A New Method for the Electronic Structure of Metals

By V. HEINE† and I. ABARENKOV‡
Cavendish Laboratory, Cambridge, England

[Received 25 October 1963]

ABSTRACT

A new method is described for setting up the effective potential for electrons in non-transition metals, including liquid metals and alloys. It is based on a model potential fitted to the spectroscopically measured energy levels of the free ions. The potential between the atomic cores is obtained from the dielectric screening calculation of Cohen and Phillips (1961) with some refinements. The method is tested on the band structures of the (solid) alkali metals. The Fermi surfaces of K, Rb and Cs are found to be considerably less distorted than calculated by Ham (1962), and thus in better agreement with experiment.

§ 1. THE POTENTIAL IN A METAL

THIS is the main paper in a series developing a new approach to calculating the electronic structure of non-transition metals. Basically it is an application of the spirit of the Quantum Defect Method (Ham 1955) to polyvalent metals taking proper account of the potential between the ion cores.

In setting up the potential or effective potential seen by a conduction electron in the metal, we have to discuss separately (*a*) the behaviour of the electron inside the ion core of one of the atoms, and (*b*) the potential in the region between the ions, with its problem of finding the self-consistent potential of the conduction electrons screening the ions. As regards (*b*), we follow the path initiated by Cohen and Phillips (1961) and recently become fashionable (see e.g. Harrison 1963, Sham 1963, Ziman 1964) in which we start with a rigid uniform jelly of electrons into which we place the bare positive ions of the metal at positions $\mathbf{R}_j$. The potential in this system is expressed in the form :

$$(\text{const}) + \sum{}' A(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{r}), \qquad (1)$$

where the $\sum'$ excludes the term $\mathbf{q} = 0$. We now unfreeze the electron jelly, allowing the electrons to move and screen the potential. We make the

† Much of the present work was done while the author was a vacation consultant at the Atomic Energy Research Establishment, Harwell.

‡ Permanent address : Department of Theoretical Physics, The University, Leningrad, U.S.S.R., British Council exchange student at Cambridge University 1962–3.

linearity approximation that each term in (1) is screened individually by some dielectric constant or screening factor $\epsilon(\mathbf{q})$, so that the self-consistent potential becomes :

$$(\text{const}) + \sum{}' \frac{A(\mathbf{q})}{\epsilon(\mathbf{q})} \exp(i\mathbf{q} \cdot \mathbf{r}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In (1), since the electron density is uniform, it does not contribute to the $\mathbf{q} \neq 0$ components of the charge density or the potential. In fact we have :

$$A(\mathbf{q}) = V(\mathbf{q}) S(\mathbf{q}), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$$S(\mathbf{q}) = \frac{1}{N} \sum_j \exp(-i\mathbf{q} \cdot \mathbf{R}_j). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here

$$V(\mathbf{q}) = (1/\Omega) \int V_{\text{ion}}(\mathbf{r}) \exp(-i\mathbf{q} \cdot \mathbf{r})\, dv, \quad . \quad . \quad . \quad . \quad (5)$$

and depends only on the potential of a bare ion. N is the total number of atoms and Ω the volume per atom. Note that the formalism covers any configuration of the atomic centres, and thus includes solid metals, liquid metals, and metals disturbed by a vacancy, dislocation or a phonon. In the case of an alloy with several atomic species α, we generalize (3) to :

$$A(\mathbf{q}) = \sum_\alpha V_\alpha(\mathbf{q}) S_\alpha(\mathbf{q}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

We shall term this approach the Screened Ion method, and we shall have nothing to add to it except a more careful discussion of some points of detail.

To take account of the inside of the atom, we use for V_{ion} the Model Potential of Abarenkov and Heine (1964, hereafter referred to as I) :

$$V_{\text{M}} = -\sum_l A_l(E) P_l \quad \text{for } r < R_{\text{M}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

$$= -Z/r \qquad \text{for } r > R_{\text{M}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

in atomic units ($e = \hbar = m = 1$), where A_l is a constant (independent of r) which varies slowly with the energy E of the incident conduction electron as well as with the chosen model radius R_{M}, and where P_l is a projection operator which picks out the lth spherical harmonic component of the incident wave function. Thus V_{M} is not simply a function of r but an l- and E-dependent operator. We reiterate that what one requires in the screened ion method is the potential seen by a single electron outside a free closed-shell ion. The use of the model potential follows the spirit of the quantum defect method (Ham 1955), firstly because the $A_l(E)$ in (7) is fitted to the spectroscopically measured energy levels of the free atom or ion (e.g. sodium atom or Al^{++} ion). Secondly the quantum defect method emphasizes that the energy band structure of the solid depends only on the logarithmic derivative of the wave function at some radius such as R_{M}, independent of what goes on inside, and this logarithmic derivative is correctly reproduced by V_{M}. Inside R_{M}, however, V_{M} produces a bogus

wave function ϕ which is slowly varying and does not have the atomic-like oscillations of the real wave function ψ produced by V_{ion}. In this respect the model potential follows the spirit of the pseudo-potential (Cohen and Heine 1961, Austin *et al.* 1962), although mathematically it does not come within the precise definition of a pseudo-potential adopted there. Thus as in the use of a pseudo-potential, what we have gained is that we have replaced a strong and unknown potential V_{ion} by a weak potential V_{M}, which is adjusted to the spectroscopic data on the free atom or ion, and which can be treated by expanding the wave function in plane waves. Note that the method works just as easily for heavy metals and metals with large valence (when the spectroscopic data are available!) as for light metals.

