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Pseudopotential Models for Pb and Mg: Convergence Properties

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The convergence properties of Fermi-surface pseudopotential calculations are discussed. It is found for Mg and for Pb that previous models which use only a relatively small number of plane waves are inadequate, particularly when pressure derivatives of Fermi-surface cross sections are calculated. Convergence studies are presented for both materials. It is found for Mg that a local-pseudopotential model if converged can be satisfactory and thus that a nonlocal model is not required. For Pb it is found that several of the discrepancies between experimental results and the model of Anderson *et al.* can be attributed directly to nonconvergence of their model. A pseudopotential model for the Pb Fermi surface is presented which gives a quite satisfactory description of the de Haas–van Alphen results both at normal volume and under pressure.

I. INTRODUCTION

Parametrization of the Fermi surface of metals has become quite common. The parametrization may be done in a manner that is obviously mathematical[1,2] such as a Kubic-harmonic expansion. Alternately, it may be considered in a more physical manner,[3–6] for example, using a pseudopotential. The latter has certain pleasing features, particularly if one wishes to extend the model to compare with something beyond normal-volume de Haas–van Alphen (dHvA) information.[6,7] The present work will be primarily concerned with the often neglected necessity for pseudopotential convergence if a pseudopotential model is to be a satisfactory physical model.

In Sec. II the pseudopotential method is reviewed. Section III considers Mg, and we will see how the use of an unconverged pseudopotential led Kimball, Stark, and Mueller (KSM)[5] to incorrectly conclude

that the normal-volume Fermi-surface data could not be fit by a local pseudopotential and hence that a nonlocal model was required. We will also see that convergence is very important in carrying out a pseudopotential study of the volume dependence of a Fermi surface. In Sec. IV, Pb is considered. The pseudopotential calculation of Anderson *et al.* (AOS)[6] for Pb had two major deviations from experiment that can be attributed directly to nonconvergence: (i) There was one orbit that simply could not be satisfactorily fit. (ii) Using the standard pseudopotential prescription to make the calculations volume dependent, all pressure derivatives were much too free-electron-like.

A model for the Pb Fermi surface is described in Sec. IV consisting of a local pseudopotential plus a spin-orbit term. This model quite satisfactorily describes the Fermi surface both at normal volume and under pressure.

II. PSEUDOPOTENTIALS

To be explicit let us write an expression for a local pseudopotential

$$V(\vec{r}) = \sum_{\vec{G}} v(\vec{G}) e^{i\vec{G}\cdot\vec{r}} , \tag{1}$$

where the $\vec{G}$'s are reciprocal-lattice vectors and $v(\vec{G})$ are the Fourier coefficients of the pseudopotential.[8] With certain loss of generality this is rewritten in the form more common to empirical pseudopotential work,

$$V(\vec{r}) = \sum_{\vec{G}} w(G) S(\vec{G}) e^{i\vec{G}\cdot\vec{r}} , \tag{2}$$

where $S(\vec{G})$ is the structure factor and $w(G)$ is called the form factor.

The pseudopotential is often discussed as if it had been further rewritten

$$V(\vec{r}) = \sum_{t} w(t) \sum_{\vec{G}ct} S(\vec{G}) e^{i\vec{G}\cdot\vec{r}} , \tag{3}$$

where t now indexes sets of reciprocal-lattice vectors which transform into themselves under symmetry operations of the appropriate space group. A typical pseudopotential calculation in a high-symmetry material will use only a few t values.

The pseudo-wave-function is represented as a plane-wave expansion,

$$\phi(\vec{k}, \vec{r}) = \sum_{\vec{G}} C_{\vec{k}}(\vec{G}) e^{i(\vec{k}+\vec{G})\cdot\vec{r}} . \tag{4}$$

For practical reasons the summation in (4) is usually truncated. The present work is primarily concerned with the consequences of this truncation. The expansion is usually truncated to include one of the following: (i) all $\vec{G}$ such that $|\vec{k}+\vec{G}| \leq G_{\max}$; (ii) some particular number of $\vec{G}$'s such that $|\vec{k}+\vec{G}|$ for those included is less than for those excluded; or (iii) a particular set of $\vec{G}$'s. One of the points to be noted in the present work is that the choice of truncation method is unimportant. If the expansion is converged, i.e., if a sufficient number of $\vec{G}$'s have been included, the variation in eigenvalue and in wave functions will be unimportant between the choices. On the other hand, if not enough $\vec{G}$'s are included, global application of any of the above prescriptions will almost assuredly run into trouble—discontinuities in $E(k)$ or in $k(\theta, \phi, E_F)$ on the order of $\frac{1}{3}$ to $\frac{1}{10}$ the magnitude of the difference between $E(k)$ calculated unconverged and converged.

For understanding convergence in Fermi-surface calculations, the $\vec{G}$'s in Eq. (4) can be separated into three classes. First, there are those such that $|\vec{G}| \leq 2k_F$. For certain directions in k space, plane waves on the Fermi surface may be coupled by $v(\vec{G})$ to other plane waves at the Fermi surface. These plane waves enter into the free-electron construction or the one-orthogonalized-plane-wave (OPW) model. It is obvious that this entire class must be included in the expansion (4).

