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Fermi-Thomas Model with Correlations*

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The Fermi-Thomas-Dirac equation is modified to include correlations between electrons. An application is made to the equation of state. No numerical work with the modified equation is reported.

I. INTRODUCTION

SINCE its invention by Fermi[1] and Thomas,[2] and later modification by Dirac,[3] the statistical model of the atom has been used by many authors[4] to study those properties of solids, and of heavy atoms, which may be expected to be reasonably independent of the detailed structure of the outer electron shells of the atom. Generally, such matters as the equation of state at high pressures,[5] and the development of the periodic system[1] are well treated by the model, indeed, in the latter case, the model is more accurate in predicting the values of the atomic number Z at which the first s, p, d, f, etc. electrons appear, than one has any right to expect. However, matters that depend upon the edge of the atom, such as the atomic diamagnetism, which is proportional to the mean square radius of the charge distribution in the atom, are poorly given by the model.

The root of the trouble is twofold. In the first place, the original model supposes, at each point in space, a degenerate free electron gas, and the interaction between electrons is ignored, except for the mean screening effect of the electron cloud. This is an approximation which is accurate for high density of electrons, therefore in the interior of heavy atoms. The first step in improving this part of the approximation was taken by Dirac,[3] who included the exchange energy of a free electron gas, thereby accounting approximately for the tendency of electrons of like spin to keep away from each other, an effect which evidently reduces the energy of the system. Various efforts have been made to take into account the tendency of electrons of unlike spin to stay apart (because of their Coulomb repulsion), an effect which is clearly in the same direction, but these have been largely frustrated for lack of an adequate theory of this so-called correlation energy. This gap has now been, if not filled, at least penetrated, by the elegant work of Gell-Mann and Brueckner,[6] and of Gell-Mann.[7] This paper will be devoted to a minor extension of their work, which will lead to a modified Fermi-Thomas-Dirac equation. As a special application, we shall deal with the equation of state, though the modified equation is generally applicable. The manner in which we shall incorporate the correlations is exact at high densities, and probably not wildly wrong at any density.

The second basic error of the model, not unrelated to the correlation energy, is rooted in the circumstance that electrons do not interact with themselves. A crude effort to take this into account was made by Fermi and Amaldi,[8] by simply multiplying the charge distribution each electron sees by the factor $(Z-1)/Z$. We shall not discuss this correction here, though it would be easy to incorporate it into the model in the manner of Fermi and Amaldi.

We shall also work at the absolute zero of temperature. The procedure for going to a finite temperature exactly is given by Feynman, Metropolis, and Teller,[5] and can be carried over with much pain, though with no difficulties of principle, for those problems in which the temperatures are comparable with the atomic energies.

II. CORRELATION ENERGY

We consider a degenerate electron gas of maximum momentum p_F, and density (number of electrons per unit volume) n. Then it is known that these are connected by the relation $n=2\times(4\pi/3)\times(p_F/2\pi\hbar)^3$, where $\hbar$ is Planck's constant divided by 2π, or $n=p_F^3/3\pi^2\hbar^3$. This relation is correct even in the presence of interactions, though p_F must then be interpreted as the maximum momentum before the interactions are turned on. We will be interested, for reasons that will appear in the next section, in the removal energy of an electron at the top of the distribution, that is, with momentum p_F. The first term is simply the kinetic energy of the electron, $p_F^2/2m$, and the second is the exchange energy, $-e^2p_F/\pi\hbar$, which was included in the Fermi-Thomas equation by Dirac. We shall show in the appendix that Gell-Mann's scheme leads to an expression for the correlation energy, correct in the high-density limit, of $-(me^4/\pi^2\hbar^2)(1-\ln 2)\ln p_F+$constant. The constant term is of no consequence for the

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[1] E. Fermi, Z. Physik **48**, 73 (1928).

[2] L. H. Thomas, Proc. Cambridge Phil. Soc. **23**, 542 (1926).

[3] P. A. M. Dirac, Proc. Cambridge Phil. Soc. **26**, 376 (1930).

[4] See, for example, P. Gombás, *Statistische Theorie des Atoms* (Springer-Verlag, Wein, 1949).

[5] Feynman, Metropolis, and Teller, Phys. Rev. **75**, 1561 (1949).

[6] M. Gell-Mann and K. Brueckner, Phys. Rev. **106**, 364 (1957).

[7] M. Gell-Mann, Phys. Rev. **106**, 369 (1957).

[8] E. Fermi and E. Amaldi, Mem. accad. sci. ist. Bologna **6**, 117 (1934).

