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Kohn-Sham Self-Consistent Calculation of the Structure of Metallic Sodium[†]

B. Y. Tong
Department of Physics, University of Western Ontario, London, Ontario 72

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The equilibrium lattice parameter, the compressibility, and the cohesive energy of metallic sodium at 0 °K are calculated *a priori* by the local-effective-potential approximation of the Kohn-Sham scheme, in which all electron wave functions are brought into self-consistency. The results are in reasonably good agreement with the measured values.

I. INTRODUCTION

The local-effective-potential approximation of the Kohn-Sham self-consistent scheme[1–3] is used to calculate the cohesive energy, the equilibrium lattice parameter, and the compressibility of metallic sodium. A preliminary report of our work was published elsewhere.[4] Since that time many self-consistent calculations on band structures have been reported.[5–11] In the preliminary report,[4] a parameter r_a was introduced to facilitate the attainment of self-consistency. The parameter r_a was chosen arbitrarily to be slightly smaller than the equilibrium value r_s^0. A full self-consistent calculation was carried out at r_a including all the core electrons. In all other values of $r_s > r_a$, the core wave functions were fixed to be the same as those at r_a, and only the valence-electron wave function was allowed to vary until self-consistency was attained. This was in a similar spirit to most self-consistent calculations[7–10] in which the core wave functions are taken to be the atomic-core wave functions. It should be better because r_a was close to the equilibrium lattice parameter r_s^0. In this previous work, only four points were calculated to give the energy vs r_s curve. It was not quite sufficient to produce accurate second derivatives which give us the compressiblity. Even so, the calculated quantities were in reasonably good agreement with experimental values. This is in contrast to the statement made by Liberman on the Kohn-Sham exchange applied to the band-structure calculation for lithium.[12]

In the present work, the calculation has been repeated with greater accuracy on a CDC 6600 computer. Each r_s calculation is carried out in full self-consistency with all the electrons. The extra parameter r_a is not introduced. Ten points on the energy vs r_s curve are obtained. The small differences of the results reported here from those in the preliminary report are mainly due to the accuracy in the self-consistency and in the interpolation differentiation.

The equilibrium lattice parameter, cohesive energy, and compressibility of metals can be studied using the model of a uniformly interacting electron gas. Good values have been obtained from such calculations, for example, those by Raich and Good[13] and by Cutler.[14] One undesirable feature of such a model is the introduction of extra parameters to take care of the core electrons. The more fundamental approach is, of course, to calculate the band structure in full. The first successful attempt from this approach to estimate the metallic binding was made by Wigner and Seitz.[15, 16] They used an effective potential fitted to spectroscopic data for sodium by Prokofjew.[17] Bardeen[18] repeated the calculation using the $\vec{k}\cdot\vec{p}$ perturbation method and obtained values in good agreement with the measured ones. Since then many authors repeated the calculation using information obtained from measured quantities, e.g., Kuhn and Van Vleck,[19] the quantum-defect method by Ham and Segall[20, 21] and Brooks and Ham,[22–24] and pseudopotential theory.[25] Recently many first-principle calculations of compressibility and other related quantities using fixed atomic-core wave functions have been reported, e.g., the augmented-plane-wave (APW) calculation of lithium by Rudge,[26] of aluminum by Ross and Johnson,[9] and the orthogonalized-plane-wave (OPW) calculation of aluminum by Scofield.[10] Here we have carried out an *a priori* calculation for sodium in which the only parameter input to the full self-consistent computation is the total number of electrons per ion: $Z = 11$.