The second class includes those plane waves (not in the first class) which have a significant coupling *directly* to plane waves at the Fermi surface. These extend approximately from $2k_F < |\vec{G}|$ to $|\vec{G}| - k_F \leq G_v^{\max}$, where $G_v^{\max}$ is the largest $|\vec{G}|$ for which $v(\vec{G})$ is significant. The error in truncating (4) within this class can be readily estimated as

$$\Delta E_{k_F} = \sum_{\vec{G}_{\mathrm{omit}}} \frac{|v(\vec{G})|^2}{|\vec{k}+\vec{G}|^2 - k_F^2} , \tag{5}$$

where $\vec{G}_{\mathrm{omit}}$ are all reciprocal-lattice vectors omitted in the truncation of Eq. (4). (Under most circumstances $\vec{G}_{\mathrm{omit}}$ may *not* be expressed as $\vec{G}$ such that $|\vec{G}|$ is greater than some $G_{\max}$.) For $|\vec{G}| \gg k_F$, Eq. (5) represents just a constant shift of states independent of position on the Fermi surface. This means that the first terms in the summation will be most important because these terms will be different at different points on the Fermi surface. Using either of the first two prescriptions for the truncation of Eq. (4), the set $\vec{G}_{\mathrm{omit}}$ can change as a single piece of Fermi surface is mapped out. If this is a change in type of $\vec{G}$ (such as from a [111] to a [200] in an fcc material), a discontinuity in the calculated Fermi surface results. This class may be slightly ambiguous since a definition of the last significant $v(\vec{G})$ is required, but it is asserted that this entire class must also be included. Note that the difficulties may be diminished if $\vec{G}$ were such that the form factor changes very little between $w(t)$ and $w(t+1)$.

The third class includes all the rest. The classes can be summarized as follows: The first class enters the calculation in first order, the second class in second order, and the third class in

higher order. In the Mg calculation of KSM, the pseudopotential has been truncated early in the second class. In the Pb calculation of AOS, the truncation has been made between the first and second classes for part of the Brillouin zone and very early in the second class elsewhere in the zone.

The foregoing discussion and Eq. (5) imply that perhaps part of the second class of plane waves could be treated in second order and thus effect a significant saving in computer time. As is quite common in pseudopotential calculations, the Löwdin partitioning scheme[9] will be used to implement this saving in the present work. After truncation, the summation in Eq. (4) will be broken into two parts; the first part of the sum will include those states to be treated exactly and the number of these states will determine the size of the "inner matrix." The influence of the second part of the sum will be folded into the inner matrix which will then be diagonalized to yield eigenvalues and eigenvectors.

One might be tempted to regard the resulting inner matrix which we diagonalize as essentially a nonlocal-pseudopotential matrix. The author's point of view is that we set up a large local-pseudopotential matrix and then, as a computational convenience, use Löwdin partitioning to hasten obtaining the desired eigenvalues. The crucial point is that we know how to make the local-pseudopotential volume dependent—but it is incorrect to simply assign that volume dependence to the individual elements in the resulting Löwdin *inner* matrix.

In a high-symmetry material a pseudopotential band-structure calculation requires values of the form factor at a few discrete points and hence these specific values may readily be used directly as the parameters. However, if the value of the form factor is needed at many values of q, such as in a low-symmetry material, or to consider a problem in which the translational symmetry has been broken by a perturbation, or to simply take into account change in lattice constant, it is convenient to use an analytic form for $w(q)$.

Theoretically derived expressions for $w(q)$ tend to fall off at large q more slowly than is convenient for use in energy-band calculations. [The more slowly $w(q)$ falls off, the more reciprocal-lattice vectors are included in the second class, having a significant coupling directly to states of interest, and hence the more reciprocal-lattice vectors that must be included in Eq. (4).] Many empirical pseudopotential calculation have been performed using *ad hoc* analytic forms that fall off more rapidly. (The use of such an *ad hoc* form is similar to setting all Fourier coefficients to zero beyond the first few, which is common practice in treating cubic semiconductors.) Jacobs[10] has addressed the question of why these *ad hoc* forms do nonetheless yield satisfactory energy-band structures. In the present work the analytic expression used by Lin and Falicov[11] in As will be adopted as a convenient form:

$$w(q) = (\Delta_0/\Delta)\, B_1(q^2 - B_2)\,(e^{B_3(q^2-B_4)}+1)^{-1}\ , \qquad (6)$$

where the volume-normalization factor has been added explicitly. The atomic volume is Δ, the normal volume is Δ_0, and the B's are parameters (which are assumed to be independent of lattice parameters). The question to be considered in what follows is, having selected a form for $w(q)$ [or a set of $w(t)$] that presumably fall off with convenient rapidity, how many reciprocal-lattice vectors must be included in Eq. (4) to yield meaningful results?

III. Mg

The Mg aspect of the present work grew out of an effort to calculate the predictions of the models of KSM[5] for the pressure dependence of the Mg Fermi surface.[12] KSM used both local and nonlocal models employing ten plane waves. Their ten-plane-wave local-model fit was sufficiently poor that they concluded a nonlocal model was necessary to fit the Fermi surface. There are two serious objections to the use of a ten-plane-wave model. First, a converged local model will fit the normal-volume data—so that use of only ten plane waves led to their wrong conclusion. Second, the predicted pressure derivatives of an unconverged model differ from those of a converged model. As will be evident when we examine the detailed convergence properties, changing the number of plane waves from ten required a complete new pseudopotential fit to the Fermi-surface data. The fitting procedure followed was essentially that of KSM. The pseudopotential Fourier coefficients and the Fermi energy were used as parameters in a least-squares program. The difference between the Fermi energy and the energy of the appropriate band at 11 points in k space defined by trial Fermi radii was minimized. (The Fermi radii were those used by KSM[13]; a 12th point was added at the approximate center of the μ_1^1 orbit. To yield the correct μ_1^1 orbit size this point was asked to be 0.01 Ry above the Fermi energy in the least-squares procedure.) Using the parameters thus determined, Fermi-surface areas were calculated, after which trial Fermi radii were adjusted on the basis of comparing calculated and experimental areas. Having a new set of Fermi radii, the whole process was repeated. This cycle was repeated until the agreement between calculated and experimental areas could not be improved. In the present work the first four $w(t)$ ($w_{10\bar{1}0}$, w_{0002}, $w_{10\bar{1}1}$, $w_{10\bar{1}2}$) were then fit to Eq. (6) which was subsequently used for

