

it is easily noticed that $\langle J_{ij} \rangle = 0$ if $i \neq j$. After performing the angular integration, the expression for the shear viscosity ($\eta = \eta_{ijij}$) reduces to

$$\eta = \frac{\beta}{15\pi^2 m^2} \int_0^\infty dk k^6 e^{\beta \epsilon_k} (e^{\beta \epsilon_k} + 1)^{-2} \tau_k, \quad (14)$$

where we have assumed that $\bar{\epsilon}_k = \epsilon_k$ and that $\tau_k = (2\Gamma_k)^{-1}$ may be identified as the relaxation time. Equation (12) can be rewritten as

$$\eta = \frac{1}{15\pi^2 m^2} \int_0^\infty (2m\epsilon)^{5/2} \left(-\frac{\partial f}{\partial \epsilon} \right) \tau(\epsilon) d\epsilon, \quad (15)$$

where $f = (e^{\beta(\epsilon - \mu)} + 1)^{-1}$ and $\epsilon = k^2/2m$. In the low-

temperature limit ($k_B T \ll \mu$), the derivative of the Fermi function can be replaced by $\delta(\epsilon - \mu)$, and we obtain

$$\eta = \frac{2}{5} n \mu \tau, \quad (16)$$

where n is the number of electrons per unit volume and the relaxation time is to be evaluated at the Fermi surface. At high temperatures the Fermi function can be replaced by the Boltzmann factor, and assuming that the relaxation is independent of the energy, one can obtain from Eq. (15) the usual kinetic-theory expression of the viscosity in the classical limit. The expression (16) is rigorously derived here by an entirely different method. We consider the present derivation more satisfactory.

Band Structure and Properties of Cesium Metal*

S. D. MAHANTI† AND T. P. DAS

Department of Physics, University of California, Riverside, California 92502

(Received 24 June 1968; revised manuscript received 9 October 1968)

Energy bands and wave functions for cesium metal have been obtained by an orthogonalized-plane-wave procedure using a conduction-electron potential constructed from first principles. The effects of correlation in the ground state have been included through a local model potential and are found to have a rather small influence on band properties. The Fermi surface is observed to be less distorted along the [110] direction than in earlier calculations, and is in better agreement with experiment. The ratios k_F/k_F^0 along three principal directions [110], [111], and [100] were found to be 1.032, 0.992, and 0.970, as compared to 1.033, 0.991, and 0.986 obtained from de Haas-van Alphen measurements. The calculated density of states is utilized to evaluate the specific heat, which, after suitable correction for electron-phonon interaction, is found to be about 1.03 times the experimental value. The spin susceptibility, after incorporating exchange enhancement effects, is predicted to be 0.7696×10^{-6} cm³ volume units, in good agreement with a recent experimental value of 0.80×10^{-6} inferred from the nuclear-magnetic-resonance measurements in liquid alkali-metal alloys. The Knight shift and the nuclear relaxation time T_1 , which depend explicitly on the wave functions, are both found to be within 60% of experiment. Possible mechanisms which could improve the agreement of these two properties with experiment are discussed.

I. INTRODUCTION

THE simplicity of the structure of alkali metals and the wealth of experimental data that are currently available for them make these systems attractive for detailed theoretical analysis. One can divide the electronic properties of interest in metals into three broad categories. First, there are those that depend only on the shape of the energy bands. Examples of such properties are the de Haas-van Alphen (dHvA) oscillations, cyclotron masses, and the density of states at the Fermi surface which is obtained from specific-heat measurements. A second class of properties are those associated with real excitations of electrons in the presence of external fields. Among these are optical

absorption, soft x-ray emission, and the Pauli paramagnetic susceptibility χ_s . These properties, in general, require a knowledge of both occupied and unoccupied states and are quite sensitive to correlation effects. In the last category are a number of properties that can be measured by magnetic-resonance techniques and which require for their interpretation an explicit knowledge of the electronic wave functions as well as band structure. Included among these properties are the isotropic and anisotropic Knight shifts, the shift in the conduction-electron g factor, the electron- and nuclear-spin relaxation times, and the indirect coupling between nuclear spins via the conduction electrons. The anisotropic Knight shift vanishes identically for the alkali metals because of their cubic symmetry.

We have singled out cesium as our choice for detailed investigation for a number of reasons. Cesium is the heaviest of the alkali metals, and its properties would

* Work supported by National Science Foundation.

† Present address: Bell Telephone Laboratories, Murray Hill, N. J.

therefore be most susceptible to relativistic corrections. However, since cesium occupies only an intermediate position in the Periodic Table as a whole, relativistic effects are not expected to be overwhelming. One can, therefore, use a nonrelativistic model to compare with experiment the predicted properties, those depending on the Fermi surface alone, and those that involve wave functions and thereby assess the importance of relativistic effects. Earlier theoretical investigations^{1,2} on cesium were primarily directed towards the Fermi-surface properties, and no specific attention was given to the conduction-electron wave functions. Thus, Ham¹ had made extensive calculations of the band structure of all the alkali metals using a combination of the quantum-defect method (QDM) and the Green's-function technique. The general features of the Fermi surfaces from his calculations are in fair agreement with experiment for other alkali metals, but there are significant disagreements for cesium. It is therefore of interest to study whether the orthogonalized-plane-wave (OPW) method can give improved results for the Fermi surface. An earlier OPW calculation by Callaway and Haase² (CH), using an ionic potential, gave a value of the Γ (Γ_1 representation) point energy in excellent agreement with that obtained by Ham. On the other hand, the energy gap $E_{N_1} - E_{N_1'}$ at the N point was found to be positive in their calculation as compared to a larger and negative value obtained by Ham.

CH were handicapped by the nonavailability of Hartree-Fock atomic functions at the time of their calculation. The apparent disagreement between CH's OPW and Ham's QDM calculations is part of the reason for our utilization of the OPW method. This method has been used extensively for obtaining the Fermi surface in more complicated metals, and it is therefore desirable that it provide accurate results for the simple alkali metals, so that one may have more general confidence in it. Secondly, the OPW procedure is particularly suitable for determining wave functions to interpret hyperfine and other magnetic properties quantitatively. Our final reason for choosing the OPW procedure is that within its framework it is convenient to analyze the importance of various contributions to the potential such as exchange and correlation effects among conduction and conduction, and conduction and core electrons. Such an analysis is carried out by a first-principles construction of the potential rather than the utilization of empirical potentials, which could take better account of exchange and correlation, but only in an indirect manner, without providing a detailed understanding of their importance.

Section II deals with a brief discussion of various choices of the potential used in the present calculation. In Sec. III the results of energy-band calculation at symmetry points is presented and compared with

earlier calculations. Finally, in Sec. IV, we compare the theoretical values of various properties (such as the specific heat, Pauli-spin susceptibility, Knight shift, and nuclear-spin relaxation time) with available experimental results.

II. POTENTIAL

It will be helpful to review briefly the currently used models for conduction-electron potentials before describing the specific choice we have made for cesium. The incorporation of exchange and correlation effects within the framework of a single-particle model is the most difficult aspect of the conduction-electron potential. We will therefore analyze these effects in some detail both to study their effects on the properties of cesium as well as for the broader purpose of critically evaluating methods available in the literature for dealing with exchange and correlation effects.

The effective single-particle Schrödinger equation for a Bloch electron in the state \mathbf{k} is

$$H\psi_{\mathbf{k}} = E(\mathbf{k})\psi_{\mathbf{k}},$$

where

$$H = -(\hbar^2/2m)\nabla^2 + V_H(\mathbf{r}) + \Sigma. \quad (1)$$

In Eq. (1), $V_H(\mathbf{r})$ is the Coulomb potential due to the nucleus, core, and other conduction electrons. This potential is \mathbf{k} -independent and therefore local in character. In constructing $V_H(\mathbf{r})$, atomic Hartree-Fock wave functions were utilized, while for the Coulomb potential due to the conduction electrons, one-OPW functions orthogonal to the atomic cores were utilized and \mathbf{k} integration was carried out over the occupied Fermi sphere.

The term Σ in (1) includes exchange and correlations among the conduction electrons themselves as well as similar effects between the conduction electrons and core electrons. This contribution to the potential is generally nonlocal in nature. The core electrons, being tightly bound as compared to the conduction electrons, possess large excitation energies. It is therefore reasonable to treat³ the core and conduction electrons as dynamically independent and core-conduction correlation effects can be safely omitted in the construction of the potential. Thus Σ in (1), often referred to as the self-energy operator, consists of two parts, one arising from the core-conduction exchange treated in Hartree-Fock approximation and the other dealing with the exchange and correlation effects among conduction electrons themselves. Brinkman and Goodman⁴ have recently given a convenient procedure for handling core-conduction exchange effects using atomic cores and OPW functions. In their procedure, one retains the nonlocality by working with matrix elements of the exchange potential between OPW states. We have

¹ F. S. Ham, Phys. Rev. **128**, 82 (1962); **128**, 2524 (1962).

