PHYSICAL REVIEW VOLUME 186, NUMBER 3 15 OCTOBER 1969

Electronic Structure of Point Defects and Impurities in Metals

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(Received 26 November 1968; revised manuscript received 25 March 1969)

The scattering of Bloch waves off point defects and impurities in metals is considered, for the following four types of defect potentials: (i) weak scatterers, (ii) strong scatterers, but with slow spatial variations in the solute potentials, (iii) strongly attractive potentials which lead to bound or resonant states, (iv) potentials leading to almost rigid-band behavior. In essence, we develop approximate wave functions or density matrices which should be valuable *zero-order* solutions in these four regimes. Iteration in the basic integral equation given for the Dirac density matrix can then be employed to refine these solutions when necessary. Thus, in case (1), we determine the linear response of the Bloch-wave system to a weak perturbation in terms of the Dirac density matrix for the periodic-potential problem. The asymptotic form of the displaced charge is discussed in some detail. For the case of a spherical Fermi surface, the Bloch-wave character does not alter the form of the long-range oscillations, though it changes the amplitude and the phase. In (ii), it is shown that the appropriate tool is a generalization of the Thomas-Fermi approximation by the introduction of an energy-dependent potential, into which we build some of the essential wave properties of the problem. By explicit calculation for repulsive potentials, we show that accurate numerical results for the energy-level shifts due to vacancies can be obtained in this way. We then deal, in (iii), with a theory motivated by the Koster-Slater treatment of defects. In this theory, we show that, usually, only the properties at the Fermi level are derivable from a local potential. This potential in the Koster-Slater model is like a square well near the defect, with Wannier-function oscillations in the tail. Systematic improvement of the Koster-Slater theory can be made via an integral equation for the Green's function. A new condition, generalizing the Koster-Slater theory to deal with solute potentials with matrix elements between Bloch functions which are energy-dependent, is proposed. It is pointed out that within this framework, conditions may arise where a rigid-band model could be regained, even for strong potentials.

1. INTRODUCTION

ATTEMPTS to formulate a theory of the electronic structure of defect crystals are generally based on the assumption that the electron states in the matrix are completely known. In the case of the pure metal, the periodic lattice structure allows the single-particle wave functions to be defined via Bloch's theorem. The dispersion relations within a fundamental Brillouin zone are also quite precisely defined, at least in the one-electron approximation.

Because of the destruction of periodicity by impurity atoms or defects, the same methods will not work for impure crystals. In particular, the wave vector is no longer a good quantum number and it seems best to develop a theory independently of $\mathbf{k}$. Then we are led to focus on the calculation of the local electron density $\rho(\mathbf{r}E)$, giving the number of electrons per unit volume at $\mathbf{r}$, with energy less than E. Our point of view here is that, if we are given complete information of the corresponding quantity $\rho_p(\mathbf{r}E)$ for the matrix metal,[1] together with the scattering potential $V(\mathbf{r})$ due to the solute atoms, then we have solved the defect problem if we can express $\rho(\mathbf{r}E)$ explicitly in terms of ρ_p and $V(\mathbf{r})$.

However, an exact solution seems out of the question at present, for realistic bands and self-consistent scattering potentials. We are concerned here, therefore, with developing a framework from which the four regimes detailed in the Abstract can be discussed. These should cover a wide range of dilute alloy systems and defect crystals of physical interest.

Throughout this paper, we use local potential theory. A basic justification for this approach can be given by the theory of Hohenberg and Kohn.[2] These workers show that, even in the presence of electron interactions, the electron density can be generated exactly from a suitably chosen local potential. This potential must have a part which is essentially the Hartree potential, but modified by a term which takes account of exchange and correlation. While we do not know how to calculate this additional part of the potential precisely, we have by now some insight into it, and can construct approximations to it from a knowledge of the electron density.[3] This means that, provided we do not go far from the Fermi level, the considerations of this paper should apply beyond the one-electron approximation.

Because, so far, methods do not exist for the direct calculation of the local density $\rho(\mathbf{r}E)$, we begin from the properties of the Dirac density matrix earlier used extensively in perturbation calculations on dilute alloys by March and Murray.[4] The present work, in contrast to these earlier studies which started from plane waves, deals primarily with the scattering of Bloch waves off the defect centers.

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[1] Or more precisely, the Dirac density matrix for the unperturbed problem. See P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[2] P. Hohenberg and W. Kohn, Phys. Rev. **136**, 864 (1964). See also W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[3] For example, the exchange term can be taken, following Dirac and Slater, to be proportional to the one-third power of the density $\rho(\mathbf{r})$. A modification of the coefficient proposed by Slater is suggested by Kohn and Sham in Ref. 2.

[4] N. H. March and A. M. Murray, Phys. Rev. **120**, 830 (1960); Proc. Roy. Soc. (London) **A261**, 119 (1961); **A266**, 559 (1962).

2. DIRAC DENSITY MATRIX IN ALLOY

We define the Dirac density matrix for the alloys in terms of the one-particle eigenstates ψ_n, and the corresponding energies E_n as

$$\rho(\mathbf{r}\mathbf{r}'E)=\sum_n \psi_n^*(\mathbf{r})\psi_n(\mathbf{r}')\theta(E-E_n)\,, \tag{2.1}$$

where

$$\begin{aligned}\theta(E-E_n)&=0 \quad \text{if } E_n>E\\ &=1 \quad \text{if } E_n\leqslant E.\end{aligned} \tag{2.2}$$

We find from (2.1) that

$$\int_{-\infty}^{E} dE'\rho(\mathbf{r}\mathbf{r}'E') =\sum_n [E-E_n]\psi_n^*(\mathbf{r})\psi_n(\mathbf{r}')\theta(E-E_n)\,, \tag{2.3}$$

and using the Schrödinger equation for the wave function ψ_n, we may write from (2.1) and (2.3) after a little algebra

$$-\tfrac{1}{2}\nabla_{\mathbf{r}}^2\rho(\mathbf{r}\mathbf{r}'E)=[E-V_p(\mathbf{r})-V(\mathbf{r})]\rho(\mathbf{r}\mathbf{r}'E) -\int_{-\infty}^{E} dE'\rho(\mathbf{r}\mathbf{r}'E')\,. \tag{2.4}$$

Here, V_p is the pure solvent lattice potential, and $V(\mathbf{r})$ is the additional potential due to the defects or impurities. To this equation we must add the idempotency condition

$$\int d\mathbf{r}_1\rho(\mathbf{r}\mathbf{r}_1E)\rho(\mathbf{r}_1\mathbf{r}'E)=\rho(\mathbf{r}\mathbf{r}'E)\,. \tag{2.5}$$

We show in Appendix A that the integrodifferential equation (2.4) can be transformed to a more useful integral equation. This may be written

$$\rho(\mathbf{r}\mathbf{r}'E)=\rho_0(\mathbf{r}\mathbf{r}'E)+\int d\mathbf{r}_1\int dE_1 f_0(\mathbf{r}-\mathbf{r}_1,E,E_1) \times[V(\mathbf{r}_1)+V_p(\mathbf{r}_1)]\rho(\mathbf{r}_1\mathbf{r}'E_1)\,, \tag{2.6}$$

where ρ_0 is the idempotent plane-wave Dirac matrix given by

$$\rho_0(\mathbf{r}\mathbf{r}'E)=\frac{k^3}{\pi^2}\frac{j_1(k|\mathbf{r}-\mathbf{r}'|)}{k|\mathbf{r}-\mathbf{r}'|}, \quad E=\tfrac{1}{2}k^2; \tag{2.7}$$

$$j_1(x)=x^{-2}[\sin x-x\cos x]$$

and

$$f_0(\mathbf{x},E,E_1)=\frac{e^{ix(2E)^{1/2}}}{4\pi x}\delta(E-E_1)-\frac{ie^{ix(2E_1)^{1/2}}}{4\pi(2E_1)^{1/2}}\theta(E-E_1) -\frac{1}{(2\pi)^2x}\int_0^{2E}dy\frac{\sin(xy^{1/2})}{[E_1-y/2]^2}. \tag{2.8}$$

A more useful form can be obtained from (2.6) in which the first term on the right-hand side of (2.6) is replaced by the Dirac matrix ρ_p for the pure solvent. The desired equation is then

$$\rho(\mathbf{r}\mathbf{r}'E)=\rho_p(\mathbf{r}\mathbf{r}'E)+\int d\mathbf{r}_1\int dE_1dE_2 \times\left[\frac{\delta(E-E_1)+\delta(E-E_2)}{(E_1-E_2+i\epsilon)^2}-2\frac{\theta(E-E_1)-\theta(E-E_2)}{(E_1-E_2+i\epsilon)^3}\right] \times\rho_p(\mathbf{r}\mathbf{r}_1E_2)V(\mathbf{r}_1)\rho(\mathbf{r}_1\mathbf{r}'E_1)\,, \tag{2.9}$$

the quantity $i\epsilon$ ensuring that we are dealing with outgoing scattered waves.

The integral equations (2.6) and (2.9) are the basic tools used in this paper. The form (2.9) incorporates the properties of the periodic lattice directly into the integral equation.

3. WEAK SCATTERING FROM SOLUTE ATOMS

We can now achieve our first objective and obtain the perturbed local density as a result of weak solute scattering in a periodic inhomogeneous gas by inserting ρ_p for ρ in the right-hand side of (2.6), or alternatively (A7). Denoting the displaced charge $\rho(\mathbf{r}E)-\rho_p(\mathbf{r}E)$ below energy E by $\Delta(\mathbf{r}E)$, it is evident that the result may be written as

$$\Delta(\mathbf{r}E)=\int d\mathbf{r}_1V(\mathbf{r}_1)F(\mathbf{r}\mathbf{r}_1E)\,. \tag{3.1}$$

F can be obtained either in terms of the periodic lattice matrix ρ_p or the Bloch functions $\psi_{\mathbf{k}\gamma}(\mathbf{r})$, labeled by wave vector $\mathbf{k}$ and band index γ. It is readily shown that the energy derivative of F is given by

$$\frac{\partial F}{\partial E}=2\,\mathrm{Re}\left\{G_p(\mathbf{r}\mathbf{r}_1E_+)\frac{\partial\rho_p(\mathbf{r}_1\mathbf{r}E)}{\partial E}\right\}, \tag{3.2}$$

where G_p is the perfect lattice Green's function, defined in terms of the Bloch waves by

$$G_p(\mathbf{r}\mathbf{r}_1E_+)=\sum_{\gamma\mathbf{k}}\frac{\psi_{\mathbf{k}\gamma}^*(\mathbf{r})\psi_{\mathbf{k}\gamma}(\mathbf{r}_1)}{E-E_\gamma(\mathbf{k})+i\epsilon}. \tag{3.3}$$

If we take the case of plane waves as a simple example, we have immediately

$$G_p\rightarrow\frac{e^{i(2E)^{1/2}|\mathbf{r}-\mathbf{r}_1|}}{4\pi|\mathbf{r}-\mathbf{r}_1|},\quad \frac{\partial\rho_p}{\partial E}\rightarrow\frac{\sin((2E)^{1/2}|\mathbf{r}-\mathbf{r}_1|)}{2\pi^2|\mathbf{r}-\mathbf{r}_1|},$$

$$F\rightarrow-\frac{k^2}{2\pi^3}\frac{j_1(2k|\mathbf{r}-\mathbf{r}_1|)}{|\mathbf{r}-\mathbf{r}_1|^2},\quad E=\frac{k^2}{2}. \tag{3.4}$$

Equations (3.1) and (3.4) lead to the well-known

$\mathbf{r}$-space equivalent of the Lindhard $\mathbf{k}$-dependent dielectric constant formulation.

