Binding of one-dimensional Bloch electrons by external fields*

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It is shown that arbitrary external fields, and in particular, antibinding ones, bind the Bloch electron in the one-dimensional one-band model. In other words, the spectrum for arbitrary nonzero field is purely discrete and the eigenfunctions are normalizable. This generalizes the Wannier-Stark effects to nonhomogeneous fields.

One of the fundamental results of quantum mechanics is that the wave function for electrons in solids is described by an extended Bloch wave. There are several known mechanisms that lead to a localization of the state vector. The most profound of these is probably the Anderson mechanism for localization in random lattices. In one dimension, it is generally believed that a random system has no continuous spectrum. Here we would like to point out another mechanism which leads to localization and which is fairly general. The following analysis shows that for any external field $V(x)$ such that $|V|\to\infty$ as $|x|\to\infty$, in one dimension, a localization takes place and the spectrum is discrete. It is only natural to expect that this one-dimensional localization will also have interesting consequences for three-dimensional systems.

The interest in this mechanism, from a theoretical viewpoint, is that it follows from an interplay between the band properties (which are purely kinematical) and the dynamics dictated by the external field. In particular, this mechanism does not apply to free electrons which have different kinematics.

Consider the Schrödinger Hamiltonian

$$H = H_B + \lambda V(x). \tag{1}$$

H_B denotes some Bloch one-electron Hamiltonians. When λ is small, one expects that the spectral representation of H_B is a suitable starting point. This is the crystal-momentum representation[1] (CMR):

$$H_B = \epsilon_n(k), \quad k \in B,$$

$$x = i\nabla_k + X_{mn}(k).$$

$\epsilon_n(k)$ are the band functions and $X_{mn}(k)$ are the interband transition matrix elements.[2] For a well isolated band it is easy to show that the transition matrix elements are small. Under these circumstances, it has been suggested that the one-band approximation (i.e., setting $X_{mn}=0$) is applicable.[3] Thus we shall analyze the Hamiltonian

$$H = \epsilon_n(k) + \lambda V(i\nabla_k), \quad k \in B. \tag{2}$$

H describes the dynamics of Bloch electrons in perturbed crystals. [A more natural mathematical definition of (2) is given in (3) below.] B is the Brillouin zone which is a d-dimensional torus. This is a very important point in what follows. Classically (or semiclassically) this means that the orbits in k space do not extend to infinity. If, in addition, the conjugate variables[4] remain bounded, the corresponding quantum mechanical motion will have eigenvalues (e.g., discrete spectrum) and normalizable eigenfunctions. That B is a torus follows from the definition of the CMR.

We shall analyze the qualitative features of the spectrum of (2) for two classes of potentials V: External fields which we define by $|V(x)|\to\infty$, $|x|\to\infty$, and impurity fields,[5] defined by $|V(x)|\to 0$, as $|x|\to\infty$. External fields are naturally classified as binding if $V(x)\to+\infty$ and antibinding if $V(x)\to-\infty$ in some sector. Hence, the positive harmonic field ω^2x^2 is binding while the negative harmonic field and the homogeneous field $-\omega^2x^2$, Ex are antibinding.

We shall analyze the qualitative features of the spectrum using general theorems. Theorem 1 applies to external fields and Theorem 2 to impurity fields. The theorems are stated to apply to Hamiltonians in arbitrary number of dimensions. In one dimension, the application of Theorem 1 gives a very general localization result namely, any external field, whether binding or unbinding, gives a purely discrete spectrum and normalizable eigenvalues to the Hamiltonian (2). This is quite surprising because one might have expected Eq. (2) to have similar spectral properties to those of the corresponding Schrödinger equation. For the latter, a discrete spectrum is typical only for binding fields.[6,7]

That antibinding fields localize in one dimension is not a completely new result. This was first suggested by Wannier for the Stark effect (i.e., homogeneous external field).[8] Wannier's result is particularly simple because the eigenvalue [Eq. (2)] can be solved explicitly for arbitrary $\epsilon_n(k)$ [see Eq. (8)]. What we show here is that this is a very general mechanism and the homogeneity of the field is not necessary for a localization.

It may be noted that our results do not depend on the differential properties of Eq. (2). In particular, V need not have a finite power series expansion and is in general a pseudodifferential operator.

As is well known, the Wannier ladder for $V=Ex$ has been the subject of controversy.[9] It is not our intention to get into this question here, but we wish to remark that claims sometimes made as to the effect of experimental inhomogeneity of E are evidently wrong.

Let L denote a d-dimensional lattice and the superscript $\hat{}$ the Fourier transform (with inverse superscript $\check{}$). The Hilbert space of square-integrable functions over the Brillouin zone $L^2(B)$ is isomorphic to the Hilbert space of sequences over the direct lattice $l^2(L)$:

$$(\cdots)^{\wedge}: L^2(B) \to l^2(L). \tag{3}$$

The one-band d-dimensional Hamiltonian [Eq. (2)] is formally defined by

$$H\psi(k)=\epsilon_n(k)\psi(k)+\lambda[V(l)\hat{\psi}(l)]^{\vee}(k)\,,$$
$$k\in B,\ l\in L. \tag{4}$$

Theorem 1: Assume that $|V(x)|\to\infty$ in the sense that for every M there is an R, such that $|V(l)|\geq M$ for all $l\in L$, $|l|\geq R$. Then (i) H has a compact resolvent for all $\lambda\neq 0$. In particular, H has purely discrete spectrum. (ii) H is self-adjoint on $\mathfrak{D}$, where $\mathfrak{D}$ is the domain of the multiplicative V. (iii) H is semibounded if and only if V is. (iv) Let $V(x)\sim\lambda x^n$ near infinity, then the number of eigenvalues of H with absolute value less than $E, n(E)$, is such that

$$\lim_{E\to\infty} n(E)\left(\frac{\lambda}{E}\right)^{d/n} = \frac{|B|}{2^{d-1}d\pi^{d/2}\Gamma(\frac{1}{2}d)}\,. \tag{5}$$

d is the dimensionality and B the volume of the Brillouin zone.

