

Comments and Addenda

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Stark Ladder in Solids? A Reply

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(Received 24 July 1968)

IN the 24 June issue of the Physical Review Letters there is a contribution by J. Zak, having the above title.¹ The paper contains two errors which involve my past work. I wish to rectify these errors and to re-examine thereupon the question raised in the title.

Zak's work, as well as my own, is based on the one-electron approximation for electrons in solids; in this approximation, the crystalline medium appears as a periodic potential. The words "approximate" and "rigorous" are to be understood in terms of this theoretical framework. We shall follow Ref. 1 in taking the crystal as one-dimensional.

The first error in Ref. 1 occurs in connection with Eq. (13). The letter describes it as "approximate." There is a rigorous proof published for it² which will now be amplified for later use. Let the Hamiltonian for the problem be

$$\mathcal{H} = p^2/2m + V(x) - eEx, \quad (1a)$$

with

$$V(x+a) = V(x). \quad (1b)$$

The development of a wave function in time is then controlled by the operator

$$\Theta(t) = \exp(-i\mathcal{H}t/\hbar). \quad (2)$$

Among these operators, the one for which the time has the value

$$T = 2\pi\hbar/eEa \quad (3)$$

is of special significance. The operator $\Theta(T)$ is periodic in x , because the nonperiodic term in (1a) is neutralized by being placed in an exponent where it takes the form $2\pi ix/a$. This time T can also be obtained by semiclassical band dynamics as the recurrence period in the motion of an electron in a tilted band. This time, the reality of which has often been questioned, has thus a rigorous mathematical significance.

Since $\Theta(T)$ is a unitary operator which is periodic in x , we can use its eigenfunctions as basic Bloch functions

Simultaneously, we are given eigenvalues in the form of phase angles; thus

$$\Theta(T)B_l(x; k) = \exp(-i\Phi_l) B_l(x; k). \quad (4)$$

The notation implies that the Bloch functions can be grouped into bands sharing the same eigenvalue Φ_l . This is not yet proved. Therefore, at the moment we accept (4) only for $k=0$. The index l is then simply a label for the complete set $B_l(x; 0)$.

The best way to get the grouping into bands is by a study of the crystal translation operators³ which define the wave vector k through their diagonal representation:

$$T(na) \equiv \exp(inpa/\hbar), \quad (5)$$

where n is an integer and the diagonalized form of (5) reads

$$[\exp(inpa/\hbar)]_{\text{diag}} \approx \exp(inka). \quad (6)$$

In the field-free case, these are constants of the motion. Now, on taking the commutator with (1), we get the equation of motion

$$\frac{d}{dt}T(na) = \frac{ineEa}{\hbar}T(na). \quad (7)$$

Equation (7) tells us that the operators are simultaneously diagonal with their time derivative, that is, they remain diagonal in time. The representation (6) can therefore be used with a time-dependent k . We find then

$$k = k_0 + eEt/\hbar. \quad (8)$$

Thus if we start out with a Bloch function having $k=0$ at $t=0$ we get a Bloch function having $k=eEt/\hbar$ at time t . We make use of this feature to generate the band from the states $k=0$ picked from (4). These bands are closed, for the defining equation (4) is such that when k has reached $2\pi/a$ then, by (3) and (8), the starting wave function is restored. We therefore define $B_l(x; k)$ for $k \neq 0$ by the formula

$$B_l(x; eEt/\hbar) = \exp[i\Psi_l(eEt/\hbar)]\Theta(t)B_l(x; 0). \quad (9)$$

Ψ_l is for the moment an unknown phase. The functions

³ G. H. Wannier, in *Elements of Solid State Theory* (Cambridge University Press, New York, 1959), p. 142.

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¹ J. Zak, Phys. Rev. Letters **20**, 1477 (1968).

