Relation Between Dirac and Canonical Density Matrices, with Applications to Imperfections in Metals*

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It is shown that the canonical density matrix in a single-particle framework may be related directly to the generalized canonical density matrix, containing the Fermi-Dirac function, and to the Dirac density matrix.

A study is then made of density matrices in central field problems. A new differential equation is derived, from the Bloch equation, for the diagonal element of the canonical density matrix. In the case of a continuum of energy levels, this is shown to lead directly to a differential equation for the diagonal element of the Dirac matrix, that is, the particle density. Free-electron density matrices are fully worked out and a perturbation theory based on these free-electron forms is presented.

It is further shown that for a nonspherical potential energy $V(\mathbf{r})$, the work of Green on the quantum-mechanical partition function may be utilized to yield a perturbation theory for the Dirac matrix. In this way, the correct formulation to replace Mott's well-known first-order approximation for dealing with imperfections in metals is obtained. A brief discussion of the way in which this removes qualitatively the difficulties of the Mott treatment is given and the possibility of direct numerical application in a self-consistent framework is pointed out.

1. INTRODUCTION

RECENTLY there has been a considerable revival of interest in the use of the density matrix in quantum-mechanical many-particle problems. If we consider a single-particle approximation to the solution of the many-body problem, then the essential tool is the matrix introduced long ago by Dirac.[1] Only recently have serious attempts been made to calculate this quantity directly.[2,3]

There are, unfortunately, a number of rather severe practical difficulties associated with the direct calculation of the Dirac density matrix. Chief among these is the awkward nature of the idempotency condition, but other points also are somewhat troublesome. Thus, while a differential equation may be obtained for the Dirac density matrix, this determines only very general properties of the solutions and must be used in conjunction with a variational principle.

The question naturally arises therefore whether some alternative formulation may be found, from which the Dirac density matrix may be obtained, but in which the calculations are eased by allowing the subsidiary conditions to be relaxed. The purpose of the present work is to show that the Dirac density matrix is rather directly related to the canonical density matrix, defined by Eq. (2.3), and since this latter quantity satisfies the Bloch equation (2.7) with a well-defined initial condition, it seems that a useful alternative approach for the calculation of the Dirac matrix is now available.

We remark at this stage that the need to develop the methods described here became apparent as a result of some earlier work on electronic wave functions around imperfections in metals[4] and we shall consider therefore examples particularly relevant to this field.

2. RELATION BETWEEN DIRAC AND CANONICAL DENSITY MATRICES

We consider the complete set of solutions of the Schrödinger equation

$$H\psi = E\psi, \tag{2.1}$$

and we denote the wave functions and energy levels by ψ_i and E_i, respectively. We now form the quantity

$$\sum_i \omega_i e^{-E_i/kT}\psi_i^*(\mathbf{r}')\psi_i(\mathbf{r}), \tag{2.2}$$

where the summation extends over all the energy levels. It will be convenient to consider the following choices of ω_i:

(a) $$\omega_i = 1,$$

leading to the usual definition of the canonical density matrix

$$C(\mathbf{r}',\mathbf{r},1/kT) = \sum_i e^{-E_i/kT}\psi_i^*(\mathbf{r}')\psi_i(\mathbf{r}), \tag{2.3}$$

(b) $$\omega_i = \frac{e^{\zeta/kT}}{1+e^{(\zeta-E_i)/kT}},$$

leading to the generalized canonical density matrix

$$D(\mathbf{r}',\mathbf{r},1/kT,\zeta) = \sum_i \frac{e^{(\zeta-E_i)/kT}}{1+e^{(\zeta-E_i)/kT}}\psi_i^*(\mathbf{r}')\psi_i(\mathbf{r}). \tag{2.4}$$

The definition (2.4) contains the Dirac zero-temperature density matrix $\rho(\mathbf{r}',\mathbf{r},\zeta)$ as a special case, namely

$$\rho(\mathbf{r}',\mathbf{r},\zeta) = \lim_{T\to 0} D(\mathbf{r}',\mathbf{r},1/kT,\zeta), \tag{2.5}$$

where ζ must be determined from the number of occu-

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[1] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).
[2] R. McWeeny, Proc. Roy. Soc. (London) **A235**, 496 (1956).
[3] N. H. March and W. H. Young, Proc. Phys. Soc. (London) **72**, 182 (1958).
[4] N. H. March and A. M. Murray, Proc. Roy. Soc. (London) **A256**, 400 (1960).

pied states N through the relation

$$\int \rho(\mathbf{r},\mathbf{r})d\tau = N. \tag{2.6}$$

Now it is well known that the canonical density matrix satisfies the Bloch equation

$$-\partial C/\partial\beta = HC; \quad \beta = 1/kT, \tag{2.7}$$

with the initial condition

$$C(\mathbf{r}',\mathbf{r},0) = \delta(\mathbf{r}'-\mathbf{r}), \tag{2.8}$$

and in Eqs. (2.7) and (2.8) is summarized the practical merit of the canonical matrix: it may be obtained without detailed knowledge of the individual wave functions and energy levels.

