartheta_{\mathbf{R}_s'},\varphi_{\mathbf{R}s'})$ by

$$\Delta\varphi_k^t=4\pi\frac{e^{i\mathbf{k}\cdot\mathbf{r}_t}}{V^{1/2}}\sum_{l,h}\sum_m i^l\alpha_{hlm}Y_{lm}^*(\vartheta_{\mathbf{k},\mathbf{r}_{ts}},\varphi_{\mathbf{k},\mathbf{r}_{ts}})Y_{hm}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})a_{hlm}^t(r_{ts},k,R_s), \tag{B2}$$

with

$$a_{hlm}^t(r_{ts},k,R_s)=\frac{2h+1}{2r_{ts}R_s}\frac{(h-m)!}{(h+m)!}\int_{|r_{ts}-R_s|}^{r_{ts}+R_s}\Omega_l^t(k,R_t)P_l^m\left(\frac{R_s^2-r_{ts}^2-R_t^2}{2r_{ts}R_t}\right)P_h^m\left(\frac{R_s^2+r_{ts}^2-R_t^2}{2r_{ts}R_s}\right)R_tdR_t, \tag{B3}$$

and

$$\alpha_{hlm}=\left(\frac{(2l+1)(l-m)!(h+m)!}{(2h+1)(l+m)!(h-m)!}\right)^{1/2}. \tag{B4}$$

Using for the Green's function G the expansion (A.3), the angular integrations in Eq. (B1) can be performed. The result is

$$\Delta(\Delta\varphi_k^t)^s = 4\pi \frac{e^{i\mathbf{k}\cdot\mathbf{r}_t}}{V^{1/2}} \sum_{l,h,m} i^l \alpha_{hlm} Y_{lm}^*(\vartheta_{\mathbf{k},\mathbf{r}_{ts}}, \varphi_{\mathbf{k},\mathbf{r}_{ts}}) Y_{hm}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}}, \varphi_{\mathbf{R}_s,\mathbf{r}_{ts}}) H_{hlm}^s(r_{ts},k,R_s), \tag{B5}$$

with

$$H_{hlm}^s(r_{ts},k,R_s) = \int_0^\infty dR_s'\, R_s'^2\, G_h(R_s,R_s',k) \Delta H^s(R_s') a_{hlm}^t(r_{ts},k,R_s'). \tag{B6}$$

APPENDIX C: DERIVATION OF $\Delta\psi_k^\mu$

The scattered wave $\Delta\psi_k^\mu$ arising from the perturbing potential $\Delta(H^M)^\mu$ associated with the displaced lattice ion μ is given by

$$\Delta\psi_k^\mu(\mathbf{R}_\mu) = \int d^3R_\mu'\, G(\mathbf{R}_\mu,\mathbf{R}_\mu',\mathbf{k}) \Delta(H^M(\mathbf{R}_\mu'))^\mu \psi_k^\mu(R_\mu'), \tag{C1}$$

with

$$\psi_k^\mu = \varphi_k^0 + \Delta\psi_k^\mu. \tag{C2}$$

To perform in Eq. (C1) the angular integration G, $\Delta(H^M)^\mu$, and ψ_k^μ are expanded into spherical harmonics as

$$G(\mathbf{R}_\mu,\mathbf{R}_\mu',\mathbf{k}) = \sum_{t,g} Y_{tg}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu}, \varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu}) Y_{tg}^*(\vartheta_{\mathbf{R}_\mu',\mathbf{v}_\mu}, \varphi_{\mathbf{R}_\mu',\mathbf{v}_\mu}) G_t(R_\mu,R_\mu',k), \tag{C3}$$

$$\Delta(H^M(\mathbf{R}_\mu'))^\mu = \sum_{p,q} Y_{pq}(\vartheta_{\mathbf{R}_\mu',\mathbf{v}_\mu}, \varphi_{\mathbf{R}_\mu',\mathbf{v}_\mu}) U_{pq}^\mu(R_\mu'), \tag{C4}$$

with

$$U_{pq}^\mu(R_\mu') = \int d\Omega\, \Delta(H^M(R_\mu'))^\mu Y_{pq}^*(\vartheta_{\mathbf{R}_\mu',\mathbf{v}_\mu}, \varphi_{\mathbf{R}_\mu',\mathbf{v}_\mu}), \tag{C5}$$

and

$$\psi_k^\mu(R_\mu') = 4\pi \frac{e^{i\mathbf{k}\cdot\mathbf{r}_\mu}}{V^{1/2}} \sum_{l,m,n} i^l Y_{lm}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu}, \varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu}) Y_{nm}^*(\vartheta_{\mathbf{k},\mathbf{v}_\mu}, \varphi_{\mathbf{k},\mathbf{v}_\mu}) F_{lnm}^\mu(v_\mu,k,R_\mu'). \tag{C6}$$