II. METHOD

We shall not describe the Kohn-Sham scheme in detail, since it has been adequately reviewed elsewhere,[4, 27] nor discuss the so-called Kohn-Sham-Gaspar[28] exchange potential which has been studied by many authors.[29–35]

As suggested by Wigner and Seitz,[15] we divide the metallic sodium into cells and use their spherical approximation. This assumes that to a first approximation the energy of a sodium atom in the metal depends only on the atomic volume, and not on the coordination number. This is supported by the experimental fact that energy remains practically unchanged in the Martensitic phase transformation of sodium from body-centered-cubic to the hexagonal-close-packed structure,[36] and the validity of the Vegard's rule in alloying metals.[37] Theoretical study on sodium by Hughes and Callaway,[38] taking into consideration the small change in such transition, found that within the accuracy of the calculation, the Fermi energy and effective mass are the same in the two structures. The cells are neutral because the ground state of a many-electron system does not allow an excess accumulation of charges in a particular cell.

The Kohn-Sham self-consistent scheme can be summarized by the following equations (in a.u.). Taking the nucleus at the center of the Wigner sphere, the energy functional is given by

$$E[n]=T_s[n]-\int\frac{Zn(\vec{r})}{r}\,d\vec{r}+\frac{1}{2}\iint\frac{n(\vec{r}\,')n(\vec{r})}{|\vec{r}\,'-\vec{r}|}\,d\vec{r}\,'\,d\vec{r}+E_{xc}[n]\,, \tag{1}$$

where E is now the total energy of all the electrons in a single cell, and $Z=11$ for sodium. $E_{xc}[n]$ is the exchange and correlation energy functional of the interacting electron gas. In the local-effective-potential approximation, it is given by

$$E_{xc}[n]=\int\epsilon_{xc}(n(\vec{r}))\,n(\vec{r})\,d\vec{r}\,, \tag{2}$$

where $\epsilon_{xc}(n(\vec{r}))$ is the exchange and correlation energy per electron of a uniform electron gas of density n. All integrations in Eqs. (1) and (2) are limited to the cell. $T_s[n]$ is the single-particle kinetic-energy functional of the homogeneous electron gas in an effective potential v_{eff}, satisfying the Schrödinger equation

$$[-\tfrac{1}{2}\nabla^2+v_{eff}(\vec{r})]\psi_i=\epsilon_i\psi_i\,,\quad i=\text{set}\{\alpha,k\} \tag{3}$$

under the appropriate boundary conditions. As emphasized before,[1-3] the nature of the single-particle equation (3) is somewhat different from the conventional Hartree-Fock picture. Here we also speak of the "core" electrons (indexed by α) and the "valence" electron (indexed by k), but always in the sense defined by the eigenvalues and eigenfunctions of Eq. (3). The values of these quantities are close enough to the conventional Hartree-Fock values that we can identify them by the conventional terminology. The effective potential in Eq. (3) is given by

$$v_{eff}(\vec{r})=-\frac{Z}{r}+\int\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,'+\mu_{xc}(n(\vec{r}))\,, \tag{4}$$

where

$$\mu_{xc}(n(\vec{r}))=\frac{d}{dn}(n\epsilon_{xc})$$

is the exchange and correlation parts of the chemical potential of a uniform gas at density n. From our knowledge of a homogeneous, interacting electron gas, we can split μ_{xc} into the exchange and correlation parts:

$$\mu_{xc}(n)=\mu_x(n)+\mu_c(n)\,, \tag{5}$$

where

$$\mu_x(n)=-(3n/\pi)^{1/3}\,, \tag{6}$$

and $\mu_c(n)$ is obtained from an interpolation between the low-density Wigner correlation formula and the high-density expression of Gell-Mann and Brueckner.[39] The interpolation curve for μ_c as a function of density n and a detailed discussion on this is given in Fig. 1 of Ref. 3, and in Ref. 40.

