$\Delta z = z' - z$ from Table II. (Note that z and z' are actually calculated from different self-consistent charge densities.) The first term gives $\delta V(r) = 0.0619$ Ry. The second term is small because the sign of $\rho(\vec{G})$ and $\cos Gr$ is different for different G's and in fact the sign of the second term is positive when the old charge density is used and negative when the new charge density is used. Because from this estimate δV is positive, we expect the one-electron energies of the new calculation to be higher than those of the old calculation as Table I confirms.

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Lattice Spacings and Compressibilities vs Pauling Radii and Valencies

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The lattice spacings and compressibilities of the nontransition-elemental solids are calculated using Ashcroft pseudopotentials to describe the cores and the von Weizsacker method to describe the valence electrons. The observed correlations of these quantities with the Pauling radii and the valencies are thereby obtained.

I. INTRODUCTION

The success of the pseudopotential method in the theory of metals is now established[1,2] and it would appear to be an appropriate time to investigate whether the method might be adapted to other systems. We have in mind, in particular, applications to molecular chemistry, a suggestion which has also been made by Harrison.[3] The aspect of the standard pseudopotential technique for metals which cannot be taken over into other problems is the method of linear dielectric screening by the valence electrons, which depends on there being a zeroth-order description in terms of plane waves.

In an earlier paper[4] it was suggested that a Thomas-Fermi (TF) type of description of the valence electrons might be a suitable alternative. Indeed, conversely, the pseudopotential description might be regarded as offering further scope for the extension of TF-like methods which often experience difficulties in the very regions, the cores, which are eliminated on using pseudopotentials.

It is well-known, however, that the TF method alone cannot produce a stable lattice. For this reason, we now generalize the previous work and show that a generalized TF method, namely, the Thomas-Fermi-Dirac-von Weizsacker (TFDW) description will give accurate interatomic spacings and compressibilities. In fact, it is probably fair to say that the average accuracy achieved is higher than in any other calculation of pseudopotential type.[3–7]

II. GENERAL THEORY

In this work we will be interested in describing the total energy E of the system as a functional of the particle density $n(\vec{r})$, the fundamental status of this viewpoint having been discussed by Kohn and coworkers.[8,9] Let us write

$$E = \int f(n)\, d\tau - \tfrac{1}{2} e \int n V_e\, d\tau + U_{ii} \quad , \tag{2.1}$$

where $e = |e|$ is the size of the electronic charge,

$$V_e = -e \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d\tau' \tag{2.2}$$

is the electrostatic potential resulting from the electron distribution, and U_{ii} represents the Coulombic ion-ion contribution. Specific forms will be taken for f later. The Euler equation for (2.1) reads

$$\frac{\delta f}{\delta n} - e(V_e - V_0) = 0 \quad , \tag{2.3}$$

where V_0 is a Lagrange multiplier arising from

the normalization requirement

$$\int n\,d\tau = N \quad , \tag{2.4}$$

where N is the total number of particles.

Equation (2.3) is derived, in the usual way, for variations in $n(\vec{r})$ but for fixed boundaries. Now, however, let us change the volume of the solid from Ω to $\Omega + \delta\Omega$. Then the corresponding change in E is

$$\delta E = [f(n) - \tfrac{1}{2} e n V_e]_b + \int \left\{ \frac{\delta f}{\delta n} - e V_e \right\} \delta n\, d\tau + \delta U_{ii} \quad , \tag{2.5}$$

where the suffix b denotes evaluation at the boundary (which in the spherical approximation we will use later is the surface of each Wigner-Seitz sphere).

This equation can be simplified on using (2.4) to write

$$\delta \int n\, d\tau = \int \delta n\, d\tau + [n]_b\, \delta\Omega = 0 \tag{2.6}$$

and noting from (2.3) that $(\delta f/\delta n) - eV_e$ is a constant. In this way, we obtain a pressure

$$p = -\frac{dE}{d\Omega} = \left[n \frac{\delta f}{\delta n} - f \right]_b , \tag{2.7}$$

the ion-ion contribution cancelling against an electron-electron electrostatic term by a theorem due to Feynman.[10]

We now take the special case

$$f = c_k n^{5/3} + \frac{c_w}{4} \frac{(\nabla n)^2}{n} - c_e n^{4/3} - e n V_N \quad , \tag{2.8}$$

where $c_k = \frac{3}{10}(3\pi^2)^{2/3}\hbar^2/m$, $c_w = \hbar^2/2m$, and $c_e = \frac{3}{4}(3/\pi)^{1/3} e^2$. The terms represent, respectively, the usual TF term, the von Weizsacker inhomogeneity contribution, the Dirac exchange energy density, and the electron-ion contribution. The basic features of these terms have been known for a long time (see, for example, March[11]) but two new developments, on which we rely, should be mentioned.

