

Treatment of the Metallic Impurity Problem Using Green's Functions*

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The calculation of the charge density or spin density at an impurity in a metal is conveniently performed using a suitably weighted density of electron states. Working in the Wannier function representation, we derive this function making use of two Green's functions, one defined for the pure metal and the other for the metal containing the impurity. The former is directly related to the usual density of states of the pure metal, the latter to the weighted density of states we require. The attractive feature of the derivation is that there is a simple relationship between the two Green's functions, as was shown by Waller for the analogous problem in lattice dynamics. The weighted density-of-states function has a continuous part coming from the band and may also have isolated parts coming from bound states which have been pulled out of the band by the perturbation. The contribution of each to a number of physical properties is discussed for the simple case of a single band of conduction electrons and a well-localized impurity potential.

THE effects which an impurity in a crystal lattice has on the distribution of phonon frequencies and on the distribution of electron states has been emphasized by Lifshitz.¹ In a recent paper concerned with the lattice vibration problem for an isotropic impurity, Waller² has derived and made use of a very simple relationship between the Green's function for the general lattice (containing the impurity) and the Green's function for the unperturbed lattice. In this paper we show that Waller's method also has attractive features for the electronic side of the impurity problem.

The effect of an impurity on the electron states in a crystal was investigated by Koster and Slater³ who determined the existence of bound states of electrons associated with the impurity. The energies of these bound states were determined for several models of increasing complexity.^{3,4} Wave functions for electronic impurity states were obtained for the bound states and for states with energies in the allowed bands (called scattering states⁴). These authors made use of a Green's function method in solving for the electron wave functions. The normalization and completeness of the perturbed electron wave functions were not explicitly obtained by these authors. One also would like to determine the electron charge density (or spin density) in addition to the wave functions, and one needs to know the normalization factors of the impurity electron wave functions. For the density problem it is far more convenient to use a more general Green's function for the density where normalization and completeness of the wave function are automatically taken into consideration. It happens that the more general Green's function relies heavily on the Green's function for the wave function as expected. In the following, we obtain an expression for the electron density making full use of the previous work of Koster and Slater.

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¹ I. M. Lifshitz, *Nuovo Cimento Suppl.* **3**, 716 (1956).

² I. Waller, *Arkiv Fysik* **24**, 495 (1963).

³ G. F. Koster and J. C. Slater, *Phys. Rev.* **95**, 1167 (1954).

⁴ G. F. Koster and J. C. Slater, *Phys. Rev.* **96**, 1208 (1954).

A convenient set of basis functions³ for electron wave functions are the Wannier functions of the pure host metal. If $\Phi_{nk}(\mathbf{r})$ is the Bloch function describing an electron of wave vector \mathbf{k} in the n th band of the pure metal, the Wannier function $a_n(\mathbf{r}-\mathbf{R}_j)$ of the n th band centered on the site \mathbf{R}_j is defined by

$$a_n(\mathbf{r}-\mathbf{R}_j) = N^{-1/2} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}_j} \Phi_{nk}(\mathbf{r}). \quad (1)$$

For simplicity, we consider a crystal of N atoms arranged on a Bravais lattice.

We shall approach our problem by first setting down a general description in which it does not matter whether the system we have in mind is the pure metal or the metal containing the impurity. In either case, if the one-electron Hamiltonian for the electrons has eigenfunctions $\Psi_p(\mathbf{r})$ and one-electron energies, E_p , then we can expand Ψ_p in terms of the Wannier functions of the pure metal

$$\Psi_p(\mathbf{r}) = N^{-1/2} \sum_{n,j} U_p(n,j) a_n(\mathbf{r}-\mathbf{R}_j). \quad (2)$$

The Wannier functions are orthonormal and since the function $\Psi_p(\mathbf{r})$ must be also, the transformation coefficients $U_p(n,j)$ form a unitary matrix:

$$N^{-1} \sum_{n,j} U_p^*(n,j) U_p(n,j) = \delta_{pp'}, \quad (3)$$

$$N^{-1} \sum_p U_p^*(n,j) U_p(n',j') = \delta_{nn'} \delta_{jj'}. \quad (4)$$

The Green's function which we work with is

$$G_{nj,n'j'}(E) = -\frac{1}{N} \sum_p \frac{U_p^*(n',j') U_p(n,j)}{E_p - E}. \quad (5)$$