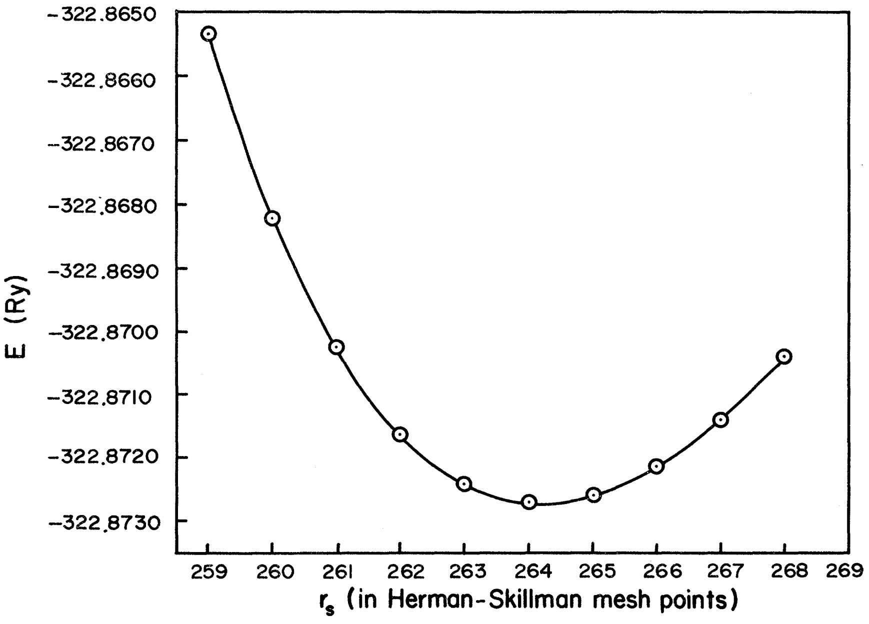

FIG. 1. Total energy E as a function of r_s, the radius of the Wigner-Seitz cell. The units of r_s are expressed in terms of Herman-Skillman mesh points: $259=3.654\,454\,4a_B$, and each step increases by $0.063\,694\,195a_B$. The minimum of E is at $r_s^0=3.982a_B$, which is equivalent to a lattice constant of 4.28 Å.

TABLE I. Equilibrium lattice constant, compressibility, and cohesive energy of metallic sodium at 0 °K.

	Author	Lattice constant (Å)	Compressibility (10^{-12} cm^2/dyn)	Cohesive energy (kcal/mole)
1	Experiment	4.225[a] (at $T = 5$ °K)	11.7[b]	26.0
		4.22[c]	13.8[d]	
2	Kohn-Sham scheme (present calculation)	4.28	10.3	(32.0)
3	Kohn-Sham scheme with free-ion core (Ref. 4)	4.11	11.5	(32.2)
4	Wigner and Seitz[e]	4.75	...	23.2
5	Fuchs[f]		11.4	
6	Bardeen[g]	4.53	12.1	23.0
7	Kuhn and Van Vleck[h]	4.14	13.0	25.9
8	Brooks[i]	4.26	16.2 (at $T = 2.93$ °K)	26.3

[a] Quoted by C. S. Barret, Acta Cryst. 9, 671 (1956).

[b] Quoted by K. Fuchs, Proc. Roy. Soc. (London) A157, 444 (1936).

[c] C. A. Swenson, Phys. Rev. 99, 423 (1955).

[d] From Eq. (5) of R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids 18, 329 (1961).

[e] E. Wigner and F. Seitz, Phys. Rev. 46, 509 (1934).

[f] K. Fuchs, Proc. Roy. Soc. (London) A157, 444 (1936).

[g] J. Bardeen, J. Chem. Phys. 6, 367 (1938).

[h] T. S. Kahn and J. H. Van Vleck, Phys. Rev. 79, 382 (1950).

[i] H. Brooks, Phys. Rev. 91, 1027 (1953).

The solutions of Eq. (3) give us the new total electron density $n(\vec{r})$, i.e., sum of the core and valence densities represented by $n_c(\vec{r})$ and $n_v(\vec{r})$, respectively:

$$n(\vec{r}) = n_c(\vec{r}) + n_v(\vec{r}) , \tag{7}$$

$$n_c(\vec{r}) = \sum_\alpha |\psi_\alpha(\vec{r})|^2 , \tag{8}$$

$$n_v(\vec{r}) = \sum_{\vec{k}} |\psi_k(\vec{r})|^2 . \tag{9}$$

Here α runs over all the core levels, and n_v is the valence density obtained by summing over all the $\vec{k}$ values below the Fermi surface. The new density $n(\vec{r})$ obtained is used to construct a new effective potential for the second cycle of the self-consistent calculation. This continues until the total energy E [Eq. (1)] has reached the accuracy we want.