A. Asymptotic Form of Displaced Charge

The correct spatial variation in the asymptotic form of the displaced charge for plane-wave scattering may be found from (3.1) and (3.4) by choosing an extreme short-range solute potential $V(\mathbf{r})=\lambda\delta(\mathbf{r})$. This evidently yields, at the Fermi level,

$$\Delta(\mathbf{r},E_F)\sim\text{const}\times\cos(2k_Fr)/r^3\,, \tag{3.5}$$

the Friedel wiggles with wavelength π/k_F where k_F is the Fermi wave number. This argument takes into account the singularity at $2k_F$ in the Fourier transform of $F(\mathbf{r}-\mathbf{r}_1,E_F)$ given in (3.4), but not, of course, the singularity which occurs when a self-consistent potential is used instead of $\lambda\delta(\mathbf{r})$. We shall come back to this point in Sec. 4.

We turn next to consider the asymptotic form of the displaced charge for Bloch wave scattering. If we choose again a δ-function scatterer in (3.1), then we find

$$\Delta(\mathbf{r}E)\sim\text{const}\times F(\mathbf{r}0E)\,, \tag{3.6}$$

and since F depends only on the properties of the perfect crystal we have an explicit result, the constant being proportional to the strength λ of the scatterer. In general, we cannot now expect $\Delta(\mathbf{r}E)$ to depend only on the distance r from the solute; directional dependence will of course enter. This could be of some importance in a variety of problems; for example, in the anisotropy of activation energies for impurity diffusion in a close-packed hexagonal crystal like zinc[5] or in nuclear magnetic resonance studies on dilute alloys.[6] In the latter case, however, it may be necessary to transcend linear response theory.

As is clear from the discussion for plane waves above, it is the singularities in the Fourier transform of the displaced charge which dominate the form in $\mathbf{r}$ space far from the solute. Fortunately, we can readily see how these singularities occur. Thus, defining $\tilde{\Delta}(\mathbf{q}E)$ by

$$\tilde{\Delta}(\mathbf{q})=\frac{1}{(2\pi)^3}\int d\mathbf{r}\,e^{-i\mathbf{q}\cdot\mathbf{r}}\Delta(\mathbf{r}E)\,, \tag{3.7}$$

we obtain from (3.1) the result

$$\tilde{\Delta}(\mathbf{q})=(2\pi)^3\int d\mathbf{k}\,\tilde{F}(\mathbf{q},\,-\mathbf{k},E)\,\tilde{V}(\mathbf{k})\,, \tag{3.8}$$

where $\tilde{F}$ is the double Fourier transform of $F(\mathbf{r}\mathbf{r}_1E)$, while $\tilde{V}(\mathbf{k})$ is the Fourier transform of the impurity potential. To display the origin of the singularities in F, the most direct procedure is to insert into (3.2) and (3.3) for F, the expansion of the Bloch wave $\psi_{\mathbf{k}\gamma}(\mathbf{r})$ in terms of plane waves, namely,

$$\psi_{\mathbf{k}\gamma}(\mathbf{r})=\sum_{\mathbf{K}_n}v_\gamma(\mathbf{k}+\mathbf{K}_n)e^{i(\mathbf{k}+\mathbf{K}_n)\cdot\mathbf{r}}\,. \tag{3.9}$$

Evidently, in (3.9), v_γ is the momentum eigenfunction for band γ, the $\mathbf{K}_n$'s denoting the reciprocal lattice vectors. Substituting (3.9) into (3.2), and performing the double Fourier transform, (3.8) becomes

$$\begin{aligned}\tilde{\Delta}(\mathbf{q},E_F)=2\,\text{Re}\sum_{\gamma_1\gamma_2}\;\sum_{\mathbf{K}_1\mathbf{K}_2\mathbf{K}_3\mathbf{K}_4}\int d\mathbf{k}_1\\ \times\frac{\theta(E_F-E_{\gamma_1}(\mathbf{k}_1))}{E_{\gamma_1}(\mathbf{k}_1)-E_{\gamma_2}(\mathbf{k}_1-\mathbf{q}+\mathbf{K}_3-\mathbf{K}_4)}v_{\gamma_1}{}^*(\mathbf{k}_1+\mathbf{K}_1)\\ \times v_{\gamma_2}(\mathbf{k}_1-\mathbf{q}+\mathbf{K}_3-\mathbf{K}_4+\mathbf{K}_2)v_{\gamma_1}(\mathbf{k}_1+\mathbf{K}_3)\\ \times v_{\gamma_2}{}^*(\mathbf{k}_1-\mathbf{q}+\mathbf{K}_3)\,\tilde{V}(\mathbf{q}+\mathbf{K}_1-\mathbf{K}_2-\mathbf{K}_3+\mathbf{K}_4)\,.\end{aligned} \tag{3.10}$$

The integration here is over the basic Brillouin zone with the restriction that $\mathbf{k}_1-\mathbf{q}+\mathbf{K}_3-\mathbf{K}_4$ must also lie in this zone.

In contrast to free electrons where a local relation exists between $\tilde{\Delta}(\mathbf{q})$ and $\tilde{V}(\mathbf{q})$, (3.10) is nonlocal, the calculation of $\tilde{\Delta}(\mathbf{q})$ involving the Fourier components of the solute potential at $\mathbf{q}+\mathbf{K}_j$, $\mathbf{K}_j$ being any reciprocal lattice vector.

The merit of (3.10) is that it shows us that singularities in $\mathbf{q}$ space can come from the term in the denominator with $\gamma_2=\gamma_1=\gamma$, where γ labels the conduction band, combined with the constraint implied by $\theta(E_F-E_\gamma(\mathbf{k}_1))$. Rewriting (3.10) as

$$\begin{aligned}\tilde{\Delta}(\mathbf{q}E)=2\,\text{Re}\sum_{\mathbf{G}}\int d\mathbf{k}_1\\ \times\frac{\theta(E_F-E_\gamma(\mathbf{k}_1))}{E_\gamma(\mathbf{k}_1)-E_\gamma(|\mathbf{k}_1-\mathbf{q}_0|)}f(\mathbf{k}_1\mathbf{q}_0\mathbf{G})\,,\end{aligned} \tag{3.11}$$

where $\mathbf{q}_0=\mathbf{q}+\mathbf{K}_3-\mathbf{K}_4=\mathbf{q}+\mathbf{G}$, we shall restrict ourselves to the case when $f(\mathbf{k}_1,\mathbf{q}_0,\mathbf{G})$, defined through (3.10) and (3.11), is a nonsingular function. Actually, as remarked above in the discussion of the free-electron case, a proper self-consistent potential $V(\mathbf{r})$ will have at least one singularity in $\mathbf{k}$ space. Generally, however, forms chosen for $V(\mathbf{r})$, for example, screened Coulomb (Yukawa) potentials, do not have such singularities. Recalling that $\mathbf{k}_1-\mathbf{q}+\mathbf{G}$ must lie inside the basic Brillouin zone, we see that a separate singularity is obtained in $\mathbf{q}$ space for each value of $\mathbf{G}$. Each such singularity will make a contribution to the asymptotic long-range oscillatory form.

This discussion of the singularities is as far as we are able to go, without choosing specific models for the band structure of the matrix metal.

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[5] Compare G. K. Corless and N. H. March, Phil. Mag. **7**, 1765 (1962); and for explicit results on Zn see A. P. Batra and H. B. Huntington, Phys. Rev. **154**, 569 (1967); J. Worster and N. H. March, AERE Report (unpublished).

[6] L. E. Drain, J. Phys. **C1**, 1690 (1968).

B. Spherical Scatterer and Spherical Energy Surfaces

If we assume spherical energy surfaces, and a spherical scattering potential, some further progress can be made. Let us assume that the dominant singularity comes from the term k_1^2 in the expansion of $E(\mathbf{k}_1)$. We may then put $\mathbf{k}_1\cdot\mathbf{q}_0=k_1q_0\mu$, where $\mu=\cos\theta$, θ being the angle between $\mathbf{k}_1$ and $\mathbf{q}_0$. Integration over μ then yields

$$\tilde{\Delta}(\mathbf{q},E_F)=\sum_{\mathbf{G}}\int dk_1\biggl(\frac{2\pi k_1}{2q_0}\biggl\{\ln\biggl[\biggl|1-\frac{q_0}{2k_1}\biggr|\biggr]f_+(\mathbf{k}_1\mathbf{q}_0\mathbf{G})$$

$$-\ln\biggl[\biggl|1+\frac{q_0}{2k_1}\biggr|\biggr]f_-(\mathbf{k}_1\mathbf{q}_0\mathbf{G})\biggr\}\theta(E_F-E_\gamma(\mathbf{k}_1))\biggr). \qquad (3.12)$$

The inclusion of higher terms in $E(\mathbf{k}_1)$ may be seen to lead to the same singularity structure (3.12) for $\tilde{\Delta}(\mathbf{q}E_F)$. In the integration over μ in (3.11) for a general spherical band structure, a singularity arises when the pole moves onto the band point $\mu=+1$ of the integration path, i.e., $\mathbf{q}_0=2\mathbf{k}_1$ or $k_1^2=(\mathbf{k}_1-\mathbf{q}_0)^2$. We may therefore take the dominant singularity from the first term $E(\mathbf{k}_1)\sim ak_1^2$, as the inclusion of higher terms does not alter the condition for a singularity to occur, nor its form. Terms involving derivatives of f, are assumed small and have been neglected. The associated singularities give a secondary contribution. Here the $\pm$ subscripts refer to $\mathbf{k}_1$ parallel or antiparallel to $\mathbf{q}_0$. As the singularity in $\mathbf{q}_0$ space comes from the first term in (3.12), the second term gives no contribution to the asymptotic form, and we may assume, with no approximation, that $f_-=f_+$, to obtain

$$\tilde{\Delta}(\mathbf{q}E_F)=\sum_{\mathbf{G}}\int dk_1\frac{\pi k_1}{q_0}\ln\biggl(\biggl|\frac{\mathbf{q}_0-2k_1}{\mathbf{q}_0+2k_1}\biggr|\biggr)$$

$$\times f_+(\mathbf{k}_1,\mathbf{q}_1,\mathbf{G})\theta(E_F-E_\gamma(\mathbf{k}_1)). \qquad (3.13)$$

The dominant singularity in $\tilde{\Delta}(\mathbf{q}E_F)$ may be obtained by assuming that $f_+(\mathbf{k}_1\mathbf{q}_0\mathbf{G})$ is a slowly varying function of $\mathbf{k}_1$, and neglecting derivatives of f_+. Forming the displaced charge $\Delta(\mathbf{r}E_F)$, we find for large $|\mathbf{r}|$ that we may replace $|\mathbf{q}_0|$ in f_+ by $2k_F$. If $\mathbf{q}_r$ is a vector of magnitude $2k_F$ along $\mathbf{r}$, we expand f_+ around $\mathbf{q}_0=\mathbf{q}_r$ and neglect derivatives to obtain the leading term in the asymptotic form of the displaced charge as

$$\Delta(\mathbf{r}E_F)=\frac{(2\pi)^3}{4}k_F\frac{\cos(2k_Fr)}{r^3}\sum_{\mathbf{G}}e^{i\mathbf{G}\cdot\mathbf{r}}f_+(\mathbf{k}_F,\mathbf{q}_r,\mathbf{G}). \qquad (3.14)$$

This is closely related to the result obtained by Kohn and Vosko,[7] though their theory is not restricted to the linear response regime.