Fermi-Thomas model, since it amounts only to a redefinition of the zero of energy. We shall modify this expression in such a way as to leave it correct in the high-density limit, but render it exact in the low-density limit,[9] thus obtaining what we hope will be a reasonable interpolation formula, correct, in any case, at the two extreme limits.

Wigner[9] has pointed out that, in order to do this, one need only note that a very dilute gas of electrons, at absolute zero, will crystallize into a body-centered cubic lattice, for which one can calculate the correlation energy exactly, by Madelung type techniques. The result[10] is (for the total energy at low density, including the exchange energy) $-0.89e^2/r_s$, where r_s, the "mean spacing between electrons" is defined by $(4\pi r_s^3/3)=n^{-1}$. [In fact, of course, the actual mean spacing between nearest electrons is not r_s but is $\Gamma(4/3)r_s$, but we conform to the standard nomenclature in the field.[11]] Since p_F is related to r_s by the equation $\alpha p_F r_s=\hbar$, where $\alpha=(4/9\pi)^{\frac{1}{3}}$, the low-density energy is

$$-0.89e^2\alpha p_F/\hbar.$$

Since the exchange energy is $-e^2p_F/\pi\hbar$, the low-density correlation energy is $-(0.89\alpha\pi-1)e^2p_F/\pi\hbar$. Remembering that the high-density limit is

$$-(me^4/\pi^2\hbar^2)(1-\ln 2)\ln p_F+\text{const},$$

a suitable interpolation formula might be[12]

$$E_{\text{corr}}\approx-\frac{me^4(1-\ln 2)}{\pi^2\hbar^2}\ln\left[1+\frac{(0.89\alpha\pi-1)\pi p_F a_0}{(1-\ln 2)\hbar}\right], \quad (1)$$

where $a_0=\hbar^2/me^2$. We take then, for the total removal energy of an electron at the top of the Fermi distribution,

$$E_{\text{tot}}=\frac{p_F^2}{2m}-\frac{e^2p_F}{\pi\hbar}+E_{\text{corr}}. \quad (2)$$

III. FERMI-THOMAS MODEL

The Fermi-Thomas model of the atom is based on the idea of a degenerate gas of electrons at each point in the atom in statistical equilibrium in the space-varying mean potential field. We will not discuss the general question of the range of validity of such a model. The condition for equilibrium is that it should not be possible to gain energy (free energy, if the temperature is not zero) by transferring an electron from one point in the atom to another, so that the removal energy should be the same at all points in the atom. So, if the electrostatic potential at a point is $V(r)$,

$$eV(r)+\frac{p_F^2}{2m}-\frac{e^2p_F}{\pi\hbar}+E_{\text{corr}}=\text{const.} \quad (3)$$

Note that e, the charge on the electron, is intrinsically negative. This equation, plus Poisson's equation

$$\nabla^2V=-4\pi ne=-4p_F^3e/3\pi\hbar^3, \quad (4)$$

completely determines the model. The boundary condition at the origin is $V\rightarrow Ze/r$, and we shall make the usual assumption of spherical symmetry, encasing each atom in a spherical cell of its own, of a volume equal to the atomic volume in the material under consideration. Thus the edge of the cell is defined by r_0 such that $V'(r_0)=0$, expressing the fact that the total charge contained within r_0 is zero.

It is customary at this point to define a collection of new variables and constants, which we do as follows:

$$\varphi(x)=\frac{r}{Ze^2}\left[\frac{p_F^2}{2m}-\frac{e^2p_F}{\pi\hbar}+E_{\text{corr}}+\frac{(1-\ln 2)e^2}{\pi^2a_0}\ln\sigma a\right], \quad (5)$$

$$x=r/\beta a_0, \quad \text{where} \quad \beta=(9\pi^2/128Z)^{\frac{1}{3}}, \quad (6)$$

$$v(x)=\frac{p_Fa_0}{\hbar}\left(\frac{r}{2Za_0}\right)^{\frac{1}{2}}=\frac{p_Fa_0}{\hbar}\cdot\frac{\pi a x^{\frac{1}{2}}}{2}, \quad (7)$$

$$a=(2\beta/\pi^2Z)^{\frac{1}{2}}, \quad (8)$$

$$b=\rho a^2, \quad \text{where} \quad \rho=\tfrac{1}{2}(1-\ln 2), \quad (9)$$

$$c=\sigma a, \quad \text{where} \quad \sigma=\frac{1-\ln 2}{2(0.89\alpha\pi-1)}. \quad (10)$$

In terms of these, Eqs. (3) and (4) become

$$\varphi''(x)=v^3x^{-\frac{1}{2}}, \quad (11)$$

and

$$\varphi=v^2-avx^{\frac{1}{2}}-\rho a^2x\ln(\sigma a+vx^{-\frac{1}{2}}). \quad (12)$$

The boundary conditions become

$$\varphi(0)=v(0)=1, \quad (13)$$

$$x_0\varphi'(x_0)=\varphi(x_0). \quad (14)$$

Equations (11) and (12) are the basic equations with which we shall henceforth deal. Neglect of the last two

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[9] E. Wigner, Phys. Rev. **46**, 1002 (1934).

