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Self-consistent field model for condensed matter

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A model for condensed matter is described in which the ions surrounding a particular atom are replaced by a positive charge distribution which is constant outside of a sphere containing the atom and zero inside. The orbital functions, both bound and free, are obtained as solutions of the Dirac equation and are used to self-consistently determine the potential function. In order to obtain the desired equation-of-state data from the calculations, three different and somewhat arbitrary prescriptions are used to separate quantities pertaining to the atom from those of the electron gas in which it is imbedded. Results are shown for 14 elements, including the 5*d* transition metals, in the neighborhood of normal solid density. Equation-of-state data for nickel, copper, and zinc are also given and are compared with experiment.

In astrophysics and in other sciences there is sometimes a need for information about the properties of matter—particularly equations of state—in extreme conditions of pressure or temperature. Experimental methods of obtaining data are limited to moderate pressures and temperatures, so one turns to theoretical models. When the atomic density is very low the appropriate picture is one of isolated atoms in equilibrium with free electrons. Isolated atoms and ions can be dealt with in a number of ways; e.g., spectroscopic data may be used or self-consistent field calculations may be performed. In the case of very high density, the statistical or Thomas-Fermi-Dirac (TFD) method is useful. However, both of these methods are poor in a large intermediate region. A model is set forth here which may be expected to be fairly good at the extremes of high and low material densities, since it closely resembles the accepted models in these limits. Also, since the model is expected to work at very low and very high densities, there is hope for it in the intermediate region. Some comparisons with experimental equation-of-state data will be given to test the model in the intermediate density region where its justification is most uncertain.

Closely related models have been proposed by Almbladh and von Barth[1] and by Bryant and Mahan[2] for the purpose of studying localized states in solids. Our concern has been mainly the calculation of equations of state and therefore our starting point—the TFD model—is different.

At very high matter densities, the TFD method applied to an atom confined in a sphere is regarded as adequate although it is uncertain just how high the density must be for the results to be trusted. Like others, we start with the notion that an appropriate generalization of the TFD model will improve its accuracy and extend its range of validity to lower densities. Part of the simplicity of the TFD model comes from the spherical symmetry of the atomic cell used in the calculations. Ordinarily the spherical cell is regarded as an approximation to a polyhedral atomic cell which is part of a large periodic array of atoms. However, another picture is possible. Instead of a polyhedral cell being regarded as surrounded by other identical cells, the nearly equivalent spherical cell can be regarded as surrounded by a uniform electron gas whose density is the same as the surface density of the atomic cell. In the TFD approximation, the electron gas outside will not alter the charge distribution inside the cell if its density is correctly chosen nor will the atom affect the electron gas.

Going back to the periodic array of atoms, we know that it is possible to do much better by using the self-consistent-field (SCF) approximation instead of the TFD method. The result is the usual band theory. It is an excellent method for equation-of-state purposes but is quite complicated from a computational point of view. What we propose here is to make a similar improvement in the model of an atom imbedded in an electron gas by using the SCF approximation.

Figure 1 illustrates the model. At the center of a spherical cavity is a point nucleus. Outside the cavity there is a uniform distribution of positive charge which takes the place of the surrounding ions. There are sufficient electrons in the system to give overall electrical neutrality, *and* the additional requirement of electrical neutrality inside the sphere is imposed. To simplify the computations somewhat, the electron density outside the sphere is replaced with its volume average in all potential-energy expressions. This is the so-called "muffin-tin" approximation which is often used in band-structure calculations.[3]

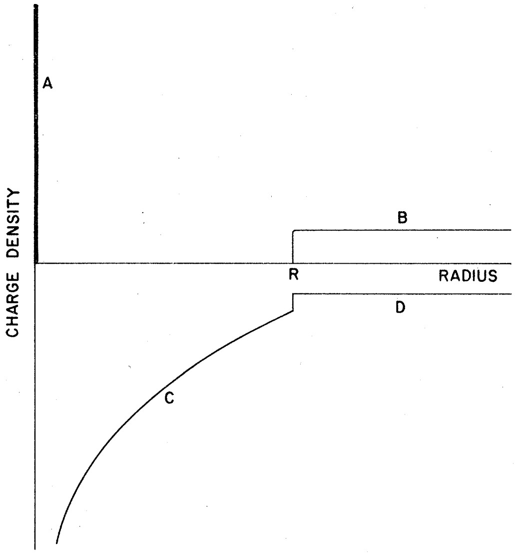

FIG. 1. A schematic distribution of charge for this model: *A*, a point nucleus at the center of a spherical cavity; *B*, a constant positive charge density outside the cavity which represents the surrounding ions; *C*, a spherically symmetric electronic charge density inside the cavity; *D*, a volume averaged electronic charge density outside the cavity. *R* is the radius of the cavity which is electrically neutral. The outside region is also neutral.