² J. Callaway and E. L. Haase, Phys. Rev. **108**, 217 (1957).

³ F. Bassani, J. E. Robinson, B. Goodman, and R. Schrieffer, Phys. Rev. **127**, 1969 (1962).

⁴ W. Brinkman and B. Goodman, Phys. Rev. **149**, 597 (1966).

instead chosen to adopt the simpler local approximation employed by Heine,⁵ Falicov,⁶ and others. The local approximation is more convenient to combine with procedures for dealing with correlation effects and is not expected to be too different from the actual exchange potential for the alkali metals with their simple structure.

One approach to the formulation of conduction-conduction exchange and correlation effects is the early Wigner-Seitz procedure.⁷ In this procedure, one assumes that correlation and exchange effects produce a hole in the Wigner-Seitz cell so that the conduction electrons essentially see an ionic potential (more explicitly, the potential seen by an atomic electron in the excited state). The other extreme point of view is to assume that correlation and exchange effects can be described reasonably well by a model of a uniform gas of interacting electrons. In this case, it has been pointed out⁵ that the combined effects of conduction-conduction exchange and correlation can be approximated by a constant correction to the potential which affects the total energy but not the band structure or wave functions. Recently, several attempts have been made to incorporate the departure of the conduction-electron distribution from the homogeneous gas model and thereby bridge the gap between the two extreme approaches. We shall now describe briefly some of these approaches which we have analyzed for our calculations.

A common approximation is to ignore the effects of Coulomb correlation and use Slater's expression

$$V_{\text{ex}}^{\text{Sl}}(\mathbf{r}) = -6[(3/8\pi)\rho(\mathbf{r})]^{1/3} \quad (2)$$

for the exchange potential, $\rho(\mathbf{r})$ being the local charge density due to the conduction electrons of both spins. In our calculation of $V_{\text{ex}}^{\text{Sl}}$, we have obtained $\rho(\mathbf{r})$ using a one-OPW approximation. For our second choice of exchange and correlation potential, we have used a procedure similar to that suggested by Kohn and Sham.⁸ In this model, one considers the exchange and correlation effects separately.

$$V^{\text{KS}}(\mathbf{r}) = V_{\text{ex}}^{\text{KS}}(\mathbf{r}) + V_{\text{c}}^{\text{KS}}(\mathbf{r}). \quad (3)$$

The exchange contribution $V_{\text{ex}}^{\text{KS}}$ is a factor of $\frac{2}{3}$ smaller than $V_{\text{ex}}^{\text{Sl}}$ in (2), the difference between the two approximations being that one uses a Fermi-volume average in one case and a Fermi-surface average for the other. The correlation part V_{c}^{KS} depends upon the local density $\rho(\mathbf{r})$ and was evaluated by an appropriate interpolation between Gellman and Brueckner's⁹ high-density result and Wigner's¹⁰ low-density result, as

given by

$$\mu_{\text{c}}^{\text{GB}}(\rho) = 0.0207 \ln(\frac{2}{3}\pi\rho) - 0.1167 \quad (4)$$

and

$$\mu_{\text{c}}^{\text{W}}(\rho) = -0.44(\frac{4}{3}\pi\rho)^{1/3} + 4.5(\frac{4}{3}\pi\rho)^{1/2}, \quad (5)$$

where μ is the chemical potential. The third choice that we have employed to incorporate exchange and correlation effects is one utilized by Hedin.¹¹ With this model one applies a static screening to the exchange potential and uses a static-hole approximation for Coulomb correlation effects. The basic idea behind this model is that in the random-phase approximation (RPA) of treating electron-electron interactions, the exchange potential gets dynamically screened by the RPA dielectric function $\epsilon(\mathbf{q},\omega)$, the effect of higher-order vertex corrections being neglected. If one further approximates the RPA dielectric constant by its static limit $\epsilon(\mathbf{q},0)$, the net contribution to the self-energy can be shown to consist of two parts, a statically screened exchange which takes care of the short-range correlation effect and a Coulomb-hole contribution arising from a static approximation to the Coulomb correlation. For the first part we have adopted a screened Slater approximation proposed by Robinson, Bassani, Knox, and Schrieffer.¹² These authors screened the bare Coulomb potential using a Thomas-Fermi approximation to the dielectric function given by

$$\epsilon_{\text{TF}}(\mathbf{q},0) = 1 + q_s^2/q^2, \quad (6)$$

where

$$q_s = 0.82k_F(r_s)^{1/2}.$$

Equation (6) for $\epsilon(\mathbf{q},0)$ leads to the screened Slater exchange potential

$$V_{\text{sc. ex.}}^{\text{Sl}}(\mathbf{r}) = -6[(3/8\pi)\rho(\mathbf{r})]^{1/3}F(\alpha),$$

where

$$F(\alpha) = 1 - \frac{4}{3}\alpha \tan^{-1}(2/\alpha) + \frac{1}{2}\alpha^2 \ln(1+4/\alpha^2) - \frac{1}{6}\alpha^2 [1 - \frac{1}{4}\alpha^2 \ln(1+4/\alpha^2)] \quad (7)$$

and

$$\alpha = 0.646[\rho(\mathbf{r})]^{-1/6}.$$

For an interacting electron gas of uniform density, the Coulomb-hole contribution to the potential is constant independent of \mathbf{k} and \mathbf{r} and is given by

$$V_{\text{ch}}(\mathbf{r}) = \frac{1}{2} \int \frac{d\mathbf{q}}{(2\pi)^3} v(\mathbf{q}) \left[\frac{1}{\epsilon(\mathbf{q},0)} - 1 \right]. \quad (8)$$

If one uses an OPW approximation for the conduction-electron wave functions, one introduces a feeble \mathbf{k}

⁵ V. Heine, Proc. Roy. Soc. (London) **A240**, 340 (1957).

⁶ L. M. Falicov, Phil. Trans. Roy. Soc. London **255**, 55 (1962).

⁷ E. P. Wigner and F. Seitz, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1955), Vol. 1, p. 97.

⁸ W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

⁹ M. Gellman and K. Brueckner, Phys. Rev. **106**, 364 (1957).

¹⁰ E. P. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

¹¹ L. Hedin, Phys. Rev. **139**, A796 (1965); Arkiv Fysik **30**, 231 (1965).

¹² J. E. Robinson, F. Bassani, R. S. Knox, and R. Schrieffer, Phys. Rev. Letters **9**, 521 (1962).

dependence leading to the modified expression

$$V_{\text{ch}}(\mathbf{r})\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{2} \int \frac{d\mathbf{q}}{(2\pi)^3} d\mathbf{r}' v(\mathbf{q}) \left[\frac{1}{\epsilon(\mathbf{q}, 0)} - 1 \right] \times e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} [\delta(\mathbf{r} - \mathbf{r}') - \langle \mathbf{r} | P_c | \mathbf{r}' \rangle], \quad (9)$$

where

$$\langle \mathbf{r} | P_c | \mathbf{r}' \rangle = \sum_t \psi_t^*(\mathbf{r}') \psi_t(\mathbf{r}),$$

with t running over occupied states. For a good metal like cesium, where the core electrons occupy a relatively small part of the Wigner-Seitz cell, the \mathbf{k} -dependent correction in (9) turns out to be quite small.

The potentials obtained by the various models can be analyzed relative to each other in two ways. One way is to compare the band structures and energies that these potentials yield. This will be done in Sec. III. Another means of comparison is to deal with the Fourier components themselves, which also permits one to anticipate the nature of the band-structure results. The Fourier components $V(\mathbf{K})$ corresponding to some of the shorter reciprocal-lattice vectors \mathbf{K} are listed in Table I for the Slater approximation, the Kohn-Sham model, and the screened-exchange Coulomb-hole approach. For purposes of comparison, we have also included the Fourier coefficients for the Wigner-Seitz ionic approximation as well as the Heine approximation discussed earlier in this section.

Barring the Fourier component for $\mathbf{K}=0$, the rest of the components are seen from Table I to be quite similar for the various approximations. This shows that differences in correlation and exchange effects which characterize the various choices are not drastic. This is an encouraging feature because it indicates that the calculated bands are not expected to vary widely with the approximations made in the incorporation of correlation and exchange effects. The $V(0)$ component, however, does show significant variation from one approximation to another. In particular, for the Heine model potential, $V(0)$ is rather different from its ionic value, while the other approximations appear to be closer to the ionic results in varying degrees. This indicates that correlation and exchange effects tend to shift the potential towards more ionic character. It should be remarked, however, that the $\mathbf{K}=0$ component which is a reflection of the long-range part of the potential, only affects the total energy and not the band shape. One also notices the anticipated near equality of the Fourier components for large \mathbf{K} for the different models, since the large- \mathbf{K} components reflect the short-range behavior of the potential, which is dominated by the attractive nuclear potential.

