SOVIET PHYSICS JETP VOLUME 32, NUMBER 5 MAY, 1971

PSEUDOPOTENTIAL THEORY

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Submitted May 27, 1970

Zh. Eksp. Teor. Fiz. 59, 1711–1715 (November, 1970)

An estimate is made of the matrix elements of the pseudopotential for the electron-ion interaction for simple metals on the assumption of the resonance nature of the scattering of s and p valence electrons. The experimentally determined values of the matrix elements are in satisfactory agreement with the universal formula obtained.

1. Direct calculations of electron states in metals (the so-called "basic principles" calculations) have now been made during several decades. Two basic approaches to the problem should be noted.

In the Wigner-Seitz method instead of solving the Schrödinger equation in a triply periodic self-consistent potential one solves the problem of an electron in an effective spherically symmetric atom which replaces the sufficiently symmetric cell of the crystal lattice. At the boundary of the cell a condition is imposed on the wave function which depends on the quasimomentum of the state. (For the bottom of the band, for example, one takes the vanishing of the derivative of the wave function at the boundary.) In such a case in the region near the nucleus where the potential is close to the atomic potential the wave function behaves as an atomic function of the valence electron with only a small admixture of the wave functions of neighboring states. The Wigner-Seitz method can be used for any degree of compression and has enabled one to predict a number of electron transitions in metals[1,2], but its defects are the large error resulting from the replacement of the polyhedron of the elementary cell by a sphere and the neglect of the specific crystal structure of the lattice.

In recent years considerable development has taken place in calculations of the band structure of specific crystals by the pseudopotential method[3] which treats the conduction electrons in the metal as being almost free while the self-consistent effective potential acting upon them is treated as a perturbation. Analysis of experimental data referring to a large number of simple metals shows that their Fermi surfaces can indeed be obtained by means of constructing "Harrison spheres", and the lifting of the degeneracy when the spheres intersect can be treated by means of perturbation theory, and in this case the corresponding matrix element of the perturbation turns out to be small compared to the Fermi energy.

The basis for the possibility of regarding the valence electrons as being almost free is the smallness of the dimensions of the ion cores which form the metal lattice, compared to the lattice parameters. If for estimating the dimensions of the ion one adopts the Thomas-Fermi model we obtain $r_i \sim a_0 Z^{-1/3}$, where a_0 is the Bohr radius, Z is the atomic number of the element, while the lattice constant is of the order of magnitude of the Bohr radius; experimental data show that the region where the potential of the ion is indeed large amounts to less than 20% of the cell volume. In the remaining part of the volume the electron moves almost as if it were free, and its wave function must be close to the solution of the Schrödinger equation for free motion.

Usually for the justification of the pseudopotential method one utilizes the expansion of the wave function in terms of "orthogonal plane waves" (OPW), which are constructed by means of adding to the wave functions for the free motion Bloch sums taken over the functions of the internal states of the atom in such a manner that the resultant wave function would be orthogonal to all the functions of the internal states. By regrouping the terms in the Schrödinger equation it can be shown that the orthogonalization procedure is equivalent to the introduction of a certain nonlocal repulsive potential which essentially compensates the initial potential of the ion. As a result there arises a comparatively weak nonlocal "pseudopotential" to which the perturbation theory is then applied.

In fact the calculation of the pseudopotential from "basic principles" is quite awkward and quantitatively yields not very reliable results. Much better results are obtained by utilizing model pseudopotentials whose parameters are chosen on the basis of the requirements of the best agreement with optical data (the method of Heine-Abarenkov[3]).

The object of the present paper is to obtain a rough estimate of the matrix elements of the pseudopotential for nontransition metals on the basis of scattering theory.

2. As has been mentioned already, in the Schrödinger equation for valence electrons their interaction with atomic nuclei and with the electrons of internal shells is strong, but of short range, and therefore in the greatest part of space the wave function can be regarded as a plane wave distorted by the presence of waves scattered at each centre of force[1)] with a scattering amplitude expressed by the usual formula in terms of the phases[4]:

$$f(\vartheta) = \sum_l (2l+1) P_l(\cos\vartheta) f_l, \qquad f_l = \sin\delta_l e^{i\delta_l}/k. \tag{1}$$

Thus, for each orbital angular momentum the modulus f_l of the partial scattering amplitude is bounded by the value 1/k independently of the strength of the po-

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[1)] Here the potential of a centre of force is the short range potential of the ion core with an added self-consistent part of corresponding to the distribution of valence electrons.