The self-consistent-field approximation, when applied to an atom imbedded in an electron gas, results in one-electron equations with a spherically symmetric potential function. The potential resembles an atomic potential inside the atomic sphere, and outside it is constant because of the muffin-tin assumption. There are a finite number of bound states and a continuum. Most atoms will have resonances in the continuum, so appropriate computational methods for handling them are necessary. Compressing an atom will change bound states into resonances and then cause the resonances to broaden. These changes should occur without any unphysical discontinuities in energy or pressure.

Since the one-electron orbitals are, to a greater or lesser extent, spread out over the entire volume of the system, there is no unambiguous way of separating the system into parts which can be associated with the atom and with the surrounding medium. Three somewhat arbitrary prescriptions for effecting this separation are tried and compared.

The model proposed here is a natural extension of the TFD method which itself is a valid high-density approximation. However, if we examine our model in the other extreme of low densities where the spherical cavity becomes very large, we find that it describes an isolated atom or an ion in equilibrium with an electron gas. The description is approximate, of course, and the approximation is that of using the method of self-consistent fields. Thus the model appears to be appropriate to both limits of high and low densities. This is encouraging for the intermediate density region which is the most interesting and the most difficult.

I. DESCRIPTION OF THE PROPOSED MODEL

A more detailed description of this model of condensed matter—so far described in general terms in the paragraphs above and in Fig. 1—will now be given.

The positive charge in the model consists of a point nucleus at $\vec{r}=0$ and a constant density distribution outside of a sphere of radius R. The positive charge outside the sphere is called $\rho_+(r)$ and equals $\bar{\rho}\Theta(r-R)$ where $\Theta(x)$ is the familiar Heavyside step function. $\bar{\rho}$ is chosen so that there is the same amount of positive as negative charge outside the cavity:

$$\int_{r>R}\bar{\rho}\,d\vec{r}=\int_{r>R}\rho_-(\vec{r})\,d\vec{r}\,. \tag{1}$$

Electrical neutrality is also required inside the atomic sphere:

$$Z=\int_{r<R}\rho_-(\vec{r})\,d\vec{r}\,. \tag{2}$$

These requirements are somewhat arbitrary, but they seem reasonable and do coincide with the TFD model discussed above. The electrical neutrality condition, expressed in (2), is achieved by varying the sphere radius or by adjusting the chemical potential.

The electron density itself is given in terms of normalized one-electron orbital functions,

$$\rho_-(\vec{r})=\sum_i n_i|\psi_i(\vec{r})|^2\,, \tag{3}$$

where the n_i's are occupation factors and the sum includes an integral over the continuum. $\rho_-(\vec{r})$ will exhibit the well-known Friedel oscillations outside the atomic sphere. Also tails of the bound-state orbital functions will extend into that region. These deviations from constant electron density outside the atomic cavity can cause some computational problems, so we resort to using an average value for the electron density there. We define

$$\rho(r)=\int\rho_-(\vec{r})\frac{\sin\theta\,d\theta\,d\phi}{4\pi} \tag{4a}$$

for $r<R$ and

$$\rho(r) = \frac{\int_{x>R} \rho_-(\vec{x})\, d\vec{x}}{\int_{x>R} d\vec{x}} = \bar{\rho} \tag{4b}$$

for $r > R$. This is very much like the well-known muffin-tin charge density[3] except that the sphere radius is somewhat larger than is usual in band-structure calculations. The name muffin-tin will be retained despite the fact that a single sphere is involved here. The potential energy will be expressed in terms of the muffin-tin charge density, and from it will come a one-electron potential function which will have the muffin-tin character also.

It is our intention to use the Kohn-Sham[4] local density scheme for obtaining the self-consistent-field equations. The obvious mean field generalization to finite temperatures will be used as we are interested in thermal effects. Also we are interested in high Z materials, so relativistic effects are included through the use of the Dirac equation.

The total energy of the system is a sum of kinetic and potential energy terms

$$E = K + U + V + W. \tag{5}$$

The kinetic energy of electrons, whose orbitals satisfy a Dirac equation, is

$$K = \sum_i n_i \int \psi_i^*(\vec{r})(c\vec{\alpha}\cdot\vec{p} + \beta c^2 - c^2)\psi_i(\vec{r})\, d\vec{r}. \tag{6}$$

(We are using atomic units with $e^2 = \hbar = m = 1$ and $c = 137.036$.) The potential energy terms are

$$U = -\int \frac{Z}{r}\,[\rho(r) - \rho_+(r)]\, d\vec{r}, \tag{7}$$

$$V = \frac{1}{2}\int\int \frac{[\rho(r) - \rho_+(r)]\,[\rho(r') - \rho_+(r')]}{|\vec{r} - \vec{r}'|}\, d\vec{r}\, d\vec{r}', \tag{8}$$

and

$$W = -\frac{3}{4\pi}\int \rho(r)[3\pi^2\rho(r)]^{1/3}\, d\vec{r}. \tag{9}$$

The Kohn-Sham local density expression for exchange is used and correlation terms are neglected. Equation (9) is really correct only for zero temperature, but at high temperatures the exchange energy is unimportant when compared to the kinetic energy, and the simple form used here should be adequate.