For the valence electron, the solution of Eq. (3) is found by solving the periodic-boundary-value problem using a variational method of Kohn.[41] Details of this method are described in the Appendix. In this method, the electron wave function ψ_k of a general wave vector $\vec{k}$ is expanded in terms of spherical harmonics. The coefficients are determined from a secular equation obtained from a variational principle. Summing over all the $\vec{k}$ points in the Fermi sea, we obtain the valence-electron density $n_v(\vec{r})$ [Eq. (A11)].

The boundary condition for the core electrons is $\psi_\alpha(\vec{r})|_{r=r_s} = 0$, for all α. This is consistent with the observation that the core wave functions die down long before they see the Wigner-Seitz cell boundary. It has been commented before[4] that this boundary condition does not give rise to essential errors in the values of E, but it may imply a more "rigid" core, leading to a smaller compressibility. It is not clear whether this is in fact one of the contributing factors to the present estimate in compressibility which is a little too small (see the results below).

For each Wigner-Seitz cell of radius r_s, we evaluate a value for E. Values of E for ten values of r_s near the equilibrium lattice r_s^0 are calculated. The equilibrium lattice parameter r_s^0 is obtained from the condition

$$\left.\frac{\partial E}{\partial r_s}\right|_{r_s = r_s^0} = 0 , \tag{10}$$

and the compressibility β is given by

$$\frac{1}{\beta} = \frac{1}{12\pi r_s^2} \frac{\partial^2 E}{\partial r_s^2} \tag{11}$$

in the spherical approximation.

III. RESULTS AND DISCUSSIONS

Each cycle in producing a new improved potential involves solving nearly 100 Schrödinger equations. Most of these are related to finding the k-dependent valence solutions, with various boundary-condition tests, determinant evaluations, and various interpolations. The program was built on the skeleton of the Herman and Skillman[42] program, with various modifications, accuracy refinements, and with additional subroutines to determine the valence-electron wave function. The success of this computation owes a lot to the Herman and Skillman program which is fast, accurate, and easy to modify.

Ten points were calculated to nine significant figures. The E vs r_s curve (Fig. 1) is very smooth. Differentiation can be carried out directly, or we can first make a least-squares fit to an inverse power series in r_s (see Bardeen[8] and Callaway[43]) and then differentiate. (The latter method is used.) The results of the full self-consistent calculation are listed in line 2 of Table I. In line 3, we also list a previous calculation[4] with the ion core fixed to be the same as the atomic-core wave functions of the Kohn-Sham scheme.[3] Experimental values and values obtained by other authors are also listed for comparison.

The calculated equilibrium lattice constant of the Kohn-Sham scheme compares very favorably with experiment values. Compressibility is a bit low compared to the new measurement of Swenson[44] and Beecroft and Swenson.[45] The compressibility-

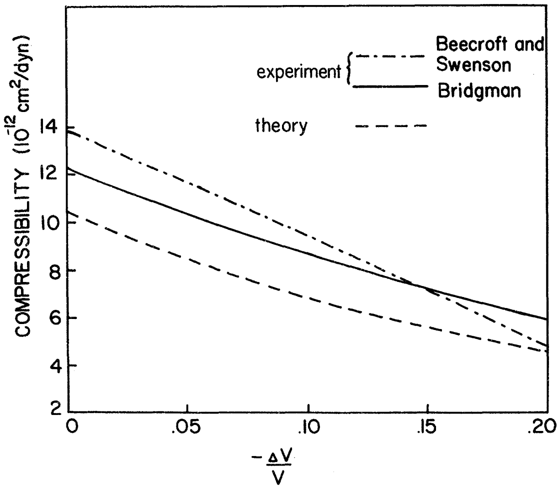

FIG. 2. Compressibility is plotted against the volume deformation $-\Delta V/V_0$.