Higher terms in the expansion of f_+ around $\mathbf{q}_r$ lead also to a $\sin(2k_Fr)/r^3$ term and thus produce a small phase shift in the dominant term (3.14). This only occurs for Bloch wave scattering, no such phase shift arising in a linear theory based on plane waves.

A simple alloy system which we expect to fall within this weak scattering regime is Li with a dilute concentration of Be solute atoms. This is not only because the valence difference is small but, more importantly, the core electrons in the solute and solvent atoms have the same character (1*s*). In contrast LiMg will not be a suitable candidate.

4. DENSITIES OF STATES AND LEVEL SHIFTS FOR SLOWLY VARYING POTENTIALS

The previous theory fails if the scattering is strong. Thus, we shall consider in this section and the next, two approaches which attempt approximate solutions of (2.6) or (2.9), when $V(\mathbf{r})$ is strong. The approach of this section should be valuable when $V(\mathbf{r})$ is not varying too rapidly in space, while the second is appropriate for strong, but rather localized solute potentials.

The method developed in this section is particularly suited for calculating the shift of an energy state $E(\mathbf{k})$ due to a perturbation, and the corresponding change in the density of states. It is less satisfactory for calculating the local density $\rho(\mathbf{r}E)$ for strong scattering potentials.

A. Plane-Wave Scattering

For free electrons, that is with $V_p=0$ in (2.6), the local density can be obtained by iteration and subsequent resummation of the perturbation expansion when $V(r)$ varies slowly in space. The result is the usual Thomas-Fermi three-halves relation for the local electron density, namely,

$$\rho(\mathbf{r}E)=\rho_0(\mathbf{r},E-V(\mathbf{r})), \qquad (4.1)$$

ρ_0 being the local density, independent of $\mathbf{r}$ for free electrons. This form suggests that we might effect a generalization by writing the correct local density, when $V(r)$ has Coulomb singularities as in impure metals, in the form

$$\rho(\mathbf{r}E)=\rho_0(\mathbf{r},E-g(\mathbf{r}E)), \qquad (4.2)$$

where $g(\mathbf{r}E)$ is now a functional of the potential. It will be seen by comparing (4.1) and (4.2) that, when the potential V is slowly varying, we can expect g to be a slowly varying function of energy. Even for strong potentials, we expect from (4.1) and (4.2) that g is roughly proportional to V, and there is now a hope that $g(\mathbf{r}E)$ can be calculated by first-order theory, even though (4.1) and (4.2) are nonlinear in V. If the potential is weak, clearly g is small, and we can write (4.2) in the form

$$\rho(\mathbf{r}E)=\rho_0(E)-g(\mathbf{r}E)\frac{\partial\rho_0}{\partial E}+O(g^2). \qquad (4.3)$$

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[7] W. Kohn and S. H. Vosko, Phys. Rev. **119**, 912 (1960).

We can in this case simply calculate $g(\mathbf{r}E)$ from (2.6) with $V_p=0$ or more directly by comparison of (4.3) with (3.1) and (3.4). The result, which we denote by g_1, is

$$g_1(\mathbf{r}E)=\frac{k}{2\pi}\int d\mathbf{r}_1 V(\mathbf{r}_1)\frac{j_1(2k|\mathbf{r}-\mathbf{r}_1|)}{|\mathbf{r}-\mathbf{r}_1|^2},\quad E=\frac{k^2}{2}. \tag{4.4}$$

For slowly varying potentials, (4.4) can be evaluated by putting $V(\mathbf{r}_1)\approx V(\mathbf{r})$ when we obtain

$$g_1(\mathbf{r}E)\approx V(\mathbf{r}), \tag{4.5}$$

giving back the Thomas-Fermi limit. Thus (4.4) has the merit that it includes first-order perturbation theory exactly, while also containing the semiclassical limit. There is a sense in which (4.4) builds wave properties into the energy-dependent potential, though we still retain the form of (4.1), based on classical mechanics.

1. Energy-Dependent Potential $g(\mathbf{r}E)$ and Displaced Charge $\tilde{\Delta}(\mathbf{q})$

One result of some interest follows immediately from (4.4). Using the property referred to in Sec. 3 that the self-consistent potential $V(\mathbf{r})$ has Fourier components which have a kink at $2k_F$, we find at large r that

$$g_1(\mathbf{r}E)\sim A(k)\frac{\cos(2k_Fr)}{r^3}+B(k)\frac{\cos(2kr)}{r^3}. \tag{4.6}$$

Thus, two wavelengths are involved in the energy-dependent potential $g(\mathbf{r}E)$: π/k_F and π/k. These, of course, coincide at the Fermi level.

One limitation of the method based on g_1 is already evident, however, from (4.6). At $E=E_F$, the displaced charge should have a nonzero phase factor[8] that is

$$\Delta\rho(\mathbf{r}E_F)\sim A\cos(2k_Fr+\phi)/r^3. \tag{4.7}$$

To obtain this correctly would necessitate a calculation of $g(\mathbf{r}E)$ beyond the first-order result (4.4). Equation (4.7) shows that the exact asymptotic form for g must be

$$g(\mathbf{r}E_F)\sim G\cos(2k_Fr+\phi)/r^3, \tag{4.8}$$

where ϕ is a functional of the potential.

We wish to point out here that the results (4.7) and (4.8) alter profoundly the nature of the singularities in $\mathbf{q}$ space of the displaced charge $\tilde{\Delta}(\mathbf{q})$ and the Fourier transform $\tilde{g}(\mathbf{q})$ of the energy-dependent potential. Writing the asymptotic form for the displaced charge $\Delta\rho(\mathbf{r}E_F)$ at the Fermi level as

$$\Delta\rho(\mathbf{r}E)\sim A\frac{\cos(2k_Fr)}{r^3}+B\frac{\sin(2k_Fr)}{r^3}, \tag{4.9}$$

we have, from (3.12), for a spherically symmetric scattering potential,

$$\tilde{\Delta}\rho(\mathbf{q})=\frac{1}{2\pi^2}\int_0^R dr\, r^2\Delta\rho(\mathbf{r})\frac{\sin(qr)}{qr}+\frac{1}{2\pi^2}\int_R^\infty dr\left(A\frac{\cos(2k_Fr)}{r}+B\frac{\sin(2k_Fr)}{r}\right)\frac{\sin(qr)}{qr}. \tag{4.10}$$

The first term of (4.10), $\tilde{\Delta}\rho_1(\mathbf{q})$, produces no singularities. The second term $\tilde{\Delta}\rho_2(\mathbf{q})$ may be rewritten when $q\sim 2k_F$ and R is chosen such that $2k_FR\gg1$,

$$\Delta\rho_2(\mathbf{q})\sim\frac{1}{2\pi^2}\left\{A\left(1-\frac{q}{2k_F}\right)\ln\left(\left|1-\frac{q}{2k_F}\right|2k_FR\right)+B\left(\frac{1}{2k_FR}-\frac{\pi}{2}\left|1-\frac{q}{2k_F}\right|\right)\right\}. \tag{4.11}$$

We see that there are two singularities in $\tilde{\Delta}\rho(\mathbf{q})$ at $q=2k_F$. One is an $x\ln|x|$ type of singularity, arising from the cosine term, while the other, from the sine term, is an $x\operatorname{sgn}(x)$ singularity. The latter causes a discontinuity in the gradient of $\tilde{\Delta}\rho(\mathbf{q})$. These singularities are illustrated in Fig. 1 and we wish to stress that the $x\operatorname{sgn}(x)$ singularity arises for the first time in second-order perturbation theory. However, when there is no singularity in the Fourier transform of the scattering potential, we have for A and B,

$$A=\frac{1}{2\pi^2}\sum_{l=0}^{\infty}(2l+1)(-1)^l\sin\eta_l\cos\eta_l \tag{4.12}$$

and

$$B=\frac{1}{2\pi^2}\sum_{l=0}^{\infty}(2l+1)(-1)^l\sin^2\eta_l, \tag{4.13}$$

where η_l is the phase shift in the lth partial wave.

It is quite possible from (4.12) and (4.13) that special cases could occur in which B is finite and $A=0$. In this case the familiar $x\ln|x|$ singularity will be absent, and the new $x\operatorname{sgn}(x)$ singularity will be dominant.

As remarked above, the phase shift in the displaced charge appears at second order for the first time, and

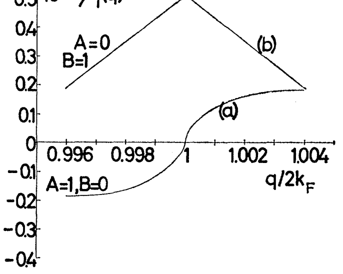

FIG. 1. Curves of $\tilde{\Delta}\rho_1(q)$ versus $q/2k_F$, illustrating the two forms of singularity at $q=2k_F$. The limit R of the numerical integration in Eq. (4.11) is given by $2k_FR=100$ in this example. Curve (a) corresponds to $A=1$, $B=0$; and curve (b) to $A=0$, $B=1$.

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[8] A. Blandin, E. Daniel, and J. Friedel, Phil. Mag. 4, 180 (1959). See also Ref. 7.

the self-consistent computations of March and Murray[4] should include this effect. The corresponding Fourier components reported by March and Boardman,[9] though revealing some change in the form of the self-consistent potential $V(q)$ around $2k_F$, do not clearly show the singularities of Fig. 1, presumably because of a coarse interval in the numerical work. We might expect that, if the sine term is dominant, arguments relating to the Kohn effect in lattice vibrations could be substantially modified.

While dealing with the asymptotic form of the displaced charge for plane-wave scattering, it is worth pointing out that the amplitude of the displaced charge, given in terms of the phase shifts η_l of the partial waves for the case of strong scattering by Blandin *et al.*,[8] is only precise when singularities in the self-consistent potential are ignored.

We have made an estimate of the effect of including the first-order self-consistent potential in a strong-scattering calculation. The amplitude A for the choice of scattering potential

$$\tilde{V}(\mathbf{q})=4\pi \Big/ \left\{q^2+\frac{2k_F}{\pi}\left[1+\frac{4k_F{}^2-q^2}{4qk_F}\times\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right]\right\} \qquad (4.14)$$

is found to be changed by the order of 15% for this case, by the singularity in V. However, there is another type of singularity, type (b) on Fig. 1, which we have seen will also arise in a nonlinear self-consistent field treatment. This will also, of course, affect the amplitude and phase of the self-consistent displaced charge.