For electrons interacting through a mean field, the entropy is

$$S = -\sum_i [n_i \ln n_i + (1 - n_i)\ln(1 - n_i)]. \tag{10}$$

Temperature is in energy units (hartrees) and the Boltzmann constant is unity.

The free energy, $F = E - TS$, is to be minimized subject to certain constraints. These are the normalization of the orbital functions,

$$\int |\psi_i(\vec{r})|^2 d\vec{r} = 1; \tag{11}$$

a fixed number of electrons in the system,

$$\sum_i n_i = N; \tag{12}$$

and the assumption of electrical neutrality of the atomic sphere,

$$\int_{r<R} \rho(r)\, d\vec{r} = Z. \tag{13}$$

The usual method for finding an extremum when there are constraints is to use Lagrange multipliers to form a functional

$$J\{\psi_i, R, n_i\} = E - TS - \mu N - \nu\int_{r<R}\rho(r)d\vec{r} - \sum_i \lambda_i \int |\psi_i(\vec{r})|^2 d\vec{r} \tag{14}$$

and then require

$$\frac{\delta J}{\delta\psi_i^*} = 0, \quad \frac{\partial J}{\partial R} = 0, \quad \frac{\partial J}{\partial n_i} = 0. \tag{15}$$

The variation of J with respect to the orbital functions gives us one-electron Dirac equations,

$$[c\vec{\alpha}\cdot\vec{p} + \beta c^2 - c^2 + v(r)]\psi_i(\vec{r}) = (\lambda_i/n_i)\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r}), \tag{16}$$

where the potential function is

$$v(r) = -\frac{Z}{r} + \int_{r'<R} \frac{\rho(r')}{|\vec{r} - \vec{r}'|}\, d\vec{r}' - \frac{[3\pi^2\rho(r)]^{1/3}}{\pi} - \nu \tag{17a}$$

if $r < R$ and

$$v(r) = -(3\pi^2\bar{\rho})^{1/3}/\pi = v_\infty \tag{17b}$$

if $r > R$.

The Lagrangian multiplier ν is determined from the condition $\partial J/\partial R = 0$. When account is taken of the explicit dependence of $\bar{\rho}$ on R as given by Eq. (4b), the result is

$$\nu = \{[4 - \bar{\rho}/\rho(R)](3\pi^2\bar{\rho})^{1/3} - 3[3\pi^2\rho(R)]^{1/3}\}/4\pi. \tag{18a}$$

If this dependence is ignored,

$$\nu = 3\{\bar{\rho}/\rho(R)(3\pi^2\bar{\rho})^{1/3} - [3\pi^2\rho(R)]^{1/3}\}/4\pi \tag{18b}$$

is obtained. Some of our earlier calculations[5] were done with the latter prescription, but none of those reported here. ν is generally quite small, particularly when defined by Eq. (18a), but equation-of-state results are rather sensitive to it.

As is usual in statistical mechanics, the variation of J with respect to the n_i's determines the average occupation factors:

$$n_i = 1/\{\exp[\beta(\epsilon_i - \mu)] + 1\}. \tag{19}$$

For computational purposes it is useful to use the Dirac equation to convert the expression for the kinetic energy from the one in Eq. (6) to

$$K=\sum_i n_i(\epsilon_i - v_\infty) - \int \rho(r)[v(r) - v_\infty]\,d\vec{r}\,. \tag{20}$$

Several of the above equations involve sums over single-particle states. Both bound and continuum states are involved. To go beyond a purely formal treatment it is necessary to separate the bound and continuum parts of these sums and examine the continuum part more closely. A typical sum is

$$G=\sum_i g_i=\sum_b g_b+\sum g_c\,, \tag{21}$$

where b and c represent bound and continuum states. The bound states are finite in number and represent no problem. The sum over the continuum is expressed in terms of integrals:

$$\sum_c g_c=\sum_s \int \frac{d\vec{k}}{(2\pi)^3}\, Vg(k) +\sum_{jlm} \int_0^\infty \frac{dk}{\pi}\frac{d\delta_{jl}(k)}{dk} g(k)\,. \tag{22}$$

The second term on the right comes from the alteration of the density of states caused by the potential.[6] $\delta_{jl}(k)$ is a scattering phase shift. While the first term on the right is proportional to the number of electrons in the entire system, the second one is similar in magnitude to the number of atomic electrons, very much less but still significant. One circumstance where it can be ignored is in calculating the electron density inside the atomic sphere.

