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The Screened Model Potential for 25 Elements

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ABSTRACT

The Fourier transform of the self-consistent screened model potential has been calculated for 25 elements. The results are presented in a form applicable to the potential in the solid or liquid metal or semiconductor, or to the electron-phonon interaction. They are reliable to about 0.01 ryd. The calculations are a continuation of the work by Heine and Abarenkov (1964), using the screening theory of Animalu (1965 a). The behaviour at high wave numbers and other points of detail are discussed much more thoroughly than before. Some average band effective masses are also calculated.

§ 1. INTRODUCTION

THE present paper is a continuation of work by Abarenkov and Heine (1965), Heine and Abarenkov (1964), Animalu (1965 a), and Heine *et al.* (1965), hereafter referred to as I, II, III and IV respectively. The purpose is to set up the potential felt by an electron in a non-transition metal or semiconductor, with a view to calculating the electronic structure of the material and such physical properties as depend on it.

In I the interaction of a conduction or valence electron with the ion core of an atom was represented by a model pseudo-potential of the form :

$$\begin{aligned} V_M &= -\sum A_l P_l \text{ for } r < R_M, \\ &= -Z/r \text{ for } r > R_M. \end{aligned} \quad \dots \dots \dots (1)$$

Here P_l is the projection operator that picks out the component of the wave function with angular momentum l , and Z is the valency of the ion. The parameters A_l are determined from the observed spectroscopic term values of the isolated ion or atom. In II it was shown how to add the conduction electron gas, and some preliminary calculations on the alkali metals showed that the use of the model potential had considerable promise. At that time the calculation of the screening of the ionic field by the conduction electrons involved treating V_M as a local potential, whereas it is non-local on account of the operators P_l in (1). The matter was put right in III, where at the same time some excellent agreement between theory and experiment was reported for the potential matrix elements determining the Fermi surface of aluminium. Sundström (1965) has calculated the resistivities of various liquid metals with the model potential, and some use has also been made of it by Ashcroft and Wilkins

(1965). It is clear that the model potential gives values for the potential in a metal sufficiently accurate for useful realistic calculations of electronic properties.

We therefore report in § 5 results for 25 elements. Given are the values of A_i relevant to electrons at the Fermi level in the solid (or liquid) and also graphs of the self-consistent screened potential in the metal. The latter is given in the following form. Let the atoms be at positions R_j in the liquid or regular solid, or solid with phonons or defects. As in II and III, the matrix element of the total potential U between plane wave states with wave vectors \mathbf{k} and $\mathbf{k} + \mathbf{q}$ can be written in the form:

$$\langle \mathbf{k} + \mathbf{q} | U | \mathbf{k} \rangle = V(q)S(\mathbf{q}), \quad (2)$$

where $S(\mathbf{q})$ is the structure factor:

$$S(\mathbf{q}) = \frac{1}{N} \sum_j \exp(-i\mathbf{q} \cdot \mathbf{R}_j). \quad (3)$$

$V(q)$ is independent of structure and represents the potential of a neutral pseudo-atom in the metal in the sense of Ziman (1964). The results go up to values of q ten times the Fermi radius, and tables more detailed than the published graphs may be had on request†. The calculations were planned to be physically realistic to about 0.01 ryd, and comparison with experiment indicates this has been on the whole achieved. Some results for the mean Hartree effective mass, calculated from the model potential, are given in § 6.

However, before reaching the results in §§ 5 and 6 it is necessary to attend to some details not adequately discussed in II and III. First, in § 2 we define more precisely the potential which we are setting up in the metal, particularly as regards our treatment of correlation and exchange, and the 'orthogonality correction' mentioned in II. By the latter we mean the following. The conduction electron states are not even in lowest order simple plane waves but contain atomic-like oscillations inside the ion cores, which are represented by the orthogonalizing terms in the orthogonalized plane wave (OPW) representation of the wave functions. The resulting non-uniformity of the total conduction electron charge density contributes both to the Hartree potential and the correlation and exchange hole.

Then the parameters A_i in (1) depend somewhat on energy E and it is necessary to evaluate them for an energy E_F of an electron at the Fermi level. Here E_F has to be not on an absolute energy scale but the energy relative to a free ion, which is defined and calculated in § 3.

In § 4 we discuss various questions related to the choice of R_M and how far the results are internally consistent in the sense of being independent of R_M . Of course it is not $V(q)$ that has to be independent of R_M but physical quantities such as band gaps, which may be given in lowest order

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directly by $V(q)$ but which also include higher-order corrections. The same total value may be distributed slightly differently between the lowest-order term and the corrections. However, for the model potential to be really useful the corrections should be small. They depend on $V(q)$ at large q , which oscillates with q due to the discontinuity in V_M at $r=R_M$. Whether any of the fluctuation of $V(q)$ is real, or whether it is *all* spurious from the artificial discontinuity in R_M is not yet clear. In any case we suggest for some purposes the use of a damping factor:

$$D(q) = \exp[-0.03(q/2k_F)^4], \quad \dots \dots \dots (4)$$

multiplying $V(q)$.

§ 2. DEFINITION OF THE POTENTIAL

We wish to set up the potential in the metal felt by an electron, including the exchange and correlation interaction with other electrons. It is convenient to choose the electron at the Fermi level ϵ_F , firstly because this is what one wants for many studies of transport properties or the shapes of Fermi surfaces, and secondly because it is only at ϵ_F that the single particle energy values ϵ_k are real and well defined in the sense of Landau quasi-particles. The ϵ_k are the eigenvalues of

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_H + \Sigma \right) \psi_k = \epsilon_k \psi_k, \quad \dots \dots \dots (5)$$

where V_H is the Hartree potential and Σ the mass operator. The latter represents the exchange and correlation hole around the electron and we can split it up at least notionally into exchange Σ_x and correlation Σ_c :

$$\Sigma = \Sigma_x + \Sigma_c. \quad \dots \dots \dots (6)$$

We could put Σ_x as the bare exchange operator of the Hartree-Fock equation and define Σ_c as $\Sigma - \Sigma_x$.

In (5) and (6), V_H , Σ_x , Σ_c and the total electron density $n(\mathbf{r})$ are the sum of three parts, due to (i) the ions, (ii) the conduction band of electrons in lowest order, pictured as simple OPW's, i.e. a uniform charge density apart from the 'orthogonality correction' at each ion, and (iii) the change in the conduction electron density when we 'unfreeze' them and allow them to screen the 'bare' model potential of (i) and (ii) as described in II, III and IV.

As regards V_H and n there is no question about the three contributions (i)-(iii) being strictly additive, and the same is true of the exchange Σ_x if we use an unscreened Coulomb interaction. Even if it is argued that one ought to imagine a modified exchange interaction, the screening radius due to the conduction electrons is sufficiently larger than an ionic radius for the Σ_x from the ion to be practically unaffected: conversely the volume of the ion is too small and the excitation frequencies of the core electrons too large to affect the intra-conduction electron exchange much, so we take them as additive.

