

The Thomas-Fermi Method for Metals

J. C. SLATER AND H. M. KRUTTER, *Massachusetts Institute of Technology*

(Received February 9, 1935)

The Thomas-Fermi method is applied to metals, by replacing each atom by a sphere, assuming the potential to be spherically symmetrical within it, and solving the Thomas-Fermi equation subject to the boundary condition that the electronic charge within the sphere shall balance the nuclear charge, rendering it electrically neutral. Calculations are presented giving potential field, charge density, and kinetic, potential, and total energy of the metal, as function of lattice spacing. The virial theorem is verified for the energy. The total energy shows no minimum, the pres-

sure being always positive. Calculations are also made using the Dirac method of correcting for exchange, for three atoms, Li, Na and Cu. The exchange lowers the energy, but still not quite enough to produce a minimum of energy and an equilibrium at zero pressure. The result should be useful as a first approximation in self-consistent field approximations for the structure of metals, and could be adapted to give approximate treatment for matter under very high pressure, as in stars.

THE application of the Thomas-Fermi equation to metals has been mentioned in an earlier paper,¹ in which some of the results to be described in the present paper were sketched. The method rests on the same fact which makes possible the Wigner-Seitz calculation:² the potential acting on an electron in the neighborhood of one of the nuclei of the metal is very nearly spherically symmetrical, the nucleus being the center, so that the same method of solving differential equations, as for example the Thomas-Fermi method or the Schrödinger equation, which is applicable in an isolated atom, can be used in the metal, simply by using different boundary conditions. More precisely, we surround each nucleus in the metal by a cell, its boundaries being the planes bisecting perpendicularly the lines joining the nucleus to its nearest or next nearest neighbors. Each such cell contains just enough electrons to neutralize the nuclear charge, so that, being of a high order of symmetry, its electric field at external points is very small, falling off very rapidly with the distance, and can be neglected. Within a cell, then, the potential arises only from the charges within that cell. Since these charges are distributed almost spherically, their resultant field is almost spherical, so that it is a self-consistent hypothesis to assume that, to a first approximation, the potential, and consequently the resultant charge distribution, are both exactly spherically symmetrical. To this approximation,

we can replace the polyhedral cell by a spherical one of the same volume. Our method, then, is to solve the Thomas-Fermi equation within this spherical cell, subject to the two boundary conditions that the potential approach Ze/r at the nucleus, and that the total electronic charge contained within the sphere (of radius R , which varies as the crystal is compressed or expanded) is equal to $-Ze$.

The Thomas-Fermi³ method as applied to isolated atoms is well known, but some of its applications to other problems have resulted in misunderstandings. For that reason it will pay to sketch briefly its application to the present case. This has been done to some extent in the paper quoted above.* There is also a treatment of the whole Thomas-Fermi problem, though without taking up the present application to metals, given by Brillouin.³ Because of the existence of these discussions, to which the reader is particularly referred, the present treatment will be brief.

First we consider the original Thomas-Fermi method, which neglects effects of exchange. We

¹ J. C. Slater, *Rev. Mod. Phys.* **6**, 209 (1934).

² E. Wigner and F. Seitz, *Phys. Rev.* **43**, 804 (1933); **46**, 509 (1934).

³ L. H. Thomas, *Proc. Camb. Phil. Soc.* **23**, 542 (1927); *E. Fermi*, *Zeits. f. Physik* **48**, 73 (1928); E. A. Milne, *Proc. Camb. Phil. Soc.* **23**, 794 (1927); J. Frenkel, *Zeits. f. Physik* **51**, 232 (1928); P. A. M. Dirac, *Proc. Camb. Phil. Soc.* **26**, 376 (1930); E. B. Baker, *Phys. Rev.* **36**, 630 (1930); E. Guth and R. Peierls, *Phys. Rev.* **37**, 217 (1931); V. Bush and S. H. Caldwell, *Phys. Rev.* **38**, 1898 (1931); W. Lenz, *Zeits. f. Physik* **77**, 713 (1932); H. Jensen, *Zeits. f. Physik* **77**, 722 (1932); H. Jensen, *Zeits. f. Physik* **93**, 232 (1934); L. Brillouin, *L'Atome de Thomas-Fermi, Actualités scientifiques et industrielles*, Hermann, Paris, No. 160, 1934. The last named reference has a more complete bibliography than is given here.

* Reference 1, p. 223.

replace the energy of interaction between electrons by an average potential depending only on position, so that the total potential energy of an electron, including the interactions with the nuclei as well as with other electrons, is a function of position, $-eV$. If the energy of an electron in such a field is $-eE$, its momentum p is given by the equation $p^2/2m - eV = -eE$, so that p is real, and the motion can occur classically, only in those regions where $-e(E - V)$ is positive. We now apply the Fermi statistics to the electrons, but otherwise treat them classically. For the absolute zero of temperature, these statistics take the form of a statement that the number of electrons per unit volume in a six-dimensional phase space is $2/h^3$ ($1/h^3$ for electrons of each spin) at all points corresponding to an energy less than an arbitrary value $-eE_0$, zero at points corresponding to energy greater than $-eE_0$. At a given point of coordinate space, those points of momentum space within a sphere of radius P , where $P = (-2me(E_0 - V))^{1/2}$, are occupied by electrons, those outside the sphere unoccupied. We can then get the charge density of electrons in ordinary space by integrating the density in phase space over this sphere, and multiplying by the charge on the electron, $-e$. Since the density in phase space is constant, the result is $-2e/h^3$ times the volume of the sphere, or