Using H to denote the matrix of the Hamiltonian in the Wannier function representation, it is easy to show using (4) that the matrix $G(E)$ whose elements are given by (5) satisfies the equation

$$(H - EI)G(E) = I, \quad (6)$$

where I is the unit matrix $\delta_{n',n''} = \delta_{nn'}\delta_{jj'}$. We now introduce a weighted density-of-states function,⁵

$$\Omega g_{nj,n'j'}(E) = N^{-1} \sum_p U_p^*(n',j') U_p(n,j) \delta(E-E_p), \quad (7)$$

in terms of which $G_{nj,n'j'}(E)$ can be expressed as

$$G_{nj,n'j'}(E) = \int_{-\infty}^{\infty} \frac{\Omega g_{nj,n'j'}(E') dE'}{E' - E}. \quad (8)$$

Here, Ω is the atomic volume. From Eq. (4), which ensures that the eigenfunctions $\psi_p(\mathbf{r})$ possess the closure property, we find the useful equation

$$\int_{-\infty}^{\infty} \Omega g_{nj,n'j'}(E) dE = \delta_{nn'}\delta_{jj'}. \quad (9)$$

We shall refer to this as the closure relationship.

In the limit of an infinite lattice $g_{nj,n'j'}(E)$ will have a continuous part $g^c(E)$ corresponding to the bands, but there may also be a number of isolated states $g^i(E) = c^i \delta(E-E^i)$, lying between the bands. For convenience, the Green's function (8) can be split into corresponding parts $G^c(E)$ and $\sum G^i(E)$. Using the well-known symbolic identity,

$$\frac{1}{E' - E - i\epsilon} = P\left(\frac{1}{E' - E}\right) + i\pi\delta(E' - E), \quad (10)$$

in which P denotes the principal value of the integral, one can write $\pi\Omega g^c(E) = \text{Im}G^c(E+i\epsilon)$. It is also easy to show from (8) that Ωc^i is equal to minus the residue of $G^i(E)$ at $E=E^i$. Hence,

$$\Omega g_{nj,n'j'}(E) = \pi^{-1} \text{Im}G_{nj,n'j'}^c(E+i\epsilon) - \sum_i [\text{Res}G_{nj,n'j'}^i(E)]_{E=E^i} \delta(E-E^i). \quad (11)$$

For the pure metal the eigenfunctions of the unperturbed Hamiltonian H^0 are the Bloch functions $\phi_{nk}(\mathbf{r})$ and the U 's are simply $e^{ik \cdot \mathbf{R}j}$. We shall denote the corresponding unperturbed functions $\bar{g}_{nj,n'j'}(E)$ and $\bar{G}_{nj,n'j'}(E)$. There are no isolated states i in this case. One can therefore use (10) to write in the usual way

$$\bar{G}_{nj,n'j'}(E) = \Omega \bar{F}_{nj,n'j'}(E) + i\pi\Omega \bar{g}_{nj,n'j'}(E), \quad (12)$$

where $\bar{F}_{nj,n'j'}(E)$ is the principal value integral

$$\Omega \bar{F}_{nj,n'j'}(E) = P \int_{-\infty}^{\infty} \frac{\Omega \bar{g}_{nj,n'j'}(E') dE'}{E' - E}. \quad (13)$$

Suppose that an impurity is introduced at \mathbf{R}_0 , and henceforth take the unbarred notation in (2) to (11) as referring to the perturbed problem with $H = H^0 + H^1$.

⁵ For simplicity, spin indices are omitted. As the index p labels space states only, $g_{nj,n'j'}(E)$ should be interpreted as belonging to states of only one spin.

In a metal the perturbation due to the impurity is localized in some degree and only a small number of bands play an important role. Thus, we may consider the problem in various approximations corresponding to allowing different number of nonzero matrix elements $H^1_{nj,n'j'}$. We suppose that these nonzero elements are contained in a $\nu \times \nu$ matrix, where, for example, in the case of one band, ν is 1 or $z+1$, z being the number of nearest neighbors. Then, multiplying (6) on the left by $\bar{G}(E)$ and using the fact that $\bar{G}(E)$ is the inverse of the matrix $(H^0 - EI)$, one obtains