It should be emphasized that there is no approximation introduced by using the model potential. Let ψ be some solution of the Schrödinger equation for energy E calculated with the actual ionic potentials, and let ϕ be the corresponding solution calculated with the model potentials at the same energy. If we integrate outwards from any nucleus, the whole point of the model potential is that it gives ϕ the same radial derivative as ψ at the radius R_{M}. Outside R_{M} in the region between the atoms, the two potentials are identical and so are ψ and ϕ. Thus to every eigenfunction of the ψ equation there corresponds an eigenfunction of the ϕ equation with the same energy, and hence the eigenvalue spectrum calculated from the model potential is the same as that from the real potential. There is of course the linear screening approximation involved in (2) and there are several approximations in the calculation of ϵ (see § 4), but this does not affect the validity of the model potential in itself. The only real doubt in the model potential comes from interpolating or extrapolating $A_l(E)$ from the atomic energy levels to the required energy in the solid.

Incidently the linear screening approximation is probably very good for most purposes. In a pure solid, $A(\mathbf{q})$ is non-zero only for reciprocal lattice vectors, which are sufficiently large for $A(\mathbf{q})$ there to be usually small. In any case $\epsilon(\mathbf{q})$ there is already as low as about 1·1 to 1·2. In the case of a long wavelength or a liquid metal, we have $S(\mathbf{q})$ small at small $\mathbf{q}$, and it is well known that the linear approximation then gives the right answer as $\mathbf{q}\to 0$ even though $V(\mathbf{q})$ and $\epsilon(\mathbf{q})$ diverge as $1/q^2$. March and Boardman (1963) have shown that the linear approximation gives rather bad results for the potential round a point charge in a free electron gas. While this may apply directly to dissolved hydrogen or injected positrons, the situation with atomic impurities is rather different. Here the pseudo-potential cancels off most of the potential at small r, where the potential of a point charge would be very strong and where the non-linearities reported by March and Boardman presumably came from. We therefore expect the linearity approximation to be much better for an impurity atom, substitutional or interstitial, than for a bare charge such as a proton or positron. It should also be noted that the approximation should be about equally good for (pure) polyvalent metals as for monovalent ones.

Although the strength of the potential increases with Z, the relevant parameter is the ratio of the strength of the potential to the Fermi energy, which is proportional to $(Z\Omega)^{1/3}$, and varies only a factor of two between the extreme cases of lithium and bismuth.

The purpose of the present calculations is to test the above method of setting up the effective potential on the band structure of the alkali metals. In § 2 we test first by itself the model potential for the inside part of the atom, retaining the older Wigner–Seitz construction of the potential between the ion cores as modified by Ham (1962). Since Ham calculated the band structures using such a potential and using a combination of the quantum defect and Kohn–Rostocker methods with the same spectroscopic data as in I, we expect to reproduce by our model potential exactly the same energy spectrum. Employing only perturbation theory, we do indeed find band gaps very close to Ham's, with a total amount of labour which must be some orders of magnitude less.

Having found a quick and satisfactory method of treating the potential from the core of the atom, we can explore different constructions for the potential in the regions in between. In § 3 we set up the Screened Ion potential (2)–(5), calculate the matrix element which determines the distortion of the Fermi surface, and compare it with that given by the Wigner–Seitz–Ham (WSH) potential. With an energy- and angular-momentum-dependent model potential, this matrix element is of course not simply equal to half the band gap. We find that the Screened Ion potential gives considerable less distorted Fermi surfaces for K, Rb and Cs than Ham's results, in accordance with the suggestion of Bienenstock (1962), and thus much better agreement with experiment (Okumura and Templeton 1962, 1963, Shoenberg and Stiles 1964).

In § 4 we give our version of how to calculate ϵ. Results on polyvalent metals, the noble metals and the resistence of liquid metals are reserved for another publication (hereafter called III).

§ 2. Test of the Model Potential

As already mentioned, we set up the WSH potential for the alkali metals, equivalent to that used by Ham (1962) modelled on the Wigner–Seitz approach. Inside R_{I}, the radius of a sphere inscribed in each atomic polyhedron, the potential is that of a bare ion, for which we use the model potential (7) with R_{M} chosen at some convenient value less than R_{I}. The values of the constants $A_0(E)$, $A_1(E)$ and $A_2(E)$ were taken from the tables in I, and we put :

$$A_l(E) = A_2(E) \quad \text{for } l \geqslant 3. \qquad (8)$$

This approximation should introduce negligible error since (*a*) it should be about right, (*b*) the wave functions in the filled band are expected to contain very little f and higher components, and (*c*) these components do not feel the potential near the nuclei much because of the centrifugal barrier. (8) should be compared with Ham's assumption which appears to be

$A_l = 0$ for $l \geqslant 3$. A further difference is that we have not incorporated a 'polarization correction' in calculating our $A_l(E)$ (see § 3).