In devising this model of condensed matter, where a single atom is imbedded in an electron gas, we introduced the electron gas to simulate the effects of the surrounding atoms on a particular one. However, it is the properties of the atom—its energy, for example—which concern us. However, the mathematical expressions for these quantities include large contributions from the electron gas. In Eq. (22) this is evident in the term that is proportional to the volume of the entire system. We want to make a separation of expressions like (22) into parts associated with the atom and with the electron gas. There is no unique way of doing this. We are forced to experiment with different prescriptions which seem plausible, and we judge them by how well they work. These will be taken up next.

II. MODEL T (REFERENCE 5)

The governing idea in this precription is the removal from expressions like (22) of the uniform electron gas terms, that is, those proportional to the volume of the electron gas. Call the volume of the atom V_T. Then the number of electrons to be associated with the electron gas is

$$N_0=\sum_s \int \frac{d\vec{k}}{(2\pi)^3}\,(V-V_T)n_k \tag{23}$$

and the remainder,

$$N_T=\sum_b n_b+\sum_s \int \frac{d\vec{k}}{(2\pi)^3}\,V_T n_k +\sum_{jlm}\int_0^\infty \frac{dk}{\pi}\frac{d\delta_{jl}}{dk}n_k\,, \tag{24}$$

are taken as belonging with the atom. [In (21) and (22), n_i has been used for g_i, and then the desired separation has been made. The total number of electrons in the system, $N=N_0+N_T$, is given by (12)]. V_T is now *defined* so that the number of electrons associated with the atom is equal to the atomic number: $N_T=Z$. V_T is not the same as the volume of the atomic sphere whose radius is R. Usually, though, it is fairly close, particularly in circumstances of high compression or high temperature.

The kinetic energy is dealt with in a similar manner. The expression for it in Eq. (20) contains an integral whose integrand is zero outside the atomic sphere. Clearly it belongs with the atom. The other term involving a sum can be handled in exactly the same way as in the case of the number of electrons, N. The potential energy terms U and V are given by (7) and (8). They also belong wholly with the atom as such terms vanish for the uniform electron gas. The exchange energy term (9) must be split between the atom and the electron gas. We have chosen to take the part inside the atomic sphere as the exchange energy of the atom. The entropy S is handled like the number of electrons, N.

The model T prescriptions for the atomic quantities are thus

$$N_T=Z=\sum_b n_b+\sum_s \int \frac{d\vec{k}}{(2\pi)^3}\,V_T n_k +\sum_{jlm}\int_0^\infty \frac{dk}{\pi}\frac{d\delta_{jl}}{dk}n_k\,, \tag{25}$$

$$K_T=\sum_b n_b(\epsilon_b - v_\infty)+\sum_s \int \frac{d\vec{k}}{(2\pi)^3}\,V_T n_k(\epsilon_k - v_\infty) +\sum_{jlm}\int_0^\infty \frac{dk}{\pi}\frac{d\delta_{jl}}{dk}n_k(\epsilon_k - v_\infty) - \int_{r<R} \rho(r)[v(r)-v_\infty]\,d\vec{r}\,, \tag{26}$$

$$U_T=-\int_{r<R}\frac{Z}{r}\rho(r)\,d\vec{r}\,, \tag{27}$$

$$V_T = \frac{1}{2} \int\int_{r,r'<R} \frac{\rho(r)\rho(r')}{|\vec{r}-\vec{r}'|} d\vec{r}\, d\vec{r}', \tag{28}$$

$$W_T = -\frac{3}{4\pi} \int_{r<R} \rho(r)[3\pi^2\rho(r)]^{1/3} d\vec{r}, \tag{29}$$

and

$$S_T = -\sum_b [n_b \ln n_b + (1-n_b)\ln(1-n_b)]$$
$$-\sum_s \int \frac{d\vec{k}}{(2\pi)^3} V_T [n_k \ln n_k + (1-n_k)\ln(1-n_k)]$$
$$-\sum_{jlm} \int_0^\infty \frac{dk}{\pi} \frac{d\delta_{jl}}{dk} [n_k \ln n_k + (1-n_k)\ln(1-n_k)]. \tag{30}$$

In Model T the various contributions to the quantities above are not limited to the region inside the atomic sphere. All deviations of the system from a uniform electron gas are regarded as connected with the atom and are assigned to it, including tails of bound-state orbitals and the continuum terms proportional to the derivatives of the phase shifts.