$$G(E) + \bar{G}(E)H^1G(E) = \bar{G}(E). \quad (14)$$

Defining $(I + \bar{G}H^1)^{-1}$ as the inverse of the $\nu \times \nu$ matrix $(I + \bar{G}(E)H^1)$ whose elements correspond to the nonzero elements of H^1 , one can manipulate (14) to obtain

$$G(E) = \bar{G}(E) - \bar{G}(E)H^1(I + \bar{G}H^1)^{-1}\bar{G}(E). \quad (15)$$

In the second term on the right the inner $\nu \times \nu$ matrices are enclosed by $\bar{G}(E)$ matrices with appropriate rectangular shapes. It is this important expression for the perturbed Green's function in terms of the unperturbed Green's function which is central to Waller's treatment of the lattice vibration problem.^{2,6} We note that $G_{nj,n'j'}(E)$ has poles at the unperturbed energies E_{nk} and also at energies E^r such that $(I + GH^1)^{-1}$ is singular. For an energy E^r which is *inside* one of the bands, there occurs resonant scattering of conduction electrons having this energy, a phenomenon corresponding to the idea of a "virtual bound state" introduced by Friedel⁷ to describe the behavior of transition metal impurities dissolved in normal metals. On the other hand, those energies E^i lying outside any of the bands are associated with electron states localized about the impurity. The properties of these electron impurity levels have been studied extensively by Koster and Slater^{3,4,8} who were, however, mainly concerned with the asymptotic form of the wave functions in the scattering problem. More recently they have been studied by Seeger, Stehle, Mann, and Bross⁹ using only the Green's function for the unperturbed system.

If there is only one band of conduction electrons (allowing us to drop the band indices), and if the perturbation is confined entirely to the impurity atom, i.e., $H^1_{jj'} = V\delta_{j0}\delta_{j'0}$, then the $j = j' = 0$ equation of (15) gives us a simple relation

$$G_{00}(E) = \bar{G}_{00}(E) / (1 + V\bar{G}_{00}(E)). \quad (16)$$

This can also be seen immediately from (14). A reso-

⁶ I. Waller (to be published).

⁷ J. Friedel, Can. J. Phys. **34**, 1190 (1956); J. Phys. Radium **23**, 692 (1962) [English transl.: *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (W. A. Benjamin, Inc., New York, 1963)].

⁸ G. F. Koster, Phys. Rev. **95**, 1436 (1954).

⁹ A. Seeger, J. Phys. Radium **23**, 616 (1962), and in *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (W. A. Benjamin, Inc., New York, 1963).

nance state or a localized state arises if there exists an energy E^0 such that $\text{Re}[1+V\bar{G}_{00}(E^0+i\epsilon)]=0$.

As an illustration of the use of (16) we calculate a first approximation to the charge density from the band of conduction electrons at the nucleus of the impurity. If E^0 is inside the band, then by putting (12) into (16) to obtain $G_{00}(E+i\epsilon)$, one obtains from (11) the weighted density-of-states function,

$$g_{00}(E) = \frac{\bar{g}_{00}(E)}{[1+V\Omega\bar{F}_{00}(E)]^2 + [\pi V\Omega\bar{g}_{00}(E)]^2}, \quad (17)$$

where $\bar{g}_{00}(E)$ is one-half the usual density of states of the band in the pure metal.⁵ If, on the other hand, E^0 is outside the unperturbed band so that $\bar{g}_{00}(E^0)=0$ as well as $1+V\Omega\bar{F}_{00}(E^0)=0$, then one must evaluate the residue in the second term of (11), giving

$$\left[\Omega^2 V^2 \int_{-\infty}^{\infty} \frac{\bar{g}_{00}(E') dE'}{(E'-E^0)^2} \right]^{-1} \delta(E-E^0), \quad (17')$$

which must be added to (17). Then summing over all occupied states of both spins and making use of (7) we obtain for the conduction electron charge density at the impurity nucleus

$$2 \sum_p |\psi_p(\mathbf{R}_0)|^2 \approx 2N^{-1} |a(0)|^2 \sum_p |U_p(0)|^2 = 2 |a(0)|^2 \times \left\{ \int_{-\infty}^{E_F} \frac{\Omega \bar{g}_{00}(E) dE}{[1+V\Omega\bar{F}_{00}(E)]^2 + [\pi V\Omega\bar{g}_{00}(E)]^2} + \left[V^2 \int_{-\infty}^{\infty} \frac{\Omega \bar{g}_{00}(E') dE'}{(E'-E^0)^2} \right]^{-1} \right\}. \quad (18)$$