The differences among the model potentials for intermediate points in the Wigner-Seitz cell are reflected in the differences of the nonzero Fourier components ($\mathbf{K} \neq 0$), which could lead to noticeable changes in band structure. The close resemblance between the conduction-electron potential, resulting from models

TABLE I. Fourier coefficients $V(\mathbf{K})$ for various choices of potential (in Ry).

\mathbf{K}	V_{ionic}	V_{Heine}	$V_{\text{sc. ex.-ch}}$	V_{Slit}	V_{KS}
(0,0,0)	-0.9696	-0.5252	-0.8938	-0.8402	-0.7898
(1,1,0)	-0.3855	-0.3627	-0.3617	-0.3565	-0.3582
(2,0,0)	-0.2517	-0.2811	-0.2784	-0.2519	-0.2568
(2,1,1)	-0.2308	-0.2351	-0.2354	-0.2355	-0.2352
(2,2,0)	-0.2178	-0.2048	-0.2065	-0.2209	-0.2179
(3,1,0)	-0.1950	-0.1821	-0.1836	-0.1961	-0.1936
(2,2,2)	-0.1689	-0.1639	-0.1645	-0.1690	-0.1680
(3,2,1)	-0.1472	-0.1491	-0.1490	-0.1467	-0.1470
(4,0,0)	-0.1327	-0.1370	-0.1365	-0.1317	-0.1325
(4,1,1)	-0.1245	-0.1271	-0.1267	-0.1230	-0.1237

utilized for exchange and correlation effects, and the potential resulting from the ionic model is only true for the $\mathbf{K}=0$ component. For $\mathbf{K} \neq 0$ components, the resemblance with the Heine model is much closer. We feel that this behavior has to do with the more realistic core-conduction Coulomb and exchange potentials used in the Heine and other models than is the case with the ionic-model approximation. The ionic-model potential would be rigorously valid if the conduction-electron wave functions were sharply localized in the Wigner-Seitz cell and had negligible penetration between cells. The QDM procedure also suffers from this restriction and further requires for its validity that the wave functions be expressible as a linear combination of excited-atom wave functions. Unfortunately, these restrictions are not met at all points in \mathbf{k} space.

For the purposes of this comparison, we have subtracted all Coulomb and core-conduction exchange contributions from the Fourier components of the total potential and have tabulated the difference in Table II. The entries in Table II thus represent the Fourier components of the exchange and correlation potential, and in our subsequent discussions in this section we shall be referring to these Fourier components as $V_c(\mathbf{K})$. The major differences in the models are again reflected in the $\mathbf{K}=0$ component, which does not influence the band shape and the density of states, but plays an important role for the cohesive energy. The components

TABLE II. Fourier coefficients $V_c(\mathbf{K})$ of exchange and correlation potential (in Ry) among conduction electrons for various models.

\mathbf{K}	$V_{\text{c. Slit}}$	$V_{\text{c. KS}}$	$V_{\text{c. sc. ex.-ch}}$
(0,0,0)	-0.3150	-0.2647	-0.3687
(1,1,0)	+0.0061	+0.0045	+0.001
(2,0,0)	+0.0292	+0.0243	+0.0027
(2,1,1)	-0.0004	-0.0001	-0.0005
(2,2,0)	-0.0161	-0.0131	-0.0018
(3,1,0)	-0.0140	-0.0115	-0.0015
(2,2,2)	-0.0050	-0.0040	-0.0005
(3,2,1)	+0.0024	+0.0021	+0.0002
(4,0,0)	+0.0053	+0.0045	+0.0005
(4,1,1)	+0.0041	+0.0037	+0.0004

$V_c(\mathbf{K} \neq 0)$ are seen to be in general one or more orders of magnitude smaller than $V_c(0)$. For any particular \mathbf{K} , all the $V_c(\mathbf{K})$'s have the same sign, although the common sign does change with \mathbf{K} . The positive sign can be interpreted as a screening effect and the negative ones as antiscreening. There is a bunching between some of the approximations because the corresponding models have certain similar features. Thus, $V_c^{\text{KS}}(\mathbf{K})$ and $V_c^{\text{Slt}}(\mathbf{K})$ exhibit similar behavior, the former being a little smaller in magnitude than the latter. The $\frac{2}{3}$ factor in Eq. (3) relative to the Slater approximation in Eq. (2) is mainly responsible for this difference, a part of which is balanced by the correlation potential included in $V_c^{\text{KS}}(\mathbf{K})$. The Fourier components of $V_c^{\text{sc. ex.-ch}}$ in the third column are seen to be an order of magnitude smaller than those in the first two columns in Table II for larger values of \mathbf{K} . These differences in Fourier coefficients for nonzero reciprocal-lattice vectors can lead to detectable effects on the band shape which can be quite significant at some of the symmetry points in the Brillouin zone. An important example is the energy difference between N_1 and N_1' . This and other features of the band structure will be discussed in Sec. III when we present the results of our band calculation. Because of the observed small differences between the various choices for incorporating the conduction-electron exchange and correlation effects and their consequent influence on ground-state properties, it is rather difficult to make a definite choice in favor of one or the other from comparison with experiment. We tend to prefer the screened-exchange-Coulomb-hole model, since it handles the screening effects explicitly, and also because it gives results closer to those obtained by Ham¹ for the Γ_1 point using the QDM procedure. We shall usually choose this screened-exchange-Coulomb-hole model for detailed comparisons with results of calculations and experiment.

III. BAND-STRUCTURE RESULTS

In the calculation of the band structure by the OPW procedure, one has to make a choice of the core wave functions in constructing the OPW functions. For the sake of consistency, one would like to use the same core wave functions both in the construction of the potential and in the OPW functions which are used as the basis set for variational calculations. For a relatively heavy metal like cesium, the choice of the core states does require some careful deliberation. Heine⁵ has studied the convergence problem for the linear combination of OPW (LCOPW) functions in some detail for aluminum metal. To improve the convergence of LCOPW calculations, he gave plausible arguments for choosing pseudocores, that is, core wave functions calculated in the same potential as that seen by the conduction electrons. Subsequently, pseudocores have been used for a number of lighter metals. However, for heavier metals the outermost pseudocore d electrons with their large centrifugal

potential term tend to be rather weakly bound since the conduction-electron potential has a longer tail than the potential seen by the real core electrons. For example, in the case of indium,¹³ the pseudocore $4d$ electrons are just barely bound (energy = -0.0897 Ry). A consequence of this weak binding is that there can be significant overlaps between pseudocore functions centered about different sites which would have to be included if good accuracy is aimed at. Inclusion of these overlaps would severely complicate the band calculation. This difficulty was also encountered by Soven¹⁴ in his calculation on thallium metal. Soven has, in fact, demonstrated that one gets equally good convergence when the OPW functions are constructed so as to be orthogonal to crystal-core functions, the eigenfunctions in the actual potential seen by the core electrons in the crystal. Fortunately, in most cases including cesium, the potential seen by atomic cores differs very little from the crystal-core potential. Thus, even for the outermost ($5s$) cores of cesium, where the greatest difference is to be expected between atomic-core and crystal-core potentials, we have found the differences to be less than 6%. One can therefore safely use atomic cores for orthogonalization purposes. Since atomic cores are much more tightly bound than pseudocores, this choice obviates the difficulties associated with the overlap.

A typical OPW function utilized in our calculation is therefore given by

$$\psi_{\mathbf{k}}(\mathbf{r}) = (1/\Omega^{1/2}) [e^{i\mathbf{k}\cdot\mathbf{r}} - \sum_t \langle \phi_t | e^{i\mathbf{k}\cdot\mathbf{r}} | \phi_t \rangle], \quad (10)$$

where $\phi_t(\mathbf{r})$ are the atomic-core functions for cesium. For determining the LCOPW by variational procedures, one has to construct elements of the Hamiltonian and overlap matrices using the OPW functions (10). These matrix elements are given by

$$\begin{aligned} H_{mn} = & |\mathbf{k} + \mathbf{K}_m|^2 \delta_{mn} + V(|\mathbf{K}_m - \mathbf{K}_n|) \\ & - (1/\Omega) \sum_t b_t(\mathbf{k} + \mathbf{K}_n) \langle \mathbf{k} + \mathbf{K}_m | H | \phi_t \rangle \\ & - (1/\Omega) \sum_t b_t^*(\mathbf{k} + \mathbf{K}_m) \langle \phi_t | H | \mathbf{k} + \mathbf{K}_n \rangle \\ & + (1/\Omega) \sum_{t't''} b_t^*(\mathbf{k} + \mathbf{K}_m) b_{t''}(\mathbf{k} + \mathbf{K}_n) \\ & \quad \times \langle \phi_t | H | \phi_{t''} \rangle, \quad (11) \end{aligned}$$

$$S_{mn} = \delta_{mn} - (1/\Omega) \sum_t b_t^*(\mathbf{k} + \mathbf{K}_m) b_t(\mathbf{k} + \mathbf{K}_n), \quad (12)$$

$$b_t(\mathbf{k}) = \langle \phi_t | e^{i\mathbf{k}\cdot\mathbf{r}} \rangle, \quad \langle \mathbf{k} + \mathbf{K}_m | H | \phi_t \rangle = \langle e^{i(\mathbf{k} + \mathbf{K}_m)\cdot\mathbf{r}} | H | \phi_t \rangle.$$

If one had used pseudocore functions which are eigenfunctions of the conduction-electron Hamiltonian with eigenvalues E_t , then the Hamiltonian matrix elements

¹³ G. D. Gaspari and T. P. Das, Phys. Rev. **167**, 660 (1968); G. D. Gaspari, Ph.D. thesis, University of California, Riverside, 1964 (unpublished).