We shall now show directly that knowledge of C enables the Dirac matrix ρ and the generalized canonical matrix D to be found. We introduce the function $Q(\mathbf{r}',\mathbf{r},E)$ defined by

$$Q(\mathbf{r}',\mathbf{r},E) = \textstyle\sum_i \psi_i^*(\mathbf{r}')\psi_i(\mathbf{r})\delta(E-E_i). \tag{2.9}$$

Hence

$$\rho(\mathbf{r}',\mathbf{r},\zeta) = \int_0^{\zeta} Q(\mathbf{r}',\mathbf{r},E)dE, \tag{2.10}$$

the Fermi level ζ being defined such that it lies just above the highest occupied level. From (2.3) and (2.9) we have

$$\begin{aligned} C(\mathbf{r}',\mathbf{r},\beta) &= \int_0^\infty Q(\mathbf{r}',\mathbf{r},E)e^{-\beta E}dE \\ &= \beta\int_0^\infty \left\{\int_0^E Q(\mathbf{r}',\mathbf{r},E)dE\right\}e^{-\beta E}dE \\ &= \beta\int_0^\infty \rho(\mathbf{r}',\mathbf{r},E)e^{-\beta E}dE, \end{aligned} \tag{2.11}$$

using (2.10). From (2.4) and (2.9) we have

$$\begin{aligned} D(\mathbf{r}',\mathbf{r},\beta,\zeta) &= \int_0^\infty Q(\mathbf{r}',\mathbf{r},E)\frac{1}{1+e^{\beta(E-\zeta)}}dE \\ &= \int_0^\infty \rho(\mathbf{r}',\mathbf{r},E)\frac{\partial}{\partial E}\left\{\frac{-1}{1+e^{\beta(E-\zeta)}}\right\}dE. \end{aligned} \tag{2.12}$$

Equations (2.11) and (2.12) reveal immediately that knowledge of the canonical matrix C is sufficient to determine both ρ and D. We shall not consider the generalized canonical matrix D further in the present paper, as our main interest is in the Dirac matrix, but shall content ourselves with the remark that (2.12) will allow direct calculation of physical properties of Fermi-Dirac assemblies from a knowledge of the canonical density matrix.

Focusing attention therefore on ρ, in what follows, it is evident from (2.11) that $C(\mathbf{r}',\mathbf{r},\beta)/\beta$ is simply the Laplace transform of $\rho(\mathbf{r}',\mathbf{r},E)$. The inverse relation can be written in the form

$$\rho(\mathbf{r}',\mathbf{r},E) = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{1}{\beta}e^{\beta E}C(\mathbf{r}',\mathbf{r},\beta)d\beta, \tag{2.13}$$

where σ is chosen such that the integrand has no poles in that part of the complex plane for which $\mathrm{R}(\beta) \geqslant \sigma$.

3. EXAMPLE: A UNIFORM ELECTRON GAS

As a first example of the use of the relation (2.11), and because the results will later be made the basis of the perturbation treatment of Sec. 7, let us consider a uniform electron gas, neglecting interactions. As Sondheimer and Wilson[5] have shown, the Bloch equation (2.7) is readily solved, subject to the initial condition (2.8) and the result, in atomic units, is

$$C(\mathbf{r}',\mathbf{r},\beta) = \exp(-R^2/2\beta)/(2\pi\beta)^{\frac{3}{2}}, \tag{3.1}$$

where

$$R^2 = (x-x')^2+(y-y')^2+(z-z')^2.$$

In obtaining ρ, we start from the result[6]

$$\frac{a}{2\pi^{\frac{1}{2}}s^{\frac{3}{2}}}\exp\left(-\frac{a^2}{4s}\right) = \int_0^\infty \frac{e^{-st}}{\pi}\sin a(t)^{\frac{1}{2}}dt, \tag{3.2}$$

and by differentiating (3.2) with respect to a we find almost immediately

$$\frac{a^3}{4\pi^{\frac{1}{2}}s^{\frac{5}{2}}}\exp\left(-\frac{a^2}{4s}\right) = \int_0^\infty \frac{e^{-st}}{\pi}[\sin a(t)^{\frac{1}{2}} - a(t)^{\frac{1}{2}}\cos a\,(t)^{\frac{1}{2}}]dt. \tag{3.3}$$

Using (3.3) we obtain directly from (3.1) the result

$$\frac{C(\mathbf{r}',\mathbf{r},\beta)}{\beta} = \frac{1}{2\pi^2R^3}\int_0^\infty e^{-\beta E}[\sin a(E)^{\frac{1}{2}} - a(E)^{\frac{1}{2}}\cos a(E)^{\frac{1}{2}}]dE, \tag{3.4}$$

where $a = 2^{\frac{1}{2}}R$.