With assumption (8), (7 *a*) becomes for $r < R_M$:

$$V_M = -A_2 - (A_0 - A_2)P_0 - (A_1 - A_2)P_1. \quad . \quad . \quad . \quad . \quad (9)$$

In the calculation of a matrix element $\langle \mathbf{k}_2 | V_M | \mathbf{k}_1 \rangle$ between plane wave states $\mathbf{k}_1$ and $\mathbf{k}_2$, the A_2 in (9) and the part of V_M at $r > R_M$ are ordinary local potentials and present no difficulty. The P_0 and P_1 in (9) pick out from the plane wave $\exp(i\mathbf{k}_1 . \mathbf{r})$ the components :

$$j_0(k_1 r) \quad \text{and} \quad 3ij_1(k_1 r) \cos \widehat{\mathbf{k}_1 \mathbf{r}}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

respectively, which because of the overall spherical symmetry of (9) combine only with the corresponding pieces of $\exp(i\mathbf{k}_2 . \mathbf{r})$. In the region between the inscribed spheres, Ham put the potential equal to a constant C, which is equal to the mean value of $-1/r$ between an inscribed (radius R_I) and an atomic sphere (radius R_a). The potential in the whole metal therefore is :

$$C + \sum v(E ; \mathbf{r} - \mathbf{R}_j), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

with

$$\begin{aligned} v(E ; \mathbf{r}) &= V_M - C \quad \text{for } r < R_I \\ &= 0 \qquad\quad \text{for } r > R_I. \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Let E_s and E_p be the energies of the first s-like and p-like states at the centre $\mathbf{k}_N$ of the Brillouin zone face. With the abbreviations :

and

$$\left.\begin{aligned} v_0(E) &= \langle \mathbf{k}_N | v(E) | \mathbf{k}_N \rangle \\ v_1(E) &= \langle -\mathbf{k}_N | v(E) | \mathbf{k}_N \rangle, \end{aligned}\right\} . \quad . \quad . \quad . \quad . \quad (13)$$

the parameter $V_1(N)$ tabulated by Ham, which is half the band gap, becomes:

$$\begin{aligned} V_1(N) &= \tfrac{1}{2}(E_s - E_p) \\ &= \tfrac{1}{2}[v_0(E_s) + v_1(E_s)] - \tfrac{1}{2}[v_0(E_p) - v_1(E_p)]. \end{aligned} \quad . \quad . \quad . \quad (14)$$

If we asume $v(E)$ varies sufficiently nearly linearly between E_s and E_p, (14) becomes :

$$\begin{aligned} V_1(N) &= \tfrac{1}{2}(E_s - E_p)\frac{\partial v_0}{\partial E} + v_1\left(\frac{E_s + E_p}{2}\right) \\ &= v_1\left(\frac{E_s + E_p}{2}\right) \times [1 - \partial v_0 / \partial E]^{-1}. \end{aligned} \quad . \quad . \quad . \quad . \quad (15)$$

We see therefore that the energy-dependent potential introduces a correction factor, and it is not adequate to use some of the simple formulae of the original nearly-free-electron approximation. Incidentally, the variation of $\langle \mathbf{k} | v(E) | \mathbf{k} \rangle$ with $\mathbf{k}$ and E contributes to the effective mass in the band in a similar way to (14), but we do not calculate this effect here.

We can improve on (15) by taking for v_1 not just the matrix element (13) itself, but by including all second-order effects (Pryce 1950) :

$$v_1 = \langle -\mathbf{k}_N|v|\mathbf{k}_N\rangle + \sum{}' \frac{\langle -\mathbf{k}_N|v|\mathbf{k}_N+\mathbf{K}_i\rangle\langle \mathbf{k}_N+\mathbf{K}_i|v|\mathbf{k}_N\rangle}{\mathbf{k}_N{}^2-(\mathbf{k}_N+\mathbf{K}_i)^2} . \qquad (16)$$

The summation is over all reciprocal lattice vectors $\mathbf{K}_i$ except 0 and $-2\mathbf{k}_N$.

The numerical results are shown in table 1. The first line is the lattice constant, which is close to the equilibrium one and is the value used by Ham (1962). The next line gives the energy $\frac{1}{2}(E_s+E_p)$ as required for calculating v_1 in (15) and (16). In a complete band structure calculation,

Table 1. Band gap with WSH potential

	Li	Na	K	Cs	Rb
a	6·65	8·11	10·05	10·74	11·46
$\frac{1}{2}(E_s+E)$	−0·311	−0·300	−0·278	−0·267	−0·253
R_M	2·8	3·4	4·2	4·6	4·8
v_1 convergence of second-order corrections	0·0951	0·0065	0·0060	−0·0145	−0·0200
	0·0973	0·0065	0·0082 −	−0·0178	−0·0259
	0·0982	0·0064	−0·0087	−0·0184	−0·0271
	0·0983	0·0064	−0·0088	−0·0184	−0·0272
R_M	2·0	2·2	2·4	3·2	3·4
v_1 with second order	0·095	0·007	−0·007	−0·014	+0·009
$(1-\partial v_0/\partial E)^{-1}$	1·00	1·07	1·16	1·21	1·27
$V_1(N)$ [WSH]	0·098	0·006	−0·010	−0·022	−0·034
$V_1(N)$ [Ham]	0·101	0·008	−0·016	−0·028	−0·042