¹⁴ P. Soven, Phys. Rev. **137**, A1706 (1965).

TABLE III. Comparison of energies (in Ry) at symmetric points.

Point	Ham (QDM)	OPW (ionic)	OPW (Heine)	OPW (sc. ex.-ch)	OPW (KS)	OPW (Stt)	APW
Γ_1	-0.4190	-0.4278	0.0209	-0.3510	-0.2668	-0.3239	-0.4667
N_1	-0.2960	-0.2915	0.1585	-0.2127	-0.1257	-0.1818	-0.3395
N_1'	-0.2110	-0.2284	0.2027	-0.1693	-0.0856	-0.1432	-0.2708
$E(N_1') - E(N_1)$	0.0850	0.0631	0.0442	0.0434	0.0401	0.0386	0.0687
H_{12}	-0.2490		0.2110	-0.1565	-0.0426	-0.0925	-0.3132
P_4	-0.0190		0.2230	-0.1483			-0.2805
$E(N_1) - E(\Gamma_1)$	0.1230	0.1363	0.1376	0.1383	0.1411	0.1421	0.1272

in (11) would simplify to the form

$$H_{mn} = |\mathbf{k} + \mathbf{K}_m|^2 \delta_{mn} + V(|\mathbf{K}_m - \mathbf{K}_n|) - (1/\Omega) \sum_t E_t b_t^*(\mathbf{k} + \mathbf{K}_m) b_t(\mathbf{k} + \mathbf{K}_n). \quad (13)$$

The more complicated matrix elements (11), which we use, represent the price one pays to avoid the difficulties associated with the overlaps of pseudocores.

Using the matrix elements in (11) and (12) and diagonalizing the appropriate secular equations, the energy eigenvalues and eigenfunctions were obtained for several symmetry points and along three principal symmetry axes. Group theory was used to reduce the order of the secular determinants as much as possible. There are various methods available for solving the matrix equation

$$(H - ES)\psi = 0. \quad (14)$$

Since $S^{-1}H$ is a nonsymmetric matrix, even though H and S are individually symmetric, one cannot use the conventional diagonalization procedures for symmetric matrices. In the past the power-series method¹⁵ has been used to diagonalize the nonsymmetric $S^{-1}H$ matrix. While this procedure is adequate for the lowest eigenvalues, it suffers from loss of accuracy and slow convergence for the higher eigenvalues and eigenfunctions. Since excellent programs utilizing algorithm are available to diagonalize symmetric (real) and Hermitian matrices, a series of transformations¹⁶ were used to reduce Eq. (14) to the form

$$(H'' - E)\psi'' = 0, \quad (15)$$

where H'' is still symmetric. The details of these transformations are given in the Appendix. For the symmetry points, we have utilized a maximum dimension of 10 for the secular equation, which is equivalent to using 165 OPW's for the Γ_1 representation. For points along symmetry axes, the highest order of the secular determinant employed was 15. The convergence in most of the cases, particularly for the low-lying eigenvalues, was found to be extremely rapid. For example, for the point $(\frac{1}{8}, \frac{1}{8}, 0)$ along the $[110]$ direction, the eigenvalues changed only 0.09% in going from a dimension 6 (13

OPW's) to 15 (39 OPW's) of the secular equation. This convergence is adequate for the accuracy that we are interested in. A rather interesting feature is the difference in the nature of convergence at points of higher and lower symmetry. Even though the use of group theory allowed larger numbers of OPW's to be included for a certain order of secular equation at points of higher symmetry, this was not found to be a distinct advantage in terms of accuracy relative to lower-symmetry points. To quote some specific examples, for the Γ_{25}' point, the energy changed by 3% in going from a secular equation of order 4 to 10, while at the point $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ on the Δ line, the rate of convergence was 0.6% on changing the order of the secular equation from 6 to 15. This convergence behavior can be physically understood as follows: The availability of a larger number of OPW's at a point of high symmetry does not necessarily imply greater flexibility for the energy calculation. This is because of the number of equal-length OPW's in various blocks that are necessary to provide the proper symmetry-restricted angular character, and which do not necessarily contribute to an improvement in the energy convergence. This question of relative accuracy at various \mathbf{k} points is of importance in our calculations, because we shall make analytic fits in Sec. IV to obtain energy contours in \mathbf{k} spaces.

In Table III, we present the energy eigenvalues at several symmetry points of interest for various choices of potential, along with the results of Ham¹ (QDM), and a recent calculation by Kenney¹⁷ using the augmented-plane-wave (APW) procedure. In addition, we have included for reference the energies obtained with the ionic-potential and OPW procedure. The results for the eigenvalue for the Γ_1 representation indicate that the inclusion of exchange and correlation among conduction electrons lowers the energy, but not enough to equal that obtained for an ionic potential. Of the various models for including correlation and exchange effects, the potential $V^{\text{sc. ex.-ch}}$ yields an energy closest to the ionic one. This was expected from the analysis of the Fourier coefficients of different potentials in Sec. II. The next important feature of the bands is the energy gap Δ between the N_1' and N_1 representations at the N point. From the fourth row of Table III, the values of Δ obtained for the different models in our calculations

¹⁵ E. Bodewig, *Matrix Calculus* (Wiley-Interscience, Inc., New York, 1959).

¹⁶ One of the authors (SDM) is grateful to K. J. Duff for suggesting this procedure.

¹⁷ J. F. Kenney, MIT Quarterly Progress Report No. 66, 1967, p. 3 (unpublished).

TABLE IV. (a) Parameters of the Kubic-harmonic fit [Eq. (16)]. (b) Parameters in the analytic expression (22) for the density of states.

Approx.	(a)						
	E_0	E_2	$E_{4,1}$	$E_{6,1}$	$E_{4,2}$	$E_{6,2}$	$E_{6,3}$
A^a	0.0210	1.3537	-1.4870	-6.2687	-0.0031	-0.5543	1.6626
B^b	-0.0110	1.3644	-1.4631	-5.9869	-0.0046	-0.5421	1.6744

Approx.	(b)		
	E_{321}	E_{621}	E_{721}
A^a	0.6686	-0.8088	+20.027
B^b	0.6442	-0.8364	+18.979

^a Without correlation.

^b Correlation included in the band-structure calculation.

all seem to be about a factor of 2 smaller than Ham's QDM result. Kenney's APW result is closer to Ham's value but is still about a factor 1.25 smaller. The value of Δ that we have obtained using an ionic potential for the OPW calculation is 0.0631 Ry, which is also lower than Ham's result but somewhat larger than for other potential models. Callaway and Haase² had obtained a value of $\Delta = -0.0569$ Ry in an earlier ionic-potential OPW calculation. Our present result for the same model supports Ham's suggestion that the opposite sign obtained by Callaway and Haase was probably due to some computational error. The larger value for Δ obtained with the ionic model as compared to the other models used in our calculation was to be anticipated from the behavior of the Fourier coefficients $V(\mathbf{K})$ discussed in Sec. II. The difference in energy between N_1 and N_1' representations is sensitively dependent on V [110], which is overemphasized in the ionic model. A similar argument can be used to explain the larger value of Δ obtained by Ham with the QDM procedure. The difference between the latter and the ionic-model-OPW calculations originates in the approximations (excited-atom) made in energy calculations by the QDM procedure. One can obtain an idea of the effects of exchange and correlation on Δ by comparing the various model potential results with those obtained with the Heine-type potential. The difference from the Heine-type potential results seems to range from about 2% for $V^{\text{sc. ex.-ch}}$ to 14% for V^{sl} . The Slater approximation tends to overemphasize exchange effects which are screened out in the case of $V^{\text{sc. ex.-ch}}$. The Coulomb-hole contribution being nearly state-independent does not influence Δ . The value of Δ has an important bearing on the degree of distortion of the Fermi surface from a sphere. Another band feature which determines the distortion of the Fermi sphere is the width W of the first band along the [110] direction given by $W = E(N_1) - E(\Gamma_1)$. The values of W for the various approximations are tabulated in the last row of Table III. All four of the model potentials that we have used give values of W which are 10 to 15% larger than that obtained by both Ham and Kenney. This result indicates that the energy bands from our OPW calculations appear to be more free-electron-like than that by earlier work.