volume relationship is shown in Fig. 2. The theoretical curve (Kohn-Sham) runs parallel to the old Bridgman data[18,46] and differs somewhat to the fitted linear relation of Eq. (5) of Beecroft and Swenson.[45] Cohesive energies from our calculations are put in brackets because they are less dependable numbers. They are obtained by subtracting the total energy of the isolated atom from the total energy per atom of metallic sodium. These are two very large numbers and are calculated from different computer programs. Besides, the theory involves approximations which may not yield an accurate difference. On the whole the results are satisfactory.

The final v_{eff} in Eq. (4) is a crystal potential obtained from the *a priori* calculation. It has included in it correlation effects not only of the valence electrons but also of all the electrons present in the solid. In Table II, we list, as a function of radial distance, (a) the bare Coulombic potential of $Z=11$, (b) v_{eff} of the full Kohn-Sham self-consistent calculation of this work, (c) the effective potential V_{AC} of a previous Kohn-Sham self-consistent calculation[4] in which the core wave functions were fixed to be the core wave functions of the free sodium atom,[3] and (d) the empirical potential of Prokofjew, V_P. It is seen that v_{eff}, V_{AC}, and V_P are quite close, and differ quite a bit from the bare Coulombic potential V_{Coul} which is strongly screened by the core electrons. Screening by other conduction electrons has not been included in V_P.

In the fitted potentials like that of Prokofjew,[17] the potential varies as $1/r$ near the Wigner-Seitz cell boundary. This feature is also present in the quantum-defect method[47] and in most pseudopotential theories.[25] This is in contradiction to the true periodic boundary condition in a metallic solid. Potentials in different cells must join smoothly at the cell boundary. V_{eff} satisfies this naturally. Several calculations after 1933 introduced artificially flattened potentials, e.g., the muffin-tin potential used by Ham.[20] Further criticisms on this subject can be found in Bienenstock and Brooks.[48]

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APPENDIX: THE VALENCE ELECTRON

In studying the solutions of the Schrödinger equation in a periodic potential, Kohn[49] developed a general variational principle. In the spherical approximation, the most convenient form is that used by Kohn.[41] We find the method particularly suitable to be incorporated into the self-consistent scheme.

The boundary-value problem of a valence electron in the spherical approximation (with a spherically, symmetric potential) can be written as

$$[-\tfrac{1}{2}\nabla^2 + v_{\text{eff}}(\vec{r}) - \epsilon_k]\psi_k(\vec{r}) = 0\,, \quad r < r_s \tag{A1}$$

$$\psi_k(\vec{r}) = e^{2ikr_s\cos\theta}\psi_k(-\vec{r})\,, \quad r = r_s \tag{A2}$$

$$\frac{\partial\psi_k(\vec{r})}{\partial\theta} = -e^{2ikr_s\cos\theta}\frac{\partial\psi_k(-\vec{r})}{\partial r}\,, \quad r = r_s \tag{A3}$$

where r_s is the radius of the Wigner-Seitz sphere,

TABLE II. Crystal potentials (in a.u.) as a function of radial distances R (in a_B). V_{Coul} is the bare Coulombic potential of $Z=11$; v_{eff} is the Kohn-Sham local effective potential of the full self-consistent calculation; V_{AC} is Kohn-Sham local effective potential of a self-consistent calculation in which the core wave functions are fixed to be the core wave functions of the free sodium atom (Ref. 3); and V_P is the fitted potential of Prokofjew.