Note : distances are in atomic units and energies in rydbergs.

this energy should be adjusted self-consistently in accordance with the position of the band. In our case we estimated the energy of the bottom of the band for sodium self-consistently as −0·600 Ryd, compared with Ham's value of −0·604 Ryd. Thus it is clear that our method gives the absolute position of the bands in substantial agreement with Ham's calculation, and the values of $\frac{1}{2}(E_s+E_p)$ were therefore taken from his work. Next in table 1 come the value of R_M, the value of the simple matrix element v_1 (13), and the effect of summing over 25, 123 and 341 reciprocal lattice vectors in (16). Also given is the corresponding result (341 $\mathbf{K}_i$'s) for a much smaller value of R_M : the potential is then far from smooth, and it is surprising that the second-order theory (16) still gives such consistent results in all cases except caesium. Actually it is not quite fair to compare v_1 itself ; it is the whole product (15) that should be invariant to choice of R_M. However, we may conclude that cutting off the series (16) at second order is quite satisfactory except possibly for caesium. In the latter case we know from the work of Ham (1962) that the lowest d-state falls only just above E_p, so that we expect (16) to be somewhat inadequate and to

underestimate the band gap. The following lines in table 1 give the v_0 correction of (15) calculated for the larger R_M, and the final value of $V_1(N)$ from (16) and (15). Comparison with Ham's (1962) results shows agreement to about 0·005 Ryd except for caesium (0·008 Ryd). We regard this as a very satisfactory and a good check on the concept of the model potential, on the usefulness of the various approximations and on the computer programmes.

§ 3. The Screened Ion Potential

We proceed to compare the screened ion potential (2)–(5) with the Wigner–Seitz–Ham potential and with experiment. We calculate not the band gap but the matrix element determining the distortion of the Fermi surface in the direction of the zone faces. The latter is more directly determined by experiment and incidentally avoids the v_0 correction factor in (15). We require the matrix element.

$$V_1(E_F) = \langle \mathbf{k}_2 | V(E_F) | \mathbf{k}_1 \rangle + (\text{second-order and higher corrections}), \qquad (17)$$

where $\mathbf{k}_1$ has magnitude k_F (the Fermi radius) in the direction $\mathbf{k}_N$, $\mathbf{k}_2 = \mathbf{k}_1 - \mathbf{K}_1$, and $\mathbf{K}_1 = 2\mathbf{k}_N$ is the first reciprocal lattice vector. Table 2 shows first of all the results for $V_1(E_F)$ using the WSH potential (12) for V. The second-order corrections were not calculated but simply taken from table 1, which is not quite right but should be within our limits of error, particularly for comparison purposes. Similarly the differences in table 1 between our values and Ham's have a systematic trend : to some extent they arise from neglect of third-order terms as already discussed in connection with caesium, and we have also added them in here as 'a higher order correction'.

In the screened ion method (2)–(5), we need :

$$\langle 2|V|1\rangle = \langle 2|V_M + V_{OC} + V_{CC}|1\rangle/\epsilon(K_1). \qquad . \; . \; . \qquad (18)$$

V_M is the full model potential (7), not cut off at R_I like the WSH potential (12). V_{OC} and V_{CC} are described below. All four quantities in (18) are shown in table 2, ϵ being taken from § 4. The second-order and 'higher' corrections were again taken from table 1.

In calculating $A_1(E)$ for V_M, we have not incorporated a 'polarization correction' such as used by Ham (1962) and by Brooks and Ham (1958). What such a correction would amount to is adding a polarization term b/r^4 to (7 b) outside R_M, with a consequent change in $A_1(E)$ inside R_M such that the whole potential still reproduces the atomic energy levels correctly. When one cuts the potential in half and throws one half away as in the WSH method, such a procedure may be physically significant. However, in the screened ion method we use the whole of V_M. In view of the rather arbitrary choice of R_M and of the form inside R_M (see I), it would appear pedantic to alter the shape of the potential slightly by a polarization correction. If the screened ion method is to be at all useful, its

Table 2. Distortion of the Fermi surface with screened ion potential

	Li	Na	K	Rb	Cs
V_1 (E_F) [WSH]	0·086	0·003	−0·018	−0·027	−0·036
$\langle 2\|V\|1\rangle$	0·100	0·017	0·004	−0·005	−0·009
$\langle 2\|V_{OC}\|1\rangle$	−0·007	−0·005	−0·005	−0·005	−0·005
$\langle 2\|V_{CC}\|1\rangle$	0·005	0·005	0·005	0·005	0·005
(K_1)	1·13	1·11	1·13	1·13	1·13
Second-order terms	0·003	0·000	−0·003	−0·004	−0·007
Higher-order corrections	0·003	0·002	−0·006	−0·006	−0·008
$V_1(E_F)$ [screened ion]	0·094	0·018	−0·004	−0·014	−0·022
error(?)	±0·010	±0·007	±0·005	±0·004	$\pm 0{\cdot}003_5$
Δk_{110} [Ham]	2·3%	0·00	0·7%	1·8%	8·0%
Δk_{110} [screened ion]	2·7–8%	0·10–0·45%	0–0·18%	0·25–0·75%	1·0–2·0%
Δk_{110} [experiment]		0(?)(*b*)	0·11%(*b*)	0·6%(*a*)	$\gtrsim$0·7%(*a*)
			<0·3%(*c*)	0·1%(*b*)	

Note : energies are in rydbergs.