Substituting these expressions into Eq. (C1) and performing the angular integrations one obtains

$$\Delta\psi_k^\mu(\mathbf{R}_\mu) = 4\pi \frac{e^{i\mathbf{k}\cdot\mathbf{r}_\mu}}{V^{1/2}} \sum_{t,g,n,m} Y_{tg}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu}, \varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu}) Y_{nm}^*(\vartheta_{\mathbf{k},\mathbf{v}_\mu}, \varphi_{\mathbf{k},\mathbf{v}_\mu}) K_{tgnm}^\mu(v_\mu,k,R_\mu), \tag{C7}$$

with

$$K_{tgnm}^\mu(V_\mu,k,R_\mu) = \sum_{l,p} i^l \sigma(plt;\,(g-m)mg) \int_0^\infty dR_\mu'\, R_\mu'^2\, G_t(R_\mu,R_\mu',k) U_{p(g-m)}^\mu(R_\mu') F_{lnm}^\mu(v_\mu,k,R_\mu'). \tag{C8}$$

It follows from Eqs. (C2), (C1), and (C6) that F_{lnm}^μ is determined by

$$F_{lnm}^\mu(v_\mu,k,R_\mu) = j_n(kR_\mu) + \sum_{t,s,p} \sigma(plt;\,(s-m)ms) \int_0^\infty dR_\mu'\, R_\mu'^2\, G_t(R_\mu,R_\mu',k) U_{p(s-m)}^\mu(R_\mu') F_{lnm}^\mu(v_\mu,k,R_\mu'). \tag{C9}$$

To determine $U_{p(s-m)}^\mu$ the potential $\Delta(H^M)^\mu$, which is given by

$$\Delta(H^M)^\mu = \mathcal{V}(\mathbf{r}-\mathbf{r}_\mu^M) - \mathcal{V}(\mathbf{r}-\mathbf{r}_\mu^0) + \Delta C^\mu(\mathbf{r}-\mathbf{r}_\mu^0) + \Delta A^\mu(\mathbf{r}-\mathbf{r}_\mu^0), \tag{C10}$$

is evaluated as follows. Expanding $\mathcal{V}(\mathbf{r}-\mathbf{r}_\mu^M)$ in a Taylor series around $\mathbf{r}_\mu^0$ and assuming that $\mathcal{V}(\mathbf{r}-\mathbf{r}_\mu^0)$ is spherically symmetric, one gets

$$\Delta(H^M)^\mu = \sum_{\alpha=1}^\infty (v^\mu)^\alpha \cos^\alpha\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu} \frac{d^\alpha \mathcal{V}(R_\mu)}{dR_\mu^\alpha} + \Delta C^\mu + \Delta A^\mu. \tag{C11}$$

Using

$$\cos^\alpha\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu} = \textstyle\sum_\beta d_\beta^{(\alpha)} Y_{\beta 0}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},0), \tag{C12}$$

with

$$d_\beta^{(\alpha)} = \int d\Omega\, \cos^\alpha x\, Y_{\beta 0}(x,0), \tag{C13}$$

Eq. (C11) can be rewritten as

$$\Delta(H^M)^\mu=\sum_{\alpha=1}^{\infty}\sum_{\beta}(v^\mu)^\alpha d_\beta{}^{(\alpha)}\frac{d^\alpha \mathcal{V}(R_\mu)}{dR_\mu{}^\alpha}Y_{\beta 0}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},0)+\Delta C^\mu+\Delta A^\mu. \tag{C14}$$