R	V_{Coul}	v_{eff}	V_{AC}	V_p
0.08957	−245.62	−196.26	−196.19	−204.0
0.11943	−184.21	−137.43	−137.36	−139.9
0.27866	−78.949	−42.438	−42.381	−39.92
0.43790	−50.240	−20.190	−20.143	−20.19
0.59713	−36.843	−11.275	−11.238	−12.22
0.91560	−24.028	−4.6604	−4.6408	−5.321
1.2341	−17.827	−2.4671	−2.4569	−2.554
1.5526	−14.170	−1.5060	−1.4997	−1.601
1.8710	−11.758	−1.0071	−1.0022	−1.214
2.1895	−10.048	−0.73133	−0.72756	−0.9788
2.5080	−8.7721	−0.57943	−0.57755	−0.8238
2.8264	−7.7837	−0.49364	−0.49333	−0.7160
3.1449	−6.9955	−0.44317	−0.44372	−0.6377
3.4638	−6.3522	−0.41434	−0.41522	−0.5783
3.7818	−5.8173	−0.40100	−0.40161	−0.5294
3.8455	−5.7209	−0.39987	−0.40053	−0.5206
3.9092	−5.6277	−0.39922	−0.39989	−0.5121
3.9729	−5.5375	−0.39901	−0.39969	−0.5038

k is the magnitude of the wave vector assumed in the z direction, and θ is the angle between $\vec{k}$ and $\vec{r}$. Assume that $\psi_k(\vec{r})$ can be expanded in terms of spherical harmonics:

$$\psi_k(\vec{r}) = \textstyle\sum_l \eta_l C_l P_l(\cos\theta)[R_{k,l}(r)/r] , \tag{A4}$$

where η_l is defined as

$$\eta_l = \begin{cases} 1 , & l \text{ even} \\ i , & l \text{ odd} \end{cases} \tag{A5}$$

and where the C_l are real.

The variational principle states that the C_l are determined by the condition that the surface integral

$$K \equiv \int_S \frac{\partial \psi_k(\vec{r})}{\partial r} \psi_k^*(-\vec{r}) e^{-2ikr_s\cos\theta} \sin\theta \, d\theta \tag{A6}$$

be stationary. Substituting Eq. (A4) into this and normalizing so that $R_{k,l}(r_s) = r_s$, we get the secular equation

$$\Delta \equiv \det | \eta_l \eta_m (L_l + L_m) I_{lm} | = 0 , \tag{A7}$$

where

$$L_l = \left(\frac{1}{R_l} \frac{dR_l}{dr} - \frac{1}{r} \right)_{r=r_s} \tag{A8}$$

and

$$I_{lm} = \int_0^\pi e^{-2ikr_s\cos\theta} P_l(\cos\theta) P_m(\cos\theta) \times P_m(\cos\theta) \sin\theta \, d\theta . \tag{A9}$$

Here the index k is suppressed.

The valence-electron density is then given by taking the sum over all $\vec{k}$ points up to the Fermi level,

$$n_v(\vec{r}) = \textstyle\sum_{\vec{k}} | \psi_k(\vec{r}) |^2 . \tag{A10}$$

With

$$\int \psi_k^*(\vec{r}) \psi_k(\vec{r}) \, d\vec{r} = 1 ,$$

we get

$$n_v(\vec{r}) = \frac{\sigma(r)}{4\pi r^2} = \frac{3}{4\pi r^2 k_F^3} \int_0^{k_F} \left[\left(\sum_l \frac{C_l R_{k,l}^2(r)}{2l+1} \right) \Big/ \left(\sum_l \frac{C_l^2}{2l+1} \int R_{k,l}^2(r)\, dr \right) \right] k^2 \, dk \tag{A11}$$

and

$$\epsilon_v = (3/k_F^3) \int_0^{k_F} \epsilon_k k^2 \, dk . \tag{A12}$$

Since the valence band of sodium is nearly a parabola, we find it quite sufficient to evaluate only seven k points equally spaced from 0 to k_F. $r_s k_F = (9\pi/4)^{1/3} = 1.919158$. This means that I_{lm}, which depends on the product $r_s k$ only, can be evaluated once for all r_s. Numerical integration with a variable number of mesh points is used (to avoid the appearance of nodal points in the integrand at a mesh point) giving values accurate up to nine significant figures. They can be checked against the values obtained by using tables of the 3-j symbols (Rotenberg *et al.*[50]):