References : (*a*) Okumura and Templeton (1962 and 1963) ; (*b*) Shoenberg and Stiles (1964) ; (*c*) Grimes and Kip (1963).

results must be roughly invarient under changes in the shape of the potential, as we have already tested with respect to changes in R_M.

In (18) V_{OC} is an 'orthogonality' correction, omitted in § 1, coming from the non-uniformity of the conduction electron density. The mean charge density of a conduction state is reduced inside the ion core due to the oscillations of the wave function, and is correspondingly enhanced, by a factor $1+\alpha$ say, in the rest of the atomic cell to preserve normalization. We therefore have an additional uniform negative charge density of $\alpha Z/\Omega$, and an extra positive charge of αZ at each atomic site spread over a radius about the size of the ion core R_c. The contribution to the Kth Fourier component of the potential is :

$$V_{OC}(K)=\frac{24\pi\alpha Z}{\Omega K^2}\left[\frac{x\cos x-\sin x}{x^3}\right]_{x=KR_c} \text{Ryd.} \quad . \; . \; . \quad (19)$$

In the past the value of α has usually been estimated from the orthogonality terms of the orthogonalized plane wave method (Heine 1957, Harrison 1963). We expect α to be proportional to the volume of the core and have used :

$$\alpha=(R_c/R_a)^3, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

with R_c taken from Seitz (1940). Since the whole correction is quite small, the precise value of α does not matter very much. However, the correction becomes more significant for polyvalent metals and (20) will be discussed further in III in connection with aluminium.

We return to V_{OC} in (18) which is a correlation correction arising as follows. In the screened ion method, the conduction electrons to a first approximation are treated as a free electron gas. The exchange and correlation hole follows the electron around and contributes an effective potential $V_{EC}(k)$ which depends on k but not on position. It is of course large, comparable with the band width, and variations of it may be important. The periodic potential causes various complications. First of all exchange with different occupied electron states is additive, and the exchange with the core orbitals is included in V_M. Secondly, however, correlation is not additive. At high electron densities it varies only very slowly (Gell-Mann and Brueckner 1957), and for our purposes we may regard it as approximately saturating at some value $\sim 0{\cdot}1$ Ryd inside the atomic core. The relatively constant figure of about 1 ev correlation energy is also well known in atomic and molecular calculations. If we regard the core as a dense electron gas, we have that V_M includes a correlation hole of $\sim -0{\cdot}1$ Ryd and $V_{EC}(k)$ one of $-0{\cdot}08$ to $-0{\cdot}06$ Ryd (Pines 1955, p. 398), whereas we only want a total correlation hole of $\sim -0{\cdot}1$ Ryd when the electron is in the core. We therefore introduce a correlation correction potential :

$$\left.\begin{aligned} V_{CC}(\mathbf{r}) &= |\text{correlation part of } V_{EC}| \quad \text{for } r<R_c \\ &= 0 \qquad\qquad\qquad\qquad\quad \text{for } r>R_c, \end{aligned}\right\} \quad . \; . \quad (21)$$

to be included in (18). Thirdly, the periodic potential causes a periodic fluctuation in the density of the electron gas and hence in $V_{EC}(k)$. This effect is included in the theory of $\epsilon(K)$ in § 4. Fourthly, there is the variation of $V_{EC}(k)$ with k round the Fermi surface if the latter is not a sphere. If one looks at the simple formula for $V_{EC}(k)$ given by Pines (1955, pp. 407–8), one finds it has a large variation with k. However, when calculating the total band width (Pines 1955, p. 411), one finds most of this is cancelled off by other effects. Experimentally the band widths are very close to the simple Hartree values (Fletcher and Larson 1958). So to a first approximation $V_{EC}(k)$ is constant. The most recent calculations (Rice 1963) indicate that $\partial V_{EC}(k)/\partial k$ increases the density of states at the Fermi level less than 10%, and effects any distortion of the Fermi surface by the same *factor*, which for present purposes is negligible (table 2). Fifthly, the wave functions are not plane waves $\exp(i\mathbf{k}.\mathbf{r})$ but if for instance the Fermi surface touches the zone face one has linear combinations like $\sin(\mathbf{k}_N.\mathbf{r})$ or $\cos(\mathbf{k}_N.\mathbf{r})$. These do not have the same exchange energy with some other state in the band, but when summed over the whole band such effects seem to cancel out (Falicov 1962).