From (3.4) and (2.11), a simple closed form for the Dirac matrix results, namely

$$\rho(\mathbf{r}',\mathbf{r},\zeta) = \frac{1}{2\pi^2R^3}[\sin a(\zeta)^{\frac{1}{2}} - a(\zeta)^{\frac{1}{2}}\cos a(\zeta)^{\frac{1}{2}}]. \tag{3.5}$$

From (2.6), ζ is to be determined from the equation

$$\rho(\mathbf{r},\mathbf{r},\zeta) = N/V = (2\zeta)^{\frac{3}{2}}/6\pi^2, \tag{3.6}$$

[5] E. H. Sondheimer and A. H. Wilson, Proc. Roy. Soc. (London) **A210**, 173 (1951).

[6] See, for example, G. Doetsch, *Theorie und Anwendung der Laplace Transform* (Dover Publications, New York, 1943), p. 24.

where V is the volume, and this is the familiar relation between the electron density and the Fermi energy.

The result (3.5) has, of course, been obtained previously by direct use of plane waves, but the present argument shows how it may be found without recourse to the wave functions, and by a method which nevertheless circumvents consideration of the awkward idempotency condition.

4. DENSITY MATRICES IN CENTRAL FIELD PROBLEMS

We turn now to a case of particular importance in the imperfections field, namely that corresponding to a spherically symmetric potential energy $V(r)$. Here it is often convenient to exploit the fact that the wave equation separates in spherical polar coordinates r, θ, ϕ, as was done, for example, in our previous computations of electronic wave functions around a vacancy in a finite metal.[4] Then the solutions of Schrödinger's equation may be written in the form

$$\chi_{il}(r)Y_{lm}(\theta,\phi),$$

where

$$Y_{lm}(\theta,\phi)=\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{\frac{1}{2}}P_l^m(\cos\theta)e^{im\phi},$$

and χ_{il} satisfies the radial Schrödinger equation

$$\frac{1}{2}\frac{d^2}{dr^2}(r\chi_{il})=\left\{\frac{l(l+1)}{2r^2}+V-E_{il}\right\}r\chi_{il}. \quad (4.1)$$

The eigenvalue E_{il} and the function χ_{il} are, of course, both independent of m. Hence from (2.3) we have

$$\begin{aligned}C(\mathbf{r}',\mathbf{r},\beta)&=\sum_l\{\sum_i e^{-\beta E_{il}}\chi_{il}(r')\chi_{il}(r)\}\\&\quad\times\{\sum_m Y_{lm}^*(\theta',\phi')Y_{lm}(\theta,\phi)\}\\&=\sum_l\{\sum_i e^{-\beta E_{il}}\chi_{il}(r')\chi_{il}(r)\}\\&\quad\times\frac{(2l+1)}{4\pi}P_l(\cos\gamma), \quad (4.2)\end{aligned}$$

where γ is the angle between $\mathbf{r}'$ and $\mathbf{r}$ and the addition theorem for spherical harmonics has been used.

We now define C_l through the equation

$$4\pi C_l(r',r,\beta)=\sum_i e^{-\beta E_{il}}\chi_{il}(r')\chi_{il}(r), \quad (4.3)$$

and thus (4.2) can be rewritten

$$C(\mathbf{r}',\mathbf{r},\beta)=\sum_l(2l+1)C_l(r',r,\beta)P_l(\cos\gamma). \quad (4.4)$$

The initial condition on $C_l(r',r,\beta)$ may be obtained by viewing (4.1) as a one-dimensional wave equation, with wave function $r\chi_{il}(r)$. From (4.3) it then follows that $4\pi rr'C_l(r',r,\beta)$ is the corresponding one-dimensional canonical density matrix and hence

$$4\pi rr'C_l(r',r,0)=\delta(r'-r). \quad (4.5)$$

This is easily shown to be consistent with the condition (2.8) on $C(\mathbf{r}',\mathbf{r},\beta)$. From (4.1) and (4.3), the equation satisfied by $C_l(r',r,\beta)$ is

$$\frac{1}{2}\frac{\partial^2}{\partial r^2}(rC_l)-\left\{\frac{l(l+1)}{2r^2}+V\right\}rC_l-\frac{\partial}{\partial\beta}(rC_l)=0. \quad (4.6)$$