On the other hand, \sum_c is highly non-additive; in fact it nearly saturates. We can see this explicitly in the approximation of Kohn and Sham (1965) who have shown that under certain conditions which are quite well fulfilled in non-transition metals, \sum_c can be approximated by:

$$\sum_c \approx \mu_c[n(\mathbf{r})]. \quad (7)$$

Here μ_c is a local correlation potential depending only on the total electron density $n(\mathbf{r})$. It is defined in terms of the correlation energy E_c (per electron) of a uniform electron gas of density n :

$$\mu_c = \frac{d}{dn}(nE_c) \quad (8)$$

The approximation (7) is the same as used intuitively and not quite correctly by Heine (1957) and in II. In the range of metallic densities E_c and μ_c vary slowly with density (see table 1) and in the limit of high densities

Table 1. Values of E_c and μ_c for a uniform electron gas

r_s (atomic units)	E_c (ryd)	μ_c (ryd)
1.6	-0.101	-0.108
1.8	-0.098	-0.106
2.0	-0.095	-0.104
2.2	-0.092	-0.102
2.4	-0.090	-0.100
2.6	-0.087	-0.098
2.8	-0.084	-0.096
3.0	-0.082	-0.094
3.2	-0.079	-0.092
3.4	-0.077	-0.090
3.6	-0.075	-0.088
3.8	-0.073	-0.085
4.0	-0.071	-0.083
4.2	-0.069	-0.081
4.4	-0.068	-0.079
4.6	-0.066	-0.076
4.8	-0.065	-0.074
5.0	-0.064	-0.072

such as inside the ions they also vary slowly as (Gell-Mann and Brueckner 1957):

$$0.0622 \ln r_s \text{ ryd}, \quad (9)$$

where r_s in atomic units is the usual radius giving the volume per electron. This justifies the statement that \sum_c is very non-additive.

The contributions from (i) to (iii) will be distinguished by subscripts *i* (ions), *b* (band), and *s* (screening) respectively. With this notation the total potential $V_{H+\Sigma}$ in (5) becomes :

$$V_i + \sum x_i + V_b + \sum x_b + \sum_{c, i+b} + (V + \sum x + \Delta \sum c)_s. \quad (10)$$

Here the final screening term, with its contribution to \sum_x and \sum_c , is all part of the screening calculation in III, and will be included in that way. It will not concern us further, except to note that in II and III the treatment of Σ was based purely on a short-range exchange interaction rather than the theory of (7), (8) and some improvement in this direction is presumably possible.

The remaining terms of (10) may be re-grouped as follows :

$$[V_i + \sum x_i + \sum c_i] + V_b + [\sum x_b + \sum c_b] + [\sum_{c, i+b} - \sum c_i - \sum c_b]. \quad (11)$$

Here the first bracket is included in the model potential of the ion, including the exact correlation terms \sum_{c_i} for one electron interacting with an isolated ion. The last bracket of (11) expresses the non-additive nature of the correlation potential and gives rise to the 'correlation correction' V_{CC} of II. We evaluate it with the approximation (7) :

$$V_{CC} = \mu_c(n_i + n_b) - \mu_c(n_i) - \mu_c(n_b). \quad (12)$$

Outside the ion core n_i is zero so that $V_{CC} = 0$, while inside the core

$$\mu_c(n_i + n_b) \approx \mu_c(n_i), \quad (13)$$

because μ_c nearly saturates and

$$V_{CC} = -\mu_c(n_b). \quad (14)$$

Comparison shows that eqn. (21) of II was not quite correct: however, to the accuracy we wish to attain, namely 0.01 ryd in the matrix elements (2) for q around the first reciprocal lattice vectors, the difference is quite negligible because from (8) we have :

$$\mu_c = E_c + n \frac{dE_c}{dn}, \quad (15)$$

where the second term is about 0.01 ryd which in the matrix element is reduced in the ratio of atomic to ionic volumes, typically nearly ten.

Returning to eqn. (11) we have that V_b is the potential from the electron density n_b which is not quite uniform because of the orthogonality correction. It is equal to a density $(1 + \alpha)Z/\Omega$ everywhere, where Z is the valency, Ω the atomic volume and α the correction, plus an extra positive charge of $Z\alpha$ electronic charges more or less uniformly spread over a sphere of radius R_c equal to that of the ion core. It remains to justify the value

$$\alpha = (R_c/R_a)^3 \quad (16)$$

suggested in II, where the atomic radius R_a is the radius of a sphere of volume Ω . Certainly we expect something of the order of magnitude of (16) because α can be calculated in the OPW method where, other things being equal, α is immediately proportional to the ratio of ionic to atomic

volume. Alternatively we can imagine a plane wave turning into atomic-like oscillations inside the core, the mean value of $|\psi|^2$ being reduced by a factor of two (mean value of $\cos^2 x$). Actually it is reduced more than this as can be seen from the factor $(E - V)^{-1/4}$ in the W.K.B. solution. Moreover the $|\psi|$ of a conduction wave function has to drop at a radius a bit larger than R_c because its outer node has to come fairly far out in the main hump of the outer shell of core states in order to get orthogonality between them. Thus we expect:

$$\alpha = (\text{factor between } \frac{1}{2} \text{ and } 1) \left(\frac{\text{radius a bit bigger than } R_c}{R_a} \right)^3, \quad (17)$$

which brings us back essentially to (16). In table 2 we compare (16) with some values of α calculated from OPW's. We note firstly that (16) fits

Table 2. Values of α

	Li	Na	K	Al
From OPW (Harrison 1963)	0.07	0.07	0.14	0.08
From OPW (Heine 1957)	—	—	—	0.15
Equation (16)	0.10	0.10	0.13	0.05

the results as well as any simple expression will, and secondly the marked discrepancy between the two OPW values for aluminium. In the OPW method there is considerable arbitrariness about the choice of auxiliary 'core' functions: Heine (1957) used functions calculated from the potential seen by a conduction electron, which are much more spread out than the actual atomic core states used by Harrison (1963). With Heine's functions the reduction in electron density would be spread over a larger radius. We have therefore computed the orthogonality correction for aluminium with the two extreme pairs of values $\alpha = 0.05$, $R_c = 1.1$ and $\alpha = 0.15$, $R_c = 2.0$. The value of the correction ranges up to 0.03 ryd in $V(q)$ for q up to $2k_F$ and is thus significant, but the difference between the two cases is everywhere less than 0.01 ryd in this range (and almost certainly beyond). We conclude that (16) is adequate for calculating the small but not quite negligible orthogonality correction.

We turn to the second bracket in (11). In zeroth order the conduction band is a uniform free-electron gas and we put (Seitz 1940):

$$\begin{aligned} \sum_{xb} + \sum_{cb} &= \mu_x(r_s) + \mu_c(r_s) \\ &= -1.224r_s^{-1} + \mu_c(r_s). \quad \dots \dots \dots (18) \end{aligned}$$

The μ_c is calculated from (8), (15), where our best estimate of E_c is derived from Hubbard (1958): we take values of his eqn. (48) given in his table I, corrected by a further 20% of eqn. (42) for the reasons discussed by him. Although (18) is independent of position and hence does not contribute

to $V(q)$, it is important for establishing the absolute energy scale for the conduction band, and we give our interpolated estimates of E_c and μ_c in table 1.