The final results for $V_1(E_F)$ with the screened ion potential are shown in table 2, to be compared with those from the Wigner–Seitz–Ham potential. The distortion of the Fermi surface depends on V_1. We see that the screened ion method gives lithium a slightly more distorted Fermi surface, but not enough to resolve the paradox of the x-ray spectrum (Ham 1962). We also see that potassium, rubidium and caesium should have more nearly spherical Fermi surfaces than calculated by Ham, while sodium receives a slight but noticeable distortion. To obtain quantitatively the bulge Δk_{110} of the Fermi surface towards the zone faces, we plotted Ham's (1962) values of Δk_{110} against the values of $V_1(E_F)$ calculated from the WSH potential (table 2). For $|V_1|/k_F^2 < 0{\cdot}25$ they lie very nearly on the curve :

$$\frac{\Delta k_{110}}{k_F} = 0{\cdot}4\frac{V_1^2}{k_F^4}, \qquad \ldots\ldots\ldots \quad (22)$$

which was anticipated theoretically. The values of Δk_{110} for the screened ion potential were then read off the graph. The results in table 2 are quoted with an error in V_1 of $0{\cdot}03\,k_F^2$, i.e. ranging from 0·010 Ryd for lithium to $0{\cdot}003_5$ Ryd for caesium, which is a reasonable guess. It is intended to cover the uncertainties of the potentials as well as approximations in the computations, both of which should be down to this magnitude now. The values of lattice constant used in table 2 are the same as in table 1 and are sufficiently near the equilibrium ones for the results not to require further correction on this account (Ham 1962). Finally in table 2 we show experimental results. Where the experimental information does not refer to Δk_{110} directly, we have used Ham's results on the ratios of area-, mass-, and radius-anisotropies to reduce the data to statements about Δk_{110}.

In conclusion, we note that the Screened Ion potential gives substantially better agreement with experiment than the Wigner–Seitz–Ham potential. The error in the Wigner–Seitz approximation for the exchange and correlation hole is therefore sufficiently large (about 0·01 Ryd) that we can probably say now for the first time it leads to significant disagreement with experiment. We regard the results both as an improved theory of the band structure of the alkali metals, and as a validation of the model potential plus screened ion approach to the potential. However, the major discrepancy (about 0·06 Ryd) with the apparent soft x-ray spectrum of lithium leaves a nagging doubt. Aside from this, the accuracy achieved is a few thousandths of a rydberg. As for instance the magnitudes of the orthogonality and correlation corrections show, to advance significantly beyond this raises several problems of self-consistency and many-body effects.

§ 4. The Dielectric Constant

For the dielectric constant or screening factor in (2) we use :

$$\epsilon(q) = 1 + X(q)m^*(1+\alpha)\left(1 - \frac{\frac{1}{2}q^2}{q^2 + k_F^2 + k_S^2}\right), \quad . \quad . \quad . \quad (23)$$

where

$$X(q) = \left(\frac{4\pi e^2 Z}{\Omega q^2}\right)\left(\frac{2}{3}E_{F0}\right)^{-1}\left(\frac{1}{2} + \frac{4k_F^2 - q^2}{8qk_F}\ln\left|\frac{2k_F - q}{2k_F + q}\right|\right), \quad . \quad . \quad (24)$$

and E_{F0} is the free-electron Fermi energy $\hbar^2 k_F^2/(2m)$. The simple Hartree approximation for the dielectric constant is $1 + X(q)$, and gives $\frac{2}{3}E_{F0}$ for the matrix element (5) in the limit as $q \to 0$.

The last term in (23) represents a correction for exchange, calculated by Sham (1963) in the spirit of Hubbard (1957, 1958). When going beyond the Hartree approximation, it is necessary to distinguish three different screening factors : (*a*) when the field is set up by some 'external' charge and measured by another 'external' charge, by which we mean that neither of them is an electron ; (*b*) when the field is generated by an 'external' charge felt by an electron which can exchange with the conduction electrons, and in particular with the screening cloud set up by the 'external' charge ; (*b'*) when the field around an electron is felt by an 'external' charge, this situation being presumably related to (*b*) by reciprocity; (*c*) the screening factor for the interaction between two of the conduction electrons. We are here concerned with (*b*) whereas Hubbard (1957–8) considered (*c*), which explains the slight difference from his result. For the screening constant k_S which screens the exchange, we have used

$$\begin{aligned} k_S^2 &= 2k_F/\pi \text{ (atomic units)} \\ &= \tfrac{1}{2}(k_S^2)_{\text{Thomas–Fermi}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25) \end{aligned}$$

as a reasonable estimate between the Thomas–Fermi and Bohm–Pines values (see also Sham 1963).

Next we consider the effect of having Bloch states or at least orthogonalized plane waves instead of free electrons. In (3) and (4), the $S(q)$ for small q comes from the long-wavelength density fluctuations due to thermal vibrations. The matrix element is well known from the theory of the electron–phonon interaction to have the limit :

$$\frac{V_{\text{ion}}(q)}{\epsilon(q)} \rightarrow \frac{Z}{n(E_{\text{F}})} \quad \text{as } q \rightarrow 0, \qquad \ldots\ldots\ldots \quad (26)$$

where $n(E_{\text{F}})$ is the density of states per atom at the Fermi level (Ziman 1960, p. 194). We therefore introduce m^* in (23) as a density-of-states mass factor, and the factor $(1+\alpha)$ to cancel the fact that our orthogonality correction (§ 3) has added an extra charge $Z\alpha$ around each atomic site. When q is not small, we want m^* to represent an average effective mass over the whole band, since it comes from a summation of type :