$$\rho_e = -8\pi e P^3 / 3h^3 = (-8\pi e / 3h^3) (-2me(E_0 - V))^{3/2}.$$

From this equation we see that once V is determined, different values of E_0 correspond to different density of charge; in any particular case, E_0 is to be so chosen that the integral of ρ_e over all space adds to the known amount of electronic charge present in the problem. We now make the requirement of self-consistency: we demand that the potential V be the electrostatic potential of the nuclei and of the electrons themselves. By Poisson's equation, $\nabla^2 V = -4\pi\rho$, where ρ is the sum of ρ_e given above in terms of V , and the charge density of nuclei. Assuming spherical symmetry, the resulting equation is:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V}{\partial r} \right) = \frac{32}{3} \frac{e}{\pi^2 h^3} P^3 \\ = \frac{32\pi^2 e}{3 h^3} (2me(V - E_0))^{3/2}.$$

We now let $r = \mu x$, where $\mu = a_0(9\pi^2/128Z)^{1/3}$, $a_0 = h^2/4\pi^2 me^2$, or numerically, μ , our new unit of length, is equal to $0.88634a_0/Z^{1/3}$ where a_0 is the radius of the first Bohr orbit for hydrogen. We also let $V - E_0 = \gamma\phi/x$, where $e\gamma$, our new unit of energy, equals Ze^2/μ , or $(2^{10}/3^2\pi^2)^{1/3} Z^{4/3} Rhc = 2.2590Z^{4/3} Rhc$, where $Rhc = 2\pi^2 me^4/h^2$, the Rydberg energy. The quantity $Ze\phi = (V - E_0)r$ is of the nature of an effective nuclear charge, or the charge which must be divided by the distance from the nucleus to give the potential, so that as r goes to zero, $Ze\phi$, the effective nuclear charge, approaches Ze , and ϕ approaches unity. In terms of these definitions, the equation takes the form $\phi'' = \phi^{3/2}/x^{1/2}$, the Thomas-Fermi equation. We have seen that the boundary condition at the nucleus is that $\phi(0) = 1$. At the boundary of the spherical cell, since the total charge contained within the cell must be zero, the electric field must vanish, or $\partial V/\partial r = 0$, which in terms of our new variables becomes $\phi' = \phi/x$. The interpretation of this condition is simply that the tangent to the curve of ϕ against x , at the distance $x = X$ corresponding to $r = R$, should pass through the origin, making a simple condition to apply graphically.

As shown in Fig. 1, the curve for ϕ starting from $x=0$ with a particular slope, $-B_0 = -1.58808$, approaches the axis asymptotically. The tangent to this curve through the origin is then the x axis itself, which is tangent at infinite distance, so that for this solution there are just enough electrons in infinite space to neutralize the nucleus. In other words, this solution is the one for the isolated atom, the familiar solution of the Thomas-Fermi equation usually discussed. The solutions we desire are those with initial slopes smaller numerically than $-B_0$, and corresponding to spheres of finite radii. The solutions of slope greater than B_0 numerically will cut the axis of abscissas. They correspond to positive ions, as is discussed by Brillouin,³ and do not concern us here.

Solutions have been carried out for a number of slopes smaller numerically than $-B_0$. A series expansion was used about $x=0$, and the function was then extended by numerical integration out to the radius X . These solutions are presented in Fig. 1, which is drawn accurately to scale. The authors will be glad to send detailed

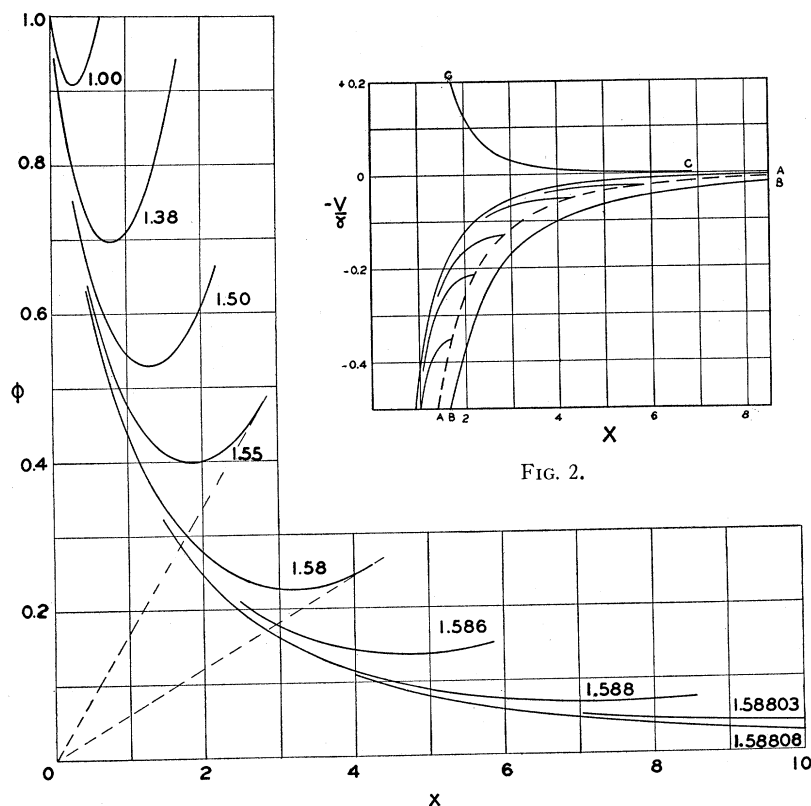


FIG. 1.