III. MODEL A

The second prescription for separating the atom from the electron gas surrounding it is a division based on location. Most of the quantities of interest are expectation values of the form

$$f_i = \int \psi_i^*(\vec{r}) f \psi_i(\vec{r})\, d\vec{r}. \tag{31}$$

We arbitrarily take that portion of the integral within the sphere bounded by $r=R$ as the atomic part, and the part outside is discarded. The volume in Model A is the atomic sphere volume: $V_A = \frac{1}{3}4\pi R^3$. The number of electrons associated with the atom is the integral of the electron density inside the sphere:

$$N_A = \int_{r<R} \rho(r)\, d\vec{r}, \tag{32}$$

which by the constraint of Eq. (13) is equal to Z. Contributions from terms proportional to $d\delta_{jl}(k)/dk$ are of order V_A/V and can be dropped because integrals now are confined to the atomic sphere.

If $\rho(r)$ is written in terms of orbital functions for the bound and continuum one-electron states as in Eq. (3), the number of electrons inside the atomic sphere may be expressed as

$$N_A = \sum_b n_b \int_{r<R} |\psi_b|^2 d\vec{r} + \sum_{jlm} \int_0^\infty \frac{2k^2 dk}{\pi} n_k \int_{r<R} |\psi_{kjlm}|^2 d\vec{r} = \sum_b n_b X_b + \sum_{jlm} \int_0^\infty \frac{2k^2 dk}{\pi} n_k X_{kjl}. \tag{33}$$

The normalization of the continuum wave functions has been changed here to

$$\int \psi^*_{k'j'l'm'}(\vec{r}) \psi_{kjlm}(\vec{r})\, d\vec{r} = \frac{\pi}{2kk'} \delta(k-k') \delta_{j'j} \delta_{l'l} \delta_{m'm} \tag{34}$$

which means that the radial parts are, asymptotically, unit amplitude spherical Bessel functions. The various energy and entropy terms can be written down in a similar form:

$$K_A = \sum_b n_b(\epsilon_b - v_\infty) X_b + \sum_{jlm} \int_0^\infty \frac{2k^2 dk}{\pi} n_k (\epsilon_k - v_\infty) X_{kjl}$$
$$- \int_{r<R} \rho(r)[v(r) - v_\infty]\, d\vec{r}, \tag{35}$$

$$U_A = -\int_{r<R} \frac{Z}{r} \rho(r)\, d\vec{r}, \tag{36}$$

$$V_A = \frac{1}{2} \int\int_{r,r'<R} [\rho(r)\rho(r')/|\vec{r}-\vec{r}'|]\, d\vec{r}\, d\vec{r}', \tag{37}$$

$$W_A = -\frac{3}{4\pi} \int_{r<R} \rho(r)[3\pi^2\rho(r)]^{1/3} d\vec{r}, \tag{38}$$

$$S_A = -\sum_b [n_b \ln n_b + (1-n_b)\ln(1-n_b)] X_b - \sum_{jlm} \int_0^\infty \frac{2k^2 dk}{\pi} [n_k \ln n_k + (1-n_k)\ln(1-n_k)] X_{kjl}. \tag{39}$$

The use of the factors X_i in the entropy is somewhat arbitrary in that entropy is not a sum of expectation values of the form in Eq. (31).

Model T and Model A use the same charge density and potential function. They differ mainly in the way the continuum contributions to the energy and entropy associated with the atom are defined. The terms containing $d\delta_{jl}/dk$ in Model T come from a few extra states which are spread out over the entire volume V. These terms are omitted in Model A, but contributions within the atomic sphere are larger or smaller in proportion to the squares of the orbital functions in that region. Despite these differences the two models are very similar in the results they give.

IV. PRESSURE FORMULA

For equation-of-state purposes, which have mainly concerned us in these spherical models of condensed matter, the pressure is the most interesting of the thermodynamic quantities. Models T and A enable us to compute free energies, and by means of numerical differentiation the pressures can be obtained. An alternative procedure is to turn to the virial theorem, and, in particular, that form of it that expresses the pressure as a surface integral over the atomic cell.[7,8] The pressure formula appropriate to the Dirac equation and a self-consistent-field local density potential function is

$$3PV_A = \sum_i n_i \int \frac{1}{2}[\psi_i^* c\vec{\alpha}(\vec{r}\cdot\vec{p}\psi) + \mathrm{c.c.}]\cdot d\vec{S} + \int_{r=R} \frac{\rho^2 d\epsilon_{xc}}{d\rho}\vec{r}\cdot d\vec{S}. \qquad (40)$$

The use of this expression for the pressure involves much the same sort of ambiguities that were encountered in the prescriptions of Models T and A. It is properly applied to the surface of a system on which the boundary conditions are specified and inside of which wave functions are normalized. We are applying it to an arbitrarily chosen part of a much larger system. If, as we expect, the atomic sphere to which we apply the pressure formula is a close approximation to the Wigner-Seitz cell of a periodic solid its use is justified, and it will give pressures that are close to those obtained from band-structure calculations.