$$\sum_{\mathbf{k}} \frac{1}{E(\mathbf{k}) - E(\mathbf{k}+\mathbf{q})}, \qquad \ldots\ldots\ldots \quad (27)$$

where $\mathbf{k}$ is inside the Fermi surface and $\mathbf{k}+\mathbf{q}$ outside (Cohen and Phillips 1961). We have in table 2 therefore used the mass values calculated by Ham (1962) for the spherical part of the band. For $q > k_{\text{F}}$, the factor $1+\alpha$ cannot correctly represent the effect of using orthogonalized plane waves instead of free electrons. However, for q equal to the first reciprocal lattice vector, $\epsilon(q)$ is already down to 1·1 to 1·2. If we say that the wave functions differ in charge density from plane waves by about 10%, then this suggests an error in $\epsilon(K)$ of 1% to 2%. Rather larger, perhaps as large as 10%, is the error from neglecting the non-local nature of the potential to be screened (Harrison 1963).

We now discuss whether there are further many-body effects. For many applications this may be somewhat pedantic at the present time. However, the electron–electron Coulomb interaction can increase the density of states in (26) by up to 10% (Rice 1963) and give quasi-particle renormalization factors N_k (Langer 1961 ; z_k in the notation of Nozières 1963) of 0·6 to 0·8. Likewise the interaction via virtual phonons increases the density of states measured in the low temperature specific heat by about 30%. If in liquid sodium for instance we hope to use the present theory to calculate the resistivity to better than a factor of two, then we must take some account of the many-body effects, because most of the scattering occurs at relatively low q where correction factors in (26) are important. Our conclusion is that m^* and (28) should contain the Coulomb corrections but not the virtual phonon one.

As regards the Coulomb interaction, this result can be proved by the Landau theory of quasi-particles. We apply a potential $V_{\text{applied}} \exp i(\mathbf{q}.\mathbf{r} - \omega t)$, which sets up a distribution of quasi-particles $\delta n(\mathbf{k}\,;\mathbf{r},t)$. An incident quasi-particle feels a scattering potential which is the sum of V_{applied}, the electrostatic Hartree field determined from δn by Poisson's equation, and the Landau field $\sum_{\mathbf{k}'} f(\mathbf{k},\mathbf{k}')\delta n(\mathbf{k}')$ determined by the Boltzmann

equation. Here $f(\mathbf{k}, \mathbf{k}')$ is the interaction energy of two quasi-particles. The equations are all set out by Nozières (1963, pp. 16, 18, 21–3) and can be solved self-consistently. The result is an effective scattering potential

$$\left.\begin{aligned} &V_{\text{applied}}/\epsilon(q) \\ \text{with}\quad &\epsilon(q)=\frac{4\pi e^2}{\Omega q^2}n(E_{\text{F}}), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where $n(E_{\text{F}})$ is the single-particle density of states including all interactions with the ground state, The following less sophisticated derivation is based on the deformation potential. We consider an electron moving from an unstrained piece of material (band structure $E_0(\mathbf{k})$) to a strained region with band structure $E_1(\mathbf{k})$. In the limit of long wavelength, each region is electrically neutral but a dipole layer of potential V_{DL} is set up between them. V_{DL} is determined by the condition that the Fermi level is the same in both regions ;

$$E_{\text{F}}=E_0(k_{\text{F}0})=V_{\text{DL}}+E_1(k_{\text{F}1})+\sum f(\mathbf{k}, \mathbf{k}')\delta n(\mathbf{k}'), \quad . \quad . \quad . \quad (29)$$

where the last term is the interaction energy with the extra distribution $\delta n(\mathbf{k})$ of quasi-particles in the strained region. $E_1(k_{\text{F}1})$ is given by :

$$E_1(k_{\text{F}1})=E_0(k_{\text{F}0})+\overline{\delta_{\text{Y}}E}-\frac{Z\Delta}{n(E_{\text{F}})}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where the term $\delta_{\text{Y}}E$ represents the change $E_1(\mathbf{k})-E_0(\mathbf{k})$ in the form of the Hartree band structure, averaged over the Fermi surface, and the last term comes from the change in the electron density and hence in k_{F} due to the dilatation Δ : see Ziman (1960, pp. 192–3) for details. We therefore have :

$$V_{\text{DL}}=\frac{\Delta Z}{n(E_{\text{F}})}-\overline{\delta_{\text{Y}}E}-\sum f(\mathbf{k}, \mathbf{k}')\delta n(\mathbf{k}'). \quad . \quad . \quad . \quad . \quad (31)$$

We now imagine a classical kind of scattering calculation with an electron wave of fixed frequency (energy) incident from the unstrained region onto the strained one. The energy (frequency) remains constant, and the scattering is produced by the change in wavelength between the two media, the scattered wave being required to match the derivative of the wave function at the boundary. We therefore consider an incident electron with wave vector $\mathbf{k}_0$, changing its wave vector to $\mathbf{k}_1$ in the strained region. The equation determining $\mathbf{k}_1$ is :

$$\begin{aligned} E&=E_0(\mathbf{k}_0) \\ &=V_{\text{DL}}+E_1(\mathbf{k}_1)+\sum f(\mathbf{k}_1, \mathbf{k}')\delta n(\mathbf{k}'). \quad . \quad . \quad . \quad . \quad . \quad (32) \end{aligned}$$