The non-homogeneity of the conduction electron density described as ‘orthogonality correction’ above also affects the charge density in the correlation and exchange hole in $\sum_x + \sum_c$. This term was overlooked in II, and it tends to cancel the orthogonality correction in the direct Hartree potential. The radius of the correlation and exchange hole is large, normally larger than R_a , and where it overlaps an ion the positive missing charge density of the ‘hole’ is modulated in the same way as the full Hartree electron density. No doubt one could write down an expression which roughly describes how this effect varies with the position of the electron. But judging from the overall magnitude of the orthogonality correction and the fact that the hole is so big that it covers the whole of an atomic cell moderately uniformly, it would seem satisfactory simply to reduce the orthogonality correction uniformly by a numerical factor β . In the centre of the hole there is zero density of parallel-spin electrons because of the exclusion principle and opposite-spin electrons are partially repelled so that β is less than one half there, whereas it tends to unity outside the hole. We choose $\beta = \frac{1}{2}$, and therefore write from (16) an effective α :

$$\alpha_{\text{eff}} = \frac{1}{2}(R_c/R_a)^3. \quad (19)$$

§ 3. CHOICE OF ENERGY PARAMETER

As discussed in § 1, we require the energy E_F relative to a free ion, of an electron at the Fermi level ϵ_F in the metal where ϵ_F is on an absolute energy scale. In the vicinity of an ion in the metal, the Schrödinger equation can be written:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + (V + \sum)_{\text{ion}} + (V + \sum)_{\text{rest}} \right] \psi = \epsilon \psi, \quad . . . (20)$$

where $(V + \sum)_{\text{ion}}$ is the potential of the single ion and $(V + \sum)_{\text{rest}}$ the potential due to all the rest of the system, i.e. the other ions and the conduction electrons, including the correlation and exchange hole. We can write (5) as:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + (V + \sum)_{\text{ion}} \right] \psi = [\epsilon - (V + \sum)_{\text{rest}}] \psi. \quad (21)$$

It is as if we were solving the wave equation for an isolated ion with electron energy:

$$E_F = \epsilon_F - (V + \sum)_{\text{rest}}. \quad (22)$$

Evidently, this is the parameter for which to evaluate $A_l(E)$ if $(V + \sum)_{\text{rest}}$ can be regarded as a constant independent of position \mathbf{r} inside R_M : any variation outside R_M is irrelevant. In practice of course $(V + \sum)_{\text{rest}}$ depends on \mathbf{r} , but a suitably weighted mean inside the sphere R_M serves well since A_l varies only slowly with E (see reference I).

In (22) we first estimate ϵ_F from the measured cohesive energy of the metal. For present purposes it is quite adequate to treat the conduction band as a free-electron gas. The absolute level of the band is simply related to the cohesive energy as described in Sietz (1940), and we obtain:

$$\epsilon_F = -[\text{M.I.E.}] - [\text{B.E.E.}] + \mu_x(r_s) + \mu_c(r_s) + \frac{2}{5} \left(\frac{\hbar^2 k_F^2}{2m^*} \right) - E_x - E_c + \frac{0.6Ze^2}{R_a} \dots \dots \dots (23)$$

Here M.I.E. is the mean of the first Z ionization energies of the free atom, B.E.E. the cohesive energy of the solid per electron (N.B. not per atom), k_F the Fermi radius, m^* an effective mass, and E_x the exchange energy of a free-electron gas:

$$E_x = -0.916r_s^{-1} \text{ ryd.} \dots \dots \dots (24)$$

With the same approximation of a uniform conduction electron density we set:

$$\sum_{\text{rest}} = \mu_x(r_s) + \mu_c(r_s) \dots \dots \dots (25)$$

The V_{rest} contains a contribution:

$$\frac{Ze^2}{2R_a} \left[3 - \left(\frac{r}{R_a} \right)^2 \right] \dots \dots \dots (26)$$

from the electrons inside the same cell as the ion we are considering. The electrons and ions in the other cells contribute practically zero potential, since they are electrically neutral and approximately spherical. As usual, we assume surface cells to have exactly the same charge distribution as cells in the interior of the solid: that is we assume zero surface dipole moment. This makes no difference to any of our results since a surface dipole moment would increase ϵ_F and V_{rest} by the same constant amount which subtracts out in (22).

Equations (22) to (26) now determine E in (21), but it is still a function of r through the term (26). The purpose of the model potential is to reproduce the correct radial derivative of ψ at R_M , and in integrating (21) outwards from the origin the $(V + \sum)_{\text{ion}}$ is, at small r , much larger than E on the right-hand side. Thus a small error or spatial dependence in E causes very little change in the wave function there. However, near R_M where the two terms are more comparable, the effect is bigger. Thus we want to take the mean value of (26) over a sphere of radius R_M with the region close to R_M weighted much more heavily than the centre. We arbitrarily choose a weighting factor of r^3 in addition to the effect of the volume element $4\pi r^2 dr$, giving a weighted mean of (26) equal to:

$$\frac{Z}{R_a} \left[3 - \frac{3}{4} \left(\frac{R_M}{R_a} \right)^2 \right] \text{ ryd.} \dots \dots \dots (27)$$

Thus the $A_l(E)$ have to be taken at an energy E_F given by (27) and (22) to (25).

§ 4. CONSISTENCY AND LARGE Q

In this section we discuss three sets of calculations in which the same quantity has been evaluated for different choices of R_M in the model potential.

We first give in table 3 values of ϵ_F in sodium for three choices of R_M , calculated from

$$\epsilon_F = \left(\frac{\hbar^2 k_F^2}{2m^*} \right) + (\mu_x + \mu_c) + \left[-A_0 \left(\frac{R_M}{R_a} \right)^3 - \frac{1.5Ze^2}{R_a} \left\{ 1 - \left(\frac{R_M}{R_a} \right)^2 \right\} + \frac{1.2Ze^2}{R_a} \right]. \quad (28)$$

Here we have used the same model of the potential as in § 3, i.e. approximating to cells as spheres and neglecting orthogonality and other corrections, some of which would give small contributions independent of R_M and hence not affecting the comparison of table 3. The three terms in the square bracket in (28) are respectively the contribution to the potential in a cell of the model potential inside R_M , the model potential between R_M and R_a , and the uniform electron density. Also given in table 3 is the value calculated from the experimentally measured quantities in (23). We have used $m^*/m = 1$. Table 3 is indicative of the accuracy obtained in lowest order, and it is not clear yet how much the comparison is improved by inclusion of second-order and other corrections.

Table 3. Energy at the Fermi level in sodium

	$R_M = 2.2$	$R_M = 3.0$	$R_M = R_a \approx 4.0$	Expt
ϵ_F (ryd)	-0.150	-0.138	-0.141	-0.153

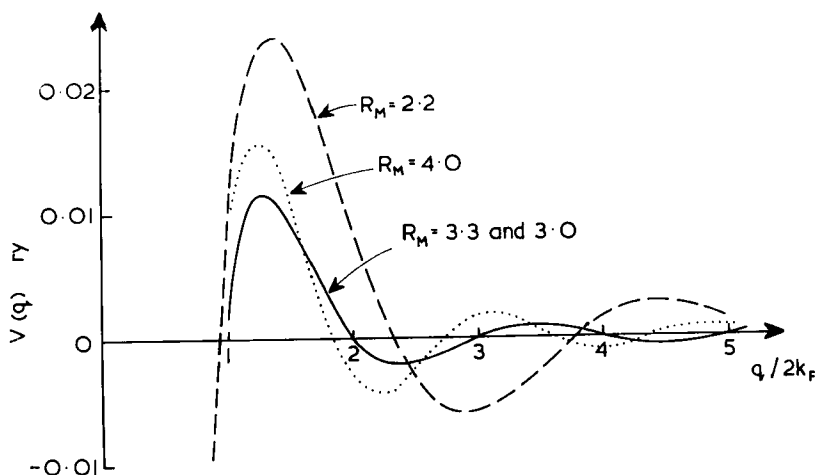
As second test we have computed $V(q)$ for aluminium for $R_M = 1.6$ and 2.2. They differ by less than 0.006 ryd in the range $0 \leq q \leq 2k_F$, which is consistent with second-order corrections for the band gap matrix elements of the order of 0.005 ryd (reference III).