Often it would be very convenient in applications if the important diagonal element $C_l(r,r,\beta)$ could be calculated directly, without the necessity of obtaining the complete matrix $C_l(r',r,\beta)$. In fact, as is shown in Appendix I, the diagonal element, which we write for convenience as $Z_l(r,\beta)$, satisfies the differential equation

$$\begin{aligned}\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2Z_l)-\frac{l(l+1)}{2r}\frac{\partial}{\partial r}(rZ_l)-\frac{1}{2}\frac{\partial V}{\partial r}r^2Z_l\\-V\frac{\partial}{\partial r}(r^2Z_l)-\frac{\partial^2}{\partial\beta\partial r}(r^2Z_l)=0. \quad (4.7)\end{aligned}$$

Turning our attention now to the corresponding Dirac matrices, we define ρ_l through the equation

$$4\pi\rho_l(r',r,E)=\sum_i\chi_{il}(r')\chi_{il}(r), \quad (4.8)$$

and then we have

$$\rho(\mathbf{r}',\mathbf{r},E)=\sum_l(2l+1)\rho_l(r',r,E)P_l(\cos\gamma), \quad (4.9)$$

which is seen to be entirely analogous to (4.4). From (2.11), (4.4) and (4.9), and using the orthogonality of the Legendre polynomials, we have

$$C_l(r',r,\beta)=\beta\int_0^\infty\rho_l(r',r,E)e^{-\beta E}dE. \quad (4.10)$$

Denoting the diagonal element of the matrix $\rho_l(r',r,E)$ as $n_l(r,E)$, it follows that

$$Z_l(r,\beta)=\beta\int_0^\infty n_l(r,E)e^{-\beta E}dE. \quad (4.11)$$

When the eigenvalues E_{il} form a continuous set, it is shown in Appendix I that the differential equation (4.7) for Z_l leads to the equation

$$\begin{aligned}\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2n_l)-\frac{l(l+1)}{2r}\frac{\partial}{\partial r}(rn_l)-\frac{1}{2}\frac{\partial V}{\partial r}r^2n_l\\-V\frac{\partial}{\partial r}(r^2n_l)+\int_0^E E\frac{\partial^2}{\partial E\partial r}(r^2n_l)dE=0, \quad (4.12)\end{aligned}$$

for the "particle density" $n_l(r,E)$.

5. CENTRAL FIELD RESULTS FOR $V(r)=0$

As an application of the above relations, as well as the fact that the results will form the basis of the perturbation theory outlined in Sec. 6, we consider now the case when $V(r)=0$. Then Eq. (4.6) satisfied by $C_l(r',r,\beta)$ reduces to

$$\frac{1}{2}\frac{\partial^2}{\partial r^2}(rC_l)-\frac{l(l+1)}{2r^2}(rC_l)-\frac{\partial}{\partial\beta}(rC_l)=0. \quad (5.1)$$

The solutions of (5.1) satisfying the boundary condition (4.5) are, for the first two l values,

$$C_0(r',r,\beta)=\frac{1}{2^{\frac{5}{2}}\pi^{\frac{3}{2}}\beta^{\frac{1}{2}}r'r}\left\{\exp\left[-\frac{(r'-r)^2}{2\beta}\right]-\exp\left[-\frac{(r'+r)^2}{2\beta}\right]\right\}, \quad (5.2a)$$

$$C_1(r',r,\beta)=\frac{1}{2^{\frac{5}{2}}\pi^{\frac{3}{2}}\beta^{\frac{1}{2}}r'r}\left\{\left(1-\frac{\beta}{r'r}\right)\exp\left[-\frac{(r'-r)^2}{2\beta}\right]+\left(1+\frac{\beta}{r'r}\right)\exp\left[-\frac{(r'+r)^2}{2\beta}\right]\right\}. \quad (5.2b)$$

Using the modified Bessel function

$$I_n(x)\equiv(-i)^nJ_n(ix)$$

the solution of (5.1) satisfying (4.5) may be obtained for all l in the form

$$C_l(r',r,\beta)=\frac{1}{4\pi\beta(r'r)^{\frac{1}{2}}}\exp\left(-\frac{r'^2+r^2}{2\beta}\right)I_{l+\frac{1}{2}}\left(\frac{r'r}{\beta}\right). \quad (5.3)$$

Setting $r'=r$, the corresponding solution of (4.7) with $V=0$ is

$$Z_l(r,\beta)=\frac{1}{4\pi\beta r}\exp\left(-\frac{r^2}{\beta}\right)I_{l+\frac{1}{2}}\left(\frac{r^2}{\beta}\right). \quad (5.4)$$