FIG. 1. Thomas-Fermi function ϕ , as function of x , for different initial slopes. The following table gives X , the minimum radius, or point of tangency of the curve and the straight line through the origin, as function of initial slope:

B	1.00	1.38	1.50	1.55	1.58	1.586	1.588	1.58803	1.58806	1.58808
X	1.19	1.69	2.20	2.80	4.23	5.85	8.59	11.3	16.	∞

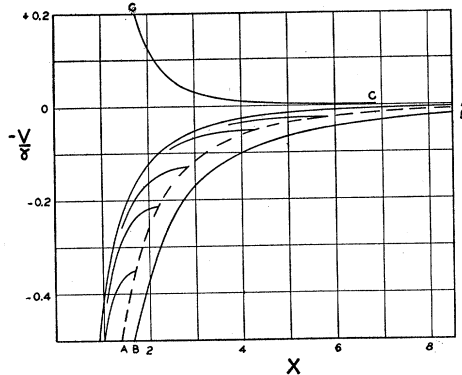


FIG. 2.

FIG. 2. Potential $-V/\gamma$ as function of distance x from nucleus, Thomas-Fermi method. The curves terminating in the dotted line AA are potentials for different lattice spacings, the values of x at the intersections being the lattice spacings X , showing that the potential $-V/\gamma$ is lowered as X decreases. The dotted line AA represents the maximum height of the potential barrier between atoms, BB represents the average potential through the cell, and CC the maximum total energy $-E_0/\gamma$ of an electron in the Fermi distribution, all as functions of X .

numerical tables to any one who may have occasion to use them, but it seems unnecessary to publish them in full.

From these solutions, we can find at once the quantity $V-E_0$, as function of x , for a number of values of X , or of the lattice spacing, and for any metal. No unique method is provided for defining the potential V and the energy E_0 separately, for as usual there is an arbitrary additive constant in the potential, and a compensating one in E_0 . This is a problem which appears in more accurate treatments, as well as in the Thomas-Fermi method. At least four

different methods of choosing the arbitrary constant have some advantages; we shall discuss them briefly. First, we may choose our constants so that the potential V in the immediate neighborhood of the nucleus has a value independent of X . This is the method adopted in the earlier paper.* When one carries out a wave-mechanical calculation, finding wave functions in the potential field V , this results in having the x-ray energy levels, which depend only on the part of V near the nucleus, independent of X , whereas

* Reference 1, p. 212, Fig. 1.

with any other choice of constant the x-ray levels will be functions of X , even when the atoms have not approached closely enough so that the wave functions in question would overlap. It is thus for most purposes the most reasonable choice physically. Mathematically the method is easily formulated. We remember that near the origin, if $-B$ is the initial slope, we can write $\phi = 1 - Bx \dots$. Substituting in the equation $V - E_0 = \gamma\phi/x$, this gives

$$V = \gamma/x + (E_0 - B\gamma) + \dots$$

For the free atom, we choose E_0 to be zero, B equal to B_0 , and we have $V_{\text{atom}} = \gamma/x - B_0\gamma + \dots$. If the potentials for the atom and metal are to agree as to the constant terms as well as to those in $1/r$, we must have $E_0 = (B - B_0)\gamma$, determining the additive constant. In Fig. 2, we show curves for $-V/\gamma$ for Na as function of x , for a number of values of X , computed on this basis. It is evident that as the atoms approach, the potential near the nucleus remains unchanged, while in the region between the atoms it decreases more and more as the inter-nuclear distance decreases. The maximum of the potential barrier, as a function of X , is shown by the dotted line AA . This is to be compared with the line AA in the Fig. 9 of the previous paper, though in that case, following Wigner and Seitz in using Prokofieff's field, the change in curvature of the potential with changing X was not considered. Also we have computed, by numerical integration, the average value of V over the sphere, for each value of X and have plotted this in the line BB , Fig. 2, to be compared with line BB , Fig. 9.¹ These potential functions as determined by the Thomas-Fermi method should be useful in the first steps of a calculation of the wave functions of electrons in metals by the method of self-consistent fields, as the corresponding functions are for isolated atoms. In Fig. 2, we also give a curve CC , representing the maximum energy $-E_0/\gamma$ of the Fermi distribution as a function of X . In contrast to the more exact wave-mechanical case, we find that this energy continuously increases as the metal is squeezed, whereas a minimum is shown by more exact methods, closely connected with the minimum of total energy of the metal. As mentioned in the

previous paper, just those electrons whose energies are greater than the amount given by the line AA , can pass the potential barrier between atoms, and take part in conduction. The energy AA , then, in a certain sense stands for the zero of energy in the Sommerfeld picture of a metal, and the difference between $-eE_0$, or CC , and AA , represents the maximum kinetic energy of a conducting electron in that model. Actually, of course, the situation is complicated by the fact that even an electron which moves slowly on the surface of the atom speeds up greatly as it approaches the nucleus. This problem of distribution of kinetic energy has been discussed in the previous paper,¹ Section 10.