Thirdly, we discuss the uncertainties at large q . The $V(q)$ for all atoms oscillates at large q , the shape of the curve depending quite markedly on the choice of R_M . As mentioned in § 1, there is no unique 'right' $V(q)$ at large q : it is possible to have different pseudo-potentials which when applied correctly to infinite order of perturbation all give in principle identical results for physically measurable quantities. This is an inescapable consequence of the rigorous theory of pseudo-potentials (Austin *et al.* 1962) and the even wider arbitrariness allowed in a model potential (reference I). However, for practical purposes one usually wishes to study quantities like phonon spectra and shapes of Fermi surfaces which are dominated by the $V(q)$ up to and including the first few reciprocal lattice vectors. One would like the $V(q)$ by itself to represent

as far as possible the physical quantities, i.e. to have higher-order corrections as low as possible. This means one would like to reduce the amplitude of the tail of $V(q)$ beyond the first few reciprocal lattice vectors as much as possible: too large a tail can lead to severe convergence difficulties, for instance, in the calculation of phonon spectra. It is undoubtedly true that the oscillating tail of $V(q)$ is mainly due to the discontinuity in the model potential at R_M . It is 'unphysical' in the sense that it could be to a large extent removed by using a more smoothly varying model potential such as that in fig. 1(d) of I. However, this is not true of the beginning of the oscillations at lower q . The fact that $V(q)$ becomes positive in many cases at q just less than the first reciprocal lattice vector, corresponds to the inversion of s and p states at the first band gaps of such metals, which is a real and important feature of their band structures.

Two measures can be taken to reduce the amplitude of the tail. The first is to choose a value of R_M such that the A_i are approximately equal to Z/R_M . The model potential (1) has a discontinuity both in the magnitude and the derivative of V_M at R_M . As expected, an investigation showed the former to be the more serious for a discontinuity of 0.1 atomic units or more, and so for each atom R_M was chosen to make it as small as possible. Secondly, we suggest eliminating the effect of the remaining discontinuity by multiplying $V(q)$ by the damping factor $D(q)$ (4) which corresponds in real space to some smoothing of V_M . The choice of this particular factor rested on the tests shown in fig. 1, which represent $V(q)$ for a fictitious atom not unlike sodium. We have set all A_i equal to A_0 so that we have

Fig. 1



$V(q)$ at large q for various R_M . The curve for $R_M = 3.0$ is not explicitly shown since it is almost indistinguishable from that for $R_M = 3.3$ on the present scale. Note the very expanded energy scale; $V(q)$ tends to -0.48 as $q \rightarrow 0$.

a local potential, ignored all orthogonality, etc. corrections, but chosen A_0 correctly for sodium for various R_M at energy (22). As expected, the smallest amplitude of oscillation is for $R_M = 3.3$ where A_0 is almost exactly equal to $1/R_M$. The oscillations for the other two R_M differ markedly in amplitude and phase, so that even at $q/2k_F = 2$ they seem physically not significant. The $D(q)$ in (4) has been chosen to cut off sharply beyond this value of q , while leaving the physically significant first positive swing of $V(q)$ as unaffected as possible. A rather more drastic smoothing of the potential in real space

$$V(r) = - \left[\frac{1}{r} + \left(A_0 - \frac{1}{r} \right) \exp(-1.5r/R_M) \right]. \quad (29)$$

was found to eliminate all oscillation of $V(q)$ including the first node.

It should be said that our damping $V(q)$ to zero at large q springs more from ignorance of what it really is, than from conviction that it is practically zero. The pseudo-potential theory suggests that the cancellation becomes less complete at large q (see eqn. (6) of Austin *et al.* (1962)). One strange result could be mentioned in this connection: in fig. 1 we have also calculated the curve for $R_M = 3.3$, which on the scale plotted is indistinguishable from $R_M = 3.0$. If the oscillations are mainly due to the remaining discontinuity at R_M , we would expect their phase to change by a factor $3.3/3.0$, or at least by 30% of the difference between the curves for $R_M = 3.0$ and 4.0 . The fact that $V(q)$ is so insensitive to choice of R_M just around $R_M = 3.0$ where the major discontinuity vanishes, suggests that the remaining oscillations may after all have physical significance. For most applications they will be too small to matter, so it will be difficult to investigate the question.

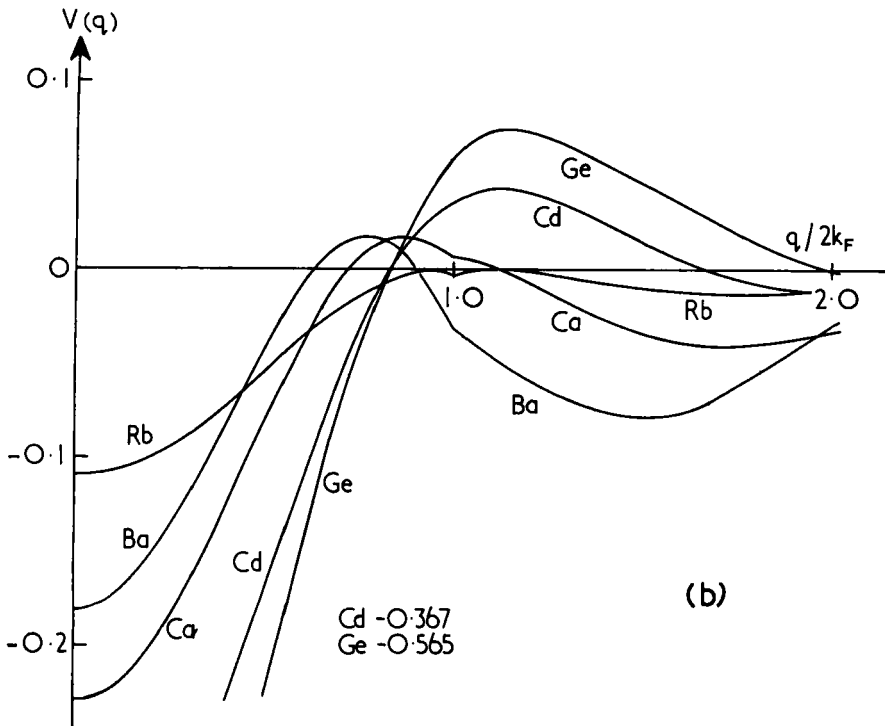
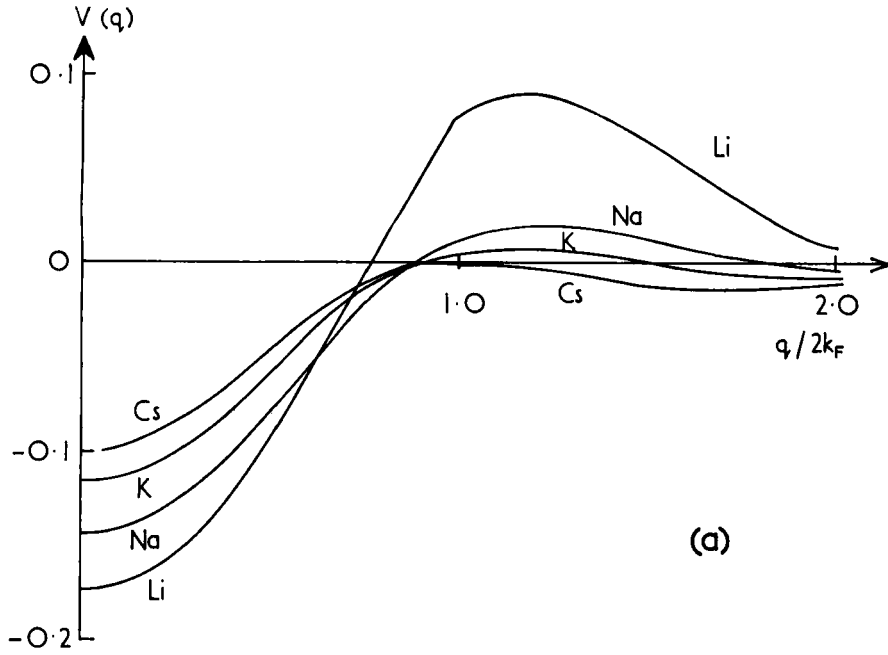
We conclude therefore from all our three tests that it is best to choose R_M such that the A_l are close to Z/R_M , but that the results do not differ significantly for variations of R_M of 10–20% around that value.