$$\begin{aligned} I_{ij} &= \int_{-1}^{1} e^{-i\rho\chi} P_i(\chi) P_j(\chi) \, d\chi \\ &= \sum_{l=0}^{\infty} (2l+1)(i)^l j_l(-\rho) \int_{-1}^{1} \rho_l(\chi) P_i(\chi) P_j(\chi) \, d\chi \\ &= \sum_{l=0}^{\infty} 2(2l+1)(-i)^l j_l(\rho) \begin{pmatrix} l & i & j \\ 0 & 0 & 0 \end{pmatrix}^2 , \quad \rho = 2kr_s . \end{aligned} \tag{A13}$$

In practice the expansion (A4) in l is terminated at $\bar{l} = 6$. Test calculations using the sodium-ion potential shows that this truncation is sufficient to guarantee that $\epsilon_k(\bar{l} = 6)$ be the same as $\epsilon_k(\bar{l})$ of a higher $\bar{l}$ to at least seven decimal places. The rapid convergence can be seen from the dominating coefficients of the s and p functions. These facts have been indicated by many authors, e.g., Kjeldaas and Kohn,[51] and are also known from calculations of transport properties in metals.

To find the correct solution of Eq. (A1) satisfying the condition (A7), we use the following iterative interpolation. For a given potential v_{eff}, we take three trial values of ϵ_k: $\epsilon_k^1 < \epsilon_k^2 < \epsilon_k^3$. Their corresponding solutions for Eq. (A1) are found by numerical integration, each giving a value of Δ. From these, we interpolate ϵ_k to $\Delta = 0$, giving us an improved value of ϵ_k^2. New values of ϵ_k^1 and ϵ_k^3 are generated close to this new ϵ_k^2 in a prescribed way. Numerical solutions for these new ϵ_k's are again obtained by integration, and the Δ interpolation is repeated. This iteration is continued until the old and the new ϵ_k^2 differ by not more than 10^{-6} Ry. As a check that the latter is the correct solution ϵ_k satisfying the boundary conditions (A2) and (A3), we follow the method suggested by Kohn[41] of testing in ten different directions θ the condition

$$\frac{C_1 P_1(\cos\theta) + C_3 P_3(\cos\theta) + \cdots}{C_0 P_0(\cos\theta) + C_2 P_2(\cos\theta) + \cdots} \Big/ \tan(kr_s \cos\theta) = 1 . \tag{A14}$$

This process to find ϵ_k is repeated for each k value. Finally, the ψ_k's and ϵ_k's are summed [Eqs. (A11) and (A12)] to give $n_v(\vec{r})$ and ϵ_v. Adding $n_v(\vec{r})$ to the calculated core density $n_c(\vec{r})$ described in the main text, we are now ready to calculate a new v_{eff}, and start a new cycle.

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[1] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[2] L. J. Sham and W. Kohn, Phys. Rev. 145, 561 (1966).

[3] B. Y. Tong and L. J. Sham, Phys. Rev. 144, 1 (1966).

[4] B. Y. Tong, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971), pp. 476–488; B. Y. Tong, Ph.D. thesis (University of Calfiornia, San Diego, 1967) (unpublished).

[5] J. D. W. Connolly, Phys. Rev. 159, 419 (1967).

[6] P. DeCicco, Phys. Rev. 153, 931 (1967).

[7] A. M. Boring, Ph.D. thesis (University of Florida, 1968) (unpublished).

[8] W. E. Rudge, Phys. Rev. 181, 1024 (1969).

[9] Marvin Ross and K. W. Johnson, Phys. Rev. B 2, 4709 (1970).

[10] D. F. Scofield, Sc.D. thesis (George Washington University, 1969) (unpublished).

