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Abstract

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THE SPECTRUM OF AN IDEAL FERMI GAS IN A LATTICE

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Let us consider a system whose Hamiltonian H possesses the symmetry of the lattice of a monatomic crystal. Let $\varphi(r)$ be a function of three spatial coordinates possessing the following properties:

1. If r_ν is the radius vector of the ν-th lattice site, $\nu = 1, 2, \ldots, N$, then the functions $\varphi_\nu(r) \equiv \varphi(r - r_\nu)$ are linearly independent and, consequently, can be orthogonalized, for example, by the Bogolyubov–Löwdin method (1). We denote the set of orthonormalized functions obtained from φ_ν by $\Phi_\nu(r)$, so that

$$\int \Phi_\nu^* \Phi_{\nu'} \, dr = \delta_{\nu\nu'}.$$

2. The dependence of the matrix elements $H_{\nu\nu'} = \int \Phi_\nu^* \Phi_{\nu'} \, dr$ on the distance between the sites ν and ν', i.e. on the radius R_η of the η-th coordination sphere, has the form

$$H_{\nu\nu'} = \beta \exp(-\alpha R_\eta^2 \pi / d^2), \qquad \eta = 1, 2, \ldots, \tag{1}$$

where β is a parameter with the dimension of energy, $\beta < 0$; α is a dimensionless parameter ($\alpha = K'/K$, where K' and K are complete elliptic integrals); d is the lattice constant.

If, under these conditions, one seeks the wave function of a (quasi-)particle in the form of a linear combination of the functions Φ_ν, then solution of the secular equation by the usual method leads to the following values for the particle energy:

for a simple cubic lattice

$$E(k_x, k_y, k_z; \alpha) = -\vartheta_3(k_x)\vartheta_3(k_y)\vartheta_3(k_z); \tag{2}$$

for a body-centered cubic lattice

$$E(k_x, k_y, k_z; \alpha) = -\vartheta_3(k_x)\vartheta_3(k_y)\vartheta_3(k_z) - \vartheta_2(k_x)\vartheta_2(k_y)\vartheta_2(k_z); \tag{3}$$

for a face-centered cubic lattice

$$E(k_x, k_y, k_z; \alpha) = -\vartheta_3(k_x)\vartheta_3(k_y)\vartheta_3(k_z) \\ -\vartheta_3(k_x)\vartheta_2(k_y)\vartheta_2(k_z) - \vartheta_2(k_x)\vartheta_3(k_y)\vartheta_2(k_z) - \vartheta_2(k_x)\vartheta_2(k_y)\vartheta_3(k_z). \tag{4}$$

Here k_x, k_y, k_z are the components of the quasimomentum divided by 2π; the energy is measured from $E_0 = H_{\nu\nu} - \beta$; the unit of energy is taken to be $|\beta|$, the unit of length d, and such notation is used for the theta functions that the period of these functions is unity (2): $\vartheta_3(\nu + 1) = \vartheta_3(\nu)$, $\vartheta_2(\nu + 1) = -\vartheta_2(\nu)$, etc.

It follows from the properties of theta functions that the region of single-valuedness of expressions (2)–(4) nearest to the origin of coordinates in k-space coincides with the Brillouin zone, defined in the usual way, and that these expressions are invariant with respect to all symmetry operations that transform the Brillouin zone into itself. Expressions (2)–(4) are valid

provided that cyclic conditions are satisfied and after passing to the limit $N \to \infty$. Let us note that the conditions of Ledermann' s theorem (^{3,12}) are not fulfilled in the present case, and the introduction of cyclic conditions must be justified separately.

In formulas (2)–(4), the smallest energy corresponds to $k_x = k_y = k_z = 0$, and the largest, for example in the case of a body-centered lattice, to $k_x = k_y = k_z = 1$. If in (3) we make the substitution $k_i \to 1 - k_i$ for all $i = x, y, z$, then it becomes

$$E = -\vartheta_3(k_x)\vartheta_3(k_y)\vartheta_3(k_z) + \vartheta_2(k_x)\vartheta_2(k_y)\vartheta_2(k_z). \tag{5}$$

Here $k = 0$ corresponds to the largest energy, $k_i = 1$ to the smallest; the counting of states is carried out from above.

For many questions it is essential to know the density of states $S(E)$, which is equal to the area of the surface S in k-space represented by equations (2)–(4) at fixed E. When written both in the form (2)–(4) and in the form of expressions of type (5), the constant-energy surfaces are closed surfaces enclosing in both cases the point $k = 0$. (To visualize this clearly, one should keep in mind that the points of the surface of the Brillouin zone are identified, generally speaking, in pairs, so that the Brillouin zone is topologically isomorphic to a torus.) Therefore $S(E)$ increases both when the energy is increased from its smallest value and when it is decreased from its largest value. On the other hand, it is obvious that the areas $S(E)$ are finite everywhere. Thus, the intersection of the monotone curves $S = S(E)$, representing the density of states, occurs at a special point where $S(E)$ is finite but its derivative is discontinuous. The existence of this special point was indicated from topological considerations (^{4}). For practically interesting α, the special point is shifted toward higher energies.