[10] It should be noted that there is some ambiguity in the literature about this number. In his original work, Wigner calculated the energy of a body-centered electron lattice, and compared it with the energy of a uniform distribution of electrons, obtaining 3/4 for the number we have given above as 0.89. Later [E. Wigner, Trans. Faraday Soc. (London) **34**, 678 (1938)], he recalculated the energy of the lattice, and obtained the answer 0.90 for the coefficient. We shall use the value 0.89, which we have obtained by an independent calculation.

[11] P. Hertz, Math. Ann. **67**, 387 (1909); see also S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

[12] This is

$$E_{\text{corr}}\ (\text{Rydbergs})=-(2/\pi^2)(1-\ln 2)\ln[1+9.0\alpha(p_Fa_0/\hbar)].$$

If we now expand this near the high density limit, we find

$$-(2/\pi^2)(1-\ln 2)\ln(\alpha p_Fa_0/\hbar)-0.137.$$

As will be shown in the appendix, the exact expansion is

$$-(2/\pi^2)(1-\ln 2)\ln(\alpha p_Fa_0/\hbar)-0.117.$$

The difference between the numbers 0.137 and 0.117 gives some measure of the error associated with our interpolation formula (1).

terms on the right-hand side of (12) would lead us to be original Fermi-Thomas model, while neglect of the last term only would yield the Fermi-Thomas-Dirac model.

For the Fermi-Thomas-Dirac equation (i.e., $\rho=0$, above), it is now possible to construct a power series solution, useful near the origin, to which one can then join a numerical integration. However, in our case, the logarithmic term in (12) changes the analytic character of the equation in the neighborhood of the origin, so that a power series does not exist. However, a double power series in x and $\ln x$ does exist, and the first few terms are given below. A is the slope parameter which determines the value of x_0, the radius of the cell, and we have defined a logarithmic slope function $Q(x)=A-(\rho a^2/4)\ln x$. Then, if $\varphi(x)=\sum_n f(n,x)x^n$, we have

$$\begin{aligned}
f(0,x)&=1,\\
f(1/2,x)&=0,\\
f(1,x)&=2A-\tfrac{1}{4}a^2,\\
f(3/2,x)&=4/3,\\
f(2,x)&=\tfrac{3}{4}a,\\
f(5/2,x)&=\frac{4}{5}Q+\left(\frac{1}{5}+\frac{16\rho}{75}\right)a^2,\\
f(3,x)&=\frac{1}{3}+\left(\frac{1}{48}+\frac{\rho\sigma}{4}+\frac{\rho}{8}\right)a^3,\\
f(7/2,x)&=\frac{6}{35}Q^2+a^2Q\left[\frac{3}{35}+\frac{282}{1225}\right]+\frac{5a}{14}+\frac{4}{35}\\
&\quad\times\left[\frac{1587\rho^2}{4900}-\frac{3\rho\sigma^2}{4}+\frac{3\rho\sigma}{4}+\frac{387\rho}{560}\right]a^4,\\
f(4,x)&=\left(\frac{4}{15}+\frac{\rho a^3}{8}\right)Q+\left(\frac{77}{480}+\frac{67\rho}{450}\right)a^2\\
&\quad+\left(\frac{\rho^2\sigma}{16}+\frac{19\rho^2}{384}+\frac{\rho\sigma^3}{24}+\frac{\rho}{192}\right)a^5.
\end{aligned}\tag{15}$$

We see that the correlations, represented by Q and ρ, do not begin to affect the interior of the atom until the terms in $x^{\frac{5}{2}}$, whereas exchange, represented by a, appears in the coefficient of x^2. [The appearance in $f(1,x)$ is meaningless, since A is an arbitrary constant.]

IV. EQUATION OF STATE

To relate a solution of (11) and (12) to the equation of state, we need to calculate the pressure associated with a given x_0. The simplest way to do this is to observe that, at the edges of the atom, there are no net forces on the electrons [this is in fact the definition of the edge, and is represented by Eq. (14)], so the pressure is just that of an electron gas at that point. Hence we need to know the density and pressure of the electron gas at $x=x_0$. The former is given by $n=p_F^3/3\pi^2\hbar^3$, so that

$$a_0^3n(x_0)=\frac{[v(x_0)]^3}{3\pi^2}\left(\frac{2Z}{\beta x_0}\right)^{\frac{3}{2}}=\frac{8}{3\pi^5}\left[\frac{v(x_0)}{ax_0^{\frac{1}{2}}}\right]^3. \tag{16}$$

For the latter, we must take into account the internal forces of the gas, since, even in this approximation,[13]

$$\tfrac{3}{2}pV=E_{\text{kinetic}}+\tfrac{1}{2}E_{\text{potential}}, \tag{17}$$

and it is necessary to know both kinetic and potential energy to find the pressure.