all values of $w(t)$. This was done as a convenience in finding $w(t)$ at different values of the lattice constant. [It should be pointed out that the values of $w(t)$ beyond $w_{10\bar{1}2}$ are sufficiently small that the conclusions to follow would be unaltered if all $w(t)$ beyond $w_{10\bar{1}2}$ were set identically to zero.]

States on the Fermi surface are coupled to other states on the Fermi surface by the first three $w(t)$ and their values are readily determined by this fitting procedure. Additional coefficients which enter only in higher order seem to be indeterminate. This led to a procedure in which the fourth coefficient was arbitrarily selected and the procedure carried out. Equally good fits to normal-volume data were obtained for two distinct values of $w_{10\bar{1}2}$; it is inferred that the same could be done for any reasonable value of $w_{10\bar{1}2}$.

In Table I the results of a convergence study on our model[12] for Mg are excerpted. To put the energy scale in perspective, note that in the local model of KSM, which was not satisfactory, the largest error was 38% on an orbit where this corresponded to a shift in E_F of only about 40 meV. KSM optimistically estimated their convergence to be within 20 meV. The present model, which is shown in column 7 of Table I, was adopted after looking at such a convergence study and the model employs over 100 (100+) plane waves folded by Löwdin partitioning into a 20×20 inner matrix.

The parameters used were selected by the fitting procedure described above using the 100+-plane-wave calculation. The same parameters are then used for all calculations in the convergence study. The parameters used are not those used by KSM. However, if there are differences in the convergence properties, this model should converge more readily than that of KSM. The reason is that the fourth Fourier coefficient is slightly smaller in our model, and the fifth coefficient in the local model of KSM is not small.

There are several things to note in Table I. Comparing with column 6, we see that the same 100+ plane waves folded into a 60×60 inner matrix change eigenvalues less than 3 meV. This test tells us whether or not the inner matrix is of adequate size. A significantly larger number of plane waves folded into the same 60×60 matrix does not produce a detectable change. Thus, the total number of plane waves used is adequate. Comparing with column 8, we see that even folding down to the size used by KSM, 10×10, produces a reasonably converged result. On the other hand, if the total number of plane waves is reduced below about 50, the convergence error is seen to begin to grow significantly. For Fermi-surface work a shift of all states together is unimportant; all that really matters is the relative (differential) motion of these energy levels (at the Fermi surface). For example, using 25 plane waves the maximum differential nonconvergence is only 16 meV. On the other hand, for ten plane waves, the number employed by KSM, the differential nonconvergence is 87 meV. It is very apparent that the influence of nonconvergence is not just a uniform shift of the energy of states on the Fermi surface.

We have just found the convergence properties of a local model. However, the convergence properties of the nonlocal model of KSM should be essentially the same as those just found since the values of the resulting matrix elements in their nonlocal model are very similar to those of the local model.

The real problem of convergence manifests itself when pressure (volume) derivatives are calculated using various numbers of plane waves. Before doing such a calculation, it seemed reasonable that most of the effects of nonconvergence would be the same for slightly different lattice constants and, thus, that pressure derivatives could be calculated from the KSM models even if they were not fully converged. As we shall see in what follows, this is not so!

To calculate pressure derivatives for Mg, the pseudopotential calculation is repeated at lattice parameters corresponding to 20 kbar. The change in convergence properties with the change in lattice parameters is shown in Table I by listing the difference in eigenvalue between the 20-kbar calculation and the normal-volume result. These values are listed in parentheses. (There is a free-electron shift of about 57 meV that has been subtracted out.)[14] These numbers are significantly different at ten and 25 plane waves from those of a converged model. This is to say that the nonconvergence error we have previously found does *not* have a negligible dependence on lattice parameters. In view of the importance of higher-order effects in the observed convergence properties of the Mg pseudopotential at normal volume, the result should not be surprising.

It should be acknowledged that the ten-plane-wave calculation described in column 1 of Table I is not a ten-plane-wave pseudopotential model for Mg. If one wanted a ten-plane-wave model, the Fourier coefficients would be readjusted to improve the normal-volume Fermi-surface fit. This would in fact result in slightly different energy distortions with pressure. This latter approach was actually followed in this investigation. From the ten-plane-wave model, we progressed through 25- and 30-plane-wave models before carrying out a detailed convergence study and selecting the 100+-plane-wave model. (The 30-plane-wave model gave an excellent fit to the normal-volume data.) The problem manifests itself as systematic changes in volume derivatives as more converged models are