First, we will choose V_N to be a pseudopotential and, specifically, we choose the empty core form[1,2,12]

$$V_N = \sum_{\vec{R}} v_N(\vec{r} - \vec{R}) \quad , \quad v_N(r) = \begin{cases} 0, & r < r_c \\ \dfrac{ze}{r}, & r > r_c \end{cases} \tag{2.9}$$

where r_c is an ionic radius. [Note that in (2.9), as in (2.2), we follow the usual practice in statistical theories by using electrostatic potentials. The definition is thus minus the usual electron-ion form used in pseudopotential theory.]

Second, the role of the von Weizsacker term has recently been clarified. For slowly varying perturbations, there is a leading order correction to the TF term which is of von Weizsacker form but with only one-ninth the original coefficient.[13] However, for rapid (though still small-amplitude) variations,[14] the leading order correction is precisely the original von Weizsacker term. In fact, direct calculation[15] shows that the two formulations become asymptotically exact for weakly perturbed systems at long and short wavelengths, respectively, and the only appropriate coefficient for the present problem (where the higher reciprocal-lattice vectors play an important role in inverse space) is the original one.

Proceeding, therefore, with (2.8), one can rewrite (2.3) as

$$\tfrac{5}{3} c_k n^{2/3} - c_w (\nabla^2 n^{1/2}/n^{1/2}) - \tfrac{4}{3} c_e n^{1/3} - ev = 0 \quad , \tag{2.10}$$

where $v = V_N + V_e - V_0$ and satisfies the Poisson equation

$$\nabla^2 v = 4\pi n e . \tag{2.11}$$

These coupled equations are to be solved subject to the conditions that the only discontinuities in v and ∇v are at the ionic radii, where they are the same as those of (2.9), and that ∇n and ∇v vanish at the ionic centers $\vec{R}$ and at the boundary.

Similarly, (2.7) and (2.8) give

$$p = [\tfrac{2}{3} c_k n^{5/3} - \tfrac{1}{2} c_w \nabla^2 n - \tfrac{1}{3} c_e n^{4/3}]_b \quad , \tag{2.12}$$

which on using (2.10) simplifies to

$$p = [env - c_k n^{5/3} + c_e n^{4/3}]_b \quad . \tag{2.13}$$

Technically this is an important result since it enables us to reduce the number of adjustable parameters at our disposal at the beginning of the calculation [see after (3.4) below].

III. NUMERICAL PROCEDURE

We know confine ourselves to one Wigner-Seitz cell and replace it by a sphere of equal volume; let the radius of the latter at pressure p be r_p. Then (2.10) yields

$$-\frac{c_w}{r} \frac{d^2}{dr^2} (rn^{1/2}) + \tfrac{5}{3} c_k n^{7/6} - \tfrac{4}{3} c_e n^{5/6} - evn^{1/2} = 0 \quad , \tag{3.1}$$

an effective Schrödinger equation for $n^{1/2}$ (Ref. 16), and (2.11) becomes

$$\frac{1}{r} \frac{d^2}{dr^2} (rv) = 4\pi n e \quad . \tag{3.2}$$

The boundary conditions now take the form

$$\begin{aligned} &v(r_c + 0) - v(r_c - 0) = ze/r_c \quad , \\ &v'(r_c + 0) - v'(r_c - 0) = -ze/r_c^2 \quad , \\ &n'(0) = v'(0) = 0 \quad , \\ &n'(r_p) = v'(r_p) = 0, \end{aligned} \tag{3.3}$$