ΔC^μ and ΔA^μ are now evaluated by using Eq. (C7). ΔC^μ is derived in the same way as ΔC^s in Appendix A. The result is

$$\Delta C^\mu(\mathbf{R}_\mu)=16e^2\sum_{l,g,n,m,q}\frac{(-1)^g}{2q+1}\sigma(nlq;m(-g)(m-g))\bigg\{i^nY_{q(m-g)}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu})\int_0^{k_F}dk\,k^2\int_0^\infty dR_\mu' R_\mu'^2 j_n(kR_\mu')$$
$$\times K_{lgnm}{}^{\mu*}(v_\mu,k,R_\mu')\gamma_q(R_\mu,R_\mu')+\text{c.c.}+Y_{q(m-g)}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu})$$
$$\times\sum_{l',g'}\int_0^{k_F}dk\,k^2\int_0^\infty dR_\mu'\,R_\mu'^2K_{lgl'g'}{}^{\mu*}(v_\mu,k,R_\mu')K_{nml'g'}{}^{\mu}(v_\mu,k,R_\mu')\gamma_q(R_\mu,R_\mu')\bigg\}. \tag{C15}$$

Using

$$\rho^\mu(\mathbf{R}_\mu,\mathbf{R}_\mu')=\frac{4}{\pi}\sum_{t,g,n,m}Y_{tg}{}^*(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu})Y_{nm}(\vartheta_{\mathbf{R}_\mu',\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu',\mathbf{v}_\mu})\rho_{tgnm}{}^\mu(R_\mu,R_\mu'), \tag{C16}$$

with

$$\rho_{tgnm}{}^\mu(R_\mu,R_\mu')=\int_0^{k_F}dk\,k^2\{j_t(kR_\mu)j_t(kR_\mu')\delta_{m,g}\delta_{n,t}+(-1)^ti^tK_{nmtg}{}^\mu(v_\mu,k,R_\mu')j_t(kR_\mu)$$
$$+i^nK_{tgnm}{}^{\mu*}(v_\mu,k,R_\mu)j_n(kR_\mu')+\sum_{t',g'}K_{tgt'g'}{}^{\mu*}(v_\mu,k,R_\mu)K_{nmt'g'}{}^\mu(v_\mu,k,R_\mu')\}, \tag{C17}$$

and expanding $[\rho^\mu(\mathbf{R}_\mu,\mathbf{R}_\mu)]^{-1}$ in a Taylor series in terms of $\Delta\rho^\mu(\mathbf{R}_\mu)/\rho^0(\mathbf{R}_\mu,\mathbf{R}_\mu)$, one obtains for ΔA^μ

$$\Delta A^\mu(\mathbf{R}_\mu)=-e^2\sum_{l,g,n,m,l',g',n',m'}\sum_{\beta,p,q}\eta_{gnmg'n'}{}^{m'\beta pq}Y_{q(g+m'-g'-m)}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu})\int_0^\infty dR_\mu'\,R_\mu'^2\gamma_\beta(R_\mu,R_\mu')$$
$$\times\bigg\{\rho_{lgnm}{}^{\mu*}(R_\mu,R_\mu')\rho_{l'g'n'm'}{}^\mu(R_\mu,R_\mu')\bigg(1-\frac{\Delta\rho^\mu(\mathbf{R}_\mu)}{\rho^0(R_\mu,R_\mu)}+\cdots\bigg)-\rho_{lgnm}{}^{0*}(R_\mu,R_\mu')\rho_{l'g'n'm'}{}^0(R_\mu,R_\mu')\bigg\}$$
$$\times[\rho^0(R_\mu,R_\mu)]^{-1}, \tag{C18}$$

where the coefficients $\eta_{gnmg'n'}{}^{m'\beta pq}$ are given by

$$\eta_{gnmg'n'}{}^{m'\beta pq}=\frac{32}{\pi}\frac{(-1)^{g'+m-m'}}{2\beta+1}\sigma(n'\beta n;m'(m-m')m)\sigma(t'\beta p;g'(m-m')(g'+m-m'))$$
$$\times\sigma(tpq;g(m'-m-g')(g+m'-m-g')). \tag{C19}$$

From Eqs. (C.14), (C.15), and (C.18) it follows that

$$U_{pq}{}^\mu(R_\mu)=(U_{pq}{}^\mu(R_\mu))_1+(U_{pq}{}^\mu(R_\mu))_2+(U_{pq}{}^\mu(R_\mu))_3, \tag{C20}$$

with

$$(U_{pq}{}^\mu(R_\mu))_1=\delta_{0,q}\sum_{\alpha=1}^\infty(v^\mu)^\alpha d_p{}^{(\alpha)}\frac{d^\alpha\vartheta(R_\mu)}{dR_\mu{}^\alpha}, \tag{C21}$$

