A. I. GUBANOV

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Abstract

Full Text

A. I. GUBANOV

ONE-ELECTRON CALCULATION OF AN ARBITRARY SYSTEM OF ATOMS

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The quantum-mechanical problem for a system of a large number of atoms, even in the one-electron approximation, has been completely solved only in the case of a crystal. In the case of a less ordered system of atoms (a liquid, an amorphous body) the theory is still far from perfect. In particular, the author (1) developed an electron theory of a liquid based on the approximate preservation of the short-range order of the arrangement of atoms. This does not hold far from the melting point, and, moreover, the theory has not been carried through to the calculation of particular liquids and to the obtaining of numerical results.

In the present article an entirely new approach to the solution of the problem is proposed, based on the statistical properties of a system of atoms at any degree of disorder. This method is suitable for glasses, liquids up to the critical temperature, compressed gas, impurities in a semiconductor, polymer semiconductors, etc.

Let there be a very large number G of atoms, for which a binary distribution function is specified. We shall seek the solution of the one-electron Schrödinger equation for this system

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k + V\psi_k = E_k\psi_k \tag{1}$$

by the tight-binding method in the form of a linear combination of functions of individual atoms $\chi(\mathbf{r}-\mathbf{R}_n)$

$$\psi_k = \frac{1}{\sqrt{G}}\sum_n c_n e^{i\varphi_n}\chi(\mathbf{r}-\mathbf{R}_n), \tag{2}$$

where $\mathbf{R}_n$ is the radius vector of the n-th atom.

For simplicity we assume that all atoms are identical and that in (2) only one function from each atom participates. For convenience in subsequent calculations the coefficients at χ_n are written as the product of a modulus $c_n > 0$ and a phase factor $e^{i\varphi_n}$; $\chi(\mathbf{r}-\mathbf{R}_n)$ satisfy the equations

$$-\frac{\hbar^2}{2m}\nabla^2\chi(\mathbf{r}-\mathbf{R}_n)+U(\mathbf{r}-\mathbf{R}_n)\chi(\mathbf{r}-\mathbf{R}_n)=E^0\chi(\mathbf{r}-\mathbf{R}_n). \qquad (3)$$

The expansion coefficients are determined, as usual, from the system of G equations

$$(E_k+\alpha_m-E^0)c_m=-\sum_{n\neq m}e^{i(\varphi_n-\varphi_m)}c_n\beta_{nm}, \qquad (4)$$

where

$$\alpha_m=-\int|\chi(\mathbf{r}-\mathbf{R}_m)|^2U'_m\,dr; \qquad \beta_{nm}=-\int\chi^*(\mathbf{r}-\mathbf{R}_m)U'_n\chi(\mathbf{r}-\mathbf{R}_n)\,dr;$$

$$U'_n=V-U(\mathbf{r}-\mathbf{R}_n); \qquad m=1,2,\dots,G. \qquad (5)$$

To restrict the number of equations, choose a compact group of atoms—the central atom 1 and $N-1$ of its neighbors, with $N \ll G$. Put $\mathbf{R}_1=0$, $\varphi_1=0$, and assume that N further values of $\mathbf{R}_n$ are specified. Restricting ourselves in (4)

values $m=1,2,\dots,N$ and equating separately the real and imaginary parts, we obtain $2N$ equations

$$(E_k+\alpha_m-E^0)c_m=-\sum_{n\neq m}\cos(\varphi_n-\varphi_m)c_n\beta_{nm}, \qquad (6)$$

$$\sum_{n\neq m}\sin(\varphi_n-\varphi_m)c_n\beta_{nm}=0, \qquad (7)$$

which make it possible to determine N values c_m and N phases for the selected group of atoms.

But equations (6) and (7) also contain c_n and the phases of "external" atoms not belonging to the group. To make the system of equations closed, we average over the configurations of all external atoms; for them we take the mean value $c_n=1$ and prescribe the mean value of the phase gradient in the external region.

The value k specifies a definite state of the system, just as the state of electrons in a crystal is specified by the wave vector k. The phase difference between an external atom n and the nearest internal atom m is on average equal to

$$\varphi_n-\varphi_m=\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_m), \qquad (8)$$

the corresponding $\beta_{nm} = \beta$, the mean value.

As a result, the system of equations (6) and (7) becomes closed. It should be noted that the coefficient c_1 for the central atom and the phase differences with its nearest neighbors are determined most accurately, since the central atom is farthest removed from the external region, which is taken into account only on the average. The remaining phases and coefficients $c_2, c_3, \ldots, c_N$ are only auxiliary. Thus, we obtain c_1 as a function of the configuration of the environment of the central atom, which makes it possible to judge the character of the wave function (2).