Further consequences of the difference in behavior between Ham's and our band-structure results will be considered in Sec. IV while making comparisons with experiment. It might appear that a quantitative comparison between Kenney's results and ours would afford a relative assessment of the OPW and APW procedures. Unfortunately, this is not the case, since Kenney employed a Slater approximation to the core-conduction exchange, which leads to a more drastic difference from Hartree-Fock core exchange than the relatively small ones among various models for conduction-conduction exchange and correlation effects that we have been discussing.

IV. COMPARISON WITH EXPERIMENT AND DISCUSSION

Our main interest in this work is in the properties of the ground state of the metal. Thus, we have to handle only the band structure on and below the Fermi surface. For properties such as optical absorption and x-ray emission spectra, a mere knowledge of occupied and excited band states is not sufficient. One requires, in addition, an intimate knowledge of correlation effects in the presence of external perturbations such as an electromagnetic field at optical frequencies¹⁸ or holes in the core states.¹⁹

The properties we shall be concerned with are the Fermi energy, density of states, dimensions of the Fermi surface, susceptibility, Knight shift, and nuclear-spin-lattice relaxation time. For these properties, one requires a detailed knowledge of the band energy $E(\mathbf{k})$ as a function of \mathbf{k} . We have utilized a Kubic-harmonic expansion for $E(\mathbf{k})$ which is particularly suitable for quantitative discussions of the properties of interest. For severe distortions from sphericity, such a representation is not very convenient from a numerical point of view, because of convergence problems. However, from our calculated energy values along the three different symmetry axes, the distortion from sphericity is seen to be small enough to justify an approximate Kubic-harmonic expansion involving terms up to order $l=6$:

$$E(k, \theta, \phi) = E_0 + E_2 k^2 + [E_{4,1} + E_{4,2} K_4(\theta, \phi)] k^4 + [E_{6,1} + E_{6,2} K_4(\theta, \phi) + E_{6,3} K_6(\theta, \phi)] k^6, \quad (16)$$

where $K_4(\theta, \phi)$ and $K_6(\theta, \phi)$ are Kubic harmonics of orders 4 and 6, respectively, (k, θ, ϕ) being the spherical coordinates of the wave vector \mathbf{k} . In principle, one can and should include higher-order Kubic harmonics. In practice, however, the presence of higher powers of k introduces errors in the numerical fit. It should be noted that the expansion in (16) does not converge for points on the Brillouin-zone (BZ) boundary; therefore, one

¹⁸ A. W. Overhauser, Phys. Rev. **156**, 844 (1967); A. O. E. Animalu, *ibid.* **163**, 557 (1967); **163**, 562 (1967).

¹⁹ S. M. Bose, Ph.D. thesis, University of Maryland, 1967 (unpublished); L. Hedin, Solid State Commun. **5**, 451 (1967).

has to avoid such points as far as possible. In our energy fit by a least-squares procedure, the closest point to the BZ boundary that we employed was along the [110] direction with Cartesian coordinates $(2\pi/a)$ (0.45, 0.45, 0). For all subsequent discussions, we shall make use of the results for the screened-exchange-Coulomb-hole approximation and the Heine approximation without exchange and correlation effects. A comparison of results with these two approximations allows an assessment of the effects of correlation for specific properties. Eighteen points in \mathbf{k} space were utilized for the seven parameter fit, the resulting parameters for the two cases being as listed in Table IV(a). The accuracy of the least-squares fit was found to be, on an average, better than 3%, and was further tested by calculating $E(\mathbf{k})$ at a general point outside of the eighteen included in making the fit and comparing it with the energy predicted by the Kubie-harmonic expansion in (16). Thus, for the point with Cartesian coordinates $(2\pi/a)$ (0.4499, 0.4499, 0) the energy was 0.1495 Ry without correlation effects, as compared to 0.1469 Ry predicted from Eq. (16). A similar good analytic fit was found for energies including correlation effects.

From Table IV(a), it appears that the parameters in Eq. (16) for the cases with and without correlation are nearly equal, except for E_0 , which is the energy for the Γ_1 representation and gives only the position of zero references. This then indicates that the band structures for the two cases are also quite close to each other, as would have been expected from the results in Table III. There are, however, small differences, the energy values including correlation being relatively lower near the Γ_1 point and a little higher for larger values of k . This leads to small differences in the density of states to be discussed later in this section.

Density of States and Fermi Energy

The number of states $g(\epsilon)$ with energy ϵ measured with respect to the bottom of the band is given by

$$g(\epsilon) = \frac{2}{(2\pi)^3} \int \frac{ds_k}{|\nabla_k \epsilon|}, \quad (17)$$

where the crystal is assumed to have unit volume, the factor of 2 arises from the two spin directions, and the integral is taken over a surface of constant energy. The Fermi energy ϵ_F can be defined in terms of the function $g(\epsilon)$ according to the relation

$$\Omega^{-1} = \int_0^{\epsilon_F} g(\epsilon) d\epsilon, \quad (18)$$

Ω being the volume of the Wigner-Seitz cell. An equivalent procedure²⁰ for determining ϵ_F is to replace the

integration of the density of states by a surface integration over contours of equal energy, which leads to

$$\Omega^{-1} = \frac{1}{12\pi^3} \int k^3(\epsilon_F, \theta, \phi) d\Omega. \quad (19)$$

To evaluate ϵ_F according to Eq. (19) one has to either invert the energy expansion given in Eq. (16) or directly obtain a Kubie-harmonic representation of $k^3(\epsilon, \theta, \phi)$. The latter procedure was found more suitable from the point of view of numerical accuracy. Thus, $k^3(\epsilon, \theta, \phi)$ was expanded in the form

$$k^3(\epsilon, \theta, \phi) = \epsilon^{3/2} [E_{321} + (E_{521} + E_{522}K_{4,1}(\theta, \phi))\epsilon + (E_{721} + E_{722}K_{4,1}(\theta, \phi) + E_{723}K_{6,1}(\theta, \phi))\epsilon^2]. \quad (20)$$

When the expansion in Eq. (20) is used, Eq. (19) reduces to

$$\Omega^{-1} = \Phi(\epsilon_F), \quad (21)$$

$$\Phi(\epsilon) = (1/3\pi^2) [E_{321}\epsilon^{3/2} + E_{521}\epsilon^{5/2} + E_{721}\epsilon^{7/2}]. \quad (22)$$

The coefficients E_{321} , E_{521} , and E_{721} in (22) are tabulated for the cases with and without correlation in Table IV(b). The power-series equation (22) was solved numerically to obtain ϵ_F , which was found to have the values 0.129 and 0.126 Ry with and without correlation effects. These values are to be compared with 0.111 Ry from Ham's QDM calculation and the free-electron value of 0.134 Ry. The rather small difference between the numbers 0.129 and 0.126 from our calculations, with and without correlation, indicates that such effects are negligible as far as the Fermi energy is concerned. For x-ray emission, one requires the absolute value of the Fermi energy rather than the difference from the bottom of the band. This difference between the two values of the parameter E_0 in Table III does indicate that the x-ray emission frequency would be appreciably influenced by correlation and so will be the cohesive energy as well. The main effect in both cases arises from the Coulomb-hole contribution. The density of states was calculated using the relation

$$g(\epsilon) = \frac{1}{(2\pi)^3} \frac{d}{d\epsilon} \int k^3(\epsilon, \theta, \phi) d\Omega, \quad (23)$$

analogous to (17). On substituting for $k^3(\epsilon, \theta, \phi)$ from Eq. (20), we get

$$g(\epsilon) = (1/3\pi^2) [\frac{3}{2}E_{321}\epsilon^{1/2} + \frac{5}{2}E_{521}\epsilon^{3/2} + \frac{7}{2}E_{721}\epsilon^{5/2}]. \quad (24)$$

For some properties, such as the Ruderman-Kittel and pseudodipolar interactions,²¹ one requires the thermal masses for the entire occupied Fermi volume. Experimentally, however, data are usually available only at the Fermi surface. On substituting $\epsilon = \epsilon_F$ in (24) and using the value for ϵ_F without correlation, $g(\epsilon_F)$, the density of states at the Fermi surface was found to be

²¹ S. D. Mahanti and T. P. Das, Phys. Rev. **170**, 426 (1968).

²⁰ J. de-Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 254.

TABLE V. Fermi momentum k_F for symmetry directions (in units of free-electron radius k_F^0).