$$(U_{pq}{}^\mu(R_\mu))^2=16e^2\sum_{l,g,n}\frac{(-1)^g}{2p+1}\sigma(nlp;(q+g)(-g)q)\bigg\{i^n\int_0^{k_F}dk\,k^2\int_0^\infty dR_\mu'\,R_\mu'^2j_n(kR_\mu')K_{lgn(q+g)}{}^{\mu*}(v_\mu,k,R_\mu')$$
$$\times\gamma_p(R_\mu,R_\mu')+\text{c.c.}+\sum_{l',g'}\int_0^{k_F}dk\,k^2\int_0^\infty dR_\mu'R_\mu'^2K_{lgl'g'}{}^{\mu*}(v_\mu,k,R_\mu')$$
$$\times K_{n(q+g)l'g'}{}^\mu(v_\mu,k,R_\mu')\gamma_p(R_\mu,R_\mu')\bigg\}, \tag{C22}$$

and

$$(U_{pq}{}^\mu(R_\mu))_3=-e^2\sum_{l,g,n,m,l',g',n',m'}\sum_{\beta,\epsilon,\vartheta}\eta_{gnmg'n'}{}^{m'\beta\epsilon\vartheta}\int_0^\infty dR_\mu'\,R_\mu'^2\gamma_\beta(R_\mu,R_\mu')\bigg\{\rho_{lgnm}{}^{\mu*}(R_\mu,R_\mu')\rho_{l'g'n'm'}{}^\mu(R_\mu,R_\mu')$$
$$\times\bigg(\delta_{p,\epsilon}\delta_{q,g+m'-g'-m}-\frac{1}{\rho^0(R_\mu,R_\mu)}\int d\Omega Y_{pq}{}^*(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_\mu},\varphi_{\mathbf{R}_\mu,\mathbf{v}_\mu})[\Delta\rho^\mu(\mathbf{R}_\mu)-+\cdots]\bigg)$$
$$-\rho_{lgnm}{}^{0*}(R_\mu,R_\mu')\rho_{l'g'n'm'}{}^0(R_\mu,R_\mu')\delta_{p,\epsilon}\delta_{q,g+m'-g'-m}\bigg\}[\rho^0(R_\mu,R_\mu)]^{-1}. \tag{C23}$$

The terms $(U_{pq}{}^{\mu})_1$, $(U_{pq}{}^{\mu})_2$, and $(U_{pq}{}^{\mu})_3$ result from Δv, ΔC^{μ} and ΔA^{μ}, respectively.

To solve now Eq. (C9) self-consistently, $(U_{pq}{}^{\mu})_2$ and $(U_{pq}{}^{\mu})_3$ are expanded as

$$(U_{pq}{}^{\mu})_2=(U_{pq}{}^{\mu})_2{}^1+\{(U_{pq}{}^{\mu})_2{}^2-(U_{pq}{}^{\mu})_2{}^1\}+\cdots, \tag{C24}$$

and

$$(U_{pq}{}^{\mu})_3=(U_{pq}{}^{\mu})_3{}^1+\{(U_{pq}{}^{\mu})_3{}^2-(U_{pq}{}^{\mu})_3{}^1\}+\cdots. \tag{C25}$$

$(U_{pq}{}^{\mu})_2{}^1$ and $(U_{pq}{}^{\mu})_3{}^1$ are first approximations for $(U_{pq}{}^{\mu})_2$ and $(U_{pq}{}^{\mu})_3$. $(U_{pq}{}^{\mu})_2{}^2$, $(U_{pq}{}^{\mu})_3{}^2$ are determined from Eqs. (C22) and (C23) by using $F_{lnm}{}^{\mu}$ which results from approximating $(U_{pq}{}^{\mu})_2$ by $(U_{pq}{}^{\mu})_2{}^1$ and $(U_{pq}{}^{\mu})_3$ by $(U_{pq}{}^{\mu})_3{}^1$. The higher terms in Eqs. (C24) and (C25) are determined in the same way.