§ 5. NUMERICAL RESULTS AND CONCLUSIONS

The self-consistent screened pseudo-potential $V(q)$ in (2) has been calculated for 25 metallic and semiconducting elements. It is important to note that in (2) the matrix element depends not only on q because of the non-local nature of the potential, but also on k and $|\mathbf{k} + \mathbf{q}|$. We have always put $k = k_F$. For $q \leq 2k_F$ we have taken $|\mathbf{k} + \mathbf{q}|$ also equal to k_F : for $q > 2k_F$ we have chosen $|\mathbf{k} + \mathbf{q}| = q - k_F$ so that \mathbf{k} and $\mathbf{k} + \mathbf{q}$ are anti-parallel. This, and the very rapid variation of the screening factor $\epsilon(q)$ near $2k_F$, produce the kink at $q/2k_F = 1$ in the results shown in fig. 2. All the quantities required in the calculation are displayed in table 4.

We now detail the numerical steps and sources of experimental information. Values of $A_l(E)$ were calculated as in I at up to three atomic energy levels for each l , the spectroscopic values of E being taken from Moore (1949). The approximation (9) of II was used for the A_l with $l > 2$. The R_M was chosen to lie between R_C and R_a at a value for which Coulomb

Fig. 2



For legend, see p. 1263.

Fig. 2 (continued)

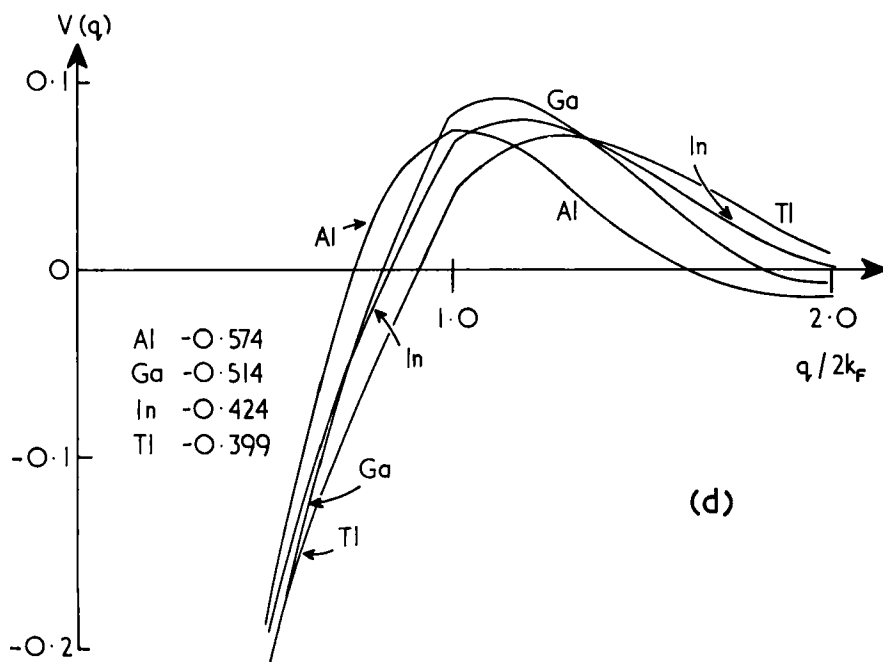
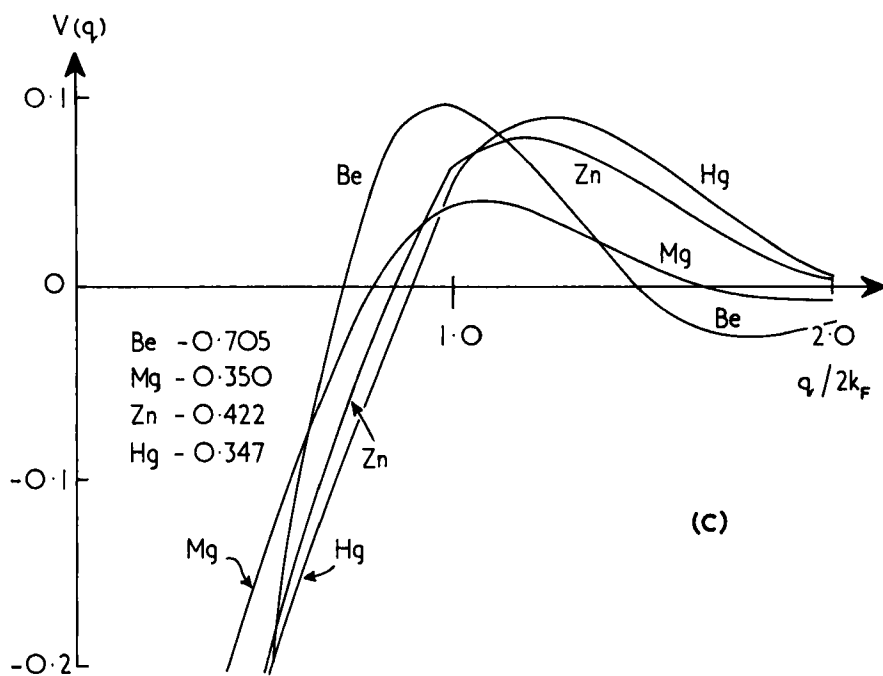
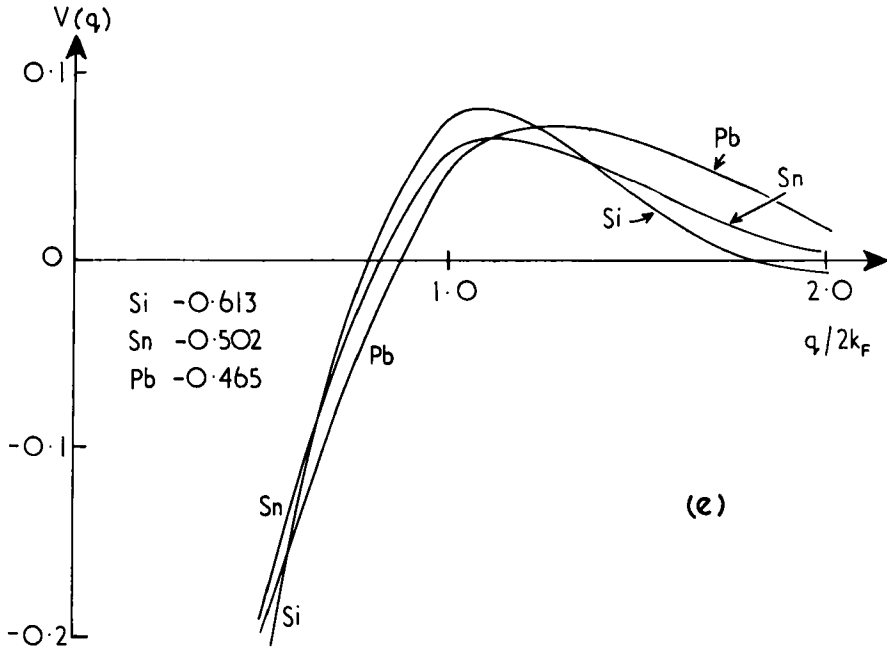
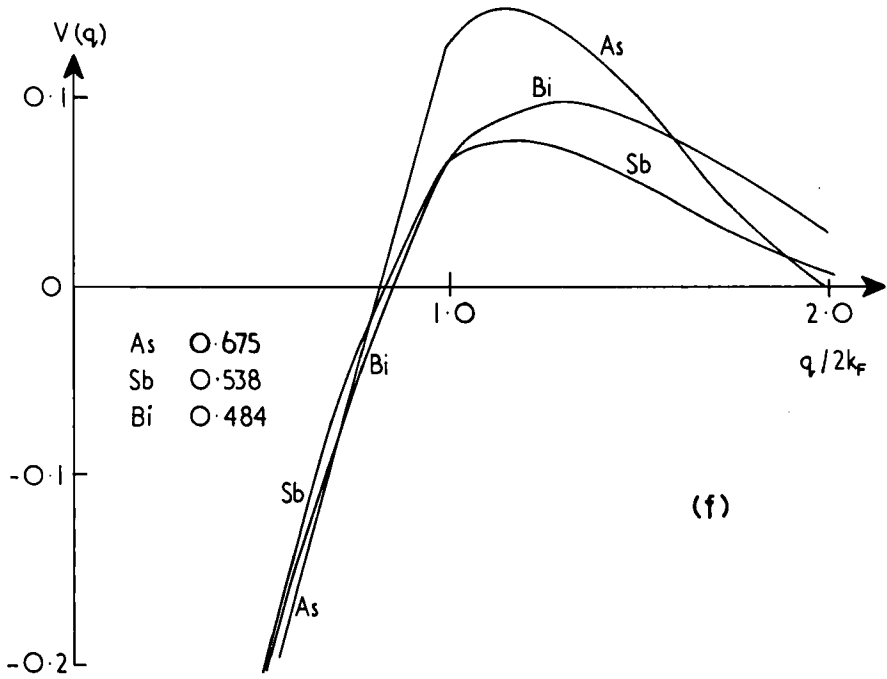