From the Laplace transform relation (4.10) we can obtain $\rho_l(r',r,E)$ from (5.2) and (5.3). Thus

$$\rho_0(r',r,E)=\frac{1}{4\pi^2r'r}\left\{\frac{\sin(r'-r)(2E)^{\frac{1}{2}}}{r'-r}-\frac{\sin(r'+r)(2E)^{\frac{1}{2}}}{r'+r}\right\}, \quad (5.5a)$$

$$\rho_1(r',r,E)=\frac{1}{4\pi^2r'r}\left\{\left(\frac{\sin(r'-r)(2E)^{\frac{1}{2}}}{r'-r}-\frac{\cos(r'-r)(2E)^{\frac{1}{2}}}{r'r(2E)^{\frac{1}{2}}}\right)+\left(\frac{\sin(r'+r)(2E)^{\frac{1}{2}}}{r'+r}+\frac{\cos(r'+r)(2E)^{\frac{1}{2}}}{r'r(2E)^{\frac{1}{2}}}\right)\right\}. \quad (5.5b)$$

Equations (5.5) are particular cases of the general formula

$$\rho_l(r',r,E)=\frac{1}{2\pi^2}\int_0^k k^2j_l(kr')j_l(kr)dk, \quad (5.6)$$

where $k=(2E)^{\frac{1}{2}}$. Setting $r'=r$ we obtain from (5.5)

$$n_0(r,E)=\frac{1}{4\pi^2r^2}\left\{k-\frac{\sin 2kr}{2r}\right\}, \quad (5.7a)$$

$$n_1(r,E)=\frac{1}{4\pi^2r^2}\left\{k+\frac{\sin 2kr}{2r}+\frac{\cos 2kr-1}{kr^2}\right\}, \quad (5.7b)$$

the general formula

$$n_l(r,E)=\frac{k^3}{4\pi^2}\{j_l^2(kr)-j_{l-1}(kr)j_{l+1}(kr)\} \quad (5.8)$$

being obtained from (5.6).

6. PERTURBATION TREATMENT FOR CENTRAL FIELDS

It appears possible for a spherical potential V to obtain a perturbation series solution of (4.12) which reduces to (5.7) or (5.8) when V vanishes. Writing

$$f=\frac{\partial}{\partial k}(r^2n_l), \quad \text{or} \quad r^2n_l=\int_0^k fdk, \quad (6.1)$$

Eq. (4.12) may be expressed as

$$\frac{\partial^3 f}{\partial r^3}+4k^2\frac{\partial f}{\partial r}-\frac{4l(l+1)}{r^2}\frac{\partial f}{\partial r}+\frac{4l(l+1)}{r^3}f-8V\frac{\partial f}{\partial r}-4\frac{\partial V}{\partial r}f=0. \quad (6.2)$$

The three independent solutions of (6.2) when $V=0$ may be written

$$f_1=k^2r^2j_l^2(kr), \quad (6.3a)$$

$$f_2=k^2r^2j_l(kr)\bar{n}_l(kr), \quad (6.3b)$$

$$f_3=k^2r^2\bar{n}_l^2(kr), \quad (6.3c)$$

where, to avoid confusion with the particle density n_l, we have written $\bar{n}_l$ for the spherical Neumann function. The free-electron solution given in Sec. 5 is obtained from (6.1) by writing

$$f=f_1/2\pi^2. \quad (6.4)$$

To second order in V, it may be verified that the solution of (6.2) is then

$$f=\frac{f_1(r)}{2\pi^2}+\frac{2}{\pi^2k}\times\left\{f_1(r)\int_r^\infty V(s)f_2(s)ds+f_2(r)\int_0^r V(s)f_1(s)ds\right\}+\frac{8}{\pi^2k^2}\left\{f_2(r)\int_0^r V(s)f_1(s)\int_s^\infty V(t)f_2(t)dtds+f_1(r)\int_r^\infty V(s)f_2(s)\int_s^\infty V(t)f_2(t)dtds-\tfrac{1}{2}f_1(r)\int_0^r V(s)f_3(s)\int_0^s V(t)f_1(t)dtds+\tfrac{1}{2}f_3(r)\times\int_0^r V(s)f_1(s)\int_0^s V(t)f_1(t)dtds\right\}. \quad (6.5)$$

Thus combining (6.5) and (6.1), the perturbed density may be obtained to the same order of approximation.

7. PERTURBATION TREATMENT FOR NONSPHERICAL $V(r)$

After developing the methods described in the preceding sections, we became aware of a paper by Green[7] in which a very general perturbation treatment yielding the canonical density matrix was developed, in order to calculate the quantum mechanical partition function. We shall restrict ourselves to a first-order calculation here, although, in principle, higher terms may be obtained using Green's work. Equation (15) of Green's paper may be expressed almost immediately in our present notation as

$$C(\mathbf{r},\mathbf{r},\beta)=\frac{1}{(2\pi\beta)^{\frac{3}{2}}}\left[1-\int\frac{V(\mathbf{r}_1)\exp(-2R_1^2)/\beta}{\pi R_1}d\mathbf{r}_1\right], \quad (7.1)$$

where

$$R_1=\{(x-x_1)^2+(y-y_1)^2+(z-z_1)^2\}^{\frac{1}{2}}.$$

All that remains is to transform this to give the diagonal element of the Dirac matrix to the same order, using (2.11), the zeroth-order result being the free-electron density given in (3.6). The perturbed density is then found to be given by

$$n(\mathbf{r},\zeta)=\frac{k^3}{6\pi^2}-\frac{k^2}{4\pi^3}\int\frac{V(\mathbf{r}_1)j_1(2kR_1)}{R_1^2}d\mathbf{r}_1, \quad (7.2)$$

where $k=(2\zeta)^{\frac{1}{2}}$. This formula is new, and appears likely to be very useful in the imperfections field, as we shall now discuss.