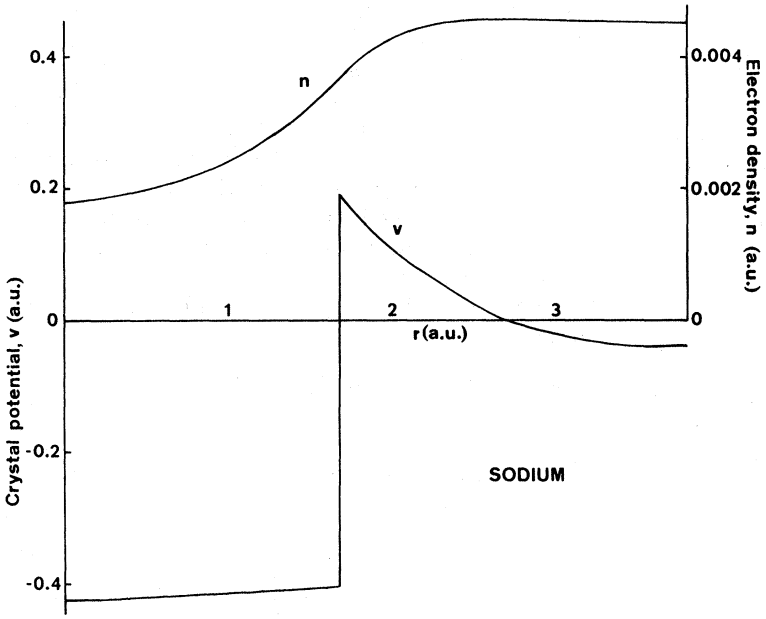

FIG. 1. Crystal potential and valence electron density for pressure $p=0$, valence $z=1$, and core radius $r_c=1.67$ a.u. This corresponds to the Ashcroft (Ref. 12) characterization of Na. The crystal potential is very close to that obtained by the TF method (Fig. 3 of Ref. 4) though, of course, there the cell radius was assumed to be given, whereas here it is predicted (to be 3.8 a.u.) by the calculation. Subsequently, for the sake of uniformity, we will characterize each element by its Pauling radius. In the case of Na, this is 1.79 a.u. The difference between the Ashcroft and Pauling radii matters very little to graphical accuracy as Figs. 4 and 5 show.

while (2.13) shows the pressure to be

$$p=n(r_p)[ev(r_p)-c_k n^{2/3}(r_p)+c_e n^{1/3}(r_p)] \quad . \quad (3.4)$$

For a specified core radius r_c, valency z, and pressure p, the procedure was as follows. First, some arbitrary trial value of r_0 is taken. Then, for a guessed $n(r_p)$, the corresponding $v(r_p)$ is given by (3.4). With these values and the knowledge [see (3.3)] that $n'(r_p)$ and $v'(r_p)$ are zero, (3.1) and (3.2) are integrated inwards until the origin is reached. In general, $n'(0)$ and $v'(0)$ will be nonzero [contrary to (3.3)] but by adjusting the guessed $n(r)_0$ appropriately one of these quantities, say $n'(0)$, can be made to vanish. Then the trial r_p is varied and the process repeated until not only $n'(0)$ but also $v'(0)$ is zero. The problem for given r_c, z, and p is thus solved and a typical solution is shown in Fig. 1.

IV. RESULTS AND COMPARISON WITH EXPERIMENT

For given r_c and z, the lattice parameter can be calculated as a function of pressure. Results ob-