The energy of the state, i.e., the relation between E_k and k, can be obtained from the normalization condition

$$\sum_{n-1}^{G} c_n^2 = G. \tag{9}$$

If G is sufficiently large, all possible configurations occur in the system; regarding each atom of the system in turn as the central one, we can replace the summation in (9) by averaging, over configurations, the values of c_1^2 for a given k, i.e.,

$$\overline{c_1^2(k)} = 1, \tag{10}$$

where the bar denotes averaging over the configurations of selected atoms, i.e., multiplication by the corresponding binary distribution functions and integration over $d\mathbf{R}_1, d\mathbf{R}_2, \ldots, d\mathbf{R}_N$. Obviously, the calculation is the more accurate the larger N is, but certain qualitative conclusions can already be drawn for $N = 1$.

The calculation can be generalized to the case where several wave functions of each atom participate in the linear combination (2) and where there are atoms of several kinds (an alloy, a solution). Instead of atomic functions one may take other localized functions, for example functions of valence strokes, as in the method of equivalent orbitals.

Let us illustrate the method described with the simplest example. There is a one-dimensional chain of atoms characterized by a distribution function $g(R)$ normalized to unity, where R is the distance between nearest neighbors. $g(R)$ is the fraction of the ordinary binary function corresponding to the region of the first maximum. We take $N = 1$. Let $R_2 = R$ be given and

$$\varphi = \mathbf{k} \cdot \overline{R} = k \int_0^\infty Rg(R)\, dR.$$

By symmetry $c_2 = c_1$; then the equations

(6) and (7) give:

$$\mathcal{E}_\varphi c_1 = -\left(c_1\beta_1\cos\varphi_2 + \beta\cos\varphi\right); \qquad c_1\beta_1\sin\varphi_2 = \beta\sin\varphi, \tag{11}$$

where

$$\mathcal{E}_\varphi = E_k + \alpha_1 - E^0; \qquad \beta_1 = \beta_{21}(R); \qquad \beta = \int \beta_{21}(R)g(R)\,dR. \tag{12}$$

From (11) we obtain

$$c_1(\varphi) = \frac{\mathcal{E}_\varphi\beta\cos\varphi \pm \beta\sqrt{\beta_1^2 - \mathcal{E}_\varphi^2\sin^2\varphi}}{\beta_1^2 - \mathcal{E}_\varphi^2}. \tag{13}$$

From (10) we obtain an equation for determining E_k

$$\int_0^\infty \left[\frac{\mathcal{E}_\varphi\beta\cos\varphi \pm \beta\sqrt{\beta_1^2 - \mathcal{E}_\varphi^2\sin^2\varphi}}{\beta_1^2 - \mathcal{E}_\varphi^2}\right] g\,dR = 1. \tag{14}$$

The last equations are simplified for $a = 0,\ \pm\pi$.

$$(c_1)_{\varphi=0,\pi} = -\frac{\beta}{\beta_1 \pm \mathcal{E}_\varphi}; \qquad \int \frac{\beta^2}{(\beta_1 \pm \mathcal{E}_\varphi)^2}\,g\,dR = 1. \tag{15}$$

For a one-dimensional crystal $\alpha_1 = \overline{\alpha}_1 = \alpha,\ \beta_1 = \beta,\ g = \delta(R - \overline{R}),\ c_1 = 1$, and (12) and (14) give

$$E_k = E^0 - \alpha - 2\beta\cos\varphi, \tag{16}$$

which coincides with the usual result of the theory of strongly bound electrons.

If the degree of disorder is small and $g(R)$ is not too diffuse, then in (12) one may put $\alpha_1 \simeq \alpha$ and, under the integral sign in (15), carry out an expansion in powers of $\beta' = \beta_1 - \beta$, accurate to β'^2, which gives

$$E_{0,\pi} = E^0 - \alpha \mp \left(2\beta + \frac{3}{2}\frac{\overline{\beta'^2}}{\beta}\right), \tag{17}$$

where

$$\overline{\beta'^2} = \int_0^\infty (\beta_1 - \beta)^2 g\,dR. \tag{18}$$

The width of the allowed energy band is

$$E_z = E_\pi - E_0 = 4\beta + \frac{3\overline{\beta'^2}}{\beta}, \tag{19}$$

i.e., the band is broadened in comparison with an ordered chain having the same mean distance between atoms, since $\beta \simeq \beta_1(\overline{R})$. This is in agreement with the conclusions of the electronic theory of liquids (1) and with numerical calculations for a one-dimensional chain of atoms (2).

In more complicated cases the system of equations (6), (7), (10) should be solved numerically with the aid of an electronic computer. Even for $N = 20$–30, the calculation is less laborious than in the numerical calculations known in the literature (2) for the one-dimensional model of a liquid, where a chain of several thousand cells was computed. Another advantage of the proposed method is that it can be applied to a three-dimensional system and takes into account (through χ or β) the properties of the specific real atoms composing the system.

Ioffe Physicotechnical Institute
Academy of Sciences of the USSR

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

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