8. APPLICATIONS TO IMPERFECTIONS IN METALS

Mott[8] developed a first-order approximation to deal with imperfections in metals, the result being expressed in the form

$$n(\mathbf{r},\zeta)=(2\zeta)^{\frac{3}{2}}/3\pi^2-q^2V(\mathbf{r})/4\pi, \quad (8.1)$$

where now we consider doubly filled levels. Here the screening radius $1/q$ is given in terms of the Fermi energy ζ by

$$q^2=2^{\frac{5}{2}}\zeta^{\frac{1}{2}}/\pi. \quad (8.2)$$

Various shortcomings of (8.1) are now well established. Thus, the density follows the potential too closely and at a point singularity, the density becomes infinite with the potential, an incorrect result. This is unfortunate, because in physically interesting problems involving positron annihilation in metals, the positron lifetime depends on the electron density at the positron and the Mott treatment is inadequate. Also, it is known from the work of Blandin *et al.*[9] and from previous computations by the present writers[4] that besides the localized screening predicted by (8.1) there are also long-range effects which Mott's treatment cannot account for.

We see now that the work presented in Sec. 7 allows the exact formulation of the first-order treatment, in which (8.1) must be replaced by

$$n(\mathbf{r},\zeta)=\frac{(2\zeta)^{\frac{3}{2}}}{3\pi^2}-\frac{k^2}{2\pi^3}\int\frac{V(\mathbf{r}_1)j_1(2kR_1)}{R_1^2}d\mathbf{r}_1. \quad (8.3)$$

The connection with Mott's treatment is seen directly when we make the assumption that the potential is slowly varying and replace $V(\mathbf{r}_1)$ by $V(\mathbf{r})$ in (8.3). Equation (8.1) then follows after a straightforward integration. Clearly, for a potential which is singular as r^{-1} the density given by (8.3) remains finite at the origin so that the qualitative defect of the Mott form is removed in this case. Also it seems that by combining (8.3) with Poisson's equation to yield

$$\nabla^2V(\mathbf{r})=\frac{2k^2}{\pi^2}\int\frac{V(\mathbf{r}_1)j_1(2kR_1)}{R_1^2}d\mathbf{r}_1, \quad (8.4)$$

we have a self-consistent field problem which should give some account of long-range effects in both the density and potential. Calculations are now being planned to enable the solutions of (8.4) to be obtained and we hope to report on this problem at a later stage.

We shall conclude by indicating the connection between the perturbation theory of Sec. 7 and that given for central field problems in Sec. 6. We have not seen at present a way to connect the two treatments completely generally in the case of a spherical potential,[9a] but we show here that they yield the same expression for the density at the origin to first order for central fields. This comparison is easily achieved, because only the partial density corresponding to $l=0$ contributes to the density at the origin when the separation in spherical harmonics is carried out. It follows from (6.5) and (6.1) that the density difference is given by

$$\frac{1}{\pi^2}\int_0^k dk\int_0^\infty V(s)\sin 2ks\,ds, \quad (8.5)$$

and the integration over k may be performed. The final result is

$$\frac{k^2}{\pi^2}\int_0^\infty j_1(2ks)V(s)ds, \quad (8.6)$$

and this is easily seen to be equivalent to that given by Eq. (7.2).

9. CONCLUSION

By exploiting the relation between the canonical and Dirac density matrices embodied in Eq. (2.11), we have

[7] H. S. Green, J. Chem. Phys. **20**, 1274 (1952).
[8] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).
[9] A. Blandin, E. Daniel, and J. Friedel, Phil. Mag. **4**, 180 (1959).

[9a] *Footnote added in proof*. This connection has now been found, and the proof is given in Appendix II.

shown how some progress may be made in the calculation of the Dirac matrix in certain cases. Suitable perturbation treatments based on free electrons may be developed, and the most important practical consequence would seem to be the exact first-order formulation which supersedes Mott's well-known treatment of imperfections in metals.

We also stress that the generalized canonical matrix D may be obtained from C, should it be required to calculate Fermi-Dirac physical properties at elevated temperatures. Furthermore we suggest that the new equations (4.7) and (4.12) for the diagonal elements of C and ρ, respectively, may have computational merit when perturbation theory fails. Generalizations of these equations when the potential is not spherical may also be obtained, but the results are complicated and will not therefore be recorded here.