Direction	Present calculation	Ham	Experiment
[110]	1.032	1.08	1.033
[100]	0.9917	0.94	0.991
[111]	0.9705	0.94	0.986

1.304 times larger than the free-electron value. The ratio m_t/m_e of the thermal mass to the free-electron mass is equal to this enhancement factor for the density of states.

In comparing the theoretical value of m_t/m_e with experiment, we have to include the effects of electron-phonon interaction which could change this ratio. Quinn and Ferrell,²² in an earlier rough estimate, obtained a 25% increase due to electron-phonon effects for all alkali metals without including umklapp processes. They suggested that umklapp processes may be quite important and comparable in effect to the normal process. In a recent calculation Robinson and Dow²³ utilized Heine-Abarenkov²⁴ pseudopotentials to calculate the electron-phonon matrix elements and elastic constants in order to determine phonon spectra, and obtained a phonon correction $\delta m_{ph}/m_e = 0.33$. Combining this with our value of m_t/m_e from band calculations, one then gets

$$(m_t/m_e)_{\text{theoret}} = 1.634. \quad (25)$$

It should be remarked that the phonon correction to m_t is considerably larger than the difference $0.03m_e$ between our values of m_t with and without correlation. This justifies a similar conclusion arrived at earlier by Ashcroft and Wilkins²⁵ and by Rice²⁶ for the alkali metals.

The experimental situation regarding m_t/m_e is somewhat uncertain at the present time. The earlier specific-heat measurements of Lien and Phillips²⁷ gave $(m_t/m_e)_{\text{expt}} = 1.6$, in good agreement with the theoretical result in (25). However, a recent measurement by Martin, Zych, and Heer²⁸ gave a value of 2.8 for this ratio. This latter value is seen to be in poor agreement with (25) and would indicate a much stronger distortion of the Fermi surface from sphericity than what we have found from our calculations. The weaker distortion

from sphericity predicted by our calculations is corroborated by de Haas-van Alphen data²⁹ to be discussed presently. An alternative explanation for a large $(m_t/m_e)_{\text{expt}}$ would be a much stronger phonon-enhancement factor than obtained by Robinson and Dow. This possibility does not seem very likely. Some recent cyclotron-resonance data³⁰ lead to an averaged cyclotron mass $m_c = 1.25m_e$, which would be the thermal mass m_t itself if the Fermi surface were exactly spherical. Since we find the departure from sphericity to be small, the cyclotron-resonance measurement would thus be close to the thermal mass and seems to be different from the values of both Lien and Phillips and Martin, Zych, and Heer, although considerably closer to the value of Lien and Phillips.

The other features of the Fermi surface that we can compare with experiment are the external dimensions obtained from dHvA measurements. Using our value of $\epsilon_F = 0.126$, we have obtained the magnitudes of the k_F vectors along three principal directions. These are listed in Table V in units of $k_F^0 = 0.339a_0^{-1}$ for a free-electron approximation. Also included for comparison are the values calculated by Ham¹ and measured experimentally by Okamura and Templeton.²⁹ Our theoretical values for k_F indicate smaller departures from sphericity than Ham's results and are in better agreement with experiment. In fact, the agreement between our results and experiment seems to be excellent for the [110] and [100] directions, while in the [111] direction, the experimental value is a little higher. A possible reason for this deviation could be some inaccuracy in our calculated energy for the P point. We would like to add, however, that Okamura and Templeton obtained their values of k_F from a Kubic-harmonic fit to experimental extremal areas. Since the analytic fits are not unique and their accuracies are somewhat sensitive to the procedure adopted, the small disagreement between theory and experiment does not appear unreasonable.

It is meaningful to compare our results for the features of the Fermi surface with those from pseudopotential calculations using the Heine-Abarenkov-Animalu model potential.²⁴ The qualitative features of pseudopotential results showing small Fermi-surface distortions are in better agreement with ours than with Ham's quantum-defect results. For example, Heine and Abarenkov²⁴ obtain a distortion of only about 1 or 2% in the [110] direction relative to the free-electron radius as compared to our result of 3.2% for the distortion and the QDM result of 8%. The improvement obtained by Heine and Abarenkov over the QDM result is a consequence of the screened ionic potential used in the construction of their model potential. The small difference between their results and ours can perhaps

²² J. J. Quinn and R. A. Ferrell, Phys. Rev. **112**, 812 (1958).

²³ J. E. Robinson and J. D. Dow (private communication). We are grateful to the authors for giving us a report of their work prior to publication.

²⁴ V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

²⁵ N. W. Ashcroft and J. W. Wilkins, Phys. Letters **14**, 285 (1965); N. W. Ashcroft, *ibid.* **23**, 48 (1966).

²⁶ T. M. Rice, Ann. Phys. (N. Y.) **31**, 100 (1965).

²⁷ W. H. Lien and N. E. Phillips, in *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960*, edited by G. M. Graham and A. C. Hollis Hallet (University of Toronto Press, Toronto, 1960), p. 675; see also Ham (Ref. 1), p. 2535.

²⁸ B. D. Martin, D. A. Zych, and C. V. Heer, Phys. Rev. **135**, 671 (1964).

²⁹ K. Okamura and I. M. Templeton, Phil. Mag. **8**, 889 (1963); Proc. Roy. Soc. (London) **A287**, 89 (1965).

³⁰ C. C. Grimes, G. Adams, and P. H. Schmidt, Bull. Am. Phys. Soc. **12**, 414 (1967).

be explained by the fact that Heine and Abarenkov utilized a linear combination of only two plane waves \mathbf{k}_F and $\mathbf{k}_F + (1,1,0)$ in obtaining their eigenfunctions. It would be interesting to test if the use of a larger basis set in the pseudopotential calculation can lead to improved agreement with experiment.

Spin Susceptibility χ_s

In the one-electron approximation, the spin susceptibility is directly proportional to the density of states at the Fermi surface. Using our calculated density of states (24), without correlation, we get

$$(\chi_s)_{\text{band}} = 0.592 \times 10^{-6} \text{ cgs vol. units.} \quad (26)$$

The ratio $(\chi_s)_{\text{band}}/(\chi_s)_{\text{free}} = 1.304$ represents the effects of band structure on the susceptibility. Theoretical arguments³¹ have been advanced to show that χ_s is not influenced by electron-phonon interactions, and so we do not have to apply the phonon-enhancement factor that was used for the specific heat. If one utilized the density of states including correlation, χ_s would be decreased by the small factor of $0.03(\chi_s)_{\text{band}}$, as in the case of the specific heat. However, there are more important exchange and correlation effects for χ_s . Thus, while χ_s does depend upon the ground state of the electrons—that is, those on the Fermi surface—strictly speaking, it is a perturbed or excited state phenomenon since it involves the energy levels and wave functions in the presence of a magnetic field. Essentially, what is involved is the magnetic response (due to spin interactions only, neglecting spin orbit) of the electrons to a magnetic field. Since a perturbed electron can influence other electrons through exchange and correlation, we have really to deal with a many-body system. This is admittedly a rather difficult problem to solve rigorously. We have used two alternative approaches to study this effect approximately. One of these is a RPA procedure, where one calculates the perturbed wave functions self-consistently in a screened-exchange approximation and thereby obtains the additional energy of the electron system in the magnetic field. This procedure has been discussed elsewhere in the literature³² and we shall merely quote our results. We have utilized two screening factors, one from a Thomas-Fermi (TF) model, the same as was utilized in the band-structure calculation, and another one obtained from plasma cutoff³³ (PCU) considerations. The enhancement factors we obtain are

$$(\chi_s)_{\text{TF}}/(\chi_s)_{\text{band}} = 1.8, \quad (27)$$

$$(\chi_s)_{\text{PCU}}/(\chi_s)_{\text{band}} = 2.2. \quad (28)$$

³¹ D. A. Simkin, Ph.D. thesis, University of Illinois, Urbana, Ill., 1963 (unpublished).

³² C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. 4, p. 17; D. R. Hamann and A. W. Overhauser, Phys. Rev. **143**, 183 (1966).

³³ A. K. Rajagopal and S. D. Mahanti, Phys. Rev. **158**, 353 (1967).