Pettifor[9] has used the same pressure formula in a spherical model with considerable success. His model is based on Anderson's[10] atomic sphere approximation and is closer to a conventional band-structure calculation. The application of the pressure formula in such circumstances should not involve the same uncertainties which affect our model.

V. SOME RESULTS

A computer program has been developed on the basis of the theory outlined in Secs. I–IV. It is an outgrowth of an earlier relativistic self-consistent-field program for atoms.[11] In most cases it functions smoothly, taking about three to ten times as much computational time as an atomic SCF calculation and being 50 or 100 times faster than a highly developed Korringa-Kohn-Rostaker (KKR) program.[12] The program has been used over a very wide range of material compressions and temperatures.

A variety of data is readily obtained. Phase shifts for elastic scattering are generated for use in Model T and have a number of well-known applications, such as in transport coefficient calculations. Wave functions, both bound and free, can be obtained. The self-consistent-field charge density can be used for band-structure calculations.

Up to now we have mostly been interested in equation-of-state information which can be obtained from the calculations and, in particular, in the density region for solids where the pressure is close to zero. Calculations based on the TFD model are known to be poor here. Recently it has become evident that for simple metals the self-consistent-field band-structure method is remarkably good.[13] It can be expected that the model we have developed here will lie somewhere in between—we hope closer to the band-structure calculations than their TFD counterparts.

To get an idea of the worth of these calculations in the low-pressure region and to learn something about the merits of the three prescriptions described above, a series of calculations have been done for the $5d$ transition metals and some other elements in the same row of the Periodic Table. Results from these calculations, from the TFD model, and experimental data are shown in Figs. 2–4.

In Fig. 2 the calculated pressure for each element at normal solid density is given. The experimental pressure is, of course, zero. For most of the elements, the TFD pressure is from 1 to 6 Mbars. Model A pressures are mostly around 100 kbars, which is a substantial improvement. Model T does not give solutions for atomic volumes V_T as large as the actual ones in most cases. [In some earlier calculations[5] reasonable values of the atomic volume were obtained with Model T. At that time the Lagrange parameter ν was chosen to be that defined by Eq. (18b). It seems likely now that Eq. (18a) is the correct one.] It may be noted that the shape of the curve of TFD pressures in Fig. 2 is a reflection of the *experimental* atomic volumes used in the calculations and is not a shell effect in the computed electron density distributions.

Another test of the calculations is a comparison of bulk moduli at normal solid densities.[14] These are shown in Fig. 3. Again Model T results cannot be shown as solutions were not found at these atomic volumes for most elements. The TFD bulk moduli are also not shown as many of them are too large to fit on the graph. Most are greater than 10 Mbars. Both Model A and the

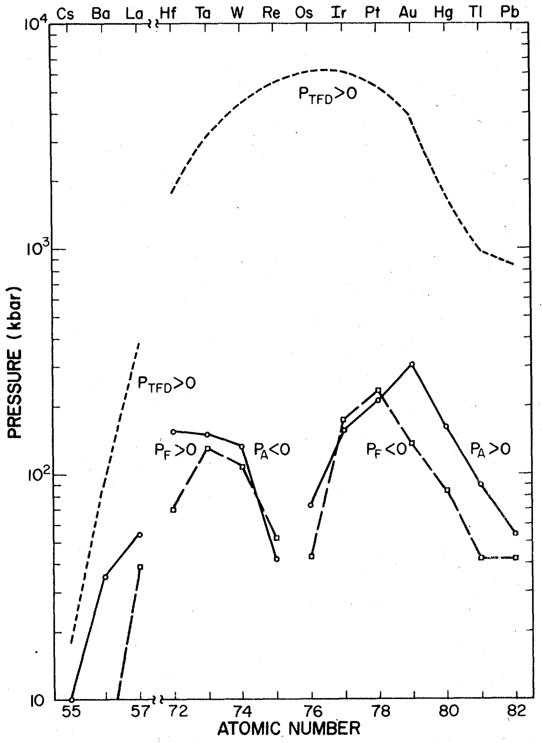

FIG. 2. Pressures calculated for cell volumes corresponding to the actual volume where the pressure is zero. The calculated pressures are a measure of the errors in the various methods. Absolute values of the pressure are plotted and their signs are indicated. P_A is the Model A pressure, P_F is from the pressure formula, and P_{TFD} is the Thomas-Fermi-Dirac pressure.