This expression provides a plausible basis for interpreting isomer shifts such as those recently measured by Mozer and Segnan¹⁰ for iron impurities in a number of nonmagnetic metals. The second term is to be included only if E^0 lies outside the band and below E_F . An interesting illustration of the contributions of both terms may be found in a paper on the x-ray emission spectrum of lithium, a situation involving essentially the charge density around an atom in an excited K state.¹¹

One can also write down an expression for the spin density at the impurity nucleus. If the host lattice is nonmagnetic so that the energy bands for spin \uparrow and spin \downarrow electrons are the same in the absence of a magnetic field, then in a weak field the contributions to the spin density from spin pairs (including possible bound states) cancel to a good approximation and one is left with the contribution from unpaired spins at the Fermi energy. Explicitly, summing over occupied states in the band as in (18), the spin density at the impurity

nucleus is¹²

$$\rho(\mathbf{R}_0) = \sum_{p\uparrow} |\psi_{p\uparrow}(\mathbf{R}_0)|^2 - \sum_{p\downarrow} |\psi_{p\downarrow}(\mathbf{R}_0)|^2 \approx |a(0)|^2 \times \left\{ \int_{-\infty}^{E_F} \Omega g_{00}(E + \frac{1}{2} g\mu_B H) dE - \int_{-\infty}^{E_F} g_{00}(E - \frac{1}{2} g\mu_B H) dE \right\} \approx |a(0)|^2 g\mu_B H \Omega g_{00}(E_F). \quad (19)$$

The corresponding hyperfine field at the nucleus is $\Delta H = (8\pi/3)\mu_B \rho(\mathbf{R}_0)$. Hence, the Knight shift $K_{\text{imp}} = \Delta H/H$ is

$$K_{\text{imp}} = (8\pi/3) g\mu_B^2 |a(0)|^2 \Omega g_{00}(E_F). \quad (20)$$

A similar argument gives for the Knight shift at an atom in the pure host metal

$$K_{\text{host}} = (8\pi/3) g\mu_B^2 |a(0)|^2 \Omega \bar{g}_{00}(E_F). \quad (21)$$

Hence, from (17),

$$K_{\text{host}}/K_{\text{imp}} = [1+V\Omega\bar{F}_{00}(E_F)]^2 + [\pi V\Omega\bar{g}_{00}(E_F)]^2, \quad (22)$$

which is equivalent to an expression obtained by Clogston.^{13,14} Measurements¹⁵ of Al in a 5% Al 95% Cu alloy give a value of 2.0 for this ratio, whereas for a 5% Cd 95% Ag alloy the value is 0.9.¹⁶

It is important to note here that the "strongly localized" approximation made in the second step of (19) prevents (20) and (21) from displaying the following physical effect. If one imagines shifting the Fermi level slightly in either direction, the Knight shift should change according to the number of states of s symmetry only, whereas (20) and (21) change according to the total number of states. A similar failing occurs in Eq. (12) of the future paper on x-ray emission which does not exhibit the expected dependence on the amount of p symmetry. However, the Green's function approach leading to (22) has the merit that it is easy to understand the approximations which have been made, in contrast with earlier considerations.¹⁷

To extend (18) or (22) to treat more than one band or to include contributions from Wannier functions on nearest neighbors, one must use Eq. (15) with $(I+\bar{G}H)^{-1}$ a matrix of order greater than unity. The complexity of the calculation is increased accordingly. Seeger⁹ describes the results of a calculation by Mann for a vacancy in a monovalent metal in which the Wannier functions of nearest neighbors are taken into account. The main difficulty, apart from increased complexity, is that one must know a great deal about

¹² For a similar development, see C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), p. 260.

¹³ A. M. Clogston, *Phys. Rev.* **125**, 439 (1962).

¹⁴ It should be noted that (22) would be drastically changed in the situation considered by Anderson (Ref. 18) in which a resonance state F^0 of one spin only lies just below the Fermi energy.

¹⁵ W. D. Knight, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2, p. 93.

¹⁶ L. E. Drain, *Phil. Mag.* **4**, 484 (1959).

¹⁷ E. Daniel, *Phys. Chem. Solids* **10**, 174 (1959).