TABLE I. Convergence study of Mg pseudopotential model.[a]

k points[c] \ Plane waves[b]	1 10(10)	2 25(25)	3 40(40)	4 50(50)	5 60(60)	6 111(60)	7 111(20)	8 111(10)
Γ (3)	−1.1691 (0.0067)	−1.2038 (0.0027)	−1.2388 (−0.0019)	−1.2403 (−0.0012)	−1.2437 (−0.0005)	−1.2469 (−0.0003)	−1.2475 (−0.0003)	−1.2483 (−0.0003)
$k^{\Gamma K}(3)$	0.1222 (0.0513)	0.0356 (0.0362)	0.0132 (0.0328)	0.0064 (0.0325)	0.0053 (0.0325)	0.0005 (0.0333)	−0.0000 (0.0333)	−0.0025 (0.0317)
$k^{\Gamma M}(3)$	0.1158 (0.0488)	0.0378 (0.0349)	0.0141 (0.0320)	0.0066 (0.0309)	0.0040 (0.0314)	0.0004 (0.0319)	−0.0000 (0.0320)	−0.0030 (0.0317)
$k^{\Gamma A}(3)$	0.0651 (0.0161)	0.0422 (0.0159)	0.0073 (0.0091)	0.0073 (0.0091)	0.0052 (0.0098)	−0.0005 (0.0104)	0.0000 (0.0105)	0.0018 (0.0103)
$k_{\text{in}}^{\Gamma M}(2)$	0.0470 (−0.0355)	0.0304 (−0.0375)	0.0133 (−0.0416)	0.0069 (−0.0420)	0.0043 (−0.0428)	0.0003 (−0.0423)	0.0000 (−0.0425)	0.0004 (−0.0427)
$k^{\Gamma' L}(2)$	0.0486 (−0.0180)	0.0298 (−0.0244)	0.0144 (−0.0292)	0.0067 (−0.0303)	0.0043 (−0.0300)	0.0009 (−0.0296)	−0.0000 (−0.0298)	−0.0008 (−0.0302)
$k_{\text{out}}^{\Gamma K}(2)$	0.0880 (−0.0180)	0.0265 (0.0041)	0.0242 (0.0042)	0.0085 (0.0008)	0.0069 (0.0007)	0.0026 (0.0015)	0.0000 (0.0010)	−0.0043 (0.0003)
$k_{\text{out}}^{\Gamma M}(2)$	0.0689 (−0.0095)	0.0368 (−0.0158)	0.0169 (−0.0212)	0.0070 (−0.0227)	0.0044 (−0.0223)	0.0013 (−0.0219)	0.0000 (−0.0221)	−0.0029 (−0.0229)
$k^{K\Gamma}(3)$	0.0598 (−0.0115)	0.0323 (−0.0280)	0.0237 (−0.0273)	0.0061 (−0.0296)	0.0053 −0.0305	0.0014 −0.0301	0.0000 (−0.0307)	−0.0021 (−0.0318)
$k^{KM}(3)$	0.0750 (−0.0013)	0.0299 (−0.0113)	0.0243 (−0.0107)	0.0076 (−0.0143)	0.0074 (−0.0143)	0.0024 (−0.0137)	0.0000 (−0.0142)	−0.0027 (−0.0150)
$k^{LH}(3)$	0.1312 (0.0344)	0.0374 (0.0219)	0.0164 (0.0185)	0.0091 (0.0184)	0.0052 (0.0204)	0.0022 (0.0209)	−0.0000 (0.0208)	−0.0097 (0.0195)
$k^{L\Sigma'}(3)$	0.1341 (0.0328)	0.0395 (0.0220)	0.0149 (0.0204)	0.0061 (0.0196)	0.0038 (0.0201)	0.0011 (0.0204)	−0.0000 (0.0204)	−0.0057 (0.0199)
Top μ_1^1	0.1914 (−0.0079)	0.1620 (−0.0157)	0.1558 (−0.0191)	0.1465 (−0.0209)	0.1420 (−0.0215)	0.1386 (−0.0209)	0.1363 (−0.0216)	0.1349 (−0.0219)

[a]Eigenvalues (in eV) of model used in Ref. 12 for various numbers of plane waves. Parameters used in Eq. (6) are $B_1 = 0.2171$, $B_2 = 1.302$, $B_3 = 1.235$, and $B_4 = 1.3426$. The partitioning energy has been selected as the average of the three lowest diagonal elements of the matrix. For the model as used in Ref. 12, which is shown in column 7, the bottom of the band occurs −7.1499 eV below E_F and $E_F - V_{0000}$ is 7.0001 eV. The numbers in parentheses are the changes in eigenvalue with 20 kbar (a constant shift of 57 meV has been subtracted out). See text for details.

[b]Number of plane waves used (and number of plane waves in inner matrix). See text. The number 111 is a nominal number. Runs so labeled used all k such that $|k|^2 \leq 7.25\ (2\pi/a)^2$.

[c]k points are those used in fitting plus the third level at Γ. The notation is that of KSM (Ref. 5). The numbers in parentheses index the band. Also see Ref. 13.

TABLE II. Pressure derivatives of Mg Fermi-surface areas.

Orbit[a]	θ[b] (deg)	Area[c]	$\frac{d\ln F}{dP}$ (%/kbar) Expt.[d]	Theory[e,f]	Free-electron ΔE_F[e,g]
λ_1^1	90	0.0727	+0.05 (± 0.02)	0.09	+0.11
μ_1^1	28.7	0.00183	−0.9 (± 0.3)	−0.78	−0.94
μ_1^5	90	0.00721	−0.17 (± 0.02)	−0.19	−0.27
μ_1^7	90	0.0457	+0.05 (± 0.02)	+0.03	−0.003
γ_1^1	0	0.00598	+0.40 (± 0.04)	+0.35	+0.42
Free-electron scaling[h]			0.18		

[a]See Ref. 5 for orbit nomenclature.
[b]Angle measured from [0001].
[c]Reference 5.
[d]Reference 12.
[e]Calculated "derivatives" are finite differences using 20 kbar and 0 pressure results.
[f]Model used in Ref. 12 and described in this work using a 20-kbar ΔE_F of 0.259 eV.
[g]Model that results from using free-electron estimate for change in E_F with 20 kbar ($\Delta E_F = 0.264$ eV).
[h]For an isotropic material, in the free-electron approximation all cross sections scale with the Brillouin zone, i.e., increase at a rate of $\frac{2}{3}$ the volume compressibility.

used. If the normal-volume fits were uniquely determined, perhaps this comparison should be presented. However, since it was found that volume derivatives did depend on the choice of the fourth Fourier coefficient, convergence properties of a model based on fixed Fourier coefficients are more transparent.