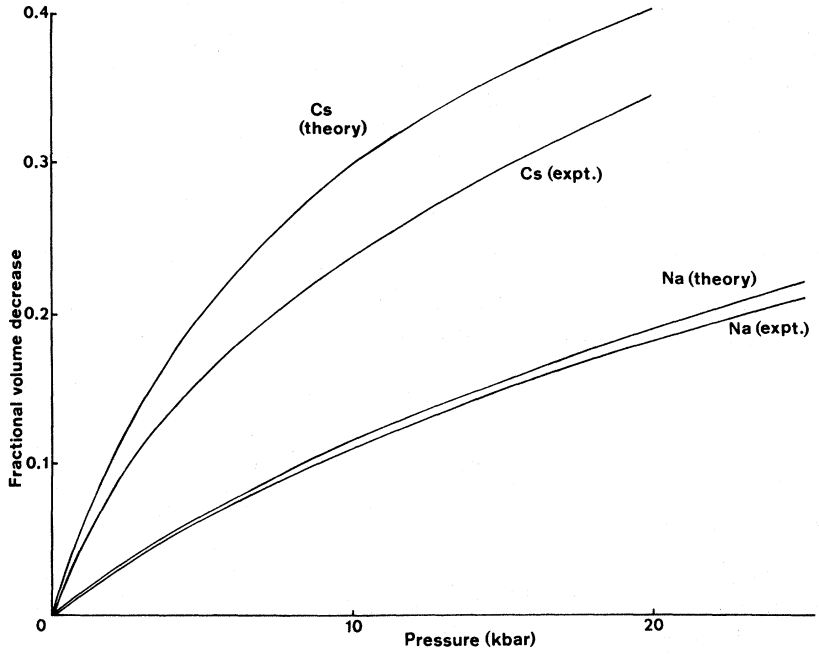

FIG. 2. Pressure-volume curves for cases with Pauling radii appropriate to Na and Cs. The experimental data are due to Bridgman (Ref. 17). The initial slopes lead to the bulk moduli (Figs. 3 and 5). The absolute theoretical specific volumes agree with the corresponding experimental data, as Fig. 4 testifies.

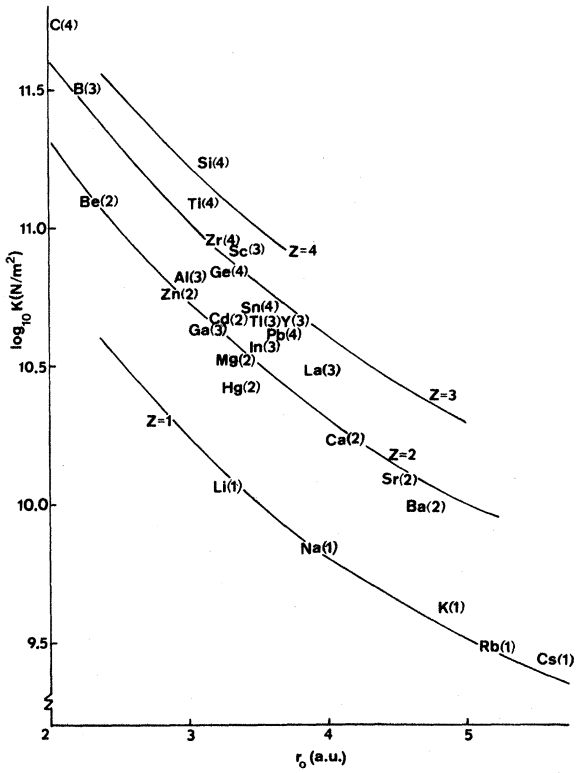

FIG. 3. Bulk moduli K versus Wigner-Seitz radii r_0. The curves are computed in our final TFDW approximation and are valence dependent. The experimental points are designated by the appropriate chemical symbols, the valencies being given in parentheses.

tained in this way are shown in Fig. 2. The bulk moduli, $K = -\Omega dp/d\Omega$, are given by the initial slopes of such curves and thus we may eliminate the auxiliary parameter r_c and plot K vs r_0, the Wigner-Seitz sphere radius at zero pressure. The results are shown in Fig. 3 along with the experimental data.

A plot of the latter, of course, indicates the extent of what we can ever hope to achieve by a two-parameter (r_c and z) model. The alkalis lie on a smooth curve which is well described by the theory. (The noble metals, incidentally, are not plotted and do not lie on the curve; the reason for this, d banding, is understood.[1-3] The divalents also yield a well-defined line and our theory reproduces this quite well. There is quite a lot of scatter on the points for the elements of higher valency. The theory produces average curves which are less satisfactory than for the lower-valency cases but the definite trend is observed, both experimentally and theoretically, of decreased compressibility as the valency is increased.

While they are not directly observed, the intermediate parameters r_c are of considerable interest. In pseudopotential perturbation theory these are found by fitting experimental results, and tables of such values are available.[1,2] It seems[12] that a good value obtained in this way correlates well with the Pauling radius.[18] Thus, since we consider some elements for which r_c's are not otherwise available, we will uniformly identity r_c with the Pauling radius in every case. In this way (Figs. 4 and 5) we may compare our $r_0(r_c)$ and $K(r_c)$ curves with experiment.

