A Treatment of the Metallic Impurity Problem

Using Green's Functions[*]

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ABSTRACT

The weighted density of electronic states (or the charge or spin density) associated with an impurity in a metal is easily derived in terms of a Green's function for the pure metal. The Green's function for either the pure metal or metal with an impurity has a particularly simple form when expressed in the Wannier function representation. The weighted density of electronic states associated with the impurity is simply related to a generalized Green's function for the impurity as shown by Waller for the analogous problem in lattice dynamics. The weighted density of electronic states so derived is useful in interpreting results on the study of impurity effects such as the isomeric shift and quadrupole splitting observed in the Mössbauer on impurities in metals. For a single conduction band and localized impurity interaction potential one easily obtains the results of Clogston for the Knight shift at an impurity. Wolff's "self consistent equations" are also readily obtained using a simple spin dependence in the matrix element of the interaction potential.

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Lifshitz[1] has emphasized the similarity of the effects which an impurity in a crystal lattice has on the distribution of phonon frequencies and on the distribution of electron states. In a recent paper concerned with the lattice vibration problem for an isotopic impurity, Waller[2] 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.

A convenient set of basis functions[3] for electron wave functions are the Wannier functions of the pure host metal. If $\emptyset_{nk}(\underline{r})$ is the Bloch function describing an electron of wave vector $\underline{k}$ in the nth band of the pure metal, the Wannier function $a_n(\underline{r}-\underline{R}_j)$ of the nth band centered on the site $\underline{R}_j$ is defined by,

$$a_n(r-R_j) = N^{-\frac{1}{2}} \sum_k e^{-i\underline{k}\cdot\underline{R}_j} \emptyset_{nk}(\underline{r}). \tag{1}$$

We shall approach our problem by first setting down a general discription 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 tor the electrons has eigen-functions $\Psi_p(\underline{r})$ and one-electron energies E_p, then we can expand $\Psi_p(\underline{r})$ in terms of the Wannier functions of the pure metal;

$$\Psi_p(\underline{r}) = N^{-\frac{1}{2}} \sum_{n,j} U_p(n,j) a_n(\underline{r}-\underline{R}_j). \tag{2}$$

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

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

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

The Green's function which we work with is,

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

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,

$$(H - EI) G(E) = I, \tag{6}$$

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

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

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

$$G_{nj,n'j'}(E) = \Omega \int [g_{nj,n'j'}(E')/(E'-E)] dE' \tag{8}$$

Here Ω is the atomic volume. 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 $\Sigma G^i(E)$. Using the well-known symbolic identity,

$$\frac{1}{E'-E-i\epsilon} = P \left(\frac{1}{E'-E} \right) + i \pi \delta (E'-E), \tag{9}$$

in which P denotes the principal value of the integral, one can write $\pi\Omega g^c(E) = Im G^c(E+i\epsilon)$. 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,

$$g_{nj,n'j'}(E) = (\pi\Omega)^{-1} \text{ Im } G^c_{nj,n'j'}(E+i\epsilon)$$

$$+ \sum_i (-\Omega)^{-1} [\text{Res } G^i_{nj,n'j'}(E)]_{E=E^i} \delta(E-E^i) \tag{10}$$

For the pure metal the eigen-functions of the unperturbed Hamiltonian H^o are the Block functions $\emptyset_{nk}(r)$ and the U's are simply $e^{i\underline{k}\cdot\underline{R}_j}$. 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 (9) to write in the usual way,

$$\bar{G}_{nj,n'j'}(E+i\epsilon) = \Omega \bar{F}_{nj,n'j'}(E) + i\pi\Omega \bar{g}_{nj,n'j'}(E), \tag{11}$$

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

$$F_{nj,n'j'}(E) = P \int_{-\infty}^{\infty} [\bar{g}_{nj,n'j'}(E')/(E'-E)] \, dE' \tag{12}$$