The experimental and calculated pressure derivatives are listed in Table II. As pointed out by Tripp *et al.*,[15] the calculated pressure derivatives of Fermi-surface cross sections are very sensitive to the value selected for the change in E_F. In Mg we initially used the free-electron estimate for this change. This led to the pressure derivatives shown in the last column of Table II. Careful comparison of calculation and experiment suggested that the agreement would be improved if ΔE_F was changed by about $\frac{1}{2}$ mRy. The change in E_F was also determined by integration over the Brillouin zone. The results of this integration are summarized in Table III. Note that calculation of E_F to the desired precision required a large number of points in the Brillouin zone even using the linear analytic method.[16] Fortunately, the difference seems to be better determined. The detailed calculation led to a shift of 0.005 eV. This is out of a total ΔE_F of 0.259 eV. This small amount significantly improved the agreement between the model and the experimental results. Note that in fact the last column in Table II does not really agree quantitatively with experiment, whereas a shift in E_F of only 5 meV produces agreement almost within experimental uncertainty.

The 100+-plane-wave model described fits the normal-volume data and the pressure dependence quite satisfactorily.[12] The ten-plane-wave local model of KSM gave a volume dependence that was more free-electron-like than the results of the pressure experiments.[12] In particular, the λ_1^1 (90°) orbit in a 10-plane-wave model had a pressure derivative of 0.14%/kbar versus the experimental value of 0.05%/kbar. The preliminary calculation indicated that the ten-plane-wave nonlocal model of KSM had a volume dependence quite similar to their ten-plane-wave local model. However, since the converged local model is satisfactory, the nonlocal model was not pursued further.

IV. Pb

For Pb, Anderson and co-workers[6,17] have used only four plane waves in their pseudopotential models. In view of the present finding in Mg, these Pb results were considered suspect and the following phase of the investigation was undertaken.

For description of the Pb Fermi surface including figures, the reader is referred to Anderson and Gold (AG).[17] The values quoted for dHvA areas will be taken from frequencies in AOS[6] and Anderson and Hines (AH).[18] Some confusion exists concerning the orbits about the arms designated $\xi[110]$ by AH and AOS. There are two orbits resulting in a beat pattern of 42 or 42.5 cycles/beat. Experimentally, one readily determines the frequency of the dominant oscillation (area = 0.0483 a.u.). Determining whether the second frequency is higher or lower is more subtle.[19] Careful measurements on a well-oriented high-quality sample indicate the nondominant orbit to have a lower frequency.[18,20,21] The original AG theoretical fit found two orbits separated by the required 2.2%. In the theoretical fit of AG the central orbit corresponded to the lower frequency.. In AOS the central orbit was fit to the dominant or larger frequency, and no additional orbit was found.[21]

AOS found very poor agreement with pressure derivatives using a local model and only achieved

TABLE III. E_F obtained by Brillouin-zone integration.[a]

Number of points[b]	45	112	180	330	546
$P = 20$ kbar	7.3866	7.4122	7.3973	7.4076	7.4043
$P = 0$	7.1253	7.1542	7.1402	7.1483	7.1455
Difference	0.2613	0.2580	0.2571	0.2593	0.2588

[a]Measured from Γ_1^+ in eV. Calculated using linear analytic method. See Ref. 16.
[b]Number of points in $\frac{1}{24}$ of Brillouin zone.

TABLE IV. Fermi radii used in least-squares fitting for Pb.

Point[a]	Origin	Direction	Radii (a.u.)	Orbits
a	0 0 0	[100]	0.6504	ψ[100] ψ[110]
b	0 0 0	[$\bar{1}$11]	0.472	ψ[110]
c	0 0 0	[$\bar{1}$10]	0.5726	ψ[110] ψ[111] ψ[100]
d	0 0 0	[11$\bar{2}$]	0.5084	ψ[111]
e	$-\frac{3}{4}\frac{3}{4}$ 0	[$\bar{1}$10]	0.1240	ξ[110] ξ[111] ξ[100]
f	$-\frac{3}{4}\frac{3}{4}$ 0	[1$\bar{1}$0]	0.2968	ξ[110] ξ[111]
g	$-\frac{3}{4}\frac{3}{4}$ 0	[001]	0.1680	ξ[110]
h	0 0 1	[100]	0.3016	ξ[100]
m	$\frac{1}{2}$ 0 1	[00$\bar{1}$]	0.4165	ν[1 1 0]
n	$\frac{1}{2}$ 0 1	[01$\bar{1}$]	0.2362	ν[110]
o	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	[$\bar{1}$10]	0.4709	θ[111]
r	$-\frac{3}{4}\frac{3}{4}$ 0	[$\bar{1}\bar{1}$2]	0.2093	ξ[111]
w	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	[11$\bar{2}$]	0.4332	θ[111]

[a]As labeled by AG, Ref. 17.

agreement within a nonlocal model by using a "R_m-scaled" volume dependence. Experimentally, almost all orbits grow more rapidly with pressure than simple free-electron scaling. The local-pseudopotential results of AOS simply do not significantly deviate from free-electron scaling. This is not surprising. This is a direct consequence of using an unconverged pseudopotential. The very-few-plane-wave model is simply much more free-electron-like than experiment.