tential. This limiting value is attained at resonance when $\delta_l \approx \pi(n + 1/2)$, and n is an integer. For making an estimate of the phases a very significant simplifying circumstance is the smallness of the Fermi energy compared to the characteristic values of the energies of the levels of internal shells in the short range potential of the core. If for rough estimates one adopts the Thomas-Fermi model, then the average energy per electron in atomic units is of order $Z^{4/3}$, where Z is the atomic number of the element, while the Fermi energy $\sim Z_{\mathrm{val}}^{2/3}$, where Z_{val} is the number of valence electrons. Thus, the scattering amplitude is determined by the behavior of the phase at low energies. In the absence of resonance all the phases (modulo π) obey the law

$$\delta_l \sim (k_F r_i)^{2l+1}$$

and are very small. Here r_i is the range of the short range potential,

$$\hbar^2 k_F^2 / 2m = \varepsilon_F, \quad k_F a_c \sim 1 \text{ and } k_F r_i \ll 1.$$

For nontransition metals, when the d- and f-levels lie very far $(\sim Z^{4/3})$ the contribution to the scattering amplitude is given only by the s- and p-states and it is just for them that the resonance situation is realized at low energies since the appearance of the corresponding states in the atom with increasing Z corresponds to the fact that in the self-consistent potential of the ion new bound electrons have appeared with a very low energy. This automatically takes into account the corrections for exchange, for correlation and for screening. With a further increase of Z the levels move deeper in and the resonance situation is violated.

As is well known, in the periodic system the s- and p-electrons appear at the beginning of a period almost simultaneously, and correspondingly for them the resonance situation is realized simultaneously (for real and virtual levels). For s- and p-electrons the width of the resonance is of the order of the Fermi energy, and in passing through resonance the s and p wave functions produce a small change in the spatial distribution of the average electron density which is characterized by the fact that the main part of the normalization integral comes from outside the core. For this reason one can neglect the reaction of the conduction electrons on the phases of the scattering effective potential of the centres of force.

For states with large values of l, conversely, it is characteristic that there is a sharp change in the probability density as we go through resonance, and the normalization integral for the free states basically comes from the region $r > r_i$, while for bound states it comes from the region $r < r_i$, and, therefore, it is necessary to take into account its reaction on the effective potential.

Thus, one can obtain a qualitative idea of the scattering amplitude in nontransition metals assuming

$$\delta_0 = \delta_1 = \pi/2, \quad \delta_l = \pi, \quad l = 2, 3, \ldots .$$

This leads to the expression

$$f(\vartheta) = \frac{i}{k_F}[P_0(\cos\vartheta) + 3P_1(\cos\vartheta)] = i\frac{1 + 3\cos\vartheta}{k_F}. \tag{2}$$

A knowledge of the scattering amplitude enables one to relate it formally by means of perturbation theory to the Fourier component of a certain pseudopotential V_q[5]:

$$f(\vartheta) = -\frac{m}{2\pi\hbar^2}\Omega_0 V_q, \tag{2a}$$

Ω_0 is the volume of the cell per single atom. In order to calculate the band structure it is sufficient to know $|V_q|$. It is convenient to find the ratio of V_q to the Fermi energy of free electrons:

$$\frac{|V_q|}{\varepsilon_F} = \frac{2\pi|f(\vartheta)|2m}{\Omega_0 m\hbar^2 k_F^2},$$

$$Z_{\mathrm{val}} = \frac{2\cdot 4\pi}{3}\frac{k_F^3\Omega_0}{(2\pi)^3}.$$

Utilizing (2) we obtain

$$\frac{V_q}{\varepsilon_F} = \frac{4(1 + 3\cos\vartheta)}{3\pi Z_{\mathrm{val}}}.$$

The scattering angle is expressed in terms of the transferred momentum:

$$q = 2k_F \sin\frac{\vartheta}{2}, \qquad \cos\vartheta = 1 - 2\sin^2\frac{\vartheta}{2} = 1 - \frac{q^2}{2k_F^2}. \tag{3}$$

Finally we obtain

$$\frac{V_q}{\varepsilon_F} = -\frac{16}{3\pi Z_{\mathrm{val}}}\left(1 - \frac{3}{8}\frac{q^2}{k_F^2}\right), \quad q_0 = k_F\sqrt{8/3}.$$

The sign in (3) is chosen in order to compare with the shape of the model pseudopotential. In the diagram the graph of formula (3) is compared with the values of V_q which are known from the measurements of the parameters of the Fermi surface for a number of nontransition metals[6]. It can be seen that the use of even the simplest expression (2) for the scattering amplitude correctly represents the general character of the variation of the pseudopotential in the most interesting range of values of $q \sim q_0$, where it is small. As $q \to 0$ a noticeable divergence in the behavior takes place. However, one should remember that as $q \to 0$ the pseudopotential $V_q \sim \epsilon_F$ and perturbation theory is inapplicable.