APPENDIX D: THE TRANSFORMATION $H(R_t,\vartheta_t,\varphi_t)=H'(R_s,\vartheta_s,\varphi_s)$

Using (see Fig. 1)

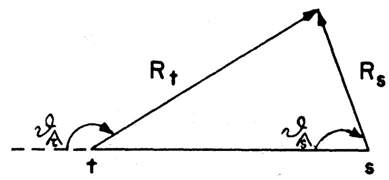

FIG. 1. Illustration to transformation ($D1$).

$$\varphi_t=\varphi_s,\quad R_t^2=R_s^2+r_{ts}^2-2r_{ts}R_s\cos\vartheta_s,\quad \cos\vartheta_s=(R_t\cos\vartheta_t+r_{ts})/R_s,\quad \cos\vartheta_t=(R_s\cos\vartheta_s-r_{ts})/R_t, \tag{D1}$$

the transformation $H(R_t,\vartheta_t,\varphi_t)=H'(R_s,\vartheta_s,\varphi_s)$ is evaluated by expanding H and H' in spherical harmonics. One gets

$$K_l(R_t)P_l{}^m(\cos\vartheta_t)=\sum\nolimits_h a_{hlm}(r_{ts},R_s)P_h{}^m(\cos\vartheta_s) \tag{D2}$$

with the coefficient functions a_{hlm} given by

$$a_{hlm}(r_{ts},R_s)=\frac{2h+1}{2r_{ts}R_s}\frac{(h-m)!}{(h+m)!}\int_{|r_{ts}-R_s|}^{r_{ts}+R_s}K_l(R_t)R_tP_l{}^m\left(\frac{R_s{}^2-r_{ts}{}^2-R_t{}^2}{2r_{ts}R_t}\right)P_h{}^m\left(\frac{R_s{}^2+r_{ts}{}^2-R_t{}^2}{2r_{ts}R_s}\right)dR_t. \tag{D3}$$

APPENDIX E: THE ANGULAR INTEGRATIONS IN $\Delta\rho^M$.

To perform the angular integrations in $\Delta\rho^M$, the integral

$$J=\int d\Omega\, Y_{l_1m_1}{}^*(\vartheta_{\mathbf{r}_1,\mathbf{r}_2},\varphi_{\mathbf{r}_1,\mathbf{r}_2})Y_{l_2m_2}(\vartheta_{\mathbf{r}_1,\mathbf{r}_3},\varphi_{\mathbf{r}_1,\mathbf{r}_3})Y_{l_3m_3}(\vartheta_{\mathbf{r}_1,\mathbf{r}_3},\varphi_{\mathbf{r}_1,\mathbf{r}_3}) \tag{E1}$$

has to be evaluated. This is done by using the expansion[12]

$$Y_{l_1m_1}(\vartheta,\varphi)Y_{l_2m_2}(\vartheta,\varphi)=\sum\nolimits_l \sigma(l_1l_2l;\,m_1m_2(m_1+m_2))Y_{l(m_1+m_2)}(\vartheta,\varphi), \tag{E2}$$

with

$$\sigma(l_1l_2l;\,m_1m_2(m_1+m_2))=\left(\frac{(2l_1+1)(2l_2+1)}{4\pi(2l+1)}\right)^{1/2}c(l_1l_2l;\,m_1m_2(m_1+m_2))c(l_1l_2l;\,000), \tag{E3}$$

where the c's are Clebsch-Gordan coefficients, and the formula[12]

$$Y_{lm}(\vartheta,\varphi)=\sum_{m'}D_{m'm}{}^l(\alpha,\beta,0)Y_{lm'}(\vartheta',\varphi'), \tag{E4}$$

which describes the transformation of spherical harmonics under the rotation of the axis of the polar coordinate system. α is the azimuthal angle and β the polar angle of the new polar axis, to which ϑ' refers with respect to the original polar axis. The Clebsch-Gordan coefficients are determined from[12]

$$c(l_1l_2l_3;\,m_1m_2m_3)=\delta_{m_3,m_1+m_2}\Bigg[(2l_3+1)\frac{(l_1+l_2-l_3)!}{(l_1+l_2+l_3+1)!}(l_3+l_1-l_2)!(l_3+l_2-l_1)!(l_1+m_1)!(l_1-m_1)!(l_2+m_2)!$$
$$\times(l_2-m_2)!(l_3+m_3)!(l_3-m_3)!\Bigg]^{1/2}\sum_r\frac{(-1)^r}{r!}[(l_1+l_2-l_3-r)!(l_1-m_1-r)!(l_2+m_2-r)!$$
$$\times(l_3-l_2+m_1+r)!(l_3-l_1-m_2+r)!]^{-1}, \tag{E5}$$

where the integral index r assumes only those values for which the factorial arguments are not negative. The matrix $D_{m'm}{}^{l}(\alpha,\beta,0)$ is given by[12]