Fig. 2 (continued)

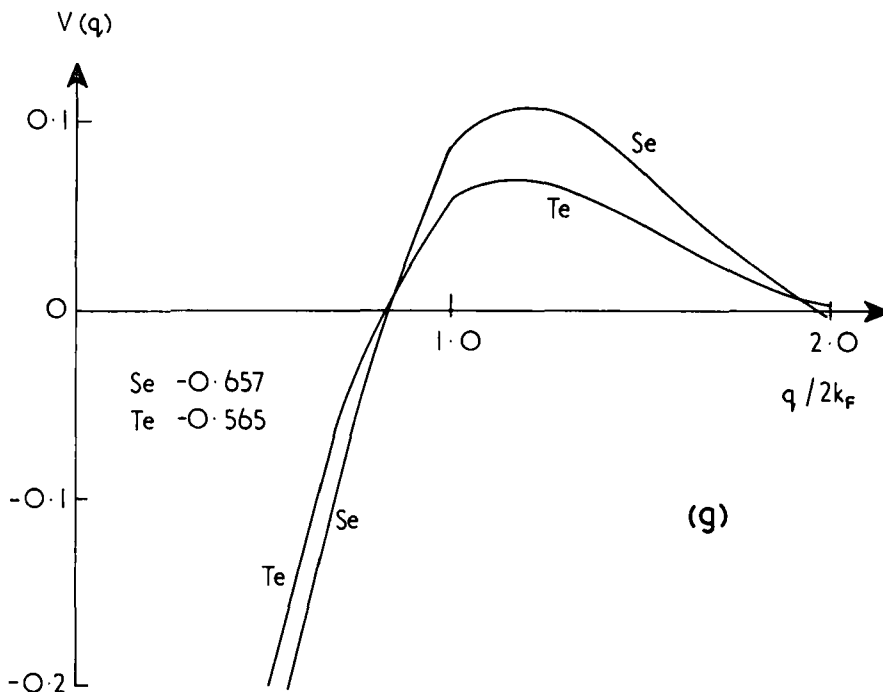


(e)



(f)

Fig. 2 (continued)



$V(q)$ for (a) Li, Na, K, Cs; (b) Rb, Ca, Ba, Cd, Ge; (c) Be, Mg, Zn, Hg; (d) Al, Ga, In, Tl; (e) Si, Sn, Pb; (f) As, Sb, Bi; (g) Se, Te. The numbers on the left give the limit of $V(q)$ as q tends to zero. Note that the curve for Cd differs from that in Harrison (1966) and Technical Report No. 3 on account of a calculation error in the earlier values: the correct table is included in Technical Report No. 4.

wave functions had been punched out for the computer, and such that A_0 is as near as possible to Z/R_M as discussed in § 4. The results for calcium should be regarded as tentative because for some computational reasons R_M had to be made much smaller than is desirable from the point of view of the latter requirement. E_F was calculated from (22)–(27) with values of M.I.E.'s from Moore (1949) and B.E.E.'s from Kittel (1956, p. 99). E_F comes approximately at the lowest valence $l=0$ level, and so A_0 for the solid can be interpolated easily from the atomic values. For $l=1$ and 2 considerable extrapolation is required, which we have done by straight line from the lowest two or three atomic values. For some ions only one atomic energy value is known, in which case the slope of the line is determined from comparison with neighbouring elements and rows in the periodic table. In all cases the weighted mean of atomic levels in one term were used, so that our calculations include no spin-orbit coupling. The extension of the model potential to spin-orbit coupling will be discussed by Animalu (1965 b). For some applications, such as the

calculation of the band mass or the thermoelectric power, the variation of model potential with energy is required. The individual $A_i(E_{ni})$ at the atomic levels E_{ni} have therefore been preserved as Technical Report No. 4, available on request from the address in § 1.