Sketch of proof: (i) $V(l): l^2(L)\to l^2(L)$ has a compact resolvent since its spectrum is purely discrete. Conditions (i)–(iii) follow from the Rellich perturbation theory for compact operators and the continuity of[10,11] $\epsilon(k)$ (iv) follows[12] from the min-max principle for compacts[13,14] and the formula for the volume of the unit sphere in d dimensions

$$\Omega = 2\pi^{d/2}/[d\Gamma(\tfrac{1}{2}d)]. \tag{6}$$

For Hamiltonians satisfying the assumptions in the theorem, the spectrum is purely discrete with infinity as the only point of accumulation of the eigenvalues. This is a well-known property of operators with compact resolvent. In addition, H has only eigenvectors, i.e., normalizable states, and no extended states.[13,15]

It is easy to see that, in one dimension, Theorem 1 holds for arbitrary external fields $[|V(x)|\to\infty,\ |x|\to\infty]$. In higher dimensions, the theorem holds for semibounded V (either from above or from below[16]). The sign of V is of no consequence. This theorem confirms the intuition one has from the nonrigorous tilted-band picture: Under the assumption on V, for every real energy E, the set S,

$$S=\{x\,|\,V(x)+\epsilon(k)=E,\quad x\in R^3,\quad k\in B\}, \tag{7}$$

is compact and the particle is localized in space.

Let us consider specific examples. For the homogeneous field in one dimension, $V(x)=Ex$, the eigenvalues E_m are

$$E_m=\frac{a}{2\pi}\int_B \epsilon_n(k)\,dk + Ema\ . \tag{8}$$

a is the lattice spacing. This is the Wannier ladder and the asymptotic distribution agrees with (5).

Consider now the harmonic field, $V(x)=\omega^2x^2$, in d dimensions. The Hamiltonian (2) is formally identical to Schrödinger's with periodic boundary conditions

$$-\omega^2\Delta_k+\epsilon(k),\quad k\in B. \tag{9}$$

In the weak-coupling limit $\omega\to 0$, we can use the semiclassical Wentzel-Kramers-Brillouin to estimate $n(E)$. $n(E)$ is proportional to the available phase space

$$n(E)=(2\pi)^{-d}\int_B d^dk\int_0^{[E-\epsilon(k)]^{1/2}/\omega} d^dq. \tag{10}$$

The integral can be calculated explicitly to yield (5).

For the sake of comparison, we conclude with a spectral theorem for the impurity Hamiltonian, $V(x)\to 0$ as $|x|\to\infty$.[17,18] Here, as expected, the continuous spectrum of the band is preserved.

Theorem 2: Let $\sum_L |V(l)| < \infty$, then the (multidimensional) Hamiltonian H has the same absolutely continuous spectrum as the bands's spectrum $\{\epsilon_n(k)\}$, H may, however, have discrete eigenvalues (impurity states) in the gaps [the resolvent set of $\epsilon_n(k)$]. This theorem is a direct application of the Kato-Kuroda trace class criterion for the existence and completeness of the wave operators.[15]

It is not very difficult to prove that, in one dimension, if V is on the average strictly attractive, $\sum_L V(l)<0$ (or repulsive), the Hamiltonian has impurity states in the gaps. This is an analog of Peierls theorem for Schrödinger Hamiltonians. Since for the latter, there is a bound state also when $\int V(x)\,dx=0$ [but not $\int V(x)\,dx>0$], we conjecture that for the Hamiltonians [Eq. (2)] there exist impurity states (either donors or acceptors) for any nonzero V. Note that whereas external fields localize all states, impurities localize only special vectors.

Theorems 1 and 2 are exact results for an approximate theory—the one-band approximation. In what sense do they approximate the spectral properties of Schrödinger Hamiltonians and real solids? In the strict mathematical sense, the answer is that they do not. For example, it is known that the spectrum of a Schrödinger Hamiltonian with an external homogeneous potential and a periodic field is absolutely continuous.[19] This obviously contradicts Theorem 1. However, we still feel that the physics is correctly described by the approximate theory (that this is not impossible, recall the perturbation expansion for the atomic Stark effect). However, the results must be suitably interpreted and in particular the "discrete spectrum" of the theorem should be loosely taken to mean "resonances" as well as " bound states." This interpretation of the one-band approximation is obviously nonrigorous, but I have gained some confidence in it by verifying it in detail for the homogeneous field.[20]

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[4]By Eq. (4), V is defined on the lattice L. From a physical point of view, this means that the one-band approximation is reasonable only for slowly varying fields. From a mathematical point of view, this is related to the fact that the quantization of classical Hamiltonians over phase space G^{2n}, requires $G^{2n}=G^n\oplus\tilde{G}^n$, with $\tilde{G}^n$ the dual of G^n.

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