$$D_{m'm}{}^{l}(\alpha,\beta,0)=e^{-im'\alpha}d_{m'm}{}^{l}(\beta), \tag{E6}$$

with

$$d_{m'm}{}^{l}(\beta)=[(l+m)!(l-m)!(l+m')!(l-m')!]^{1/2}\sum_K \frac{(-1)^K[\cos(\beta/2)]^{2l+m-m'-2K}[-\sin(\beta/2)]^{m'-m+2K}}{(l-m'-K)!(l+m-K)!(K+m'-m)!K!}, \tag{E7}$$

where the sum is over the values of the integer K for which the factorial arguments are greater or equal to zero. Now the integral J is easily evaluated. One gets

$$J=\sigma(l_3l_2l_1;\, m_3m_2(m_3+m_2))D_{(m_2+m_3)\,m_1}{}^{l_1*}(\varphi_{\mathbf{r}_2,\mathbf{r}_3},\vartheta_{\mathbf{r}_2,\mathbf{r}_3},0). \tag{E8}$$

In performing the angular integrations in $\Delta\rho^M$ with the help of Eq. (E8), the relationship

$$D_{m0}{}^{l}(\alpha,\beta,0)=\left(\frac{4\pi}{2l+1}\right)^{1/2}Y_{lm}{}^{*}(\beta,\alpha) \tag{E9}$$

is used.

APPENDIX F: FURTHER EVALUATION OF SOME TERMS IN $\Delta\rho^M$

To determine the interaction energy of point defects and the electric field resulting from the electron redistribution all terms in $\Delta\rho^M$ need be expressed with respect to one coordinate system. In principle, this can be easily performed by using the transformation formulas (D2) and (E4). The following results are obtained:

$$\Delta\rho_3{}^{\text{s.s.}}=\sum_{s,t(s\neq t)}\ \sum_{l,l',\alpha,m,h,q} A_{ll'\alpha}{}^{mhq}Y_{q(2m)}{}^{*}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})\int_0^{k_F}dk\, k^2\Omega_l{}^{s*}(k,R_s)a_{hl'm}{}^{t}(r_{ts},k,R_s)j_\alpha(kr_{ts}), \tag{F1}$$

with

$$A_{ll'\alpha}{}^{mhq}=16(-1)^{l+m}i^{l+l'+\alpha}\alpha_{hl'm}\left(\frac{2\alpha+1}{4\pi}\right)^{1/2}\sigma(ll'\alpha;\, m(-m)0)\sigma(hlq;\, mm(2m)); \tag{F2}$$

$$\Delta\rho_4{}^{\text{s.s.}}=\sum_{\mu,\nu(\mu\neq\nu)}\ \sum_{l,g,n,m,l',g',n'}\ \sum_{\alpha,\beta,\gamma,f,h,g'',q} B_{lgnml'g'n'}{}^{\alpha\beta\gamma fhg''q}Y_{q(g''-f)}(\vartheta_{\mathbf{R}_\mu,\mathbf{v}_{\nu\mu}},\varphi_{\mathbf{R}_\mu,\mathbf{r}_{\nu\mu}})$$
$$\times\int_0^{k_F}dk\, k^2K_{lgnm}{}^{\mu*}(v_\mu,k,R_\mu)b_{hg''l'g'n'(\alpha+\gamma)}{}^{\nu}(v_\nu,r_{\nu\mu},k,R_\mu)j_\beta(kr_{\nu\mu}), \tag{F3}$$

with

$$B_{lgnm'l'g'n'}{}^{\alpha\beta\gamma fhg''q}=16i^\beta(-1)^f\sigma(n\beta n';\,\alpha\gamma(\alpha+\gamma))\sigma(hlq;\, g''(-f)(g''-f))\alpha_{hlg''}D_{\alpha m}{}^{n}(\varphi_{\mathbf{V}_\mu,\mathbf{V}_\nu},\vartheta_{\mathbf{V}_\mu,\mathbf{V}_\nu},0)$$
$$\times D_{g''g'}{}^{l'}(\varphi_{\mathbf{V}_\nu,\mathbf{r}_{\nu\mu}},\vartheta_{\mathbf{V}_\nu,\mathbf{r}_{\nu\mu}},0)D_{fg}{}^{l*}(\varphi_{\mathbf{V}_\nu,\mathbf{r}_{\nu\mu}},\vartheta_{\mathbf{V}_\nu,\mathbf{r}_{\nu\mu}},0), \tag{F4}$$