The effective scattering potential V_{s} is now defined as that potential, which when placed as a perturbation in the unstrained medium with band

structure $E_0(\mathbf{k})$, produces exactly the same change in wave vector : i.e.

$$E = E_0(\mathbf{k}_0) = V_s + E_0(\mathbf{k}_1). \quad \ldots\ldots\ldots \quad (33)$$

Combining (31)–(33), we have :

$$V_s = \frac{Z}{n(E_F)}\Delta, \quad \ldots\ldots\ldots \quad (34)$$

which leads again to (26) since for small $\mathbf{q}$ the structure factor $S(\mathbf{q})$ of (3) is simply the Fourier transform of the dilation $\Delta(\mathbf{r})$ (Ziman 1961).

We return now to the effect on $n(E)$ of the excitation of virtual phonons. As is well known, it changes the effective band structure $E(k)$ and enhances $n(E_F)$ as measured by the electronic specific heat by some 30%. However, it only produces a narrow kink in $E(k)$ of width $\hbar\omega_D$ (ω_D = Debye frequency) just at the Fermi level. This is seen for instance in the theory of superconductivity or is evident from the fact that the total energy of the system is only changed to order m/M (electron to ion mass). In (27) the excitation by wave-vector $\mathbf{q}$ carries the energy right across the kink for all but exceptionally small $\mathbf{q}$'s. Alternatively in the argument of (29)–(34), the kink in $E(k)$ rides up and down with the Fermi level and does not contribute to the last term in (30) which is the change in E_F. We conclude therefore that the virtual phonon correction to the density of states should not be included in m^*, and must be subtracted out before experimental values of m^* are used.

Acknowledgments

One of us (I. A.) wishes to thank the British Council and the Ministry of Higher Education of the U.S.S.R. for an exchange studentship, and the other (V. H.) to thank the Theoretical Physics Division, Harwell, for their kind hospitality during the summer of 1963. We are indebted to Drs. A. Bienenstock, C. C. Grimes, A. F. Kip, W. A. Harrison, T. M. Rice, L. Sham, D. Shoenberg, P. J. Stiles and J. Ziman for showing us their results prior to publication, and to several of these for helpful discussions.

References

Abarenkov, I., and Heine, V., 1964, to be published. (Referred to as I.)
Austin, B. J., Heine, V., and Sham, L. J., 1962, *Phys. Rev.*, **127,** 276.
Bienenstock, A., 1962, Thesis, Harvard University, and to be published.
Brooks, H., and Ham, F. S., 1958, *Phys. Rev.*, **112,** 344.
Cohen, M. H., and Heine, V., 1961, *Phys. Rev.*, **122,** 1821.
Cohen, M. H., and Phillips, J. C., 1961, *Phys. Rev.*, **124,** 1818.
Falicov, L. M., 1962, *Phil. Trans.* A, **255,** 55.
Fletcher, J. G., and Larson, D. C., 1958, *Phys. Rev.*, **111,** 455.
Gell-Mann, M., and Brueckner, K. A., 1957, *Phys. Rev.*, **106,** 364.
Grimes, C. C., and Kip, A. F., 1963, *Phys. Rev.*, **132,** 1991.
Ham, F. S., 1955, *Solid State Physics*, **1,** 127 ; 1962, *Phys. Rev.*, **128** 82, 2524.
Harrison, W. A., 1963, *Phys. Rev.*, **129,** 2503, 2512 ; **131,** 2433.
Heine, V., 1957, *Proc. roy. Soc.* A, **240,** 361.

HUBBARD, J., 1957, *Proc. roy. Soc.* A, **240,** 539 ; 1958, *Ibid.*, **243,** 336.
LANGER, J. S., 1961, *Phys. Rev.*, **124,** 1003.
MARCH, N. H., and BOARDMAN, A. D., 1963, *Conference Jour. of the Phys. Soc. of Japan*, **18,** supplement II, p. 80.
NOZIERÈS, P., 1963, *Le Problème à N Corps* (Paris : Dunod). Translation : *The Theory of Interacting Fermion Systems* (New York : Benjamin, 1963).
OKUMURA, K., and TEMPLETON, I. M., 1962, *Phil. Mag.*, **7,** 1239 ; 1963, *Ibid.*, **8,** 889.
PINES, D., 1955, *Solid State Physics*, **1,** 367.
PRYCE, M. H. L., 1950, *Proc. phys. Soc., Lond.* A, **63,** 25.
RICE, T. M., 1963, Thesis, Cambridge University and to be published.
SEITZ, F., 1940, *Modern Theory of Solids* (New York : McGraw-Hill).
SHAM, L. J., 1963, Thesis, Cambridge University (available on microfilm from Micromethods Ltd., East Ardsley, Wakefield, Yorkshire).
SHOENBERG, D., and STILES, P. J., 1964, Private communication and to be published.
ZIMAN, J. M., 1960, *Electrons and Phonons* (Oxford : Clarendon Press) ; 1961, *Phil. Mag.*, **6,** 1013 ; 1964, to be published.