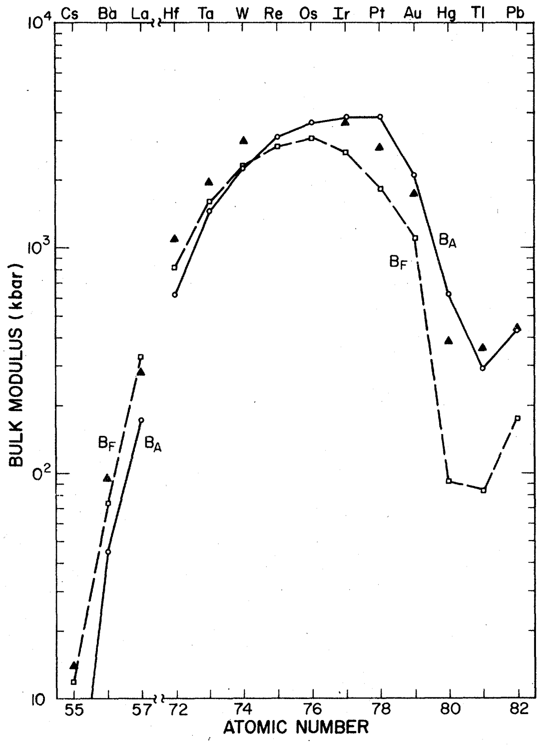

FIG. 3. Computed bulk moduli at normal density and experimental values from the article by Birch (see Ref. 12). No values are quoted for rhenium and osmium. Experimental values are shown with triangles (▲). B_A and B_F are Model A and pressure formula results, respectively.

pressure formula give bulk moduli in fair agreement with the experimental values, but some discrepancies of a factor of 2 or more do exist.

Another way of viewing the calculations for the same series of elements in the solid state is to compare atomic cell sizes at zero pressure. In Fig. 4, the three prescriptions for the zero-pressure cell radii are given together with the experimental values. The calculations follow very well the trend of the observed cell sizes which shows a minimum near where the 5*d* shell is half filled. The TFD model radii are almost constant at about 4.7 a.u. The Model T radii are consistently small, but are not unreasonable. Model A fails to show cohesion for three elements. The pressure formula seems to do best overall. Most of the calculated radii differ from the correct ones by a few percent which is fairly good agreement, but the band-structure results of Moruzzi, *et al.*[13] are distinctly better.

It is hoped that the model developed in this paper will be useful for calculating equations of state of compressed solids. As pressures get higher, experimental data becomes scarcer and less accurate, and eventually must be supplemented with calculated results. At present, the usual procedure is to use the TFD model for the extreme high-pressure region. Experimental data are used for low pressures, and the two regions are joined together by an interpolation. With a better theoretical model, the high-pressure equation of state can be improved and the task of interpolating made easier.

Two elements for which our model works very well are copper and zinc. In Fig. 5 the zero-temperature isotherms based on shock wave data[15] are shown together with the pressures calculated using Model A. Above about 2 Mbars the calculations are within estimated experimental errors.[15] Experimental data does not exist for pressures higher than those shown in the graph, but we have carried our calculations to the neighborhood of 100 Mbars and could easily have gone much higher. The pressures computed from our other two prescriptions are in poorer agreement with experiment and are omitted to avoid cluttering the graph. The TFD pressures are very much too

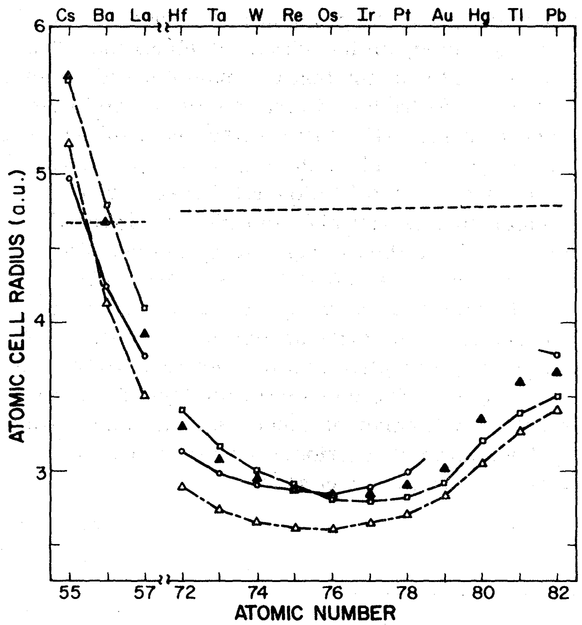

FIG. 4. Cell radii at which computed and experimental pressures are zero. Triangles (▲) are experimental values; open triangles (△) correspond to Model T; circles (○) to Model A; and squares (□) to the pressure formula. The TFD radii are represented by a dashed line. Gold, mercury, and thulium did not bind according to Model A prescriptions.

high and cannot conveniently be shown on the graph.