The three other methods of determining the additive constants in E_0 and V , which we mentioned above, are less useful, because they are less plausible physically. The second method is to let E_0 be zero, for all R 's. The third is to let V be zero at the outer boundary of the sphere, for $x = X$. Neither of these methods has much to recommend it. The fourth, however, is more plausible: it is to consider a finite sample of metal, and let the potential be zero at infinite distance from the uncharged sample. This is more complicated, for it involves a discussion of the potential barrier and electrical double layer at the surface of the metal. With this definition of potential, the potential energy within the atom, the x-ray levels, and $-eE_0$, the top of the Fermi distribution, will all move up or down together as the jump of potential at the boundary changes, for any such reason as the addition of a surface layer of foreign atoms. For purposes of thermionic and photoelectric emission, this last definition of potential is the most useful. But since it involves a discussion of the surface effects, a problem outside the range of the present paper (though, as has been shown by Frenkel and Brillouin,³ a treatment on the basis of Thomas-Fermi theory is possible), it is a less practical method when dealing with the interior of the metal, and we shall not follow it further at the moment.

From the values of $V - E_0$ as function of x , we can compute the charge density, and find how it changes as X is changed. The point of particular interest is the way in which the density at the edge of the sphere, midway

between atoms, increases continuously as X decreases, so that the number of electrons capable of carrying current is much greater for tightly packed than for loosely packed metals. This conclusion seems to have no counterpart in the actual metals, where, as Mott⁴ has shown, the alkalis have the largest number of effective free electrons. The discrepancy arises undoubtedly from the fact that the Thomas-Fermi method cannot be expected to account for the periodic properties of the elements.

Knowing the potential, and the charge density, we can find the total energy of the crystal, kinetic and potential. The potential energy per atom is $\frac{1}{2} \int \rho_e V dv + \frac{1}{2} ZeV_0$, where ρ_e is the charge density due to electrons, V is the whole potential, and V_0 is the potential at the nucleus, whose charge is Ze , due to the electrons. By using partial integrations similar to those of Milne,³ the potential energy becomes

$$\text{P.E.} = (6/7)Ze\gamma[\phi_0' - \frac{1}{3}X^{1/2}\phi_X^{5/2}],$$

where ϕ_0' is the slope of the ϕ curve at the origin, which we have denoted by $-B$, and ϕ_X is the value of ϕ at the edge of the sphere. For the kinetic energy, we note that the maximum kinetic energy at any point is $e(V-E_0)$, and that according to the Fermi statistics the mean kinetic energy is $3/5$ of this. Weighting the mean kinetic energy at each point by the charge density of electrons at that point and integrating over the volume, we obtain the total kinetic energy, which is

$$\text{K.E.} = -(3/7)Ze\gamma[\phi_0' - (4/5)X^{1/2}\phi_X^{5/2}].$$

The potential, kinetic and total energy are plotted in Fig. 3, as functions of X . At infinite separation, where ϕ_X is zero, the potential energy becomes $-(6/7)B_0Ze\gamma$, the kinetic energy is $(3/7)B_0Ze\gamma$, evidently verifying the result of the virial theorem that the potential energy should be minus twice the kinetic energy. These limiting values of potential, kinetic and total energy are subtracted from the curves of Fig. 3, so that they really represent changes in energy on compression. We see that the total energy increases continuously with decreasing X , with no mini-

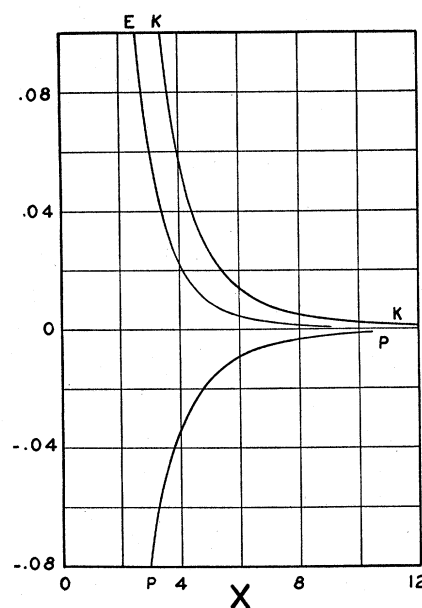


FIG. 3. Kinetic, potential and total energies as function of lattice spacings X , Thomas-Fermi method. The quantities plotted, K , P and E , are in units of $(3/7)Ze\gamma$, and represent differences between the corresponding energies at spacing X and the values of the isolated atom.

mum, so that this model cannot explain the cohesion of metals. The increase of kinetic energy with decreasing X , because of the adiabatic compression of the Fermi gas, is partly but not wholly compensated by the decrease of potential energy, arising because the electrons on the average are closer to the nucleus in the compressed state.