Table 4. Parameters for screened model potential

	A_0	A_1	A_2	R_M	Ω	Z	m^*	R_C	α_{eff}	$ E_c $
Li	0.336	0.504	0.455	2.8	144.9	1	1.33	1.47	0.046	0.078
Na	0.305	0.339	0.402	3.4	254.5	1	1.096	1.85	0.052	0.072
K	0.240	0.256	0.368	4.2	481.4	1	0.884	2.51	0.069	0.065
Rb	0.224	0.226	0.384	4.4	587.9	1	0.827	2.82	0.080	0.063
Cs	0.205	0.207	0.366	4.8	745.5	1	0.775	3.12	0.085	0.060
Be	1.01	1.22	1.48	2.0	54.4	2	1.0	0.64	0.010	0.097
Mg	0.78	0.88	0.99	2.6	155.9	2	1.0	1.47	0.043	0.086
Ca	0.54	0.50	1.49	2.6	293.5	2	1.0	2.00	0.057	0.078
Ba	0.45	0.34	1.07	3.4	424.1	2	1.0	2.70	0.097	0.074
Zn	0.99	1.14	0.98	2.2	102.0	2	1.1	1.57	0.079	0.091
Cd	0.88	0.98	1.11	2.6	144.8	2	1.0	1.95	0.107	0.087
Hg	0.97	1.11	0.85	2.6	157.8	2	1.0	2.12	0.126	0.086
Al	1.38	1.64	1.92	2.0	111.3	3	1.0	1.08	0.024	0.094
Ga	1.44	1.58	1.41	2.4	131.4	3	1.0	1.17	0.026	0.092
In	1.32	1.46	1.10	2.4	175.3	3	1.0	1.74	0.063	0.090
Tl	1.44	1.51	0.98	2.4	191.7	3	1.0	1.98	0.085	0.089
Si	2.08	2.39	2.44	2.0	134.3	4	1.0	0.74	0.006	0.095
Ge	2.10	2.34	2.09	2.0	151.8	4	1.0	0.83	0.008	0.094
Sn	1.84	2.04	1.62	2.0	181.5	4	1.0	1.40	0.032	0.092
Pb	1.92	(2.00)	0.90	2.1	203.4	4	1.0	1.59	0.041	0.091
As	2.71	(3.08)	(2.0)	2.0	145.2	5	1.0	0.89	0.010	0.096
Sb	2.42	2.66	(1.8)	2.0	204.0	5	1.0	1.17	0.017	0.093
Bi	2.38	2.58	0.25	2.0	239.4	5	1.0	1.40	0.024	0.091
Se	3.42	(3.77)	(3.0)	2.0	181.6	6	1.0	0.66	0.003	0.096
Te	3.04	3.32	(2.80)	2.0	227.5	6	1.0	1.04	0.010	0.094

Note: All quantities are in atomic units except E_c which is in rydbergs. The numbers in brackets had to be determined by extrapolation from a single point as described in § 6.

The value of Ω in table 4 corresponds to the solid state at the lowest temperature tabulated by Pearson (1958). $V(q)$ is not very sensitive to change of Ω for q at and beyond the first reciprocal lattice vector since the dielectric screening factor $\epsilon(q)$ of I is already down to 1.1 to 1.2 there and Ω only really comes into the screening. In order to apply the present results at slightly different Ω one must remember the matrix elements are for wave functions normalized to unity over Ω , and $V(q)$ is insensitive to Ω for fixed q , not fixed $q/2k_F$. The screening theory of III has been

used, as if all the elements were free-electron metals. Thus for the semi-conducting elements the $V(q)$ at low q are meaningless, but certainly for $q/2k_F \geq \frac{1}{2}$ the present screening theory should be as good as for a metal. It should be emphasized that we are only calculating the screening in linear perturbation theory, and that further hybridization effects which are certainly very important in group IV semiconductors have to be calculated in the manner of Bennemann (1964) using our linear theory as starting point. The m^* for the alkalis are taken from Ham (1962) and the remainder set equal to unity in ignorance. This should be quite a good guess, since the usual large electron-phonon contribution to the electronic specific heat mass does not enter into our screening m^* as discussed in II and IV: also the electron-electron contribution, which does enter our m^* , is rather small (Rice 1965). We could have re-calculated all the $V(q)$ using the somewhat uncertain estimated band masses of §6, but it does not seem worth re-calculating all the $V(q)$ just with this modification. R_c has been taken from Winkler (1955, table II), and α_{eff} in table 4 corresponds to (19). The $|E_c|$ was used by mistake instead of $-\mu_c$ in (14) for the correlation correction, but the error is negligible as already remarked in §2.

The final results for $V(q)$ shown in fig. 2 include the factor $D(q)$ from eqn. (4). As mentioned in §1, detailed numerical tables, with and without the factor $D(q)$, are available on request. They will also be included without $D(q)$ by Harrison (1966). Finally table 5 shows the comparison with values of $V(q)$ at the first few reciprocal lattice vectors, determined from the observed shape of the Fermi surface in the metals and from the optical spectra in the case of the semiconductors. As discussed in §§1 and 4 and in II, one is not exactly comparing like with like because the experimental values of $V(q)$ are determined from truncated secular equations so that they include some higher-order corrections which are calculated to be about 0.01 ryd or less even for a metal with relatively large $V(q)$ like lead. In the case of Si and Ge, the analysis of the optical spectra did not take into account any variation of $V(q=0)$ with position in the band: this effect is appreciable and thus the 'experimental' $V(q)$ will be distorted to some extent.

The agreement in table 5 between calculation and experiment is on the whole most gratifying, and shows that we have basically arrived at our objective of setting up the potential in a solid to about 0.01 ryd. In some cases the error is a bit greater: in the group IV semiconductors, as is well known, the linear screening theory is inadequate because of the large magnitude of V_{111} and the presence of many reciprocal lattice vectors of magnitude less than or comparable with $2k_F$. There is also some doubt about many-body effects in the screening, as discussed in IV. However, the calculations show that we have more or less arrived at the end of the line. Perhaps the treatment of correlation and exchange in the screening theory could be improved somewhat along the lines of Kohn and Sham (1965), but otherwise it is clear that improving significantly on

the accuracy of 0.01 ryd would raise a whole host of difficult many-body problems and self-consistency problems. The correlation and orthogonality corrections, including the orthogonality correction to the valence-valence exchange and correction, are all of this magnitude, and our approximations to them are rather crude. Furthermore, the treatment of the conduction electrons as a free-electron gas in the screening theory while satisfactory to 0.01 ryd, would probably not do at the level of 0.001 ryd. The importance of non-linearity in screening has already been mentioned. Finally there is the question of the additivity of the model potential and the V_{rest} in (20), which we could only deal with by taking quite arbitrarily some weighted mean of (26): this is an inherent limitation of the model

Table 5. Comparison between calculated $V(q)$ and experiment

	Recip. lattice vector	$\frac{q}{2k_F}$	$V(q)$ calc. ryd	$V(q)$ expt. ryd	Refce.
Si	(111)	0.55	-0.18	-0.21	} Brust (1964)
	(200)	0.90	+0.05	+0.04	
	(311)	1.07	+0.08	+0.08	
Ge	(111)	0.55	-0.19	-0.23	} Brust (1964)
	(200)	0.90	+0.03	+0.01	
	(311)	1.07	+0.07	+0.06	
Al	(111)	0.78	+0.020	+0.0179	} Ashcroft (1963)
	(200)	0.88	+0.057	+0.0562	
Pb	(111)	0.69	-0.085	-0.084	} Anderson and Gold (1965)
	(200)	0.81	-0.032	-0.039	

potential, as is the need to extrapolate the $A_i(E)$ from the atomic values. Thus it seems doubtful if anyone will ever wish to compute the potentials to much higher accuracy.