There are less favorable cases also. Nickel is an example—see Fig. 6. The error in the calculated density grows from 0.5% to 6% at 7 Mbars. The quoted[15] experimental error is 3.5%. Probably the main source of error in the calculations is the assumption that the medium in which the compressed atom is imbedded is a simple electron gas. Also we have made no allowance for magnetic effects.[16] Despite these shortcomings our calculations should still be preferred to those based on the TFD model.

We conclude that we have a useful model for equation-of-state calculations—much better than the old Thomas-Fermi-Dirac method but falling somewhat short of the best self-consistent-field band-structure calculations. However, it is more flexible in use and more economical, and perhaps it can be further improved.

ACKNOWLEDGMENT

I have had helpful discussions with several of my colleagues in the Los Alamos Scientific Laboratory. The collaboration of Bard Bennett in many aspects of this work has been of particular value.

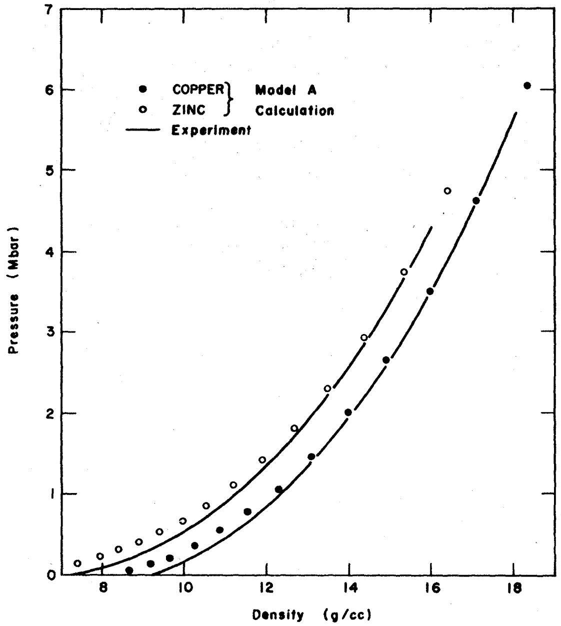

FIG. 5. Zero-temperature equations of state of copper and zinc. The lines are experimental data as reduced to zero temperature by Al'tschuler *et al.* (Ref. 13). The circles (● and ○) are the results of Model A calculations.

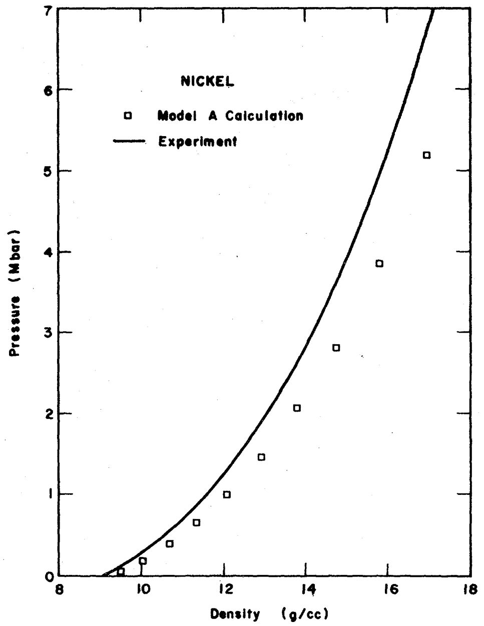

FIG. 6. Zero-temperature equation of state of nickel. The line is based on experimental data as reduced to zero temperature by Al'tschuler *et al.* (Ref. 13). The boxes (□) are the results of Model A calculations.

APPENDIX

A matter of concern in using the local density approximation for exchange is that eigenvalues of the one-electron equations are not good representations of the electron binding energies. For example, in neutral argon the magnitude of the eigenvalue of a $3p$ electron is 0.33 hartree while the measured binding energy is 0.58 hartree. It is usual for the magnitude of the eigenvalue corresponding to a particular electron in an atom or ion to be less than the actual binding energy, as in this case. This seems to indicate that a model such as ours based on local density SCF calculations will systematically predict ionization at a lower temperature than it should, but this is not quite the case. Suppose that the temperature is high enough for half the atoms in a gas to lose an electron. In an "average atom" model this is represented by an ion with $Z-\frac{1}{2}$ electrons. It is then found for argon that the magnitude of the eigenvalue is 0.54 hartree which is quite close to the correct value. (If a local density correlation energy had been included, the eigenvalue probably would have been still closer.) Finally, when the temperature is just high enough to remove one electron from the average atom, the magnitude of the eigenvalue is 0.76 hartree. What happens in this calculational model is that ionization of a particular level starts at too low a temperature and is only complete at a temperature higher than it should be. The 50% ionization level for a given electron will occur at about the right temperature.

The matter of fractional occupation has been discussed by Slater *et al.*[17]

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