In the general case, for arbitrary X , the kinetic and potential energies are related through the virial theorem,⁵ which for a solid in which all forces are derived from the Coulomb law, takes the form $\text{K.E.} + 1/2\text{P.E.} = 3/2pv$, where p is the pressure, v the volume. For the Thomas-Fermi method, Fock has shown in general that this theorem must apply, and we can easily check it in the present case. Thus we substitute in the expression above the values of kinetic and potential energies already derived, and compute pv in that way. Next we find the total energy as a function of X , differentiate to get dE/dX and from that find dE/dv , which must be equal $-p$.

⁴ N. F. Mott, Proc. Phys. Soc. **46**, 680 (1934); N. H. Frank, Phys. Rev. **47**, 282 (1935).

⁵ V. Fock, Physik. Zeits. Sowjetunion **1**, 747 (1932); J. C. Slater, J. Chem. Phys. **1**, 687 (1933); H. Hellmann, Zeits. f. Physik **85**, 180 (1933).

Comparing, and going through considerable mathematical manipulation, it can be shown that the two expressions for pressure are equal. By either method we have

$$pv = (2/15)Ze\gamma X^{1/2}\phi_X^{5/2}.$$

Since we have used the energy per atom, the volume in question is that associated with an atom, or $(4/3)\pi(\mu X)^3$, so that

$$p = \{(2/15)Ze\gamma X^{1/2}\phi_X^{5/2}\} / \{(4/3)\pi(\mu X)^3\}.$$

This value has a simple interpretation: it is simply the gas pressure exerted by the electrons on the wall of the sphere. This should be given according to kinetic theory by $p = \frac{2}{3}(N/v)\text{K.E.}$, where N/v is the number of electrons per unit volume at the surface of the sphere, K.E. is their mean kinetic energy. The number per unit volume at any point can be found from the density which enters into the formulation of the Thomas-Fermi method, and in our present notation it is

$$N/v = \{\frac{1}{3}Z(x\phi)^{3/2}\} / \{(4/3)\pi(\mu x)^3\}.$$

The mean kinetic energy of the electrons at any point is $\frac{3}{8}e\gamma\phi/x$. Substituting $x = X$, and putting these values into the formula for p , we immediately verify the statement as to the interpreta-

tion of the pressure. Since the pressure is that of a perfect Fermi gas, it is obvious that no cohesive forces are found in this model. Such forces could come only from electrostatic attraction of one atom for its neighbors, and that is impossible with the uncharged spherical atom which we have considered.

A considerable improvement over the Thomas-Fermi method can be attained by introducing the effect of exchange, as Dirac has done, and as Brillouin³ describes. The principle of the method can best be described in terms of the Fock⁶ equation. These equations can be written

$$-(\hbar^2/8\pi^2m)\nabla^2 - e(V_i(x) - E_i)u_i(x) = 0,$$

where $u_i(x)$ is the wave function corresponding to the i th state of an electron, so that the whole wave function is made of a determinant of functions $u_i(x_k)$, and $-eE_i$ is the corresponding one electron energy. Here the potential V_i is different for each stationary state, and is given by

$$V_i(x) = \int [\rho_i(x, x')dv' / |r - r'|],$$

where $\rho_i(x, x')$ is the effective charge density at x' of all electrons but the one we are considering, when that one is at x , and is in the i th stationary state. Analytically, $\rho_i(x, x') = \text{charge density of nuclei}$

$$-e \sum_k \frac{u_k^*(x')u_k(x')u_i^*(x)u_i(x) - u_k^*(x')u_i(x')u_i^*(x)u_k(x)}{u_i^*(x)u_i(x)}.$$

The latter term, involving the summation, is the charge density of other electrons, and consists of two parts. The first, which can be rewritten $-e \sum_k u_k^*(x')u_k(x')$, is simply the density of all electrons including the one we are considering. It is this density which, added to the density of nuclei, we identified with the density ρ in the Thomas-Fermi method, so that that method corresponds to neglecting the last term above, which can be rewritten $e \sum_k u_k^*(x')u_i(x')u_k(x)/u_i(x)$. Remembering the orthogonality of the u 's in the Fock method, this term, the so-called exchange term, can be immediately shown to represent a charge of total amount e , so that the density $\rho_i(x, x')$ is that of the nuclei and $N-1$ electrons, if there are N electrons in the problem.

The correction which we have neglected in the Thomas-Fermi method, in other words, arises from the fact that an electron exerts no forces on itself, only on other electrons.

If now we assume a perfect gas of free electrons, obeying Fermi statistics in a field free space, it has been shown⁷ that we can compute the charge density $\rho_i(x, x')$, and consequently the potential $V_i(x)$ acting on an electron of any arbitrary momentum (corresponding to the

⁶ V. Fock, *Zeits. f. Physik* **61**, 126 (1930). For a new discussion of these equations see L. Brillouin, *Les Champs "self-consistents" de Hartree et de Fock*, Actualit es scientifiques et industrielles, Hermann, Paris, No. 159 (1934).