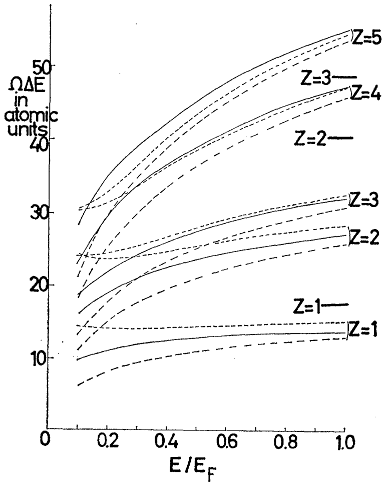

FIG. 2. Level shift ΔE multiplied by the volume of the crystal as function of E/E_F, for repulsive potentials (4.15) with the screening lengths q^{-1} shown in Table I. Solid curves. Exact values given by Eq. (4.16). Lower dashed curves for each Z. Values calculated from $g_1(rE)$ of Eq. (4.4), together with Eq. (4.17). Upper dashed curves for each Z. Values calculated by replacing g_1 above by $V(r)$. Horizontal lines on the right of the figure denote the first-order perturbation energy shifts, which are independent of energy, for $Z=1$, 2, and 3.

TABLE I. Inverse screening radii used in calculation of level shift ΔE, using Eqs. (4.15) and (4.16).

Z	Metal	k_F	q	$q_{\text{Thomas-Fermi}}$
1	Cu	0.720	0.846	0.957
2	Mg	0.728	0.789	0.963
3	Al	0.928	0.883	1.086
4	Pb	0.836	0.791	1.032
5	Sb	0.899	0.806	1.070

2. Results for Level Shift for a Strong Repulsive Potential

In order to demonstrate the utility of our method based on the energy-dependent potential $g(rE)$, we have carried out some numerical calculations for the case of a repulsive potential given by

$$V(r)=+(Z/r)e^{-qr}. \qquad (4.15)$$

This is of interest in the case of a vacancy,[10] and the exact phase shifts have been calculated by numerical integration of the radial Schrödinger equation. Using these phase shifts η_l as a function of incident energy E, the level shift/vacancy in the defect crystal has been calculated from the formula

$$\Delta E=\int \psi_{\mathbf{k}}{}^*(\mathbf{r})V(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r})d\mathbf{r}\Big/\int \psi_{\mathbf{k}}{}^*(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r})d\mathbf{r}, \quad (4.16)$$

where $\psi_{\mathbf{k}}{}^*(\mathbf{r})$ is a plane wave and $\phi_{\mathbf{k}}(\mathbf{r})$ the scattered wave. Equation (4.16) is readily expressed in terms of the phase shifts. The calculations based on these phase shifts, in which q in (4.15) was adjusted to satisfy the Friedel sum rule, are shown in the solid curves of Fig. 2 for $Z=1$ to 5, the values of q being recorded in Table I along with the linear Thomas-Fermi values.

For comparison, the level shift given by the new method has been calculated using the same potentials and the expression

$$\Delta E=-\int d\mathbf{r}[\rho(\mathbf{r},E)-\rho_0(\mathbf{r},E)]\Big/\frac{\partial\mathfrak{N}_0(E)}{\partial E}, \qquad (4.17)$$

where

$$\begin{aligned}\rho(\mathbf{r},E)&=0, \quad E<g_1(\mathbf{r}E)\\ &=\rho_0[\mathbf{r},E-g_1(\mathbf{r}E)], \quad E\geqslant g_1(\mathbf{r}E)\end{aligned}$$

and $\mathfrak{N}_0(E)$ is the integrated density of states, $\mathfrak{N}_0(E)=\int d\mathbf{r}\rho_0(\mathbf{r}E)$, given by (4.4). The results for the exact $g_1(\mathbf{r},E)$ are shown in curves 2 and those for the Thomas-

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[9] N. H. March and A. D. Boardman, J. Phys. Soc. Japan **18**, 80 (1963).

[10] Exact calculations of the charge displaced by a square barrier of the type proposed by Fumi in Phil. Mag. **46**, 1007 (1955), for the representation of a vacancy have been carried out by Baranovsky and March. Some results are reported by N. H. March and J. C. Stoddart, Rept. Progr. Phys. **31**, 533 (1968).

Fermi approximation, Eq. (4.5), in curves 3. The first-order perturbative results for $Z=1$, 2, and 3 are also shown. These are independent of energy and given by $4\pi Zq^{-2}$.

It can be seen that there is pretty good agreement between the exact level shifts as a function of energy, and the two approximate theories. For large Z, the new approximation is better than the Thomas-Fermi approximation except at low energies. Both sets of approximate curves are good, however. The indications are that, had we used attractive potentials, the method based on $g(\mathbf{r}E)$ would be a substantial improvement on the Thomas-Fermi method.

For $Z=1$, the level shift varies only weakly with energy, leading to the almost rigid-band-model characteristic of first-order perturbation theory for plane waves. Already, however, for $Z=2$ perturbation theory is seriously breaking down.

These results encourage us to believe that the method proposed here is very useful for calculating level shifts, and hence, straightforwardly, densities of states. However, the trouble in the Thomas-Fermi method, that there is a classically forbidden region for a repulsive potential, is not wholly removed by our energy-dependent potential. Thus, the method is less useful for getting $\rho(\mathbf{r}E)$ and is best thought of as a procedure for calculating the density of states.

In view of the accuracy of these results, we shall go on to discuss how the density of states can be got for Bloch-wave scattering from slowly varying potentials.

B. Bloch-Wave Scattering

Having illustrated the method for plane-wave scattering, we now turn to the Bloch-wave case. The generalization of (4.2) is clearly

$$\rho(\mathbf{r}E)=\rho_p[\mathbf{r},E-g(\mathbf{r}E)], \tag{4.18}$$

where $\rho_p(\mathbf{r}E)$ is the local density in the pure metal. To first order in the impurity potential, we find

$$g_1(\mathbf{r}E)=-\left(\frac{\partial\rho_p(\mathbf{r}E)}{\partial E}\right)^{-1}\int d\mathbf{r}_1\int dE_1dE_2 \times\left[\frac{\delta(E-E_1)+\delta(E-E_2)}{(E_1-E_2)^2}-2\frac{\theta(E-E_1)-\theta(E-E_2)}{(E_1-E_2)^3}\right] \times\rho_p(\mathbf{r}\mathbf{r}_1E_2)V(\mathbf{r}_1)\rho_p(\mathbf{r}_1\mathbf{r}E_1)\,, \tag{4.19}$$

by comparison of (4.18) for weak potentials with (3.1). However, we cannot expect that such a theory will deal carefully (if indeed at all) with virtual states. Nevertheless, it gives us an explicit way of "deforming" the pure metal local density $\rho_p(\mathbf{r}E)$ to account for scattering off the solute atoms. We can also obtain the off-diagonal elements of $g(\mathbf{r}E)$, and this is dealt with in Appendix B. This may be useful if we regard the introduction of $g(\mathbf{r}\mathbf{r}'E)$ into $\rho(\mathbf{r}\mathbf{r}'E)$ as a first approximation to insert in the basic integral equation (2.9).

In the case of a strongly attractive potential, we should want to orthogonalize to the bound states introduced by the solute potential before such iteration. To do this, we would write

$$\rho(\mathbf{r},\mathbf{r}',E)=\rho_p[\mathbf{r},\mathbf{r}',E-g_1(\mathbf{r}\mathbf{r}'E)] +\lambda(E)\phi_0^*(\mathbf{r})\phi_0(\mathbf{r}') \tag{4.20}$$

if a single bound state, with localized wave function $\phi_0(\mathbf{r})$, is formed. The quantity $\lambda(E)$ is then calculated from the orthogonality relation

$$\int\rho(\mathbf{r}\mathbf{r}'E)\phi_0^*(\mathbf{r})\phi_0(\mathbf{r}')d\mathbf{r}d\mathbf{r}'=1\,, \tag{4.21}$$

yielding

$$\lambda(E)=1-\int\rho_p(\mathbf{r}\mathbf{r}'E-g_1)\phi_0^*(\mathbf{r})\phi_0(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{4.22}$$

Inserting this in (4.20), and writing the left-hand side as $\rho(\mathbf{r},\mathbf{r}',E-g)$, we get a new approximation transcending g_1. This is then inserted in the right-hand side of (2.9) to obtain the next approximation. Clearly, full knowledge of the Dirac matrix for the perfect crystal is now a pressing need. When it becomes available, we can calculate the modifications in the band density of states induced by the scattering potential $V(\mathbf{r})$.

Finally, we want to point out that if we integrate the displaced charge over all $\mathbf{r}$, we regain after some calculation the first-order result for the integrated density of states.[11] We expect from the discussion in Sec. 4 A that Eqs. (4.18) and (4.19) will be very useful in the problem of Bloch-wave scattering from a strong repulsive potential, such as is afforded by a vacancy in polyvalent metals.

5. VIRTUAL AND BOUND STATES: KOSTER-SLATER MODEL

Though the approximate theory of Sec. 4 is applicable to problems of strong scattering, it is not suitable for dealing with strong and localized potentials which can lead to resonances in the conduction band, i.e., to virtual bound states. The merit of the approach initiated by Koster and Slater[12] is that it can deal very naturally with bound and resonant states. The price paid for this, however, is to assume a solute potential $V(\mathbf{r})$ which seems very restrictive. Indeed, it has been suggested that the two assumptions of the Koster-Slater model, namely, the one-band assumption and the

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[11] A. D. Boardman and N. H. March, J. Phys. Chem. Solids **25**, 1435 (1964).

[12] G. F. Koster and J. C. Slater, Phys. Rev. **96**, 1208 (1954).

assumption about the matrix elements of the solute potential, set out in Eq. (5.1) below, are so restrictive that they will not be compatible in real impurity situations.[13]

The special property assumed for the solute potential in the simplest form of the Koster-Slater model may be expressed in terms of the Wannier functions $\omega_\gamma(\mathbf{r})$ by

$$\int d\mathbf{r}\,\omega_\gamma^*(\mathbf{r}-\mathbf{t}_i)V(\mathbf{r})\omega_{\gamma'}(\mathbf{r}-\mathbf{t}_j)=\lambda_\gamma\delta_{\gamma\gamma'}\delta(\mathbf{t}_i-\mathbf{t}_0)\delta(\mathbf{t}_j-\mathbf{t}_0)\,, \tag{5.1}$$

where $\mathbf{t}_i$ denotes the ionic positions and $\mathbf{t}_0$ is the site at which the impurity is substituted. This assumption, as shown by Koster and Slater, enables the eigenfunctions in the impure crystal to be obtained in closed form.

