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MOTION OF A PARTICLE IN A LINEAR PERIODIC ARRAY OF SMALL-RADIUS POTENTIAL WELLS IN QUANTUM MECHANICS

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The problem of the motion of a particle in a one-dimensional periodic array of small-radius potential wells is considered. Expressions are obtained in closed form for the energy band, the band width, and the effective mass of a particle moving in such a field. It is shown that a negative-energy state should exist in this case for a well of arbitrarily small depth. The wave function obtained is in fact a Green's function and can be employed to solve the general problem of motion of a particle in the field of a linear periodic array in three-dimensional space.

1. The method of small-radius potentials has been widely used of late in different branches of quantum mechanics. It was first used by Smirnov and Firsov[1] and by Demkov[2,3] in the problem of interaction of negative ions with atoms. This method was used by Demkov and Drukarev[4,5] to study the properties of a particle moving in an electric or magnetic field, by Adamov et al.[6] for molecular systems, and by Subramanian[7] in the problem of elastic scattering of electrons by molecules, and also for an approximate solution of the Schrödinger equation and to find the eigenvalues of the bound states of a particle in a potential of rather general form[8]. In this method, as is well known, the true potential is replaced by certain small-radius potentials, each of which in turn is replaced by a boundary condition on the wave function in the vicinity of the point where it is located:

$$\psi \sim A\left(\frac{1}{|\mathbf{r}-\mathbf{r}_i|}-\alpha_i\right). \tag{1}$$

The parameter α_i characterizes here the depth of the well.

2. In all the aforementioned applications of the method, a study was made of the motion of the particles in the summary field of a finite number of small-radius wells of constant or variable depth and of an external electromagnetic field. When there is an infinite number of such wells, the Schrödinger equation for the wave function of a particle in this field can usually not be solved in closed form. An interesting exception, however, is the case of a one-dimensional periodic chain of small-radius potentials in three-dimensional space. This problem can be used for an approximate study of the negative ion of a linear polymer molecule. We must emphasize here the difference between the investigated problem and the Kronig-Penney model. In the latter they studied the wave functions of particles moving in the field of a one-dimensional periodic chain in one-dimensional space, whereas in our case the particle moves in three-dimensional space, although the potential wells lie at points forming a one-dimensional chain.

3. Let us assume that an infinite number of small-radius wells lie along the x axis at points x = na, where n runs through all integer positive and negative values (including zero). We can immediately write down an expression for the wave function of the particles in such a field:

$$\psi(\mathbf{r})=\sum_n A_n\frac{\exp(-k|\mathbf{r}-na\mathbf{i}|)}{|\mathbf{r}-na\mathbf{i}|}, \tag{2}$$

where i is a unit vector along the x axis and $E=-k^2\hbar^2/2m<0$. According to the Bloch theorem, the solution of the Schrödinger equation in the field of this periodic potential should be of the form

$$\psi(\mathbf{r})=\exp(i\varkappa\mathbf{r}\mathbf{i})u_\varkappa(\mathbf{r}), \tag{3}$$

where the function $u_\kappa(\mathbf{r})$ has the periodicity of the chain:

$$u_\varkappa(\mathbf{r}+ma\mathbf{i})=u_\varkappa(\mathbf{r});$$

κ is the particle quasimomentum. This requirement is satisfied if one chooses $A_n=\exp(i\kappa na)$ and one omits the normalization factor, which is of no significance in the solution of the problem. We thus obtain for the wave function of the particle the following expression

$$\psi(\mathbf{r})=\sum_n\frac{\exp(i\varkappa na-k|\mathbf{r}-na\mathbf{i}|}{|\mathbf{r}-na\mathbf{i}|}. \tag{4}$$

Applying to the function $\psi(\mathbf{r})$ the boundary condition (1), which it must satisfy in the vicinity of each node of the chain (we put $\alpha_i=\alpha$), we obtain a relation between κ and k, i.e., the connection between the quasimomentum and the energy:

$$\alpha=k-\sum_{n=1}^{\infty}\frac{\exp(-nka)\cos(n\varkappa a)}{na}, \tag{5}$$

which yields after summing the series in the right-hand side

$$\operatorname{ch} ka=\tfrac{1}{2}[\exp(\alpha a)+2\cos(\varkappa a)]. \tag{6}$$

It is easy to show that for positive particle energies we get in place of (6)

$$\alpha a=\ln|2(\cos(k'a)-\cos(\varkappa a))|, \tag{6'}$$

where $k'=(2mE/\hbar^2)^{1/2}$. The dependence of the particle energy on the parameter αa is shown in Fig. 1 for different values of the quasimomentum. At any value of

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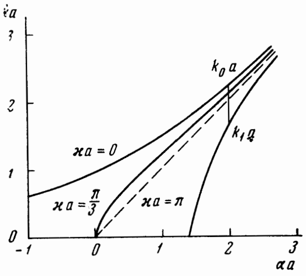

FIG. 1

αa, there exists one and only one band in the region of negative energies.