⁷ See P. A. M. Dirac, *Proc. Camb. Phil. Soc.* **26**, 376 (1930), and particularly Brillouin, *L'Atome de Thomas-Fermi*, quoted above.

quantum number i). The charge of one electron which must be removed from ρ to get ρ_i proves to be localized about the point x with spherical symmetry. The linear dimension of the sphere from which the charge e is removed is a function of the density of the electron gas, if it is compressed, changing proportionally to the linear dimension of the sample of gas. The correction to the potential on account of this removed charge can be shown to be $4eP/h F(p/P)$, where P is the maximum momentum of the electrons in the gas, p the momentum of the electron in question, and

$$F(\eta) = \frac{1}{2} + [(1-\eta^2)/4\eta] \log [(1+\eta)/|1-\eta|],$$

where $\eta = p/P$. Now the Thomas-Fermi method consists essentially of assuming that the electrons at any point within the system can be treated as a small part of an infinite perfect gas of free electrons of the same maximum kinetic energy. Hence it is a reasonable extension of this method to assume that the correction above, which is strictly correct only for a field-free gas where P is independent of position, can be applied in general by making P the appropriate function of position. This is the essence of the method which can be called the Thomas-Fermi-Dirac method.

Now let us apply the correction we have just discussed to the Thomas-Fermi method. In phase space, we assume as before that the number of electrons per unit volume is $2/h^3$ within a certain energy surface $-eE_0$, zero outside this energy surface. At any point of the coordinate space, the electrons will fill a sphere in momentum space, the momentum of the fastest electron being P . This fastest electron, corresponding to $\eta=1$ in the expression above, will be in a potential field equal to the potential of all charges, corrected by the exchange term for $\eta=1$. If we call the uncorrected potential V_0 , and if we note that $F(1) = \frac{1}{2}$, then the potential V_P appropriate for this fastest electron is $V_P = V_0 + 2eP/h$. The kinetic energy of this electron is $-e(E_0 - V_P) = -e(E_0 - V_0 - 2eP/h)$, and of course equals $P^2/2m$. Equating these, we have the quadratic $P^2/2m - 2e^2P/h + e(E_0 - V_0) = 0$, whose solution is $P = 2e^2m/h \pm (4e^4m^2/h^2 + 2em(V_0 - E_0))^{1/2}$, where the positive sign for the square root must be chosen to agree with the Thomas-Fermi case. The charge density is again $-8\pi eP^3/3h^3$, to be expressed in terms of the revised formula for P . As before, we apply Poisson's equation, stating that the Laplacian of the potential V_0 of all charge should equal -4π times the density of charge, so that

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial V_0}{\partial r} \right) = \frac{32\pi^2 e}{3h^3} \left\{ \frac{2e^2m}{h} + \left[\frac{4e^4m^2}{h^2} + 2em(V_0 - E_0) \right]^{1/2} \right\}^3.$$

As changes of variables, we introduce $r = \mu x$ as before, and let $V_0 - E_0 + 2me^3/h^2 = \gamma\psi/x$, where γ is as before. We also introduce $d = (3/32\pi^2)^{1/3} Z^{-2/3} = 0.211783Z^{-2/3}$. In terms of these, the equation becomes $\psi'' = x(d + \psi^{1/2}/x^{1/2})^3$, which differs from the Thomas-Fermi equation by the term d . On closer examination, the boundary conditions prove to be, as before, $\psi(0) = 1$, and $\psi_{x'} = \psi_x/X$, the latter defining the radius μX of the sphere which contains Z electrons.

Integration of the equation above has been carried out as for the Thomas-Fermi problem, expanding in series for small values of x , and integrating numerically from there out. Calculations have been made for three different values of d , corresponding to Li, $Z=3$, Na, $Z=11$, and

Cu, $Z=29$, as well as for $d=0$, the Thomas-Fermi case. In each of these three cases, a number of initial slopes were chosen, and curves computed for each of them. For each value of d , there is a particular value of the initial slope, $-B_0$, for which the ψ curve is tangent to the x axis. For the Thomas-Fermi case, this tangency is for infinite x , but for the general case it comes at a finite value of x . Brillouin has tried to connect these solutions with the neutral atoms, assuming that the charge density was given by the relations we have used out to the point of tangency, at which point the nuclear charge is just neutralized by the electrons, and assuming the charge density and field to be zero from there out. This does not seem a particularly

satisfactory suggestion, for it involves a discontinuity of charge density at the sphere. The charge density is proportional to ψ''/x , and as we see this attains its minimum value, d^3 , when ψ is zero, and can never fall to zero. We prefer to consider, as Dirac did in his original paper on the subject, that the Thomas-Fermi-Dirac method is not applicable to neutral atoms without modification. We should interpret the solution of initial slope $-B_0$, which becomes tangent to the axis at distance X_0 , simply as the solution of the metallic problem in which the radius of the cell equals X_0 . For any radius larger than X_0 , the method does not provide a solution. It is fortunate, however, that X_0 is much larger than the interatomic distance, except for the lightest atoms, so that this limitation is not of practical importance. Unfortunately for large radii the numerical integration is very sensitive to small errors, as well as to small changes in the initial slope, so that even approximately accurate values of X_0 have not been obtained, except for the case of Li. Here X_0 is in the neighborhood of 6, only slightly larger than the normal value of x in the metal. For heavier atoms, X_0 is much larger than 6, but its value cannot be accurately stated. The values of B_0 as function of d , however, can be found within narrow limits, and the curve is plotted in Fig. 4. It is practically a straight line, and should be useful for starting integrations for other atoms. For values of B less numerically than B_0 , the boundary condition $\psi x' = \psi x/X$ can be satisfied for a value of X smaller than X_0 , so that these values correspond to states of the metal more compressed than the limiting case X_0 . In Fig. 5 these curves of ψ against x are given, for Cu, for a number of values of B , again accurately to scale.