It is straightforward to verify that a solution in closed form for the Dirac matrix may be obtained from (2.4) and (2.9) using the result (5.1). The Green's function may also be obtained using the usual dynamical equation. To obtain these solutions, we use the fact that (5.1) is equivalent to assuming that the interband matrix elements of $V(\mathbf{r})$ between Bloch states are zero. However, the intraband matrix elements are either assumed independent of the wave vectors involved, or are replaced by their averages λ_γ over the band. Thus we have

$$\int d\mathbf{r}\psi_{\mathbf{k}_1\gamma}^*(\mathbf{r})V(\mathbf{r})\psi_{\mathbf{k}_2\gamma}(\mathbf{r})=\lambda_\gamma\,. \tag{5.2}$$

We will not describe the procedure in detail, as the result for the Green's function has already been given by Dawber and Turner.[14] Rather, we shall restrict ourselves to the relevant expressions required for the discussion of the precise nature of the impurity potential in the Koster-Slater theory.

A. Nonlocal Potential Reproducing Koster-Slater Density Matrix

Though we are principally concerned here with local potential theory, it is fruitful to effect a generalization of (2.4) to define a nonlocal potential $V_{\mathrm{KS}}{}^\gamma(\mathbf{rr}'E)$, which is related to the Koster-Slater density matrix $\rho_{\mathrm{KS}}{}^\gamma(\mathbf{rr}'E)$ through Eq. (2.4) with $V(\mathbf{r})$ replaced by $V_{\mathrm{KS}}(\mathbf{rr}'E)$. Using the results of Dawber and Turner,[14] the nonlocal potential for an impurity at the origin turns out to be

$$V_{\mathrm{KS}}{}^\gamma(\mathbf{rr}'E)=\lambda_\gamma\omega_\gamma(\mathbf{r})\sum_{\mathbf{t}_n}\omega_\gamma^*(\mathbf{r}'-\mathbf{t}_n)A_\gamma(\mathbf{t}_nE)\Big/\sum_{\mathbf{t}_n\mathbf{t}_m}\rho_{\mathrm{KS}}{}^\gamma(\mathbf{t}_n,\mathbf{t}_m,E)\omega_\gamma(\mathbf{r}-\mathbf{t}_n)\omega_\gamma^*(\mathbf{r}'-\mathbf{t}_m)\,, \tag{5.3}$$

where the function $A_\gamma(\mathbf{t}_nE)$ is given in Appendix C.

Near the impurity site, i.e., $|\mathbf{r}|$ small, only the contribution from $\mathbf{t}_n=0$ will be important in the denominator. Then we find that considerable cancellation occurs, giving $V_{\mathrm{KS}}{}^\gamma(\mathbf{rr}'E)\sim\lambda_\gamma$ for $|\mathbf{r}|$ small and for any $\mathbf{r}'$ and E. As $|\mathbf{r}|$ becomes larger, we can again use such cancellations to show that the dependence of $V_{\mathrm{KS}}{}^\gamma(\mathbf{rr}'E)$ on $\mathbf{r}'$ and E should be small if the Wannier functions are well localized. Often, therefore, a good approximation to the Koster-Slater impurity potential could be constructed from (5.3) by evaluating the local one-body potential $V_{\mathrm{KS}}(\mathbf{rr}E_F)$. An alternative form of V_{KS} could have been defined from the Green's function, rather than the Dirac matrix, and is recorded in Appendix C.

B. Local Potential from Koster-Slater Density at Fermi Level

As shown above, we could test the nonlocal character of $V_{\mathrm{KS}}{}^\gamma(\mathbf{rr}_1E)$ explicitly by evaluating (5.3). When the result is such that it is well approximated through the band by $V_{\mathrm{KS}}{}^\gamma(\mathbf{rr}E_F)$, the Koster-Slater theory must be almost exact. However, even when the nonlocality is marked, we emphasize that it is still possible to use the Koster-Slater method near the Fermi level, for local potentials having the form discussed below.

Thus we shall seek a one-body potential $V_p(\mathbf{r})+V(\mathbf{r})$ which defines a density matrix $\rho(\mathbf{r},\mathbf{r}',E)$ through the equation of motion (2.4) such that

$$\rho^\gamma(\mathbf{rr}E_F)=\rho_{\mathrm{KS}}{}^\gamma(\mathbf{rr}E_F)\equiv\rho_{\mathrm{KS}}{}^\gamma(\mathbf{r})\,. \tag{5.4}$$

Here $\rho_{\mathrm{KS}}{}^\gamma(\mathbf{r})$ is the density of electrons in the given band at the Fermi energy E_F, and we have assumed that the interband matrix elements of $V(\mathbf{r})$ are zero. Hence the solution for ρ is diagonal in the band indices and we can write

$$\rho(\mathbf{rr}'E)=\sum_\gamma\rho^\gamma(\mathbf{rr}'E)\,. \tag{5.5}$$

Kohn and Sham[2] have suggested that, even with an exact density $\rho(\mathbf{r})$ calculated for the many-body system of N electrons, a one-body local potential can always be defined such that $\rho(\mathbf{r})$ is generated by summing the squares of N single-particle wave functions calculated from this local potential. A prescription for calculating this potential exactly from a known density has been given by Stoddart and March[15] as an expansion in the displaced charge $(\rho-\rho_0)$, but so far it has not proved

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[13] See, for example, the discussion by J. L. Beeby in Phys. Rev. **137**, A933 (1964). Beeby's criticism was based on the assumption of extreme localization of the solute potential. We show below that this is not a general consequence of the Koster-Slater assumptions. We find, in fact, that the range of the solute potential is the same as the range of the Wannier functions in the band under discussion. This result had also been anticipated by G. E. Kilby in Proc. Phys. Soc. (London) **90**, 181 (1967).

[14] P. Dawber and R. E. Turner, Proc. Phys. Soc. (London) **88**, 217 (1966).

[15] J. C. Stoddart and N. H. March, Proc. Roy. Soc. (London) **A229**, 279 (1969).

possible to sum this expansion. Thus, another method is adopted below, but we stress that the potential defined above will only be exactly the Kohn-Sham potential if E_F lies in the lowest-energy band. If, however, γ is a higher band, then the potential need not correspond to the Kohn-Sham choice, as we require only that the electron density in one chosen band be obtained correctly. To be quite precise, we should label the one-body potential with a band index.

From (2.4) it can be seen immediately that

$$(\nabla_{\mathbf{r}}^2-\nabla_{\mathbf{r}'}^2)\rho^\gamma(\mathbf{rr}'E_F) =2[V_p(\mathbf{r})+V(\mathbf{r})-V_p(\mathbf{r}')-V(\mathbf{r}')]\rho^\gamma(\mathbf{rr}'E_F). \quad (5.6)$$

Introducing sum and difference variables $2\boldsymbol{\xi}=(\mathbf{r}+\mathbf{r}')$, $2\boldsymbol{\eta}=(\mathbf{r}-\mathbf{r}')$, we expand the density matrix in the form

$$\rho(\mathbf{rr}'E_F)=\rho(\boldsymbol{\xi\eta}E_F) =\rho(\boldsymbol{\xi}0E_F)+\sum_{i\geqslant j}\eta_i\eta_j a_{ij}(\boldsymbol{\xi})+\cdots, \quad (5.7)$$

following the method proposed in one-dimension by Young and March.[16] The coefficients a_{ij} then define a potential corresponding to a given density $\rho(\boldsymbol{\xi}0E_F)\equiv\rho(\boldsymbol{\xi})$ through

$$\frac{\partial V(\boldsymbol{\xi})}{\partial\xi_i}=\frac{1}{4\rho(\boldsymbol{\xi})}\left[\sum_{l=1}^{3}\frac{\partial a_{li}(\boldsymbol{\xi})}{\partial\xi_l}+\frac{\partial a_{ii}(\boldsymbol{\xi})}{\partial\xi_i}\right]. \quad (5.8)$$

To find the local potential which yields the Koster-Slater density, we now calculate the coefficients $a_{ij}(\xi)$ from the known Koster-Slater density matrix $\rho_{\mathrm{KS}}(\mathbf{rr}'E_F)$.

Use of the equation of motion for $\rho_{\mathrm{KS}}(\mathbf{rr}'E_F)$ in the form (5.6) simplifies the procedure, and we obtain

$$\frac{\partial V(\boldsymbol{\xi})}{\partial\xi_i}=\frac{\lambda_\gamma}{2\rho(\boldsymbol{\xi})}\sum_{\mathbf{k}_1\mathbf{k}_2}\left\{\frac{\partial\psi_{\mathbf{k}_1\gamma}(\boldsymbol{\xi})}{\partial\xi_i}\psi_{\mathbf{k}_2\gamma}^*(\boldsymbol{\xi}) -\psi_{\mathbf{k}_1\gamma}(\boldsymbol{\xi})\frac{\partial\psi_{\mathbf{k}_2\gamma}^*(\boldsymbol{\xi})}{\partial\xi_i}\right\}S_\gamma(k_2,E_F), \quad (5.9)$$

where S_γ is given by (C14), and $\rho(\boldsymbol{\xi})$ is the Koster-Slater density at $E=E_F$. Again the use of the Wannier representation leads to a simpler form, and we find

$$\frac{\partial V(\boldsymbol{\xi})}{\partial\xi_i}=\frac{\lambda_\gamma}{\rho(\boldsymbol{\xi})}\operatorname{Re}\sum_{\mathbf{t}_n}\left[\frac{\partial\omega_\gamma(\boldsymbol{\xi})}{\partial\xi_i}\omega_\gamma^*(\boldsymbol{\xi}-\mathbf{t}_n)A_\gamma(\mathbf{t}_n,E_F) -\frac{\partial\omega_\gamma(\boldsymbol{\xi}-\mathbf{t}_n)}{\partial\xi_i}\omega_\gamma^*(\boldsymbol{\xi})A_\gamma^*(\mathbf{t}_n,E_F)\right], \quad (5.10)$$

where A_γ was introduced in (5.3).

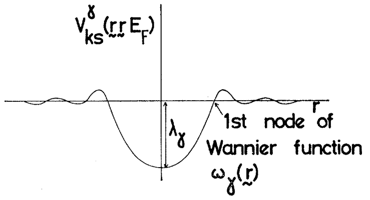

FIG. 3. Schematic form of local potential derived from Koster-Slater density at the Fermi level. The range of the potential is determined largely by the range of the Wannier function. However, the nodes further out are not necessarily associated solely with the oscillations of the Wannier function [cf. Eq. (5.3)]. The amplitude of the oscillations in the potential is small compared with λ_γ. The solute potential in the Koster-Slater theory is not, in general, spherically symmetric. The potential shown is a spherically averaged form.

As with the nonlocal form (5.3), the presence of $\omega_\gamma(\boldsymbol{\xi})$ implies localization of $V(\boldsymbol{\xi})$, which may, in principle, be obtained from (5.10) by integration, since the boundary condition as $\xi_i\rightarrow\infty$ is known. The derivative form (5.10) is, on closer examination, found again to give a potential very similar to $V_{\mathrm{KS}}(\mathbf{rr}E_F)$. Both have approximately square-well form near the impurity, with oscillations in the tail arising from the oscillations in the Wannier function, as shown schematically in Fig. 3.