4. It is obvious that in the case of large values of αa (αa $\gg$ 1) the interaction of the potential wells is small and the band lies entirely near the energy level of the isolated well, i.e., k $\approx$ α. This follows directly from (6), if cos κa is neglected compared with cosh ka, and cosh ka is replaced by $\frac{1}{2}$exp(ka). The width of the band in this limiting case can be readily estimated: for the upper (κa = π) and the lower (κa = 0) boundaries of the band we have respectively

$$k_1a \sim \ln[\exp(\alpha a) - 2) \sim \alpha a - 2\exp(-\alpha a),$$

$$k_0a \sim \ln[\exp(\alpha a) + 2] \sim \alpha a + 2\exp(-\alpha a).$$

From this we get for the width of the band the expression (which is valid when αa $\gg$ 1)

$$\Delta E = \hbar^2(k_0^2 - k_1^2)/2m \approx 4\alpha\hbar^2 \exp(-\alpha a)/ma. \tag{7}$$

Thus, the width of the band decreases exponentially with increasing αa.

With decreasing αa, the band broadens, and the energy level of the isolated well remains at all times inside the band. This follows from the inequality

$$\tfrac{1}{2}(\exp|x| + 2) > \operatorname{ch} x > \tfrac{1}{2}(\exp|x| - 2).$$

when αa = ln 4, the upper edge of the band (αa = π) coincides with the boundary of the continuous spectrum (E = 0). At low values of αa (including negative ones) the boundary of the continuous spectrum is reached at values of αa smaller than π. However, the lower edge of the band always remains in the region of negative energies. Indeed, Eq. (6) with κ = 0 has a solution for any value of αa. This is connected with the fact that in this case the problem is analogous to a certain two-dimensional problem regarding the motion of a particle in a field of one potential well, where a bound state always exists.

A consequence of this result is that in sufficiently long linear polymer molecules there are always bound states. It should be noted that this result is general and does not depend on the form of the potential, whereas at small values of the energy the approximation of small-radius potentials is, in the limit, exact for any potential (that decreases sufficiently rapidly with the distance).

5. At large negative values of αa, we can estimate for a polymer molecule the number of links N_0 at which a bound state of an electron appears. In this case each link is a minute well, incapable of retaining the electron. For the lower energy level of a finite chain of N links we have Nκa $\approx$ π. From this, assuming that κa and ka are small and using (6), we obtain the condition for the existence of the bound state:

$$\frac{\pi^2}{2N^2a^2} < \frac{1}{2a^2}\exp(\alpha a),$$

$$N > \pi \exp\left(-\frac{1}{2}\alpha a\right).$$

On the other hand, if we take a chain nN links long, it will contain n bound states.

6. We can also obtain within the framework of this model an expression for the effective mass of a particle moving in the field of a one-dimensional chain of small-radius wells.

Using (6) and the relation between E and k, we obtain after few calculations

$$\frac{d^2E}{d\varkappa^2}_{\varkappa=0} = -\frac{\hbar^2}{m}\left[k\frac{\partial^2 k}{\partial\varkappa^2}\right]_{\varkappa=0} = \frac{\hbar^2}{m}\frac{k_0a}{\operatorname{sh} k_0a},$$

where k_0 is the value of k at κ = 0. For the effective mass of the particle m* we obtain the formula

$$m^* = \hbar^2\left(\frac{\partial^2 E}{\partial\varkappa^2}\right)_{\varkappa=0} = m\frac{\operatorname{sh} k_0a}{k_0a}. \tag{8}$$

With the aid of (6) we can rewrite this relation in the form

$$\frac{m^*}{m} = \frac{(\Lambda^2 - 1)^{1/2}}{\ln[\Lambda + (\Lambda^2 - 1)^{1/2}]}, \tag{9}$$

where Λ = $\frac{1}{2}$exp(αa) + 1.

The dependence of m*/m on the parameter αa is shown in Fig. 2. The ratio m*/m increases, as expected, with increasing αa (i.e., with increasing depth of the wells). At large negative values of αa (very shallow wells) we have m*/m $\approx$ 1, i.e., the effective mass almost coincides with the true mass. This corresponds to free motion of the particle.

7. The proposed model is well suited for low energies of an electron moving in the field of the chain. It is possible, however, to propose a modification of this model also for not very small E, when several small-radius wells are situated in each cell of the chain. In this case it is necessary to calculate the value of the wave function (4) not only at the points r = nai, but also to points where other wells are located. It is easy to propose a rapidly converging program for the calculation of the function (4). The problem of calculating E(κ) then becomes purely algebraic, and, by replacing the real link of the polymer molecule by a sufficiently large number of wells, we can attain, in principle, an arbitrary high accuracy for a real problem.

8. We have considered here only negative energies E < 0. When E > 0 it is also easy to obtain analogous solutions of the Schrödinger equation; they can be used to describe the scattering of electrons by a polymer chain.

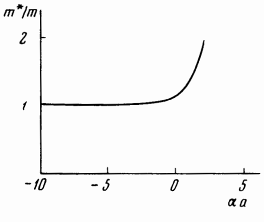

FIG. 2

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