¹⁰ B. Mozer and R. Segnan (to be published).

¹¹ B. Mozer and D. A. Goodings (to be published).

the unperturbed host metal and also about the matrix elements of the perturbation. In the "strongly localized" approximation there is only one matrix element V , which can be conveniently treated as a parameter, and the band structure of the host metal enters only through the density of states. For the "moderately localized" case, Mann found it useful to use the tight-binding approximation to describe the band structure. However, this is unnecessarily restrictive. The Green's function method offers the possibility of performing calculations for energy bands of arbitrary form. Unfortunately, because of difficulties connected with the calculation of certain principal value integrals, these have not yet been performed.

Finally it is worth mentioning that the Green's function approach described here can be used in study-

ing the phenomenon of localized magnetic moments associated with iron atoms dissolved in various $4d$ elements and alloys.¹⁸⁻²⁰ For example, Wolff's "self-consistent equations" for the existence of a localized moment [Eqs. (18) and (19) of Ref. 19] follow at once from (18), introducing a simple spin dependence into the matrix element V . As Wolff does not consider the case in which a bound state separates from the band, the second term of (18) does not appear in his equations.

This study was stimulated by a series of lectures on the lattice impurity problem by Professor Waller, to whom we are grateful for many interesting discussions.

¹⁸ A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, *Phys. Rev.* **125**, 541 (1962).

¹⁹ P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

²⁰ P. A. Wolff, *Phys. Rev.* **124**, 1030 (1961).

Ultrasonic Investigation of Open Orbits in Cadmium and Zinc*

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An experimental investigation of the frequency and temperature variation of ultrasonic resonance absorption by open-orbit electrons moving parallel to [0001] in Cd and Zn is presented. The observations indicate conclusively that the Fermi surfaces of Cd and Zn are open parallel to [0001]. The Brillouin zone dimensions along [0001] calculated from the experimental data are $1.20 \pm 0.005 \times 10^{-19}$ g cm/sec for Cd and $1.36 \pm 0.01 \times 10^{-19}$ g cm/sec for Zn. These values agree very well with x-ray data and provide experimental evidence against the possibility of there being an effective charge carrier e^* different from the electronic charge e . The frequency dependence of the resonance is found to agree quite well with theory, and no evidence for magnetic breakdown is seen up to 2000 G. The width of the open-orbit resonance is directly related to the electron mean free path l , thus allowing a determination of l for the open-orbit electrons from sample to sample or as the temperature varies in a particular sample.

I. INTRODUCTION

THE effects of open-orbit electrons on the various transport properties of metals are well recognized.¹ In a preliminary communication, a resonant absorption of ultrasonic waves by conduction electrons moving along open orbits in cadmium was reported.² The present study is concerned with a detailed analysis of the absorption of ultrasonic waves by open-orbit electrons in cadmium and zinc, the phenomena having been investigated experimentally with compressional and shear waves as a function of temperature from 1.0 to 4.2°K at frequencies from 10 to 110 Mc/sec.

The possibility of resonant absorption of ultrasound by open-orbit electrons was first discussed by Galkin, Kaner, and Korolyuk³ who showed that the open-orbit electrons would absorb energy resonantly from the sound field when the period of the open orbit is a multiple of the sound wavelength. Initial observations on a tin single crystal allowed the pertinent Brillouin zone dimension corresponding to the open orbit electrons to be selected.

The Fermi surfaces for cadmium and zinc proposed by Harrison⁴ and corrected by Cohen and Falicov⁵ to include spin-orbit coupling effects are connected in the

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¹ *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960).

² J. D. Gavenda and B. C. Deaton, *Phys. Rev. Letters* **8**, 208 (1962).

³ A. A. Galkin, E. A. Kaner, and A. P. Korolyuk, *Dokl. Akad. Nauk SSSR* **134**, 74 (1960) [English transl.: *Soviet Phys.—Doklady* **5**, 1002 (1961)]; *Zh. Eksperim. i Teor. Fiz.* **39**, 1517 (1960) [English transl.: *Soviet Phys.—JETP* **12**, 1055 (1961)].

⁴ W. A. Harrison, *Phys. Rev.* **118**, 1190 (1960); **126**, 497 (1962).

⁵ M. H. Cohen and L. M. Falicov, *Phys. Rev. Letters* **5**, 544 (1960).