APPENDIX I

In this appendix we derive (4.7), the equation satisfied by $Z_l(r,\beta)\equiv C_l(r,r,\beta)$, from (4.6) which is satisfied by $C_l(r',r,\beta)$. Multiplying (4.6) through by r' we obtain

$$\frac{1}{2}\frac{\partial^2}{\partial r^2}\{r'rC_l(r',r,\beta)\} - \left\{\frac{l(l+1)}{2r^2}+V(r)\right\}r'rC_l(r',r,\beta) - \frac{\partial}{\partial\beta}\{r'rC_l(r',r,\beta)\}=0. \quad \text{(A1.1)}$$

We now introduce new variables ξ, η defined by the relations

$$\xi=(r'+r')/2, \quad \eta=(r'-r)/2,$$

and hence $r=\xi+\eta$, $r'=\xi-\eta$. Since $r'rC_l(r',r,\beta)$ is symmetrical with respect to interchange of r and r' we may expand it in the form

$$r'rC_l(r',r,\beta)=\textstyle\sum_n \eta^{2n}c_n(\xi), \quad \text{(A1.2)}$$

where

$$r^{-2}c_0(r)=C_l(r,r,\beta)=Z_l(r,\beta).$$

We also expand $l(l+1)/2r^2+V(r)$ in the form

$$l(l+1)/2r^2+V(r)=\textstyle\sum_m \eta^m v_m(\xi), \quad \text{(A1.3)}$$

where

$$v_0(r)=l(l+1)/r^2+V(r),$$

and

$$v_1(r)=dv_0(r)/dr.$$

Writing (A1.1) in terms of ξ and η we obtain

$$\left\{\frac{1}{8}\frac{\partial^2}{\partial\eta^2}+\frac{1}{4}\frac{\partial^2}{\partial\eta\partial\xi}+\frac{1}{8}\frac{\partial^2}{\partial\xi^2}-\frac{\partial}{\partial\beta}\right\}\sum_n \eta^{2n}c_n(\xi) - \sum_m\sum_n \eta^{m+2n}c_n(\xi)v_m(\xi)=0.$$

Therefore it follows that

$$\sum_n\left\{\frac{n(2n-1)}{4}\eta^{2n-2}c_n+\frac{n}{2}\eta^{2n-1}c_n'+\tfrac{1}{8}\eta^{2n}c_n''-\eta^{2n}\frac{\partial c_n}{\partial\beta}\right\} - \sum_m\sum_n \eta^{m+2n}c_nv_m=0,$$

where primes on c_n denote derivatives with respect to ξ. We now equate to zero the coefficient of each power of η. The coefficient of η^0 gives then

$$\tfrac{1}{4}c_1+\tfrac{1}{8}c_0''-\frac{\partial c_0}{\partial\beta}-c_0v_0=0, \quad \text{(A1.4)}$$

and the coefficient of η,

$$\tfrac{1}{2}c_1'-c_0v_1=0. \quad \text{(A1.5)}$$

Hence, using the fact that v_1 is the derivative of v_0 and eliminating c_1 between (A1.4) and (A1.5) we obtain

$$\tfrac{1}{8}c_0'''-\tfrac{1}{2}v_0'c_0-v_0c_0'-\partial c_0'/\partial\beta=0. \quad \text{(A1.6)}$$

Replacing ξ by r, introducing the explicit form for v_0, and substituting $c_0(r)=r^2Z_l(r,\beta)$, (A1.6) is readily shown to be equivalent to (4.7).

Finally we show that (4.12) may be obtained directly from (4.7). Substituting (4.11) into (4.7), we obtain

$$\beta\int_0^\infty\left\{\frac{1}{8}\frac{\partial^3}{\partial r^3}(r^2n_l)-\frac{l(l+1)}{2r}\frac{\partial}{\partial r}(rn_l) - \frac{1}{2}\frac{\partial V}{\partial r}r^2n_l-V\frac{\partial}{\partial r}(r^2n_l)\right\}e^{-\beta E}dE - \frac{\partial}{\partial\beta}\left[\beta\int_0^\infty e^{-\beta E}\frac{\partial}{\partial r}(r^2n_l)dE\right]=0. \quad \text{(A1.7)}$$

Partial integration of the last term in the above yields

$$\beta\int_0^\infty\left\{\int_0^E E\frac{\partial^2}{\partial E\partial r}(r^2n_l)\right\}e^{-\beta E}dE,$$

and since (A1.7) must hold for all β, (4.12) follows.