C. Improved Approximations

1. Perturbative Approach

Clearly, the nonperturbative solution for the scattering of Bloch waves off potentials of the general form shown in Fig. 3 is of considerable interest, even though in almost all problems of impurities and defects, we would want to deal with impurity potentials with a Coulomb singularity eventually.

We want therefore to show how the Koster-Slater theory can be refined, so that we have a systematic procedure for converging on the solution for the local potential $V(\mathbf{r})$ discussed in Sec. 5 B, or any rather similar potentials. It is not clear to us, unfortunately, that the perturbation theory developed below will converge satisfactorily if $V(\mathbf{r})$ contains a Coulomb singularity.

Writing the Green's function for the impurity potential $V(r)$ in the form

$$G(\mathbf{rr}'E_+)=-i\sum_{\mathbf{q}_1\mathbf{q}_2\gamma}\psi_{\mathbf{q}_1\gamma}^*(\mathbf{r})\psi_{\mathbf{q}_2\gamma}(\mathbf{r}')\tilde{G}_\gamma(\mathbf{q}_1\mathbf{q}_2E_+) =\sum_\gamma G^\gamma(\mathbf{rr}'E_+), \quad (5.11)$$

the integral equation giving the Green's function G^γ for one band may be written down, and, as shown in

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[16] W. H. Young and N. H. March, Nucl. Phys. **12**, 237 (1959).

Appendix C, the result is

$$
\begin{aligned}
\tilde{G}_\gamma(\mathbf{q}_1\mathbf{q}_2E_+)
&=\frac{i\delta(\mathbf{q}_1-\mathbf{q}_2)}{E-E_\gamma(\mathbf{q}_1)+i\epsilon}+\frac{i}{(E-E_\gamma(\mathbf{q}_1)+i\epsilon)(E-E_\gamma(\mathbf{q}_2)+i\epsilon)}\\
&\quad\times\left\{\frac{\lambda_\gamma}{1-\lambda_\gamma F_\gamma(E_+)}-\lambda_\gamma+\sigma_\gamma(\mathbf{q}_1\mathbf{q}_2)\right.\\
&\quad-\sum_{\mathbf{k}_1}\frac{\lambda_\gamma[\lambda_\gamma-\sigma_\gamma(\mathbf{q}_1\mathbf{k}_1)]+\lambda_\gamma[\lambda_\gamma-\sigma_\gamma(\mathbf{k}_1\mathbf{q}_2)]}{(E-E_\gamma(\mathbf{k}_1)+i\epsilon)(1-\lambda_\gamma F_\gamma(E_+))}\\
&\left.\quad-\sum_{\mathbf{k}_1\mathbf{k}_2}\frac{\lambda_\gamma^2[\lambda_\gamma-\sigma_\gamma(\mathbf{k}_1\mathbf{k}_2)]}{(E-E_\gamma(\mathbf{k}_1)+i\epsilon)(E-E_\gamma(\mathbf{k}_2)+i\epsilon)(1-\lambda_\gamma F_\gamma(E_+))^2}\right\},
\end{aligned}
\tag{5.12}
$$

where now, in contrast to (5.2),

$$\int d\mathbf{r}\psi_{\mathbf{k}_1\gamma}{}^*(\mathbf{r})V(\mathbf{r})\psi_{\mathbf{k}_2\gamma}(\mathbf{r})=\sigma_\gamma(\mathbf{k}_1\mathbf{k}_2). \tag{5.13}$$

$F_\gamma(E)$ is the quantity characteristic of the Koster-Slater theory

$$F_\gamma(E_+)=\int\frac{n_\gamma(\epsilon)d\epsilon}{\epsilon-E-i\delta}=P_\gamma(E)-i\pi n_\gamma(E), \tag{5.14}$$

$n_\gamma(E)$ being the density of states in band γ.

Obviously, if $\sigma_\gamma(\mathbf{k}_1\mathbf{k}_2)$ deviates but little from the constant λ_γ, the perturbation series will converge rapidly and the analytic properties of the Green's function are not going to be greatly altered. In particular, there are still singularities in (5.12) when $1-\lambda_\gamma P_\gamma(E)=0$, P_γ being as defined in (5.14). This condition, of course, determines the positions of the real and virtual bound states. In any nonperturbational treatment of the matrix elements $\sigma_\gamma(\mathbf{k}_1\mathbf{k}_2)$, the positions of the bound state and virtual state are shifted somewhat.

2. *Nonperturbative Method Using Energy-Dependent Matrix Elements*

In order to improve on the solution (5.12), we must obviously have some more explicit information about the matrix elements $\sigma_\gamma(\mathbf{k}_1\mathbf{k}_2)$ of the impurity potential. In view of the fact that we are assuming an impurity potential $V(\mathbf{r})$ similar to the one-body potential which gives the Koster-Slater density, a reasonable approximation is to take

$$\sigma_\gamma(\mathbf{k}_1\mathbf{k}_2)=\sigma_\gamma[E_\gamma(\mathbf{k}_1),E_\gamma(\mathbf{k}_2)]. \tag{5.15}$$

As can be seen from the perturbation series, this is equivalent to assuming that $G_\gamma(\mathbf{k}_1\mathbf{k}_2E)$ is a function of $E(\mathbf{k}_1)$ and $E(\mathbf{k}_2)$ and not of the wave vectors.

Using (5.15) and with the definition

$$\tilde{G}_\gamma=\frac{i\delta(\mathbf{q}_1-\mathbf{q}_2)}{E-E_\gamma(\mathbf{q}_1)+i\epsilon}+\tilde{\mathcal{G}}_\gamma(\mathbf{q}_1\mathbf{q}_2E), \tag{5.16}$$

we have from the usual integral equation for the Green's function

$$
\begin{aligned}
\tilde{\mathcal{G}}_\gamma(E_1E_2E_+)&=\frac{i\sigma_\gamma(E_1,E_2)}{(E-E_1+i\epsilon)(E-E_2+i\epsilon)}\\
&\quad+\int\frac{dE_0n_\gamma(E_0)\sigma_\gamma(E_1E_0)\tilde{\mathcal{G}}_\gamma(E_0E_2E_+)}{E-E_1+i\epsilon}.
\end{aligned}
\tag{5.17}
$$

We also have

$$\tilde{\mathcal{G}}_\gamma(E_1E_2E_+)=\tilde{\mathcal{G}}_\gamma(E_2E_1E_+). \tag{5.18}$$

The solution of (5.17), subject to (5.18), would give the Green's function for the one-body potential $V_\gamma(\mathbf{r})+V(\mathbf{r})$, with intraband matrix elements of $V(\mathbf{r})$ between Bloch states of the form (5.15) and zero interband matrix elements. Equation (5.17) seems to be a great simplification over the full problem and appears to be soluble by numerical iteration, without enormous computational problems.

6. GENERALIZED KOSTER-SLATER RELATION FOR BOUND STATES

Some further analytic progress is possible in solving the integral equation (5.17), if we remind ourselves that the Koster-Slater theory is regained from (5.17) by assuming $\sigma_\gamma(E_1,E_2)$ is independent of E_1 and E_2.

This suggests that an improved approximation will be to average over E_1 say, within band γ. Though, at first sight, this seems to violate the symmetry requirement (5.18), we can subsequently symmetrize readily as we shall see below. Once $\sigma_\gamma(E_1E_2)$ is averaged over E_1 to give $\sigma_\gamma(E_2)$, then the solution of (5.17) is readily found as

$$\tilde{G}_\gamma(E_1,E_2,E_+)=\frac{i\sigma_\gamma(E_2)}{(E-E_1+i\epsilon)(E-E_2+i\epsilon)[1-a_\gamma(E_+)]}, \tag{6.1}$$

where

$$a_\gamma(E_+)=\int dE_0\frac{n_\gamma(E_0)\sigma_\gamma(E_0)}{E-E_0+i\epsilon}. \tag{6.2}$$

The density of states may now be calculated from

$$n(E)=-\frac{1}{2\pi i}\int d\mathbf{r}[G(\mathbf{r}\mathbf{r}E_+)-G^*(\mathbf{r}\mathbf{r}E_+)], \tag{6.3}$$

where

$$
\begin{aligned}
G(\mathbf{r}\mathbf{r}_0E_+)&=G_p(\mathbf{r}\mathbf{r}_0E_+)\\
&\quad-i\sum_{\mathbf{k}_1\mathbf{k}_2\gamma}\psi_{\mathbf{k}_1\gamma}{}^*(\mathbf{r})\psi_{\mathbf{k}_2\gamma}(\mathbf{r}_0)\tilde{G}_\gamma(E_\gamma(\mathbf{k}_1),E_\gamma(\mathbf{k}_2),E_+).
\end{aligned}
\tag{6.4}
$$

Then we find, from (6.1), (6.3), and (6.4),

$$n(E)=n_\gamma(E)+\frac{1}{\pi}\operatorname{Im}\left[\frac{\partial a_\gamma(E_+)}{\partial E}\,\frac{1}{1-a_\gamma(E_+)}\right]. \tag{6.5}$$

If we write, as $\epsilon\rightarrow 0^+$,

$$a_\gamma(E_+)=P_\gamma'(E)-i\pi n_\gamma(E)\sigma_\gamma(E), \tag{6.6}$$

then we find from (6.5)

$$n(E)=n_\gamma(E)-\frac{n_\gamma(E)\sigma_\gamma(E)\partial P_\gamma'(E)/\partial E+[1-P_\gamma'(E)](\sigma_\gamma(E)\partial n_\gamma(E)/\partial E+n_\gamma(E)\partial\sigma_\gamma(E)/\partial E)}{[1-P'(E)]^2+[\pi n_\gamma(E)\sigma_\gamma(E)]^2}. \tag{6.7}$$

This result remains unchanged if we replace $\sigma_\gamma(E_2)$ in (6.1) by the symmetrized form $\frac{1}{2}[\sigma_\gamma(E_1)+\sigma_\gamma(E_2)]$.

The condition for a bound state to occur is now

$$1-P\int dE_0\frac{n_\gamma(E_0)\sigma_\gamma(E_0)}{E-E_0+i\epsilon}=0. \tag{6.8}$$

Wave Functions and Rigid-Band-Like Behavior

Equation (6.8) is the generalization of the Koster-Slater condition for bound states. It enables a more general matrix element to be discussed, and evidently relaxes somewhat the conditions on the Koster-Slater potential.

While (6.7) is obviously leading back to the rigid-band-model result to first order in $\sigma_\gamma(E)$, we feel that the above argument could, in contrast to the Koster-Slater model, lead to rigid-band-like behavior when the energy dependence of $\sigma_\gamma(E)$ is strong, for a strongly attractive potential.