Suppose that an impurity is introduced at $\underline{R}_o$, and henceforth take the unbarred notation in (2) to (10) as referring to the perturbed problem with $H = H^o + H^1$. 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 numbers of non-zero matrix elements $H^1_{nj,n'j'}$. We suppose that these non-zero elements are contained in an SxS matrix, where, for example, in the case of the one band, S is 1 or Z+1 being the number of nearest neighbors. Then, mulitplying (6) on the left by $\bar{G}(E)$ and using the fact that $\bar{G}(E)$ is the inverse of the matrix (H^o-EI), one obtains,

$$G(E) + \bar{G}(E) H^1 G(E) = \bar{G}(E). \tag{3}$$

Defining $(I + \bar{G} H^1)^{-1}$ as the inverse of the SxS matrix $(I + \bar{G}(E) H^1)$ whose elements correspond to the non-zero elements of H^1, one can manipulate (13) to obtain,

$$G(E) = \bar{G}(E) - \bar{G}(E) H^1 (I + \bar{G} H^1)^{-1} \bar{G}(E). \tag{4}$$

In the second term on the right the inner SxS 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.[2,4] We note that $G_{nj,n'j'}(E)$ has poles at the unperturbed energies $E_{n\underline{k}}$ and also at energies E^r such that $(I + G \, H^1)^{-1}$ is singular. For an energy E^r which is inside one of the bands there occurs resonant scattering of conduction electrons having this energy. 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[3,5,6] who were, however, mainly concerned with the form of the wave functions in the scattering problem.

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., $H^1_{jj'} = V\delta_{jo}\delta_{j'o}$, then the j=j'=o equation of (14) gives us a simple relation;

$$G_{oo}(E) = \bar{G}_{oo}(E)/[1 + V \, \bar{G}_{oo}(E)]. \tag{15}$$

This can also be seen immediately from (11). A resonance state or a localized state arises if there exists an energy E^o such that $Re(1 + V \, \bar{G}_{oo}(E^o + i\epsilon)) = 0$.

As an illustration of the use of (15) we calculate a first approximation to the charge density from the band of conduction electrons at the nucleus of the impurity. If E^o is inside the band, then by putting (11) into (15) to obtain $G_{oo}(E+i\epsilon)$, one obtains from (10) the weighted density of states function,

$$g_{oo}(E) = \bar{g}_{oo}(E)/\{[1 + \Omega V \bar{F}_{oo}(E)]^2 + [\pi \Omega V \bar{g}_{oo}(E)]^2\}, \tag{16}$$

where $\bar{g}_{oo}(E)$ is the usual density of states of the band in the pure metal.

If, on the other hand, E^O is outside the unperturbed band so that $g_{oo}(E^O) = 0$, as well as $1 + \Omega V \bar{F}_{oo}(E^O) = 0$, then one must evaluate the residue in the second term of (10), giving,

$$\{\Omega^2 V^2 \int [\; \bar{g}_{oo}(E')/(E'-E^O)^2] \; dE'\}^{-1} \; \delta(E-E^O), \qquad (16')$$

which must be added to (16). Since it is clear how this extra term parti-cipates when it occurs, we shall for convenience drop it, supposing E^O to lie inside the band. Then summing over all occupied states p and making use of (7) and (16) we obtain,

$$\sum_p |\Psi_p(R_o)|^2 \approx N^{-1} |a(0)|^2 \sum_p |U_p(0)|^2$$

$$= \Omega |a(0)|^2 \int_{-\infty}^{E_F} dE \; \bar{g}_{oo}(E)/\{[1 + \Omega V \bar{F}_{oo}(E)]^2 + [\pi \Omega V \bar{g}_{oo}(E)]^2\}$$

$$\qquad (17)$$

This expression provides a plausible basis for interpreting isomer shifts such as those recently measured by Mozer and Segnan[7] for iron impurities in a number of non-magnetic metals.