APPENDIX II

We demonstrate in this Appendix the equivalence, to first order in V, of the methods of paragraphs 6 and 7, for the central field problem. The first-order terms of Eq. (6.5) may be written

$$\frac{1}{k}\frac{\partial}{\partial k}\{r^2(n_0-n)\} = -\frac{2k^2}{\pi^2}\sum_l(2l+1)\left[\int_0^r dsV(s)r^2s^2j_l(kr)\bar{n}_l(kr)j_l^2(ks) + \int_r^\infty dsV(s)r^2s^2j_l^2(kr)j_l(ks)\bar{n}_l(ks)\right] \quad \text{(A2.1)}$$

and we first focus attention on the quantity S defined by

$$S=-4k^2rs\sum_l(2l+1)j_l(kr)\bar{n}_l(kr)j_l^2(ks). \quad (A2.2)$$

To proceed, we wish to differentiate S with respect to k, using the results of Schiff.[10] Strictly, terms corresponding to $l=0$ should be considered separately, but for convenience they may be included if we identify $j_{-1}(\rho)$ and $\bar{n}_{-1}(\rho)$ with $-\bar{n}_0(\rho)$ and $j_0(\rho)$, respectively. It then follows after some manipulation that

$$\frac{\partial S}{\partial k}=-4\sum_l(2l+1)k^2rs[r\{j_{l-1}(kr)\bar{n}_l(kr)-j_l(kr)\bar{n}_{l+1}(kr)\}\times j_l^2(ks)+sj_l(kr)\bar{n}_l(kr)\times\{j_{l-1}(ks)j_l(ks)-j_l(ks)j_{l+1}(ks)\}].$$

Using Schiff's Eq. (15.10) we obtain

$$\frac{\partial S}{\partial k}=-4k^3r^2s^2\sum_l[j_{l-1}(kr)\bar{n}_l(kr)j_l(ks)j_{l-1}(ks)+j_l(kr)\bar{n}_{l-1}(kr)j_{l-1}(ks)j_l(ks)-j_l(kr)\bar{n}_{l+1}(kr)j_{l+1}(ks)j_l(ks)-j_{l+1}(kr)\bar{n}_l(kr)j_l(ks)j_{l+1}(ks)]$$
$$=-4k^3r^2s^2[j_{-1}(kr)\bar{n}_0(kr)j_0(ks)j_{-1}(ks)+j_0(kr)\bar{n}_{-1}(kr)j_{-1}(ks)j_0(ks)],$$

since all other terms in the summation cancel. Interpreting $j_{-1}(\rho)$ and $\bar{n}_{-1}(\rho)$ in the manner discussed above we find

$$\frac{\partial S}{\partial k}=\frac{4}{k}(\cos^2kr-\sin^2kr)\sin ks\cos ks=\frac{1}{k}\{\sin 2k(r+s)-\sin 2k(r-s)\}. \quad (A2.3)$$

[10] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), p. 78, Eq. (15.10).

Since $S(0)=0$, we have on integration, for $s\leqslant r$,

$$S(k)=\int_{2k(r-s)}^{2k(r+s)}du\frac{\sin u}{u}. \quad (A2.4)$$

Thus, in (A2.1) we may write

$$\frac{1}{k}\frac{\partial}{\partial k}\{r^2(n_0-n)\}=\frac{1}{2\pi^2}\left\{\int_0^r dsV(s)rs\int_{2k(r-s)}^{2k(r+s)}du\frac{\sin u}{u}+\int_r^\infty dsV(s)rs\int_{2k(s-r)}^{2k(s+r)}du\frac{\sin u}{u}\right\}$$
$$=\frac{1}{2\pi^2}\int_0^\infty dsV(s)rs\int_{2k|r-s|}^{2k(r+s)}du\frac{\sin u}{u}. \quad (A2.5)$$

As may be verified by differentiation, the integral of (A2.5) is

$$r^2(n_0-n)=\frac{k^2}{2\pi^2}\int_0^\infty dsV(s)rs\times\int_{2k|r-s|}^{2k(r+s)}du\left(\frac{\sin u}{u^3}-\frac{\cos u}{u^2}\right). \quad (A2.6)$$

Now when V has spherical symmetry, Eq. (7.2) may be written

$$n_0-n=\frac{k^2}{2\pi^2}\int_0^\pi d\theta\int_0^\infty dsV(s)\frac{s^2\sin\theta}{R_1^2}\times\left\{\frac{\sin 2kR_1}{(2kR_1)^2}-\frac{\cos 2kR_1}{2kR_1}\right\},$$

where $R_1^2=r^2+s^2-2rs\cos\theta$. Substituting $u=2kR_1$, it follows that

$$n_0-n=\frac{k^2}{2\pi^2}\int_0^\infty dsV(s)\frac{s}{r}\int_{2k|r-s|}^{2k(r+s)}du\left(\frac{\sin u}{u^3}-\frac{\cos u}{u^2}\right),$$

which is evidently equivalent to (A2.6).