We can best see this via the eigenfunctions $\phi_{\mathbf{k}}(\mathbf{r})$. These may be obtained by expanding in terms of the Bloch functions of a single band γ,

$$\phi_{\mathbf{k}}(\mathbf{r})=\sum_{\mathbf{k}'}p_\gamma(\mathbf{kk}')\psi_{\mathbf{k}'\gamma}(\mathbf{r}). \tag{6.9}$$

Substitution into the integral equation for $\phi_{\mathbf{k}}(\mathbf{r})$ gives the following equation for the coefficients p_γ, with $E\equiv E_\gamma(\mathbf{k})$:

$$p_\gamma(\mathbf{kq})=\delta(\mathbf{k}-\mathbf{q})+\sum_{\mathbf{k}'}\frac{p_\gamma(\mathbf{kk}')\sigma_\gamma(\mathbf{qk}')}{E-E_\gamma(\mathbf{q})+i\epsilon}. \tag{6.10}$$

This equation may be solved by replacing $\sigma_\gamma(\mathbf{qk}')$ by its average over either $\mathbf{q}$ or $\mathbf{k}'$, in the same way as the Green's function was obtained earlier in this section. We replace $\sigma_\gamma(\mathbf{qk}')$ by $\sigma_\gamma(\mathbf{k}')\equiv\sigma_\gamma(E_\gamma(\mathbf{k}'))$ and obtain the eigenfunctions

$$\phi_{\mathbf{k}}(\mathbf{r})=\psi_{\mathbf{k}\gamma}(\mathbf{r})+\frac{\sigma_\gamma(E)}{1-a_\gamma(E_+)}\sum_{\mathbf{q}}\frac{\psi_{\mathbf{q}\gamma}(\mathbf{r})}{E-E_\gamma(\mathbf{q})+i\epsilon}. \tag{6.11}$$

It does seem possible to choose $\sigma_\gamma(E)$ even for a strongly attractive potential, so that the condition (6.8) for a bound state or resonance is never satisfied, even if (6.8) would be satisfied in the corresponding Koster-Slater theory with parameter λ_γ = average of $\sigma_\gamma(E)$ over band energies. We then expect that the corresponding eigenfunctions (6.11) will describe approximately the behavior in a rigid-band-like alloy.

If we rewrite (6.11) in terms of the Wannier function $\omega(\mathbf{r})$ and for a first orientation neglect the Wannier functions on other than the impurity site, then we obtain

$$\phi_{\mathbf{k}}(\mathbf{r})=\psi_{\mathbf{k}\gamma}(\mathbf{r})+\mu_\gamma(E)[P_\gamma(E)-i\pi n_\gamma(E)]\omega_\gamma(\mathbf{r}), \tag{6.12}$$

where

$$\mu_\gamma(E)=\sigma_\gamma(E)/1-a_\gamma(E_+). \tag{6.13}$$

We note that the eigenfunction (6.11) may be obtained from the integral equation for $\phi_{\mathbf{k}}(\mathbf{r})$ by assuming

$$\mu_\gamma(E)=\int d\mathbf{r}_1\psi_{\mathbf{q}\gamma}^*(\mathbf{r}_1)V(\mathbf{r}_1)\phi_{\mathbf{k}}(\mathbf{r}_1),\quad E=E_\gamma(\mathbf{k}). \tag{6.14}$$

This is obviously a generalization of the Koster-Slater condition on the impurity potential, and is of interest in view of the fact that the exact level shift $\Delta E(\mathbf{k})$ is given by

$$\Delta E(\mathbf{k})=\int\psi_{\mathbf{k}\gamma}^*(\mathbf{r})V(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r})d\mathbf{r}\Bigg/\int\psi_{\mathbf{k}\gamma}^*(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r})d\mathbf{r}. \tag{6.15}$$

Thus if $\mu_\gamma(E)$ is a slowly varying function, as discussed earlier, we expect an almost rigid-band model to emerge if the denominator in (6.15) is almost independent of $\mathbf{k}$.

If μ_γ in (6.13) is assumed to be real, then the corresponding $\sigma_\gamma(E)$ will be complex, and this leads to difficulties in the formalism. This is why we have preferred the approach based on (6.1) with $\sigma_\gamma(E)$ taken to be real. However, if we require σ_γ in (6.13) to be real, then the eigenfunctions lead to the density of states given by (6.7).

It will be an interesting matter for the future to see whether, with realistic Bloch functions, a strongly energy-dependent $\sigma_\gamma(E)$ could, in some circumstances, suppress bound or virtual states and lead to roughly rigid-band behavior. An alloy system like Ag-Pd, where the rigid-band model appears to be a useful first approximation, might perhaps be tackled eventually by a theory like the one outlined in this section.

7. CONCLUSION

As soon as detailed information is forthcoming on the Dirac density matrix in perfect crystals, the kernel F in Eq. (3.1) of the linear response theory can be estimated, and the general features of the displaced charge $\Delta(\mathbf{r}E)$ round an impurity or defect can then be mapped out. The effect of anisotropic Fermi surfaces and the related problem of the angular dependence of the displaced charge could then be estimated. As indicated in Sec. 3, such knowledge is now becoming important in a variety of problems in metallic alloys.

Secondly, for defect potentials that are repulsive, but not necessarily weak, Eqs. (4.18) and (4.19) offer a direct route to the calculation of the modified density of states, when the same information on the perfect crystal as required in the linear response theory becomes available. This method should also be fruitful for the scattering of Bloch waves off attractive potentials which are not strong enough to induce real or virtual bound states.

For the latter class of problem, the best approach to date seems to be afforded by the Koster-Slater theory, and the refinements presented here. We have displayed the essential form of the Koster-Slater defect potential, and it would, we think, be of considerable interest to solve numerically the integral equation (5.17) for a particular dilute alloy, to see how the Koster-Slater condition for bound states is to be modified.

Forms of wave functions are presented which should afford a starting point in alloys where almost rigid-band models or energy surfaces of undeformed shape apply.

Clearly, in making numerical calculations on the basis of the zero-order solutions presented in this paper for specific defect crystals, the greatest care should be exercised in deciding within which regime the solute or defect potential is likely to lie. A good choice should allow ready refinement by iteration in (2.9).

Finally, the bottleneck in impurity and defect problems is now, unquestionably, the lack of accurate usable information for the perfect crystal. The first task is to find explicitly the local density $\rho(\mathbf{r}E)$ in pure metals. Such a program is now under way in this Department.

APPENDIX A: INTEGRAL EQUATIONS FOR DIRAC MATRIX

The integral equation (2.6) for the Dirac matrix is readily obtained from the Bloch matrix $C(\mathbf{r}\mathbf{r}_0\beta)$ defined by

$$C(\mathbf{r}\mathbf{r}_0\beta)=\sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}_0)e^{-\beta E_i} \tag{A1}$$

in terms of one-electron wave functions ψ_i and energies E_i. This satisfies the well-known integral equation, for electrons moving in a total potential $V(\mathbf{r})$,

$$C(\mathbf{r}\mathbf{r}_0\beta)=C_0(\mathbf{r}\mathbf{r}_0\beta)-\int d\mathbf{r}_1\int_0^\beta d\beta_1 C_0(\mathbf{r}\mathbf{r}_1\beta-\beta_1)V(\mathbf{r}_1)C(\mathbf{r}_1\mathbf{r}_0\beta_1)\,, \tag{A2}$$

where C_0 is the free-electron Bloch matrix. Using the Laplace transform relation between ρ and C,

$$\rho(\mathbf{r}\mathbf{r}_0E)=\frac{1}{2\pi i}\int_{C-i\infty}^{C+i\infty} d\beta\frac{e^{\beta E}}{\beta}C(\mathbf{r}\mathbf{r}_0\beta)\,, \tag{A3}$$

we then obtain

$$\rho(\mathbf{r}\mathbf{r}_0E)=\rho_0(\mathbf{r}\mathbf{r}_0E)+\int d\mathbf{r}_1\int dE_1 f_0(\mathbf{r}-\mathbf{r}_1,E,E_1)V(\mathbf{r}_1)\rho(\mathbf{r}_1,\mathbf{r}_0,E_1)\,, \tag{A4}$$

where

$$f_0(\mathbf{r}-\mathbf{r}_1,E,E_1)=\frac{1}{2\pi i}\int_{C-i\infty}^{C+i\infty} d\beta\frac{e^{\beta E}}{\beta}\times\int_0^\beta d\beta_1 C_0(\mathbf{r}\mathbf{r}_1\beta-\beta_1)\beta_1 e^{-\beta_1 E_1}. \tag{A5}$$

Use of the standard form for C_0 in momentum space enables (A5) to be rewritten as

$$f_0(\mathbf{r}-\mathbf{r}_1,E,E_{1+})=\frac{1}{(2\pi)^3}\int\frac{d\mathbf{p}_2 e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}_1)}}{(E_1+i\epsilon-p^2/2)^2}\times\left[\left(E_1-\frac{p^2}{2}\right)\delta(E-E_1)+\theta(E-E_1)-\theta\left(E-\frac{p^2}{2}\right)\right], \tag{A6}$$

and from this we may obtain directly the form given in Eq. (2.8).

To obtain the form (2.9) we return to (A2), but now choose the unperturbed solution as the Bloch matrix C_p generated by the lattice potential $V_p(\mathbf{r})$. Then, replacing C_0 by C_p and interpreting $V(\mathbf{r}_1)$ in (A2) as the impurity potential, we can again use (A3) to yield

$$\rho(\mathbf{r}\mathbf{r}_0E)=\rho_p(\mathbf{r}\mathbf{r}_0E)-\int d\mathbf{r}_1 dE_1 f_p(\mathbf{r},\mathbf{r}_1,E,E_1)\times V(\mathbf{r}_1)\frac{\partial\rho(\mathbf{r}_1\mathbf{r}_0E_1)}{\partial E_1}, \tag{A7}$$

where

$$f_p(\mathbf{r},\mathbf{r}_1,E,E_1)=\int dE_2\left[\frac{\theta(E-E_2)-\theta(E-E_1)}{E_1-E_2+i\epsilon}\right]\frac{\partial\rho_p(\mathbf{r}\mathbf{r}_1E_2)}{\partial E_2}. \tag{A8}$$

The form (2.9) is then obtained by performing the integrations over E_1 and E_2 in (A7) and (A8) by parts.

APPENDIX B: OFF-DIAGONAL ELEMENTS OF ENERGY-DEPENDENT POTENTIAL

In Sec. 4 B on Bloch-wave scattering, a method was proposed for obtaining the Dirac matrix ρ for a strongly attractive solute potential which could include any bound states associated with this potential. To calculate the orthogonality function $\lambda(E)$ defined by (4.17) we require the off-diagonal elements $g(\mathbf{rr}'E)$ defined by

$$\rho(\mathbf{rr}'E)=\rho_p[\mathbf{rr}',E-g(\mathbf{rr}'E)]. \tag{B1}$$

To first order in solute potential we may obtain from (4.19),

$$g(\mathbf{rr}'E)=\left[\frac{\partial\rho_p(\mathbf{rr}'E)}{\partial E}\right]^{-1} \times\int d\mathbf{r}_1dE_1dE_2\left[\frac{\theta(E-E_2)-\theta(E-E_1)}{E_1-E_2+i\epsilon}\right] \times V(\mathbf{r}_1)\frac{\partial\rho_p(\mathbf{rr}_1E_2)}{\partial E_2}\frac{\partial\rho_p(\mathbf{r}_1\mathbf{r}'E_1)}{\partial E_1}. \tag{B2}$$

The density matrix defined by (B1) and (B2) may be a good first-order solution which could in principle be improved by iteration in (2.9).