§ 6. APPLICATION TO EFFECTIVE MASS

In this section we calculate an average Hartree effective band mass at the Fermi level. By this we mean that the pseudo-wave functions are taken as single plane waves with no mixing of waves by the periodic potential, and we calculate their energy expectation value :

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} + \langle \mathbf{k} | U | \mathbf{k} \rangle. \quad \dots \dots \dots (30)$$

The effective mass m^* is defined by :

$$\frac{\hbar k}{m^*} = \frac{d\epsilon}{dk} = \frac{\hbar k}{m} + \frac{dW}{dk}, \quad \dots \dots \dots (31)$$

where

$$W(k, E) = \langle \mathbf{k} | U | \mathbf{k} \rangle. \quad \dots \dots \dots (32)$$

The second term in (31) contributes in two ways: firstly the parameters A_i in the model potential depend on the energy E and hence on ϵ ; secondly the projection operators in (1) mean that the potential is not simply a local one, so that $\langle \mathbf{k} | U | \mathbf{k} \rangle$ is not independent of k . We have:

$$\frac{dW}{dk} = \frac{\partial W}{\partial k} + \frac{\partial W}{\partial E} \frac{d\epsilon}{dk}, \dots \dots \dots (33)$$

whence

$$\frac{m^*}{m} = \frac{1 - \partial W / \partial E}{1 - (m / \hbar^2 k) \partial W / \partial k} \dots \dots \dots (34)$$

The model potential at $r > R_M$ is purely local and independent of E , as are the screening potential of the electrons and the orthogonality and correlation correction. They therefore contribute only a constant to W and nothing to (34). The only contribution comes from the model potential of the bare ion at $r < R_M$, which we again take in the form (9) of II.

Table 6. Effective masses

Element	Li	Na	Na	Na	Na	K	Rb
R_M	2.8	2.2	3.0	3.4	4.0	4.2	4.4
m^*/m	1.36	0.57	0.99	1.13	1.13	0.90	0.88
m^*/m (Ham 1962)	1.33	—	—	1.10	—	0.88	0.83
Element	Cs	Be	Mg	Zn	Hg	Al	Ga
R_M	4.8	2.0	2.6	2.2	2.6	2.0	2.4
m^*/m	0.75	1.80	1.09	0.89	0.69	1.10	0.87
m^*/m (Ham 1962)	0.78						
Element	In	Tl	Si	Ge	Sn	Pb	Bi
R_M	2.4	2.4	2.0	2.0	2.0	2.1	2.0
m^*/m	0.74	0.66	1.00	0.91	0.88	0.67	0.61

The results of evaluating (34) are shown in table 6. They are compared for the alkalis with the masses fitted by Ham (1962) to the results of his detailed band structure calculations. The values of A_i used were the same as in table 4, and the derivatives dA_i/dE taken from the $A_i(E)$ in Technical Report No. 4. In the case of sodium we have used four different R_M . As in fig. 1, two are extreme values, and the difference between $R_M = 3.0$ and 3.4 is probably a good measure of the reliability of the m^* . When the A_i are not nearly equal to Z/R_M it is not a good approximation to take the pseudo-wave functions as single plane waves: as one would expect, the effective mass, being a derivative with respect to energy, is much more sensitive to such an approximation than the absolute position of the Fermi level in table 3. The comparison for the alkalis with the effective masses of Ham (1962) is quite good, but it is not clear

how reliable the results are for the polyvalent metals. At least they show the qualitative trend with row in the periodic table expected from the theory of Cohen and Heine (1958).

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APPENDIX

In (2), $V(q)$ depends not only on q , but also to some extent on k and $k' = |\mathbf{k} + \mathbf{q}|$, while our calculations refer to a particular choice of k and k' as discussed in § 5. Since for many purposes matrix elements are required for other values of k , k' , we give here the complete formulae derived on the basis of II and III:

$$V(q; k, k') = \frac{G(q)}{\epsilon(q)} + F(q, k, k') + I(q). \quad \quad (34)$$

Here $G(q)$ is the local part of the unscreened potential and $\epsilon(q)$ the screening factor defined in (23)–(25) of II. We use the approximation (8) of II, and obtain:

$$\begin{aligned} G(q) = & -\frac{8\pi A_2}{\Omega q^3} [\sin(qR_M) - qR_M \cos(qR_M)] \\ & -\frac{8\pi Z}{\Omega q^2} \cos(qR_M) \\ & + \left[\frac{4\pi |\mu_c(n_b)|}{\Omega q^3} - \frac{24\pi Z \alpha_{\text{eff}}}{\Omega q^2 (qR_c)^3} \right] [\sin(qR_c) - qR_c \cos(qR_c)]. \end{aligned} \quad (35)$$

Here the last term comes from the correlation and orthogonality corrections defined by (14), (15), (19). The same α_{eff} is also to be used in the formula (23) of II for $\epsilon(q)$. Note that in these formulae the A_i must be in atomic units (i.e. double rydbergs) and μ_c in rydbergs, as given in the tables. All other quantities are in atomic units. $V(q)$ is then in rydbergs. In (34) F comes from the non-local part of the bare ion model potential. For $k = k'$ we have

$$\begin{aligned} F(q, k, k') \\ = & -4\pi \Omega^{-1} R_M^3 (A_0 - A_2) \{ [j_0(kR_M)]^2 - [kR_M]^{-1} \cos(kR_M) j_1(kR_M) \} \\ & - 12\pi \Omega^{-1} R_M^3 (A_1 - A_2) \left(1 - \frac{q^2}{2k^2} \right) \{ [j_1(kR_M)]^2 - j_0(kR_M) j_2(kR_M) \}, \end{aligned} \quad (36)$$

where

$$\begin{aligned} j_0(x) &= x^{-1} \sin x, \\ j_1(x) &= x^{-2} \sin x - x^{-1} \cos x, \\ j_2(x) &= (3x^{-3} - x^{-1}) \sin x - 3x^{-2} \cos x. \end{aligned}$$

For $k \neq k'$ we have :

$$\begin{aligned} F(q, k, k') = & - \frac{8\pi R_M^2 (A_0 - A_2)}{\Omega [k^2 - k'^2]} [kj_1(kR_M)j_0(k'R_M) - k'j_1(k'R_M)j_0(kR_M)] \\ & - \frac{24\pi (A_1 - A_2) R_M^2}{\Omega [k^2 - k'^2]} \left(\frac{k^2 + k'^2 - q^2}{2kk'} \right) [kj_2(kR_M)j_1(k'R_M) \\ & - k'j_2(k'R_M)j_1(kR_M)]. \end{aligned} \quad (37)$$

This formula is the same as eqn. (4.5) of III except for correcting an error of a factor R_M^2 . Finally in (34) the $I(q)$ is the potential produced by the electrons screening the non-local part of the model potential and is defined by :

$$\begin{aligned} I(q) = & - \frac{32m^* [1 - f(q)]}{\pi \Omega q^2 \epsilon'(q)} [(A_0 - A_2)L_0 + 3(A_1 - A_2)L_1] R_M^2, \\ L_1 = & \int_{\kappa < k_F} (\kappa^2 - \kappa'^2)^{-2} [\kappa j_{l+1}(\kappa R_M) j_l(\kappa' R_M) - \kappa' j_{l+1}(\kappa' R_M) j_l(\kappa R_M)] \\ & \times P_l(\cos \theta_{\kappa\kappa'}) d^3 \kappa, \end{aligned} \quad (38)$$

where $\kappa' = \kappa + \mathbf{q}$ and $f(q)$ is given by (2.3) of III. There is no simple correct way of including in this the effect of the orthogonality correction in the screening electrons, but since the whole term is small this effect can be ignored. The $\epsilon'(q)$ in (38) is therefore the same as (23) of II except for omitting the factor $(1 + \alpha_{\text{eff}})$.

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