The R_m-scaled model is somewhat disturbing. A key assumption of empirical pseudopotential theory is that the pseudopotential describes properties of the ion core that are nearly independent of crystalline environment. This is directly contradicted by a prescription for calculating as a function of volume that says that the ion radius changes in direct proportion to the lattice constant. AOS offer no physical rationale for the R_m-scaled model—except that it works!

The model to be discussed here is a local pseudopotential with a spin-orbit term added which is modeled after the corresponding term in the relativistic OPW method[22]:

$$H_{so}^{l=1}(\vec{k}_i s', \vec{k}_j s) = -i\lambda\, \hat{k}_i \times \hat{k}_j \cdot \vec{\sigma}_{s's}\, C(k_i) C(k_j), \quad (7)$$

where $\vec{k}_i$ are vectors in reciprocal space [$\vec{k}_i = \vec{k} + \vec{G}_i$ in the notation of Eq. (4)], $\vec{\sigma}$ are the Pauli matrices, and λ is the parameter describing the strength of the spin-orbit interaction. The wave-function Fourier transforms $C(k_i)$ have been modeled as $C_0 k_i (1 - a k_i^2)$, where a (= 0.269 a.u.) was selected to approximate the Fourier transform of the Pb 5p wave function. [For computational reasons the $C(k_i)$ are set equal to zero beyond the 30th plane wave.] This is not the same form used by AOS. Note that we no longer have a strictly local model; the spin-orbit term is k dependent. The spin-orbit calculation proceeds by a double-expansion technique. The local pseudopotential without spin is set up using about 90 plane waves. This is solved using Löwdin partitioning to fold it into a 30×30 matrix. The eigenvectors within about 1.75 Ry of the Fermi energy are then used as a basis set for expanding H_{so}. Finally, the eigenvalues of the resulting matrix (including the part from the local pseudopotential which is diagonal) are determined. This latter matrix ranges from about 20×20 to 30×30.

The fitting procedure is essentially the same as that used in Mg. Table IV lists the points used in the fitting procedure and the orbit on which each lies. As previously noted in Mg, it is again found that Fourier coefficients that do not directly couple states on the Fermi surface are indeterminate in a fit to zero-pressure data. Consequently, V_{220} and V_{311} were arbitrarily set at 0.04 and 0.02 Ry. The final values for the other coefficients were $V_{111} = -0.1022$ Ry, $V_{200} = -0.0210$ Ry, $\lambda C_0^2 = 0.02329$ Ry, and $E_F = 0.6526$ Ry.

Table V lists the orbits calculated. The table contains the orbits listed in Table I of AOS plus a second ξ[110]. Included for compariosn is the percent deviation of AOS. AOS excluded the ξ[100] orbit from their rms-error calculation because it was fit so poorly. Using a more converged model, it is possible to fit this orbit (and all others AOS compared with) with a rms error of about 0.4% compared to 0.8% for AOS. (The 0.8% error of AOS excludes a 3.4% deviation on ξ[100] and ig-

TABLE V. Areas of de Haas–van Alphen orbits in Pb.

		Area (a.u.)		% deviation		$\frac{d\ln F}{dP}$[a]	
				This			
Center	Orbit	Expt.	Calc.	work	AOS[b]	Expt.[b]	Calc.
W	ν[100]	0.1369	0.1369	0.0	−0.1	2.3[c] 2.7[d]	1.9
K	ξ[110]	0.04831	0.04833	0.04	0.3	2.5[c] 2.4[d]	2.9
	ξ[110]	0.04717	0.0476	0.09	Ref. e		
K	ξ[111]	0.0597	0.0593	−0.8	0.6	2.7	2.9
L	θ[111]	0.2924	0.2927	0.1	−0.2	1.2	1.4
X	ξ[100]	0.09625	0.09645	0.2	(−3.4)[f]	0	−0.9
Γ	ψ[110]	0.4249	0.4260	0.2	0.1	2.9	2.9
Γ	ψ[111]	0.4161	0.4144	−0.4	−1.4	2.1	2.8
Γ	ψ[100]	0.5459	0.5479	0.4	−1.3	2.4	3.6
			rms	0.45	0.8[f]		

[a]Units of 10^{-3} kbar^{-1}. Free-electron scaling value is 1.37×10^{-3} kbar^{-1}. (In the free-electron approximation all orbits scale with the Brillouin zone, i.e., increase at a rate of $\frac{2}{3}$ the volume compressibility.)

[b]Reference 6.

[c]Fluid He < 25 bar. See Ref. 6.

[d]Solid He ≤ 4 kbar. See Ref. 6.

[e]A noncentral orbit was not found in the model of AOS. See Ref. 21.

[f]ξ[100] orbit excluded in AOS calculation of rms deviation.

TABLE VI. Energies at Γ and W in Pb (eV).