APPENDIX C: SOME FURTHER RESULTS RELATING TO KOSTER-SLATER MODEL

Here the basic equations used to refine the Koster-Slater solution for the Green's function, in perturbation theory, will be summarized. First of all, the impurity potential will be assumed to have zero interband matrix elements, though subsequently this restriction will be dropped.

A brief comment on the boundary conditions obeyed by the matrices generated by the impurity potentials discussed above is first necessary. Throughout the text we have focused attention on one band. Then, when the interband matrix elements are zero, an "effective" nonlocal impurity potential for each band may be defined, as discussed in Sec. 5 B. Although these potentials for the various bands all have the same functional form, the strength of each is measured by the parameters λ_γ, which are effectively independent in the Koster-Slater theory. Thus, for the Bloch matrix given in Eq. (A1), this model leads to the complete solution $C_{\mathrm{KS}}=\sum_\gamma C_{\mathrm{KS}}{}^\gamma$. The matrix C_{KS} is required to satisfy the completeness condition

$$C_{\mathrm{KS}}(\mathbf{rr}_0 0)=\delta(\mathbf{r}-\mathbf{r}_0). \tag{C1}$$

Because of the way in which the impurity potential separates the scattering in each band, the partial matrix $C_{\mathrm{KS}}{}^\gamma$ for band γ is required to satisfy

$$C_{\mathrm{KS}}{}^\gamma(\mathbf{rr}_0 0)=C_p{}^\gamma(\mathbf{rr}_0 0)=\sum_{\mathbf{k}}\psi_{\mathbf{k}\gamma}{}^*(\mathbf{r})\psi_{\mathbf{k}\gamma}(\mathbf{r}_0). \tag{C2}$$

We turn now to discuss the Green's function G for an impurity potential $V(\mathbf{r})$ which has zero interband matrix elements. In terms of the Koster-Slater theory, for which $G_{\mathrm{KS}}=\sum_\gamma G_{\mathrm{KS}}{}^\gamma$, we can write the integral equation for the Green's function, assuming that it has the form (5.11), as

$$G^\gamma(\mathbf{rr}_0E)=G_{\mathrm{KS}}{}^\gamma(\mathbf{rr}_0E)+\int d\mathbf{r}_1G(\mathbf{rr}_1E) \times[V(\mathbf{r}_1)-\mathcal{V}_{\mathrm{KS}}{}^\gamma(\mathbf{r}_1\mathbf{r}_0E)]G_{\mathrm{KS}}{}^\gamma(\mathbf{r}_1\mathbf{r}_0E). \tag{C3}$$

The nonlocal potential $\mathcal{V}_{\mathrm{KS}}{}^\gamma$ is defined by

$$\mathcal{V}_{\mathrm{KS}}{}^\gamma(\mathbf{rr}_0E)G_{\mathrm{KS}}{}^\gamma(\mathbf{rr}_0E) =-i\lambda_\gamma\sum_{\mathbf{k}_1\mathbf{k}_2}\psi_{\mathbf{k}_1\gamma}{}^*(\mathbf{r})\psi_{\mathbf{k}_2\gamma}(\mathbf{r}_0)\sum_{\mathbf{k}}B^\gamma(\mathbf{kk}_2E), \tag{C4}$$

where

$$B^\gamma(\mathbf{kk}_2E)=\frac{i\delta(\mathbf{k}-\mathbf{k}_2)}{E-E_\gamma(\mathbf{k})+i\epsilon} +\frac{i\lambda_\gamma}{[E-E_\gamma(\mathbf{k})+i\epsilon][E-E_\gamma(\mathbf{k}_2)+i\epsilon][1-\lambda_\gamma F_\gamma(E_+)]}. \tag{C5}$$

Upon substitution of (5.11) into (C3) we obtain the integral equation for $\tilde{G}_\gamma$,

$$\tilde{G}_\gamma(\mathbf{q}_1\mathbf{q}_2E)=B^\gamma(\mathbf{q}_1\mathbf{q}_2E) +i\sum_{\mathbf{qk}}\tilde{G}_\gamma(\mathbf{q}_1\mathbf{q}E)[\lambda_\gamma-\sigma_\gamma(\mathbf{qk})]B^\gamma(\mathbf{kq}_2E), \tag{C6}$$

where

$$\sigma_\gamma(\mathbf{qk})=\int d\mathbf{r}\psi_{\mathbf{q}\gamma}{}^*(\mathbf{r})V(\mathbf{r})\psi_{\mathbf{k}\gamma}(\mathbf{r}). \tag{C7}$$

The perturbation series for $\tilde{G}_\gamma$ may be generated by iteration of (C6). By replacing $\tilde{G}_\gamma$ by $\tilde{A}_\gamma$ in the right-hand side of (C6), we obtain the result of (5.12).

Nonzero Interband Matrix Elements

The assumption that the impurity part of the one-body potential $V(\mathbf{r})$ has zero interband matrix elements is not necessary, and we may again set up a perturbational treatment.

The integral equation giving $G(\mathbf{rr}_0E)$ in terms of G_{KS} for an impurity potential with small interband matrix elements is

$$G(\mathbf{rr}_0E)=G_{\mathrm{KS}}(\mathbf{rr}_0E)+\int d\mathbf{r}_1G(\mathbf{rr}_1E) \times[V(\mathbf{r}_1)-\mathcal{V}_{\mathrm{KS}}(\mathbf{r}_1\mathbf{r}_0E)]G_{\mathrm{KS}}(\mathbf{r}_1\mathbf{r}_0E). \tag{C8}$$

In (C8), we have used G_{KS} given in Ref. 15 upon summing over band index γ, and the nonlocal potential

$\mathcal{V}_{\mathrm{KS}}$ is defined by

$$\mathcal{V}_{\mathrm{KS}}(\mathbf{r}\mathbf{r}_0E)G_{\mathrm{KS}}(\mathbf{r}\mathbf{r}_0E)=-\delta(\mathbf{r}-\mathbf{r}_0)-[-\tfrac{1}{2}\nabla_{\mathbf{r}}^2-E-V_p(\mathbf{r})]G_{\mathrm{KS}}(\mathbf{r}\mathbf{r}_0E)\,. \tag{C9}$$

We assume that G takes the nondiagonal form

$$G(\mathbf{r}\mathbf{r}_0E)=-i\sum_{\mathbf{q}_1\mathbf{q}_2,\alpha_1,\alpha_2}\psi_{\mathbf{q}_1\alpha_1}{}^*(\mathbf{r})\psi_{\mathbf{q}_2\alpha_2}(\mathbf{r}_0)\tilde{G}_{\alpha_1\alpha_2}(\mathbf{q}_1\mathbf{q}_2E)\,. \tag{C10}$$

Upon substitution of (C10) into (C8), we obtain an equation for $\tilde{G}$ which may be solved as a perturbation expansion based upon small wave-vector dependence of the matrix elements of the impurity potential between Bloch states. We obtain to first order,

$$G_{\gamma_1\gamma_2}(\mathbf{q}_1\mathbf{q}_2E)=B^{\gamma}(\mathbf{q}_1\mathbf{q}_2E)\delta_{\gamma_1\gamma_2}+i\sum_{\mathbf{q}\mathbf{k}}B^{\gamma_1}(\mathbf{q}_1\mathbf{q}E)\times[\lambda_{\gamma_2}\delta_{\gamma_1\gamma_2}-\sigma_{\gamma_1\gamma_2}(\mathbf{q})]B^{\gamma_2}(\mathbf{k}\mathbf{q}_2E)+\cdots\,. \tag{C11}$$

In (C11), we have

$$\sigma_{\alpha\beta}(\mathbf{q}\mathbf{k})=\int d\mathbf{r}\psi_{\mathbf{q}\alpha}{}^*(\mathbf{r})V(\mathbf{r})\psi_{\mathbf{k}\beta}(\mathbf{r})\,, \tag{C12}$$

and λ_γ is the average of $\sigma_{\gamma\gamma}$ over band γ. Hence we have a quite explicit way of correcting, when necessary, for nonzero interband matrix elements.

Finally, we record here for completeness the explicit form of the function $A_\gamma(\mathbf{t}_nE)$ which was used in Sec. 5 A to define the most fundamental of the nonlocal potentials $V_{\mathrm{KS}}{}^{\gamma}(\mathbf{r}\mathbf{r}_0E)$. We have

$$A_\gamma(\mathbf{t}_nE)=\sum_{\mathbf{k}_2}e^{-i\mathbf{k}_2\cdot\mathbf{t}_n}S_\gamma(\mathbf{k}_2E)\,, \tag{C13}$$

where $S_\gamma(\mathbf{k}_2,E)$ can be obtained from the Dawber-Turner Green's function, and has the form

$$\begin{aligned}S_\gamma(\mathbf{k}_2E)=\theta(E-E_2)&+\lambda_\gamma P\int dE_0\frac{\theta(E-E_0)n_\gamma(E_0)}{[E_0-E_2][(1-\lambda_\gamma P_\gamma(E_0))^2+\pi^2\lambda_\gamma{}^2n_\gamma{}^2(E_0)]}+\frac{\lambda_\gamma\theta(E-E_2)P_\gamma(E_2)}{(1-\lambda_\gamma P_\gamma(E_2))^2+\pi^2\lambda_\gamma{}^2n_\gamma{}^2(E_2)}\\&+2\lambda_\gamma{}^2P\int dE_0\frac{\theta(E-E_0)P_\gamma(E_0)n_\gamma(E_0)}{(E_0-E_2)\{[1-\lambda_\gamma P_\gamma(E_0)]^2+\pi^2\lambda_\gamma{}^2n_\gamma{}^2(E_0)\}}\\&-\frac{\lambda_\gamma{}^2\theta(E-E_2)[P_\gamma{}^2(E_2)-\pi^2n_\gamma{}^2(E_2)]}{\{[1-\lambda_\gamma P_\gamma(E_2)]^2+\pi^2\lambda_\gamma{}^2n_\gamma{}^2(E_2)\}}-\lambda_\gamma\sum_n r_n{}^{\gamma}\frac{P_\gamma(E_n)\theta(E-E_n)}{E_n-E_2}\,.\end{aligned} \tag{C14}$$

P denotes the principal value and $E_2\equiv E_\gamma(\mathbf{k}_2)$. $r_n{}^{\gamma}$ is the residue of $[1-\lambda_\gamma F_\gamma(E)]^{-1}$ at the pole $E=E_n$, representing a bound state in the Koster-Slater formalism.

ACKNOWLEDGMENTS

The motivation for the search for a local potential consistent with the Koster-Slater assumptions arose out of a question posed to one of us (NHM) by Dr. Arthur Bienenstock during a lecture course given at the Nordic School in Gothenberg. Two of us (JCS and NHM) wish to acknowledge partial contractual support from the U. S. Army through the European Research Office. One of us (MJS) became interested in the alloy problem through work on soft x-ray emission in alloys, supported by contract with the Royal Radar Establishment, Malvern.