To achieve this, we consider a virtual expansion of the electron gas, keeping the number of particles constant. Then

$$p=-nV(\partial\bar{E}/\partial V)=\tfrac{1}{3}np_F(\partial\bar{E}/\partial p_F), \tag{18}$$

where $\bar{E}$ is the mean energy per particle, including kinetic, exchange, and correlation energy. In the appendix, we show that this is simply related to the difference between the mean energy per particle, and the energy at the top of the Fermi distribution, namely,

$$p=n[E(p_F)-\bar{E}]. \tag{19}$$

Since, as is shown in the appendix, the correlation part of the difference in parentheses in (19) no longer contains a logarithm, but is just -0.021 Rydbergs, we have, if we introduce $w(x_0)=(p_Fa_0/\hbar)=2v(x_0)/\pi ax_0^{\frac{1}{2}}$,

$$p=\frac{\hbar^2}{ma_0^5}\frac{w^5}{15\pi^2}\left[1-\frac{5}{4\pi w}-\frac{0.052}{w^2}\right]. \tag{20}$$

We should observe that a free atom is defined by zero pressure at the boundary so that, for a free atom,

$$w^2-(5w/4\pi)-0.052=0. \tag{21}$$

This leads to a minimum value of $(p_Fa_0/\hbar)$ at the edge of an atom of 0.50, as contrasted with the value 0.40 without correlations.

APPENDIX

We want to establish our expression for high-density limit of the correlation energy of an electron at the top of the Fermi distribution. This expression, given in the text, is

$$E_{\text{corr}}(\text{Rydbergs})=-2\pi^{-2}(1-\ln 2)\ln p_F+\text{const.} \tag{22}$$

There are two ways to do this. Gell-Mann and

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[13] See Feynman, Metropolis, and Teller, reference 5. Their arguments apply equally well to our case.

Brueckner have calculated the average correlation energy per electron by writing down the important part of the perturbation expansion for the energy of the electrons in Coulomb interaction with each other, summing over the electrons, and summing the perturbation series. One can do just this, summing over all electrons but one, then setting the momentum of that one equal to p_F. This will give the correlation energy of one electron of momentum p_F, due to its interaction with all the other electrons, and, in fact, leads to (22).

A simpler procedure is as follows, exploiting the mean energy expression of Gell-Mann and Brueckner,

$$\bar{E}_{\text{corr}} = -2\pi^{-2}(1-\ln 2)\ln(\alpha p_F a_0/\hbar) - 0.096, \quad (23)$$

where the bar over the E_{corr} indicates that this is not the correlation energy of an electron at the top of the Fermi distribution, but is the mean correlation energy per particle. To obtain the former, we consider the variation of (23) with change of p_F. A change in p_F means that the density of electrons is being changed, since that is proportional to $p_F{}^3$, say $Ap_F{}^3$. The total energy per unit volume is, then

$$Ap_F{}^3 f(p_F), \quad (24)$$

where $f(p_F)$ is the mean energy per electron, in particular (23). If we now change p_F by Δp_F, the change in energy density is

$$A\Delta p_F \frac{d}{dp_F}[p_F{}^3 f(p_F)]. \quad (25)$$

The change in the number of electrons is

$$3Ap_F{}^2\Delta p_F, \quad (26)$$

and all these extra electrons are added to the top of the Fermi distribution. So the removal energy of an electron at the top of the distribution is the quotient of (25) and (26), or

$$f(p_F) + \frac{p_F}{3}\frac{df(p_F)}{dp_F}, \quad (27)$$

and this relation is valid for kinetic, exchange, or correlation energy. Applying it in particular to (23), we find

$$E_{\text{corr}}(p_F) = -2\pi^{-2}(1-\ln 2)\ln(\alpha p_F a_0/\hbar) - 0.117, \quad (28)$$

measured in Rydbergs, which is the expression given in the text. The difference $\bar{E}_{\text{corr}} - E_{\text{corr}}(p_F) = 0.021$ Rydbergs remains correct, even when we use our interpolation formula (1) for $E_{\text{corr}}(p_F)$, provided we connect the two through (27). The number 0.021 is just $\frac{2}{3}\pi^{-2}(1-\ln 2)$.