² G. H. Wannier and D. R. Fredkin, Phys. Rev. **125**, 1910 (1962), especially Sec. 3.

so defined do share with the starting function the eigenvalue Φ_l . This is seen as follows:

$$\begin{aligned}\Theta(T)B_l(x; eEt/\hbar) &= e^{i\Psi_l}\Theta(T)\Theta(t)B_l(x; 0) \\ &= e^{i\Psi_l}\Theta(t)\Theta(T)B_l(x; 0) \\ &= e^{-i\Phi_l}e^{i\Psi_l}\Theta(t)B_l(x; 0) \\ &= e^{-i\Phi_l}B_l(x; eEt/\hbar).\end{aligned}$$

The full implications of the notation used in (4) are thus verified. Furthermore, each band is closed in time, that is, interband tunneling is transformed out.

The controversial relation (13) of Ref. 1 now follows from (9) simply by differentiation with respect to time. The result of such a differentiation is

$$\left(\mathcal{H} - ieE\frac{\partial}{\partial k}\right)B_l(x; k) = eE\frac{d\Psi_l(k)}{dk}B_l(x; k). \quad (10)$$

The relation is therefore proved.

Examination of (10) shows that the energy band function $W_l(k)$ is related to the phase Ψ_l of the wave functions by the relation

$$W_l(k) = eEd\Psi_l(k)/dk. \quad (11)$$

We now come to the second error in Zak's paper, namely, the statement in connection with his Eq. (17) that ϵ is arbitrary. This is not correct. The arbitrariness of the phase Ψ_l in (9) is partially restricted, because the same wave functions repeat as t increases and that, for such repetitions, (9) must not be in contradiction with (4). This yields

$$\Psi_l(k + 2\pi/a) - \Psi_l(k) = \Phi_l. \quad (12)$$

The connection between ϵ_l and $W_l(k)$ is given in Eq. (16) of Ref. 1. The equation contains a misprint. There should be a factor $a/2\pi$ in front of the integral. It then becomes

$$\epsilon_l = \frac{a}{2\pi} \int_0^{2\pi/a} W_l(k) dk.$$

This yields, with (11) and (12),

$$\epsilon_l = eEa(\Phi_l/2\pi). \quad (13)$$

The eigenvalue relation (4) thus determines ϵ_l precisely even though other aspects of the energy band function are indeterminate.

The conclusions drawn by Zak will be unaffected by the two errors if the eigenvalue equation (4) yields a continuous spectrum devoid of structure. That this case can arise was anticipated in Ref. 2. The theory is applied there to the case of free electrons with an artificially imposed period a ("empty lattice" test). A similar situation must prevail when the periodic potential is very weak. Even in strong periodic potentials, the following result is now proved.⁴ While it is possible to solve Eq. (13) of Ref. 1 in powers of the electric field, starting with a field-free band, the resultant power series is divergent. Thus a truly discrete spectrum for Φ_l is unlikely. However, in all cases except that of free particles, there is a periodic recurrence of structure which has the Stark ladder spacing. This structure might very well resemble a set of discrete levels in some cases. In order to see this we can turn to the case of atoms for comparison. In that case also, the energy spectrum is continuous, and a correction of the atomic wave functions in powers of the field leads to a divergent expansion. Nevertheless, the Stark levels in atoms come out correctly from such a computation as metastable states, which are different from the background continuum. In a similar way, the Stark levels computed in a straightforward way from a single band are likely to be present as metastable states, limited by interband tunneling.

In estimating the likelihood that Stark levels occur in an actual crystal, one might be tempted to follow up the reasoning of the preceding paragraph and say that Stark levels can only be prominent if the field configuration and the relaxation times for the sample permit return of the electrons to their starting configuration. This takes a time T given by (3), which is of the order 10^{-10} sec. Such an argument neglects, however, that the energy spacing in question can be derived in a second independent way. Suppose we take a molecular crystal in which the probability of passage of an electron from molecule to molecule is small, and suppose we apply to the crystal a uniform electric field \mathbf{E} . There is then an energy difference $e\mathbf{E} \cdot \mathbf{a}$ between two equivalent energy states for an electron in neighboring cells. Thus the presence of such a splitting transcends the band picture on which the argument was based originally.

⁴ G. H. Wannier and J. P. Van Dyke, J. Math. Phys. 9, 899 (1968).