	Pseudopotential		ROFW	
	Energy[a]	Difference	Energy[b]	Difference
W_7	0.48		0.50	
		1.23		1.21
$W_6(W_3)$	−0.75		−0.71	
		1.57		1.13
W_7	−2.32		−1.84	
		2.33		3.75
$W_6(W_1)$	−4.65		−5.58	
$\Gamma_8^-(\Gamma_{15})$	8.87		9.13	
		4.17		3.15
$\Gamma_6^-(\Gamma_{15})$	4.69		5.98	
		14.49		17.19
$\Gamma_6^+(\Gamma_1)$	−9.79		−11.21	

[a]With respect to Fermi energy.
[b]Energy zero chosen to make $E(W_7)=0.5$ eV.

nores the second $\xi[100]$ orbit.) (Estimated experimental errors ranged from 0.02 to 0.5% for various orbits.)

The least satisfying feature of the normal-volume fit concerns the two $\xi[110]$ orbits and the $\xi[111]$ orbits. It was not possible to fit the central $\xi[110]$ and the $\xi[111]$ orbit without a combined uncertainty of 0.8%. That is to say, it was not possible to achieve the correct ratio of $\xi[110]$ to $\xi[111]$. A fit was also obtained assuming the nondominant $\xi[110]$ orbit to be larger than the dominant one.[23] The fit was of very comparable quality to the one shown in Table V, but the combined deviation between the central $\xi[110]$ and $\xi[111]$ was still about 0.8% ($\xi[111]$ was then too big). In both of the above fits the central orbit had the larger frequency in contrast to the models of AG and AOS. In neither of these fits was the lower-frequency orbit in satisfactory agreement with the experimental results. Comparing these two fits, it would appear possible to fit $\xi[111]$ very well and simultaneously obtain a 2.4% difference between the two $\xi[110]$ orbits; however, this would result in the experimental frequency being approximately equal to the average of the two calculated frequencies instead of to the dominant one.

In the [100] direction a beat pattern of about 600 cycles is observed experimentally on the ν orbit.[17] The model does not give this. d^2A/dz^2 for ν was about 0.5 and the area increases monotonically off the symmetry position well beyond the 0.16% required for such a beat pattern.[24]

AOS were unable to keep the fourth band empty at W in a local model. The model described in Table V has the fourth level at W 0.48 eV above the Fermi energy. However, this is higher than AH infer it should be from alloying experiments. For completeness, the pseudopotential energy levels at W and Γ are listed in Table VI. For comparison, values obtained from a relativistic OPW (ROPW) calculation are also listed.[25] The $\Gamma_8^- - \Gamma_6^-$ spin splitting affords the only clean comparison of the strength of the spin-orbit parameter. (The W_3 level is not simply split but is spin-orbit mixed with W_2'.) We see that the pseudopotential model estimates the spin-orbit interaction about 30% larger than the first-principles calculation.

In the Mg section there were only two convergence questions to consider—the total number of plane waves and number of plane waves in the inner matrix. In the Pb work we must also consider the effects of the spin-orbit term. Does the double-expansion include enough states; and since the spin-orbit interaction is included only in the Löwdin inner matrix, is that matrix large enough? The results of the convergence study on the pseudopotential model for Pb are shown in Table VII. To get an energy perspective for this table we note that on the ν orbit, which is the most prominent feature in the dHvA spectra, an error of 10 meV corresponds roughly to a 1% error in area. The difference between 50 and 100 plane waves is seen to be 5 meV differentially; thus, 100 plane waves should be reasonably well converged. The differences between an inner matrix of 20 and 30 are 7 meV or less, so that 30 is also adequate (both for Löwdin and spin-orbit splitting). Including basis states for an additional 1.25 Ry above E_F produces changes on the order of 10 meV so that, in fact, this is the poorest aspect of the convergence.

One very quickly observes from Table VII that a four-plane-wave model is so far from converged that discussion of 10- or 20-meV details with it is meaningless. Thirty plane waves would seem about the bare minimum one might reasonably employ.

In order to obtain pressure derivatives, the calculation was repeated for the lattice parameter corresponding to 20 kbar.[26] The 20-kbar Fermi energy was adjusted to fit the experimental derivatives as well as possible. With so many hole and electron orbits, careful application of this procedure can be expected to yield results comparable to doing the volume integration and calculating the change in Fermi energy. The 20-kbar shift in E_F was only about 75% of the amount predicted by the free-electron model (with respect to the bottom of the band). The calculated and experimental pressure derivatives are listed in Table V. The agreement is not as good as that claimed for the R_m-scaled model by AOS. However, the trends in large deviation from free-electron scaling are reproduced in a converged pseudopotential calculation using the usual prescription for a volume-dependent pseudopotential. [The spin-orbit term has been made volume dependent by noting that in addition to the dependence of k on the lattice constant, the $C(k_i)$ are

TABLE VII. Convergence study for Pb model.[a]