and

$$b_{hg''l'g'n'(\alpha+\gamma)}{}^{\nu}(v_\nu,r_{\nu\mu},k,R_\mu)=\frac{2h+1}{2r_{\nu\mu}R_\mu}\frac{(h-g'')!}{(h+g'')!}\int_{|r_{\nu\mu}-R_\mu|}^{r_{\nu\mu}+R_\mu}dR_\nu R_\nu K_{l'g'n'(\alpha+\gamma)}{}^{\nu}(V_\nu,k,R_\nu)$$
$$\times P_{l'}{}^{g''}\left(\frac{R_\mu{}^2-r_{\nu\mu}{}^2-R_\nu{}^2}{2r_{\nu\mu}R_\nu}\right)P_h{}^{g''}\left(\frac{R_\mu{}^2+r_{\nu\mu}{}^2-R_\nu{}^2}{2r_{\nu\mu}R_\mu}\right); \tag{F5}$$

$$\Delta\rho_5{}^{\text{s.s.}}=\sum_{s,\mu}\left(\sum_{l,t,g,n,\alpha,\beta,\gamma,g',h,q,\alpha'} C_{ltgn\alpha\beta}{}^{\gamma g'hq\alpha'}Y_{q(g'+\alpha')}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{\mu s}},\varphi_{\mathbf{R}_s,\mathbf{r}_{\mu s}})\right.$$
$$\left.\times\int_0^{k_F}dk\, k^2\Omega_l{}^{s*}(k,R_s)b_{hg'tgn(\alpha+\gamma)}{}^{\mu}(v_\mu,r_{\mu s},k,R_s)j_\beta(kr_{\mu s})+\text{c.c.}\right), \tag{F6}$$

with

$$C_{ltgn\alpha\beta}{}^{\gamma g'hq\alpha'}=16(-1)^{l+\alpha}i^{l+\beta}\sigma(\beta ln;\,\gamma\alpha(\gamma+\alpha))\alpha_{htg'}\sigma(hlq;\, g'\alpha'(g'+\alpha'))D_{g'g}{}^{t}(\varphi_{\mathbf{V}_\mu,\mathbf{r}_{\mu s}},\vartheta_{\mathbf{V}_\mu,\mathbf{r}_{\mu s}},0)$$
$$\times D_{\alpha'(-\alpha)}{}^{l}(\varphi_{\mathbf{V}_\mu,\mathbf{r}_{\mu s}},\vartheta_{\mathbf{V}_\mu,\mathbf{r}_{\mu s}},0)Y_{\beta\gamma}{}^{*}(\vartheta_{\mathbf{r}_{\mu s},\mathbf{V}_\mu},\varphi_{\mathbf{r}_{\mu s},\mathbf{V}_\mu}); \tag{F7}$$

$$\Delta\rho_2{}^{\text{m.s.}}=\sum_{s,s',t(s\neq t,s\neq s')}\left(\sum_{l,m,h,n,\alpha,\beta,h',q} D_{lmhn}{}^{\alpha\beta h'q}Y_{q\beta}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})\int_0^{k_F}dk\, k^2H_{hlm}{}^{s}(r_{ts},k,R_s)\right.$$
$$\left.\times a_{h'n(m-\beta)}{}^{s'*}(r_{ts},k,R_s)j_\alpha(kr_{ts'})+\text{c.c.}\right), \tag{F8}$$

with

$$D_{lmhn}{}^{\alpha\beta h'q}=16(-1)^{n+m-\beta}i^{l+n+\alpha}\alpha_{lhm}\alpha_{h'n(m-\beta)}\sigma(n\alpha l;\,(m-\beta)\beta m)$$
$$\times\sigma(hh'q;\,m(m-\beta)(2m-\beta))Y_{\alpha\beta}{}^*(\vartheta_{\mathbf{r}_{ts'},\mathbf{r}_{ts}},\varphi_{\mathbf{r}_{ts'},\mathbf{r}_{ts}});\quad\text{(F9)}$$

$$\Delta\rho_3{}^{\text{m.s.}}=\sum_{\mu,s,t(s\neq t)}\Bigg(\sum_{l,g,n,m,f,h,\alpha,\beta,\gamma,g',h',g'',q}E_{lgnmfh\alpha}{}^{\beta\gamma g'h'g''q}Y_{q(\gamma+\alpha+g'')}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})$$
$$\times\int_0^{k_F}dk\;k^2H_{fh(\gamma+\alpha)}{}^s(r_{ts},k,R_s)b_{h'g'lgnm}{}^{\mu*}(v_\mu,r_{\mu s},k,R_s)j_\beta(kr_{t\mu})+\text{c.c.}\Bigg),\quad\text{(F10)}$$