[11] See many other articles, including a review by J. C. Slater, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971).

[12] David A. Liberman, in Ref. 11, pp. 489–494; Phys. Rev. B 2, 244 (1970).

[13] J. C. Raich and R. H. Good, Jr., J. Phys. Chem. Solids 26, 1061 (1965). This paper contains references to other papers which make use of similar models.

[14] Melvin Cutler, J. Chem. Phys. 46, 2044 (1967).

[15] E. P. Wigner and F. Seitz, Phys. Rev. 43, 804 (1933); 46, 509 (1934).

[16] E. P. Wigner and F. Seitz, Solid State Phys. 1, 97 (1955).

[17] W. Prokofjew, Z. Physik 58, 255 (1929).

[18] J. Bardeen, J. Chem. Phys. 6, 367 (1938); 6, 372 (1938).

[19] T. S. Kuhn and J. H. Van Vleck, Phys. Rev. 79, 382 (1950).

[20] F. S. Ham, Phys. Rev. 128, 82 (1962); 128, 2524 (1962).

[21] F. S. Ham and B. Segall, Phys. Rev. 124, 1786 (1961).

[22] H. Brooks, Nuovo Cimento Suppl. 7, 165 (1958).

[23] H. Brooks and F. S. Ham, Phys. Rev. 112, 344 (1958).

[24] H. Brooks, Trans. Met. Soc. AIME 227, 546 (1963).

[25] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[26] W. E. Rudge, Phys. Rev. 181, 1033 (1969).

[27] W. Kohn, in *Many-Body Theory*, 1965 *Tokyo Summer Lectures in Theoretical Physics*, Pt. I (Benjamin, New York, 1966), pp. 73–85.

[28] R. Gaspar, Acta Phys. Acad. Sci. Hung. 3, 263 (1954).

[29] David A. Liberman, Phys. Rev. 171, 1 (1968).

[30] F. Herman, J. P. Van Dyke, and I. B. Ortenburger, Phys. Rev. Letters 22, 807 (1969).

[31] J. C. Slater and J. H. Wood, Intern. J. Quantum Chem. (to be published).

[32] A. M. Boring, Phys. Rev. B 2, 1506 (1970).

[33] A. W. Overhauser, Phys. Rev. B 2, 874 (1970).

[34] J. R. Smith, Phys. Rev. A 3, 513 (1971).

[35] L. J. Sham, in Ref. 11, pp. 458–468.

[36] C. S. Barrett, Acta Cryst. 9, 671 (1956).

[37] J. Friedel, Advan. Phys. 3, 446 (1954); Phil. Mag. 7, 46 (1955); 7, 516 (1955); N. F. Mott, Rept. Progr. Phys. 25, 218 (1962).

[38] A. J. Hughes and J. Callaway, Phys. Rev. 136, A1390 (1964).

[39] D. Pines, *Elementary Excitations in Solids* (Benjamin, New York, 1963).

[40] B. Y. Tong, Phys. Rev. A 4, 1375 (1971).

[41] W. Kohn, Phys. Rev. 96, 590 (1954).

[42] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, N. J., 1963).

[43] J. Callaway, *Energy Band Theory* (Academic, New York, 1964).

[44] C. A. Swenson, Phys. Rev. 99, 423 (1955).

[45] R. I. Beecroft and C. A. Swenson, J. Phys. Chem. Solids 18, 329 (1961).

[46] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 207 (1938).

[47] F. S. Ham, Solid State Phys. 1, 127 (1955).

[48] A. Bienenstock and H. Brooks, Phys. Rev. 136, A784 (1964).

[49] W. Kohn, Phys. Rev. 87, 472 (1950).

[50] M. Rotenberg *et al.*, *The* 3-*j and* 6-*j Symbols* (MIT, Cambridge, Mass., 1959).

[51] T. Kjeldaas, Jr. and W. Kohn, Phys. Rev. 101, 66 (1956).