Fig. 1

Figure 1: Fig. 1

Therefore the low-energy branch of the density of states may be roughly approximated by a parabola, and the high-energy branch by a vertical straight line. It is precisely this circumstance that explains the fact that Sommerfeld' s model for electrons satisfactorily explains certain properties of metals.

Fig. 1

Let us consider, for definiteness, an electron gas in a lattice for which the interaction between electrons is taken into account in some self-consistent form. In this model, small α corresponds to the approximation of almost free electrons, and large α to the strong-coupling approximation. Therefore α may be regarded as a quantitative measure, respectively, of the "metallicity" or covalency (ionicity) of the crystal. The parameters α and β specify all characteristics of the band, except for its position; the position of the band is determined by the quantity E_0. In particular, the density of states, up to normalization, is determined only by α. For metals, α is not very large, and at small $|k|$ the constant-energy surfaces are not very anisotropic. Therefore below the Fermi level the dependence of S on E may be estimated as follows. By the mean-value theorem we have $S = 4\pi R_E^2$.

To estimate the dependence of R_E on E, for example for a body-centered lattice, consider a sphere of radius R in k-space. Let the energies corresponding to the points of intersection of this sphere with the directions $\langle 200\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ be E_1, E_2, and E_3. Then for E corresponding to the chosen R, one may take $E = (E_1 + E_2 + E_3)/3$ or $E = (E_1 E_2 E_3)^{1/3}$. For $\alpha \lesssim 1$ these two quantities differ only slightly from one another. The Fermi level may be identified with the energy thus obtained for the sphere that cuts out one half of the volume of the Brillouin zone. In Fig. 1 the density of states calculated by

from tables (5) in this way, for sodium, $\beta = 0.6$ eV, $\alpha = 1.1$ ($\theta = 40^\circ$, where θ is the modular angle, $\sin^2\theta = g_2^4/g_3^4$). For this α, the ratio of the zone widths for the directions $\langle 002\rangle$ and $\langle 111\rangle$ is close to the value of this ratio obtained by the cell method (6). The dotted line denotes Skinner' s data, obtained from measurements of the intensity of soft X-ray radiation (7). For copper, also by comparison with the cell method (8), it was found that $\beta = 1.4$ eV, $\alpha = 1.0$; in this case the variation of E with increasing k along fixed directions is close to calculations based on the interpolation LCAO method (9). For lithium, the density of states at approximately the same α differs only slightly from calculations by the orthogonalized-plane-wave method (10).

Thus, the parametric method set forth here for solving the one-body problem in a lattice field can give results no worse than other methods. Among the advantages of the method are, above all, the absence of special assumptions about the structure of the Hamiltonian and broad freedom in the choice of trial functions.

As is known (11), it is precisely an arbitrary choice of the self-consistent potential, of boundary conditions (in the cell method), or of trial functions (in the form, for example, of linear combinations of atomic functions) that is a source of uncontrollable errors. The parameters α and β can be compared directly with experiment and their optimal values determined.

Let us show that the requirements imposed on the trial function can be modified. Suppose, for example, that the integrals $\int \Phi_\nu^* H \Phi_\nu dr$ diverge, the functions Φ_ν are orthogonal but not normalized to unity, and the limits $\lim_{V\to\infty} \frac{1}{V} \int_V \Phi_\nu^* H \Phi_\nu dr$ and $\lim_{V\to\infty} \frac{1}{V} \int_V \Phi_\nu^* \Phi_\nu dr$ exist. Then, modifying conditions 1 and 2, one can express the energy as a function of the wave vector in the form (2)–(4).

It is also possible to replace the exponential dependence (1), for example, by a power-law dependence: $H_{\nu\nu} = aR^{-s/2}$, $s > 0$. Then, on the basis of Born' s method of summation over lattice sites (12), it can be shown that the energies are proportional to the Mellin transforms of the functions (2)–(4):

$$E_1(k_x, k_y, k_z) = A(a, s) \int_0^\infty E(k_x, k_y, k_z; u)\, u^{s/2-1}\, du.$$

Finally, the restriction to monatomic crystals is also immaterial, at least for electrons. Namely, in the definition of r_k, one may regard r_k not as the coordinates of the sites, but as the coordinates of the corresponding points of the primitive cells.

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Note: Figure translations are in progress. See original paper for figures.