The second procedure is one utilized by Silverstein,³⁴ where one interpolates between the high- and low-momentum expressions and introduces effects of band structure in an effective-mass approximation. Using this method, we obtain

$$(\chi_s)_{\text{interpol}}/(\chi_s)_{\text{band}} = 1.301. \quad (29)$$

The spread in the enhancement factors in Eqs. (27)–(29) indicates the uncertainties in the present theoretical models for inclusion of this type of many-body effect. Of the three, Silverstein's estimate seems somewhat more realistic because, whereas the RPA procedure is strictly justified for high-density systems, the interpolation procedure does bring in some features of the more realistic intermediate densities. We shall therefore utilize the enhancement factor in Eq. (29), which makes our theoretical value for χ_s including band and correlation effects

$$(\chi_s)_{\text{theoret}} = 0.7696 \times 10^{-6} \text{ cgs vol. units.} \quad (30)$$

This value is in excellent agreement with a recent experimental value inferred by Kaeck³⁵ from Knight-shift measurements on liquid alkali-metal alloys containing cesium. While this good comparison between theory and experiment is reassuring, not too much emphasis should be placed on the exact quantitative nature of the agreement because of uncertainties in both the theoretical and experimental values. On the theoretical side, the major uncertainty is in the exchange enhancement factor. To make the situation about the latter more definite, what is required is a complete analysis of many-body effects in the presence of a magnetic field, taking explicit account of the proper density and spatial inhomogeneities arising out of the lattice potential. This is a formidable problem requiring detailed study. On the experimental side, there are some assumptions in the determination of χ_s from liquid-alloy studies, particularly about the spin density at the nucleus as a function of concentration. A direct spin-resonance measurement,³⁶ which obviates these assumptions, would be desirable.

Knight Shift

The Knight shift is given by

$$K_s = (8\pi/3)\chi_s\Omega\langle|\psi_{k_F}(0)|^2\rangle_{\text{av}}, \quad (31)$$

when the average is $\langle|\psi_{k_F}(0)|^2\rangle$ taken over the Fermi surface. In Table VI are listed the values of $|\psi_{k_F}(0)|^2$ for the three principal directions [100], [110], and [111]. In the second column, results quoted are from the wave functions resulting from eleventh-order secular equations using the potential V^{Heine} of Table I.

³⁴ S. D. Silverstein, Phys. Rev. **130**, 1703 (1963).

³⁵ J. A. Kaek, Ph.D. thesis, University of Cornell, Ithaca, N. Y., 1968 (unpublished).

³⁶ R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids **24**, 297 (1963).

TABLE VI. Wave-function densities at nucleus (in a_0^{-3}) for symmetry directions and average value. (wc indicates without correlation and c with correlation for the sc. ex.-ch approximation.)

Direction	$ \psi_{k_F}(0) _{wc}^2$	$ \psi_{k_F}(0) _c^2$	Weight factor α_2	$\langle \psi_{k_F}(0) ^2 \rangle_{av}$	$ \psi_{k_F}(0) _{1OPW}^2$
[110]	1.994	2.024	0.5584	1.826	2.239
[111]	1.615	1.653	0.2307		
[100]	1.615	1.652	0.2109		

To examine the influence of correlation in the ground state, the corresponding values of $|\psi_{k_F}(0)|^2$ for $V^{sc. ex.-ch}$ are tabulated in the third column of Table VI. It is seen that correlation effects lead to only a 3% increase in the spin density and are therefore not very significant in their influence. From the results of Table VI the values of $|\psi_{k_F}(0)|^2$ for the [100] and [111] directions are seen to be nearly equal, while that for [110] is about 20% higher. This trend of the variation in the density at the nucleus can be understood by an examination of the symmetry of the relevant regions of the BZ. Thus, starting from the Γ point, the Δ [100] and Λ [111] directions terminate at the points H_{12} and P_4 on the BZ boundary, these points having d and p symmetry, respectively. The terminal point N_1 for the Σ [110] line, on the other hand, has s symmetry. There is, thus, a somewhat faster decrease in s character along the Δ and Λ lines than along Σ . The fact that the variation in $|\psi_{k_F}(0)|^2$ is only 20% is a reflection of the near-spherical nature of the Fermi surface.

To obtain the value of $\langle |\psi_{k_F}(0)|^2 \rangle_{av}$ required in Eq. (31), one has to carry out an average using proper weighting factors^{37,38}: $w = |\nabla_k E|^{-1}$, associated with density of states, and t , arising from the geometry of the BZ. Thus, for any property g , using a discrete number of points in \mathbf{k} space,

$$\langle g \rangle_{av} = \frac{\sum_i t_i w_i g_i}{\sum_i t_i w_i} = \sum_i \alpha_i g_i. \quad (32)$$

Since the band is relatively flatter near the Fermi surface along the [110] direction, this region makes a dominant contribution to the average. Using Eq. (32) and the results for the three directions in the second column of Table VI, we obtain

$$\langle |\psi_{k_F}(0)|^2 \rangle_{av} = 1.826 a_0^{-3}, \quad (33)$$

where a_0 is the Bohr radius, the atomic unit of length. From the convergence in energy in the present calculation as well as from earlier calculations on alkali metals, it appears that the one-OPW energy is quite satisfactory for the occupied regions of the Fermi surface. One would like to inquire whether similar conclusions hold for the wave function, and the Knight shift is an appropriate property to test this point. In Table VI, we have included the results for $|\psi_{k_F}(0)|^2$ for the

one-OPW approximation. The one-OPW result is seen to be 22% higher. To study the convergence, we have analyzed the values of $|\psi_{k_F}(0)|^2$ for various orders of the secular equation, and find that a major change occurs in going from first to third order, encompassing three OPW's at general points and a larger number of symmetry points.

Brooks³⁹ has also obtained $\langle |\psi_{k_F}(0)|^2 \rangle_{av}$ by the QDM procedure and finds a value of $2.47 a_0^{-3}$, which is about 30% higher than our value in Eq. (33). Since the QDM result utilizes approximate procedures based on atomic spin densities, it may include uncertain amounts of atomic correlation and relativistic effects. A quantitative comparison with our results is therefore not meaningful. However, it may be pointed out that, not unexpectedly, the difference in band energies by the two procedures is much less pronounced than that in the wave-function densities.

Using the value for χ_s in Eq. (30) and $\langle |\psi_{k_F}(0)|^2 \rangle_{av}$ in (33), the theoretical value of the Knight shift is found to be

$$(K_s)_{theoret} = 0.885\%, \quad (34)$$

as compared with the most recent experimental value⁴⁰

$$(K_s)_{expt} = 1.58\%. \quad (35)$$

In assessing the nature of the agreement between $(K_s)_{theoret}$ and $(K_s)_{expt}$, we are handicapped by the uncertainty in the value of the spin susceptibility discussed earlier. For purposes of this discussion, the choice of χ_s in Eq. (30) may be considered to be the most reliable to date and reasonably close to the actual value. The theoretical and experimental results for K_s in Eqs. (34) and (35) then indicate that some additional contributions may have to be included in K_s . Three possible effects that have not been considered are relativistic and core-polarization⁴¹ (CP) effects, and correlation between the core electrons themselves as well as between the core and the conduction electrons. Calculations of the CP effect in lithium metal⁴² have indicated that there is cancellation between the CP contributions from the s and p components of the conduction-electron wave

³⁹ H. Brooks (unpublished), quoted in G. B. Benedek and T. Kushida, *J. Phys. Chem. Solids* **5**, 241 (1968).

⁴⁰ D. F. Holcomb, J. A. Kaeck, and J. H. Strange, *Phys. Rev.* **150**, 306 (1967); G. P. Carver, D. F. Holcomb, and J. A. Kaeck, *ibid.* **164**, 410 (1967).

⁴¹ M. H. Cohen, D. A. Goodings, and V. Heine, *Proc. Phys. Soc. (London)* **73**, 811 (1959).

⁴² G. D. Gaspari, W. M. Shyu, and T. P. Das, *Phys. Rev.* **134**, A852 (1964).

³⁷ J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964), p. 154.

³⁸ P. Jena, S. D. Mahanti, and T. P. Das, *Phys. Rev. Letters* **20**, 544 (1968).

functions. It is difficult to conclude without actual calculations whether similar cancellation occurs for cesium metal, but such a possibility does not seem unlikely. Correlation effects among the core electrons alone cannot directly contribute to the hyperfine field, because their spins are paired. Core-conduction correlation is an uncertain factor, but from the arguments in Sec. II one might expect its effect to be small. Since cesium is moderately heavy, we believe that relativistic effects may be the predominant additional source of contribution. Further analysis of all these effects will be very informative since their relative contributions are independent of the uncertainties in χ_s .