with

$$E_{lgnmfh\alpha}{}^{\beta\gamma g'h'g''q}=16(-1)^g i^{f+\beta}\alpha_{fh(\gamma+\alpha)}\alpha_{h'lg'}\sigma(\beta nf;\,\gamma\alpha(\gamma+\alpha))\sigma(h'hq;\,g''(\gamma+\alpha)(g''+\gamma+\alpha))D_{\alpha m}{}^n(\varphi_{\mathbf{v}_\mu,\mathbf{r}_{ts}},\vartheta_{\mathbf{v}_\mu,\mathbf{r}_{ts}},0)$$
$$\times D_{g'(-g)}{}^l(\varphi_{\mathbf{v}_\mu,\mathbf{r}_{\mu s}},\vartheta_{\mathbf{v}_\mu,\mathbf{r}_{\mu s}},0)D_{g''g'}{}^{h'}(\varphi_{\mathbf{r}_{\mu s},\mathbf{r}_{ts}},\vartheta_{\mathbf{r}_{\mu s},\mathbf{r}_{ts}},0)Y_{\beta\gamma}{}^*(\vartheta_{\mathbf{r}_{t\mu},\mathbf{r}_{ts}},\varphi_{\mathbf{r}_{t\mu},\mathbf{r}_{ts}});\quad\text{(F11)}$$

$$\Delta\rho_4{}^{\text{m.s.}}=\sum_{s,t,s',t'(s\neq t,s'\neq t',s'\neq s)}\Bigg(\sum_{l,m,h,l',m',h',\alpha,\beta,m'',h'',q}F_{lmhl'm'h'}{}^{\alpha\beta m''h''q}Y_{q(m''-m)}(\vartheta_{\mathbf{R}_s,\mathbf{r}_{ts}},\varphi_{\mathbf{R}_s,\mathbf{r}_{ts}})$$
$$\times\int_0^{k_F}dk\;k^2H_{hlm}{}^{s*}(r_{ts},k,R_s)d_{h''m''h'l'm'}{}^{s'}(r_{t's'},r_{s's},k,R_s)j_\beta(kr_{t't})+\text{c.c.}\Bigg),\quad\text{(F12)}$$

with

$$F_{lmhl'm'h'}{}^{\alpha\beta m''h''q}=16(-1)^{l+m}i^{l+l'+\beta}\alpha_{hlm}\alpha_{h'l'm'}\alpha_{h''h'm''}\sigma(\beta ll';\,(\alpha-m)m\alpha)\sigma(h''hq;\,m''m(m''+m))$$
$$\times D_{\alpha m'}{}^{l'*}(\varphi_{\mathbf{r}_{t's'},\mathbf{r}_{ts}},\vartheta_{\mathbf{r}_{t's'},\mathbf{r}_{ts}},0)D_{m''m'}{}^{h'}(\varphi_{\mathbf{r}_{t's'},\mathbf{r}_{ts}},\vartheta_{\mathbf{r}_{t's'}\mathbf{r}_{ts}},0)Y_{\beta(\alpha-m)}{}^*(\vartheta_{\mathbf{r}_{t't},\mathbf{r}_{ts}},\varphi_{\mathbf{r}_{t't},\mathbf{r}_{ts}}),\quad\text{(F13)}$$

and

$$d_{h''m''h'l'm'}{}^{s'}(r_{s's},r_{t's'},k,R_s)=\frac{2h''+1}{2r_{s's}R_s}\frac{(h''-m'')!}{(h''+m'')!}\int_{|r_{s's}-R_s|}^{r_{s's}+R_s}H_{h'l'm'}{}^{s'}(r_{t's'},k,R_{s'})P_{h'}{}^{m''}\left(\frac{R_s{}^2+r_{s's}{}^2-R_{s'}{}^2}{2r_{s's}R_{s'}}\right)$$
$$\times P_{h''}{}^{m''}\left(\frac{R_s{}^2-r_{s's}{}^2-R_{s'}{}^2}{2r_{s's}R_s}\right)R_{s'}dR_{s'}.\quad\text{(F14)}$$