We also note that the agreement of the experimental points with formula (3) or, more accurately, with its linearized modification

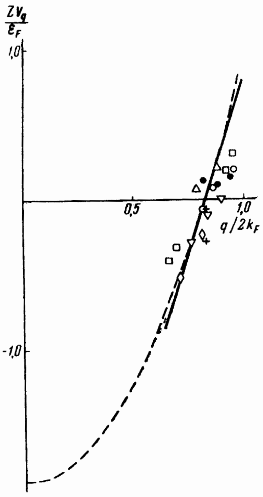
$$V_q = \frac{32}{3\pi Z_{\mathrm{val}}}\sqrt{\frac{3}{2}}\,\varepsilon_F\left(\frac{q}{2k_F} - \sqrt{\frac{2}{3}}\right) \tag{3a}$$

is satisfactory only on the average and is much worse for each separate element. This is more understandable, if we remember that the modulus of the complex scattering amplitude can vanish only for exact resonance in the s- and p-phases, and therefore an error of the order of magnitude of the effect itself is quite natural for the approximate formula (3a) which only enables one to assert that the smallness of the matrix elements compared with the Fermi energy in normal metals is due principally to the cancellation of s- and p-scattering for $q \sim q_0 = k_F\sqrt{8/3}$.

Thus, the short range of the potential leads to the fact that it acts on the electrons only through the scattering amplitude, and the strong potential leads only to a moderate effect: $|f(\vartheta)| \sim k_F^{-1}$. In this the well-known "compensation theorem"[3] manifests itself. In this case the effective pseudopotential has, as can easily be seen, matrix elements of the order of the Fermi energy. In order to determine the band structure the values of

Values of the parameter β (Ryderg · at.unit^3) in accordance with formula (4) and from Table 5 in[3] (in brackets)

I	II	III	IV	V
Li—26 (33,3)	—	—	—	—
Na—41 (31,8)	Mg—35 (31.4)	Al—35 (29,4)	Si—43 (42,6)	—
K—62 (44)	—	—	—	
—	Zn—27 (24.5)	—	Ge—46 (46.5)	As—50 (45.5)
Rb—73 (32)	—	In—47 (43.8)	Sn—51 (41.1)	Sb—61 (51.4)
Cs—86 (44)	Hg—38 (45.9)	Tl—50 (40.1)	Pb—56 (46.0)	Bi—68 (61.0)



Graphs of universal formulas (3)-dotted line and (3a)-solid line. Experimental values taken from the review [6]: ●–Mg, ○–Zn, +–Hg, △–Al, ▽–In, □–Sn, ◇–Pb.

the matrix elements for the Bragg planes closest to the centre of the Brillouin zone are of greatest interest. It is just this range of values of $q \sim q_0$ which has direct physical meaning, and here formula (2a) of perturbation theory is applicable. But the general problem of reconstructing the whole pseudopotential from the values of the scattering amplitude in a restricted range of arguments does not have a unique solution. This corresponds to the theorem of the nonuniqueness of the pseudopotential[3].

Quantities determined by the whole dependence of V_q, as is well known, are calculated not very reliably with the aid of pseudopotential theory, although good estimates can be obtained for them if one utilizes a model semiempirical potential. In this case with the aid of (3) one can attempt to determine the parameters of the model potential. Thus, for example, for the formula (cf.,[3])

$$W^0(r) = -Z_{\text{val}}/r + \beta\delta(r), \quad V_q \sim 4\pi Z_{\text{val}}/q^2 - \beta,$$

an estimate of β on the basis of the universal, in accordance with (3), condition $V(q_0) = 0$ for $q_0 = k_F\sqrt{8/3}$ yields

$$\beta = 3\pi Z_{\text{val}}/2k_F^2. \tag{4}$$

For "good" metals the values obtained with the aid of (4) are in satisfactory agreement with other data.

For alkali metals the agreement is poor since the argument of the matrix element lies outside the range $0 < q < 2k_F$ allowed by single scattering, and formula (2a) loses its meaning. The quantity determined by formula (4) clearly depends on the volume and would be of interest for calculating characteristics of compressed substances, in particular, of phonon spectra under pressure.

In conclusion I express my gratitude to V. Heine for sending me his paper[6] prior to publication.

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Translated by G. Volkoff
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