Relaxation Time T_1

The relaxation time T_1 complements the Knight shift K_s in providing a test of the accuracy of the conduction-electron wave functions. The dominant relaxation mechanism in the case of alkali metals is through the contact interaction, leading to the expression⁴³

$$(T_1T)_{\text{cont}}^{-1} = (64/9)\pi^3\hbar^2\gamma_e^2\gamma_N^2k_B\langle|\psi_{k_F}(0)|^2\rangle_{\text{av}}^2g^2(\epsilon_F), \quad (36)$$

where k_B is the Boltzmann constant; γ_e and γ_N are the electronic and cesium nuclear gyromagnetic ratios, respectively; the suffix "cont" refers to the contact mechanism; and the other symbols have been defined earlier. Since T_1^{-1} involves $\langle|\psi_{k_F}(0)|^2\rangle_{\text{av}}^2$, it is more sensitively dependent on the accuracy of the wave functions. On substituting the calculated values of $\langle|\psi_{k_F}(0)|^2\rangle_{\text{av}}^2$ and density of states $g(\epsilon_F)$ from Eqs. (33) and (24), we obtain

$$(T_1T)_{\text{cont}} = 0.33 \text{ deg sec}, \quad (37)$$

as compared to the most recent experimental value⁴⁰ of

$$(T_1T)_{\text{expt}} = 0.13 \pm 0.03 \text{ deg sec}. \quad (38)$$

In looking for an explanation of the nearly 2.5 times faster relaxation rate observed experimentally as compared to theory, one can classify the possible causes into two categories: corrections to the calculated relaxation rate itself and additional mechanisms that could also contribute to T_1 . We shall consider the former type first. Equation (36) has been derived assuming the electrons to be interacting independently with the nucleus. However, as in the case of Pauli susceptibility χ_s , we have to take account of the influence of exchange and correlation between conduction electrons on the relaxation process. In the case of χ_s , one is interested in the response of the electrons to a uniform and steady magnetic field. On the other hand, for the relaxation process, one has to deal with the fluctuating inhomogeneous field of the nucleus. Thus, the appropriate response function is now $\chi(\mathbf{q},\omega)$ instead of $\chi(0,0)$ ($\equiv \chi_s$) for the

⁴³ C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, Publishers, Inc., New York, 1963), p. 126.

TABLE VII. Values of T_1T (deg sec) for different mechanisms.

Approximation	Contact mechanism (without exchange enhancement)	Moriya model [Eq. (39)]	Mitchell mechanism (dipole and electric quadruple)	Expt
T_1T	0.3296	0.2160	1.10×10^2	0.13 ± 0.04

steady uniform field. This problem has been discussed by a number of authors.^{44,45} Moriya⁴⁵ has carried out a calculation of the correction to T_1^{-1} using, for simplicity of analysis, a δ -function interaction between the electrons. The resulting expression for $(T_1T)^{-1}$ is

$$(T_1T)_{\text{Moriya}}^{-1} = (T_1T)_{\text{cont}}^{-1} \langle [1 - \alpha_{\text{band}} F(q)]^{-2} \rangle_{\text{av}}, \quad (39)$$

α_{band} being a parameter depending on the strength of the assumed δ -function interaction between the electrons. The function $F(q)$ in Eq. (39) is the linear dielectric function⁴⁶ which for the case of a spherical Fermi surface has the form

$$F(q) = \frac{1}{2} \left[1 + \frac{4k_F^2 - q^2}{4k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right]. \quad (40)$$

The average in (39) is over all q 's which connect states on the Fermi surface. The parameter α_{band} can be evaluated from the enhancement factor for the uniform static susceptibility using a δ -function model, namely,

$$(\chi_s)_{\text{theoret}} / (\chi_s)_{\text{band}} = 1 / (1 - \alpha_{\text{band}}). \quad (41)$$

In Eq. (41) we have utilized the value of $(\chi_s)_{\text{theoret}} / (\chi_s)_{\text{band}}$ obtained from Silverstein's expression [Eq. (29)] and obtained $\alpha_{\text{band}} = 0.236$. On substituting this value of α_{band} and Eq. (40) in (39), we obtain the value of $(T_1T)_{\text{Moriya}}$ given in the second column of Table VII (after making appropriate corrections⁴⁷ for numerical errors in Moriya's⁴⁵ Table I). This value (0.2160 deg sec) is still substantially larger than experiment. It is possible that further improvement could be attained with a more realistic treatment of the electron-electron interaction. However, as in the case of Knight shift, there can be significant corrections to the contact mechanism from CP and relativistic effects. A detailed treatment of these effects is beyond the scope of the present work. It is suggested, however, that a convenient procedure for dealing with CP effect would be an adaptation of the moment-perturbation method⁴² that has been used previously for the Knight shift. For relativistic effects a Dirac formulation of the OPW procedure¹⁴ would be desirable.

⁴⁴ J. Korringa, *Physica* **16**, 601 (1950); L. P. Kadanoff, *Phys. Rev.* **132**, 2073 (1963).

⁴⁵ T. Moriya, *J. Phys. Soc. Japan* **18**, 516 (1963).

⁴⁶ D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1962).

⁴⁷ S. D. Mahanti, Ph.D. thesis, University of California, 1968 (unpublished).

Mitchell⁴⁸ has proposed two other mechanisms that could contribute to the relaxation process. These are the electron-nuclear dipole interaction and electric-quadrupole interaction between the nucleus and the electrons. He has derived expressions for $(T_1T)^{-1}$ for these mechanisms in the case of nuclear spin $I=1$.

$$\frac{(T_1T)_{\text{dip}}^{-1}}{(T_1T)_{\text{cont}}^{-1}} = \frac{1877}{240} \frac{\langle 1/r^3 \rangle_{k_F}^2}{\langle |\psi_{k_F}(0)|^2 \rangle^2}, \quad (42)$$

$$\frac{(T_1T)_{\text{dip}}^{-1}}{(T_1T)_{\text{quad}}^{-1}} = \frac{68}{6} \frac{\gamma_N^2 \gamma_e^2 \hbar^4}{e^4 Q^2}, \quad (43)$$

where Q is the quadrupole moment. In Eq. (42), $\langle 1/r^3 \rangle_{k_F}$ represents the expectation value of $(1/r^3) \times (3 \cos^2\theta - 1)$ over the p component of the conduction-electron wave function with wave vector k_F . These expressions are adequate for order-of-magnitude estimates of the relaxation times due to these mechanisms. From the calculated OPW wave functions, it is found that

$$\frac{\langle 1/r^3 \rangle_{k_F}}{|\psi_{k_F}(0)|^2} \approx 0.03. \quad (44)$$

On substituting (44) in Eq. (42), we obtain

$$(T_1T)_{\text{dip}} \approx 1.1 \times 10^2 \text{ deg sec}. \quad (45)$$

Using this result and the value of the quadrupole moment Q ($Q=0.004$ b) for Cs¹³³, Eq. (43) yields

$$(T_1T)_{\text{quad}} \approx 1.5 \times 10^6 \text{ deg sec}. \quad (46)$$

The ineffectiveness of the dipolar and electronic-quadrupole mechanisms is a consequence of the small p character of the conduction-electron wave function, the quadrupole mechanism being rendered even less important by the rather small value of Q . It appears, therefore, that the major additional contributions to the relaxation process would have to come from CP and relativistic effects, if improved agreement with experiment is to be attained.

V. CONCLUSION

A first-principles OPW calculation has been carried out for the energy bands and wave functions for cesium metal. Correlation effects are incorporated explicitly through their influence on the conduction-electron potential. The shape and dimensions of the calculated Fermi surface were found to be in good agreement with available experimental information. The value of specific heat, obtained from the density of states, after

correcting for electron-phonon effects, is also found to be in reasonable agreement with the experimental value. The calculated Knight shift and relaxation time were found to be in fair agreement with experiment. It is suggested that the incorporation of CP and relativistic effects can provide improved agreement with experiment for both these properties. Other hyperfine properties of interest are the Ruderman-Kittel and pseudodipolar coupling between the nuclei, and these owe their origin to the entire occupied k space rather than the Fermi surface alone. An analysis of these properties is presented in a separate publication.²¹

ACKNOWLEDGMENTS

We are grateful for the cooperation and assistance rendered to us by the staff of the Computing Center, University of California, Riverside. Some helpful discussions with Dr. L. Tterlikkis and Dr. A. K. Rajagopal are also gratefully acknowledged.

APPENDIX

One has to solve the following matrix equation:

$$H - ES = 0. \quad (A1)$$

The matrices H and S in Eq. (A1) are real and symmetric in our case, but in general they can be complex but Hermitian. Defining a unitary transformation U_1 which diagonalizes the S matrix, one obtains from Eq. (A1)

$$(H' - ED)\psi' = 0, \quad (A2)$$

where

$$H' = U_1^\dagger H U_1,$$

$$\psi' = U_1^{-1} \psi,$$

and

$$U_1^\dagger S U_1 = D. \quad (A3)$$

To eliminate D from Eq. (A2), one defines another transformation (not unitary) U_2 whose matrix elements are given by

$$(U_2)_{ij} = (D_{ii})^{-1/2} \delta_{ij}. \quad (A4)$$

Utilizing the second transformation U_2 , one obtains from Eq. (A2)

$$(H'' - E)\psi = 0, \quad (A5)$$

where

$$H'' = U_2^\dagger H' U_2$$

and

$$\psi = U_2^{-1} U_1^{-1} \psi. \quad (A6)$$

It is rather easy to show that H'' is still symmetric and Eq. (A5) can be solved by using the standard matrix diagonalization technique, giving E and ψ'' . Equation (A6) can then be used to obtain ψ .

⁴⁸ A. H. Mitchell, J. Chem. Phys. **26**, 1714 (1957).