One can also write down an expression for the spin density at the impurity nucleus. If the host lattice is non-magnetic 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 cancel to a good approximation and one is left with the contribution from unpaired spin at the Fermi energy. Explicitly, summing over occupied states in the band as in (17), the spin density at the impurity nucleus is,[8]

$$\rho(R_o) = \sum_{p\uparrow} |\Psi_{p\uparrow}(R_o)|^2 - \sum_{p\downarrow} |\Psi_{p\downarrow}(R_o)|^2$$

$$\approx \Omega |a(0)|^2 \{\int_{-\infty}^{E_F} \tfrac{1}{2} g_{oo} (E+\mu_B H) dE - \int_{-\infty}^{E_F} \tfrac{1}{2} g_{oo} (E-\mu_B H) \; dE\}$$

$$\approx \Omega |a(0)|^2 \; \mu_B \; H \; g_{oo} (E_F). \qquad (18)$$

Here we have taken the g-factor of the electrons to be 2. The corresponding hyperfine field at the nucleus is $\Delta H = (8\pi/3) \, \mu_B \, \rho(\underline{R}_o)$. Hence, the Knight shift $K_{imp} = \Delta H/H$ is,

$$K_{imp} = (8\pi/3) \, \mu_B^2 \, \Omega |a(0)|^2 \, g_{oo} \, (E_F). \tag{19}$$

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

$$K_{host} = (8\pi/3) \, \mu_B^2 \, \Omega \, |a(0)|^2 \, \bar{g}_{oo}(E_F). \tag{20}$$

Hence, from (16),

$$K_{host}/K_{imp} = [1 + \Omega \, V \, \bar{F}_{oo}(E_F)]^2 + [\pi \, \Omega \, V \, \bar{g}_{oo} \, (E_F)]^2, \tag{21}$$

which is equivalent to an expression obtained by Clogston.[9,10] Measurements[11] 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.[12] The Green's function approach leading to (21) has the merit that it is easy to understand the approximations which have been made, in contrast with earlier considerations.[13]

There is a possibility that semi-quantitative calculations can be performed using (17) or (21). The difficulty is that one needs to know a great deal about the unperturbed host lattice. At the present time it would probably be expedient to assume some form for $\bar{g}_{oo}(E)$ from which $\bar{F}_{oo}(E)$ can be found analytically.[9]

To extend (17) or (21) to treat more than one band or to include contributions from Wannier functions on nearest neighbors, one must use Eq. (14) with $(I + \bar{G} \, H^1)^{-1}$ a matrix of order greater than unity. The complexity of the calculation is increased accordingly.

Finally it is worth mentioning that the Green's function approach described here can be used in studying the phenomenon of localized magnetic moments associated with iron atoms dissolved in various 4d elements and alloys.[9,14-16]

For example, Wolff's "self-consistent equations" for the existence of a

localized moment (Eqs. (18) and (19) of reference 17) follow at once from

(17) introducing a simple spin dependence into the matrix element V.

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.

References

1. I. M. Lifshitz, Suppl. Nuovo cimento $\underline{3}$, 716 (1956).

2. I. Waller, Arkiv für Fysik $\underline{24}$, 495 (1963).

3. G. F. Koster and J. C. Slater, Phys. Rev. $\underline{95}$, 1167 (1954).

4. I. Waller, to be published.

5. G. F. Koster, Phys. Rev. $\underline{95}$, 1436 (1954).

6. G. F. Koster and J. C. Slater, Phys. Rev. $\underline{96}$, 1208 (1954).

7. B. Mozer and R. Segnan, to be published.

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

9. A. M. Clogston, Phys. Rev. $\underline{125}$, 439 (1962).

10. It should be noted that (21) would be drastically changed in the situation considered by Anderson (reference 16) in which a resonant state E^o of one spin only lies just below the Fermi energy.

11. W. D. Knight, Solid State Phys. $\underline{2}$, 93 (1956).

12. L. E. Drain, Phil. Mag. $\underline{4}$, 484 (1959).

13. E. Daniel, J. Phys. Chem. Solids $\underline{10}$, 174 (1959).

14. A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corchzwit and R. C. Sherwood, Phys. Rev. $\underline{125}$, 541 (1962).

15. P. W. Anderson, Phys. Rev. $\underline{124}$, 41 (1961).

16. P. A. Wolff, Phys. Rev. $\underline{124}$, 1030 (1961).