k points[c] \ Plane waves[b]	1 4(4)	2 10(10)	3 30(30)	4 50(30)	5 100(30)	6 100(20)	7 100(10)	8 3.0[b]	9 3.5[b]
Γ_{15}[d]	11.333	9.656	8.899	8.896	8.866	8.884	8.666	8.866	8.866
Γ_{15}	9.831	9.656	8.899	8.896	8.866	8.877	8.860	8.866	8.866
Γ_{15}	8.865	6.773	4.729	4.722	4.694	4.703	5.862	4.694	4.694
Γ_1	−9.166	−9.653	−9.754	−9.790	−9.794	−9.801	−9.889	−9.794	−9.794
$W(4)$	1.510	0.732	0.512	0.497	0.482	0.479	0.469	0.482	0.481
$W(3)$	−0.345	−0.414	−0.722	−0.738	−0.751	−0.767	−0.851	−0.751	−0.752
a	1.500	0.578	0.035	0.024	0.000	0.007	0.195	−0.013	−0.013
c	1.262	0.613	0.036	0.022	0.000	0.001	0.207	−0.002	−0.005
b	1.244	0.505	0.032	0.021	0.000	0.000	0.113	0.001	0.001
e	0.902	0.255	0.026	0.013	0.000	0.001	−0.009	0.015	−0.015
f	0.546	0.385	0.030	0.014	0.000	0.001	−0.042	−0.006	−0.006
d	1.303	0.515	0.032	0.020	0.000	0.001	0.125	−0.004	−0.005
m	0.532	0.386	0.030	0.014	0.000	0.001	−0.042	−0.005	−0.006
n	0.633	0.337	0.029	0.015	0.000	0.003	0.005	−0.005	−0.006
h	0.746	0.352	0.029	0.014	0.000	0.003	−0.003	−0.008	−0.009
w	0.832	0.358	0.031	0.015	0.000	0.003	0.007	−0.010	−0.010
o	0.633	0.337	0.029	0.015	0.000	0.005	0.005	−0.005	−0.006
g	0.875	0.309	0.027	0.017	0.000	0.006	−0.004	−0.010	−0.010
r	0.733	0.320	0.028	0.015	0.000	0.007	−0.004	−0.007	−0.007

[a]Eigenvalues eV.

[b]Number of plane waves used and in parentheses the number of plane waves in inner matrix. See text. Last two columns labeled by number of Ry above E_F included in spin-orbit expansion using 100(30) plane waves. All other columns used states to 1.75 Ry above E_F.

[c]k points are defined in Table IV.

[d]Γ_{15} is spin-orbit split into Γ_6^- and Γ_8^-.

inversely proportional to the square root of the unit cell volume.]

V. SUMMARY

Convergence studies of Fermi-surface pseudopotential calculations have been presented for Pb and Mg. These studies show that previous works which used ten or less plane waves were not adequately converged. Converged models for both Pb and Mg are described which fit normal-volume dHvA data. In Pb the fit is significantly better than that of AOS. In Mg the local-pseudopotential model described fits the data as satisfactorily as the nonlocal model of KSM. Hence, contrary to the conclusion of KSM, a nonlocal pseudopotential model is *not* required for Mg. For both materials the pressure dependence of the Fermi surface has also been calculated. The convergence study for Mg under pressure indicates that calculated pressure derivatives are quite sensitive to convergence. These findings also explain why the calculated pressure derivatives of the local model of AOS are so much more free-electron-like than the experimental results. For both materials the models presented satisfactorily describe the Fermi surface—both at normal volume and under pressure. The important conclusion of this work is that if a pseudopotential model is to be a "physical model" rather than only a Fermi-surface parametrization scheme—that is, if the model is to be used for other than just fitting normal-volume Fermi-surface data—it is necessary that the pseudopotential model be converged.

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[14]The free-electron shift in Fermi energies with 20 kbar for Mg is 0.264 eV; however, one measures the latter value with respect to Γ_1^+, whereas the numbers in text are absolute and Γ_1^+ also shifts. For 20-kbar lattice parameters we used $a=5.9181$ a.u. and $c=9.6040$ a.u. compared to $a=6.0260$ a.u. and $c=9.7811$ a.u. at zero pressure, which assumes volume-independent compressibilities. See L. J. Slutsky and C. W. Garland [Phys. Rev. 107, 972 (1957)] for Mg compressibilities.

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[25]ROPW results based on crystal-potential model made up of superimposed spherically symmetric free-atom *potentials*. Free-atom potentials were obtained using the Kohn–Sham exchange coefficient.

[26]The lattice constant used for 20 kbar was 9.1331 a.u. compared to 9.2597 a.u. at normal volume. The Fourier coefficients obtained from Eq. (6) were $V_{111}=-0.0976$, $V_{200}=-0.0152$, $V_{220}=0.0403$, and $V_{311}=0.0191$. E_F was 0.6759 Ry.

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Effect of Reconstruction on the Electronic Free Energy of a Simple Model of Transition Metals

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We present the results of theoretical studies of the change in free energy associated with surface reconstruction for one simple model of transition metals. We study the dependence of the free energy on reconstruction for a semi-infinte simple cubic lattice with one tight-binding Wannier orbital per unit cell. For this model, we compare the free energy of the unreconstructed surface with that when the surface is deformed into a 2×1 configuration. The effect of the distortion is introduced into the model by allowing the overlap integrals to vary with interatomic separation. We find that this particular mode of reconstruction always lowers the electronic free energy, with maximum effect when the band is half-filled. The physical origin of the changes in electronic density of states with reconstruction is discussed. The variation with temperature of the given gain in the electronic free energy is also studied.

I. INTRODUCTION

There has been a considerable effort on the part of experimentalists and theorists devoted to the study of the effect of a surface on the elementary-excitation spectrum of solids. The effect of a surface on the nature of the electronic states, phonons, and spin waves has been explored extensively in the theoretical literature.

Most of the theoretical models used in this work presume that in the surface layer, the geometrical arrangement of the atoms is identical to the arrangement in the appropriate bulk atomic plane. While this assumption greatly simplifies the theoretical analysis, it is often true that the atomic arrangement in the surface differs significantly from the bulk. For one thing, the atomic layers near the surface may relax, so that the separation between adjacent layers differs from the bulk.[1] It is also found that in many crystals, the atoms in and near the surface layer shift away from the lattice sites appropriate to the bulk layer, to produce an atomic