From ψ , we can calculate the charge density, and by the equation already given find $V_0 - E_0$ and $V_P - E_0$. A convenient choice of E_0 is made as follows. Since we cannot solve the problem of the isolated atom, we choose the case of maximum radius, $X = X_0$, as a standard, and demand that V_0 in the neighborhood of the nucleus have the same value for any X that it has for $X = X_0$. For $X = X_0$, at the edge of the sphere, we have

$$\psi = (x/\gamma)(V_0 - E_0 + 2me^3/h^2) = 0.$$

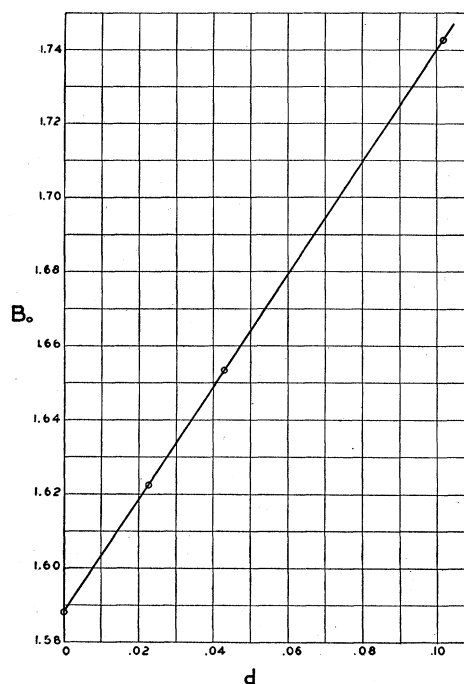


FIG. 4. Initial slopes B_0 , in Thomas-Fermi-Dirac method; for solutions where ψ curves are tangent to x axis, as function of d ; parameter depending on atomic number. The four points plotted are as follows:

atom	Z	d	B_0
Thomas-Fermi		0	1.58808
Cu	29	0.022437	1.6225
Na	11	0.042818	1.6536
Li	3	0.101815	1.7427

Let us determine E_0 by assuming that in this case $V_0 = 0$ at the edge of the sphere, giving $E_0 = 2me^3/h^2 = \gamma d^2$. Now near the nucleus for $X = X_0$, we have $\psi = 1 - B_0 x + \dots$, where B_0 is given in Fig. 4. Thus we have $V_0 = \gamma/x - B_0 \gamma \dots$. Next, for an arbitrary X , we have $V_0 - E_0 + 2e^3 m/h^2 = \gamma/x - B \gamma \dots$. To make this agree with the limiting case, we must have $E_0 = 2me^3/h^2 + (B - B_0)\gamma$. Making this choice of E_0 , the potential is definitely determined, and in Fig. 6 we plot curves of V_0 , V_P and E_0 , as functions of X , similar to the Thomas-Fermi curves of Fig. 2. Qualitatively the curves resemble those of Fig. 2, and it is seen that V_0 closely resembles the V of Fig. 2. The potential energy $-eV_P$ of an electron, however, is decidedly lower on account of exchange than with the original Thomas-Fermi method, and as a result the exchange leads to a tighter binding.

To find the total energy, and the potential and kinetic energies, with the Thomas-Fermi-

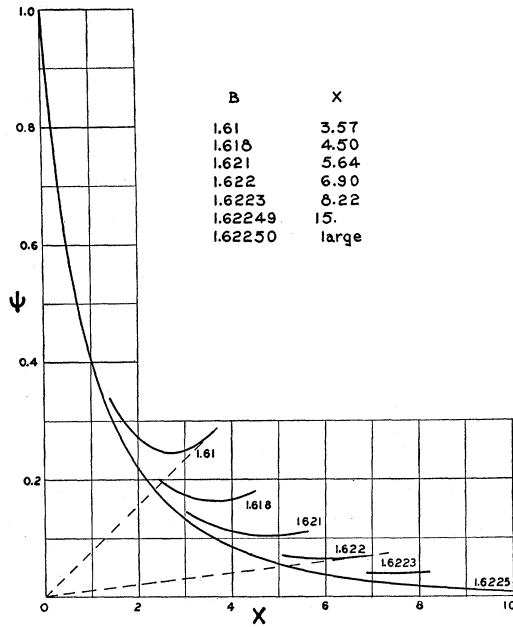


FIG. 5. Thomas-Fermi-Dirac function ψ as function of x , for Cu, $Z=29$. Table of X as function of B .