The first thing to note about Fig. 4 is that the theoretical r_0-vs-r_c relationship turns out to be valence independent and linear over the physical range. This is in contrast with the TFD results (with von Weizsacker term omitted) which were also calculated. The experimental results support the idea of a valence-independent line and the theoretical result we obtain is almost as good as any that could be drawn through the experimental data. Because of the simplicity of this relationship, Fig. 5 is a recognizable distortion of Fig. 3

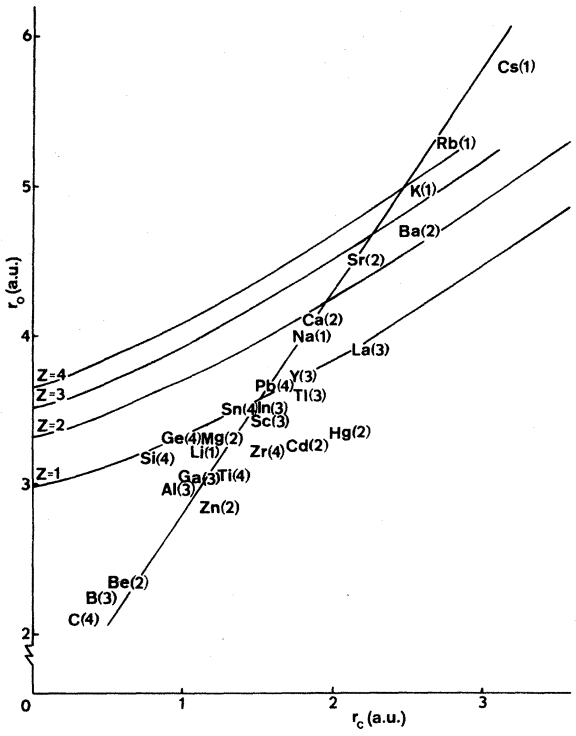

FIG. 4. Wigner-Seitz radii r_0 vs Pauling radii r_c. The TFD curves are valence (z) dependent and do not correspond to experiment. The single TFDW curve is valence independent and provides a good average description of experiment. The experimental points are designated by the appropriate chemical symbols, the valencies being given in parentheses.

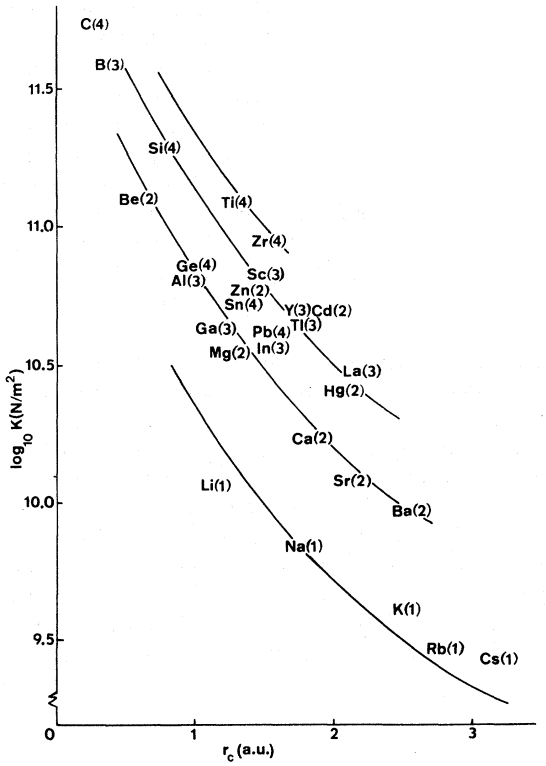

FIG. 5. Bulk moduli K vs Pauling radii r_c. The curves are computed in TFDW approximation and the experimental points are designated by the appropriate chemical symbols, the valencies being given in parentheses.

and about the same degree of success is obtained when comparison is made with the experiment.

It will be noted that some elements, which appear to be quite normal from Fig. 3, present difficulties on the basis of Figs. 4 and 5. In fact, to assign core values consistent with those employed in standard pseudopotential perturbation theory would improve the situation in some cases and worsen it in others. In other words, the results displayed perhaps typify the kind of overall agreement we can expect, from the present model, on the basis of any one method of allocating core radii.

V. CONCLUSIONS

The present method is able to account for the main features of the observed pressure-volume relationship of the elemental solids having valencies between one and four. It also seems possible that if the more obvious improvements were made (the use of more sophisticated pseudopotentials and the elimination of the sphere approximation) the present results would be improved and other elements could also be described.

Though the results, taken as a whole, are at least as good as any yet obtained from first principles, it is the particular technique of combining the pseudopotential concept with a TF-like description of the valence electrons to which we attach importance. For the latter type of technique is useful in problems (for example, molecules) where the more usual linear dielectric screening method is not available. Applications in such areas would now appear to be desirable and potentially fruitful.

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