Dirac method, we proceed much as in the Thomas-Fermi method. The problem is complicated, however, by the fact that the electron of momentum p moves in a potential $V_p = V_0 + 4eP/h F(p/P)$, which is a function of p . At a point of space where V_0 has a particular value, the density of electronic charge connected with electrons with momentum between p and $p+dp$ is equal to $-(8\pi e p^2/h^3) dp$ if p is less than P , zero if p is greater than P , where P is the root of the quadratic written above. For the potential energy of interaction between electrons, instead of the simple expression $\frac{1}{2} \int \rho_e V dv$ of the Thomas-Fermi method, we must multiply the charge density for each value of p by the corresponding value of V_p , and integrate over p , as well as over v . In this way we obtain

$$\frac{1}{2} \int \rho_e V_0 dv + \frac{1}{2} \int \int (-8\pi e p^2/h^3) (4eP/h) F(p/P) dp dv,$$

where the integration with respect to p is from 0 to P . Carrying out the integration over p , the result is

$$\frac{1}{2} \int \rho_e V_0 dv - 4\pi e^2/h^4 \int P^4 dv.$$

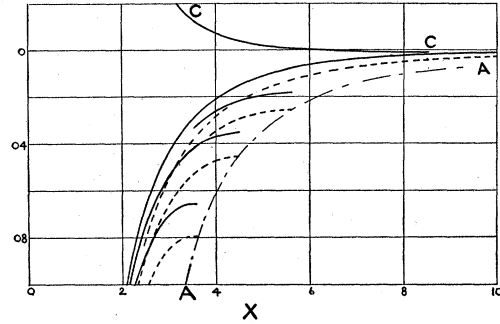


FIG. 6. Uncorrected potential $-V_0/\gamma$ (full lines), and potential acting on an electron $-V_p/\gamma$ (dotted lines), for Thomas-Fermi-Dirac method, for several lattice spacings. Line AA represents the maximum potential barrier of the potential acting on an electron. CC represents the maximum total energy of an electron, $-E_0/\gamma$.

The total potential energy is the sum of these terms, and $\frac{1}{2} Ze V_{00}$, where V_{00} is the value of the potential due to the electrons, at the nucleus. In contrast to the Thomas-Fermi method, no method has been found for carrying out all the integrations explicitly in terms of the values of known quantities at $x=0$ and $x=X$. Instead, most of the integration must be performed numerically.

The kinetic energy of an electron of momentum p is $p^2/2m$, as with the Thomas-Fermi case, and the mean kinetic energy at a given point of space is $\frac{3}{5} P^2/2m$. To get the total kinetic energy, we multiply this by the number of electrons per unit volume, and integrate over all space. As with the potential energy, the integrals have not all been evaluated, and some had to be computed by numerical integration, so that it is not worth while to give the details of the integration. In Fig. 7 we give the total energy as function of X for Cu. In comparison with the Thomas-Fermi method, the effect of including exchange is to lower the total energy decidedly. It is still not lowered enough, however, to give a minimum, but the energy is practically constant within the error of the calculation in the neighborhood of the observed distance of separation.⁸ It is to be noted, however, that Wigner and Seitz² have found that a considerable part of the cohesive energy of sodium comes from the

⁸ In the earlier paper (reference 1, p. 234) it was stated that approximate calculations appeared to give a minimum in the curve. This is not verified in more accurate computations.

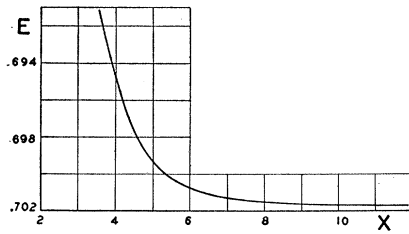


FIG. 7. Total energy, in units of $-Ze\gamma$, as function of X , for Cu, $Z=29$, Thomas-Fermi-Dirac method.

correlation energy between electrons of opposite spin, a feature which the Fock and Thomas-Fermi-Dirac methods neglect, so that we could not expect to get nearly as low an energy as is observed.

The virial theorem, as far as the writers are aware, has not been discussed in general for the Thomas-Fermi-Dirac model, and since we have not obtained analytical forms for the kinetic and potential energies, it has not been possible to verify it analytically in the present case. However, we have computed pv both from the virial method and from the slope of the total energy curve, and the two values agree within the error of the numerical calculation, so that we infer that the theorem holds in the present case. The pressure is quite different in physical interpretation from what it was in the Thomas-Fermi method. There, as we have pointed out, it is the perfect gas pressure of the electrons striking the boundary of the sphere. Here, a

larger density of free electrons is allowed at the surface of the sphere than in the Thomas-Fermi case, so that their pressure as a perfect gas would be greater than before. The exchange, however, gives a negative term in the potential and the total energy, which becomes greater numerically as the metal is compressed. Thus it gives rise to an attraction, and negative pressure, which just result in zero pressure. If our model were sufficiently good to give the cohesive effect, this attraction would slightly outweigh the repulsive effect of the gas pressure.

From the foregoing discussion we see that neither the Thomas-Fermi nor the Thomas-Fermi-Dirac method as applied to metals gives results of sufficient accuracy to use for investigating the energy in the neighborhood of equilibrium. On the other hand, the potential field, momentum distribution, and various other features promise to be of decided value as first approximations in more accurate treatments of the metals. One further field in which the method might be advantageous is in investigating the limiting behavior of matter under high pressure, as it is found particularly in astrophysics. Stellar material, either at low temperature and very high density as in the dense stars, or at high temperature and more normal density, as in hot stars, could be approximated as in the present paper, and a much better approximation to the equation of the state could be found than has been so far obtained.