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Topics in the Spectral Theory of Crystals

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I. Introduction

The purpose of this article is to describe two results in the quantum mechanical spectral theory of crystals. The first result [1] concerns a single particle moving in a periodic potential in $\mathbb{R}^3$ and asserts that the resulting Schrodinger Hamiltonian $H = p^2 + V(\underset{\sim}{x})$ with V locally L^2 and periodic has only absolutely continuous spectrum. This results serves as a convenient starting point for considering the problem of scattering from an impurity in which $H_1 = p^2 + V(\underset{\sim}{x}) + W(\underset{\sim}{x})$ and the perturbation $W(\underset{\sim}{x})$ is a short range perturbation corresponding to the impurity. An elementary theorem regarding the existence and completeness of wave operators in this situation is included.

The second topic (work done in collaboration with J.P. Eckmann [2]) concerns the following problem: Let $H_M(N,a,m)$ be the Schrodinger operator for M quantum mechanical spinless "electrons" of mass m in the presence of N classical fixed "protons" regularly arranged in a finite lattice with lattice constant a. Assume that the electrons are either Bosons or Fermions and assume that they interact with one another and with the protons by $v_R(\underset{\sim}{x}_i - \underset{\sim}{x}_j)$ and $-v_A(\underset{\sim}{x}_i - \underset{\sim}{y}_j)$ respectively with v_R, v_A positive, continuously differentiable and short range. Here, $\underset{\sim}{x}_i$ is the position of the i^{th} electron and $\underset{\sim}{y}_j$ is the position of the j^{th} proton. $H_M(N,a,m)$

acts in $\otimes_S L^2(\mathbb{R}^3)$ where $\otimes_S$ denotes the appropriately symmetrized tensor product. Then $H_M(N,a,m)$ has a ground state eigenvalue λ_{MN} uniformly isolated from the continuous spectrum for all N and $M \leq N$ if a and m are sufficiently large. Hence, there is a $g > 0$ such that for all N and $M \leq N$, $\text{dist}(\lambda_{MN}, \sigma_{MN}) \geq g$ where σ_{MN} is the continuous spectrum of $H_M(N,a,m)$.

The quantity g is a lower bound for the work function familiar from the photo electric effect, i.e. the amount of energy required to ionize an electron from the crystal. A non-vanishing work function insures that the electrons do not spontaneously escape from the crystal. The result is related to the more general problem concerning the stability of solids, particularly in the limit as the crystal becomes very large.

II. Single Electron Problem

Let H be the self adjoint operator acting in $\mathcal{H} = L^2(\mathbb{R}^3)$ defined in the momentum representation

$$H\phi(\underset{\sim}{p}) = p^2\phi(\underset{\sim}{p}) + \sum_{q \in \Gamma} v_q \phi(\underset{\sim}{p} + \underset{\sim}{q}), \quad \underset{\sim}{p} \in \mathbb{R}^3 \qquad (2\text{-}1)$$

where Γ is the reciprocal lattice and v_q are the Fourier coefficients of the locally square integrable periodic potential $v(\underset{\sim}{x})$,

$$(V(\underset{\sim}{x}) = V(\underset{\sim}{x} + \underset{\sim}{a}) = V(\underset{\sim}{x} + \underset{\sim}{b}) = V(\underset{\sim}{x} + \underset{\sim}{c}) \text{ with } \underset{\sim}{a},\underset{\sim}{b},\underset{\sim}{c}$$

linearly independent.) The main result is the following.

Theorem 1 H has only absolutely continuous spectrum.

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In order to outline the proof, we first set up some notation [3]. Let k be any point in the first Brillouin zone B and set $\Gamma_k = \{ j \in \mathbb{R}^3 \mid j = k + q,\ q \in \Gamma \}$. Denote by ℓ^2_k the Hilbert space of square summable functions defined on Γ_k with inner product $\langle \phi^k, \psi^k \rangle_k = \sum_{j \in \Gamma_k} \bar{\phi}^k(j) \psi^k(j)$. We obtain a direct integral decomposition of H,

$$H = \int_B^{\oplus} \ell^2_k \, d^3k$$

which reduces H, i.e. if $\phi = \int_B^{\oplus} \phi^k \, d^3k$, then

$$H\phi = \int_B^{\oplus} H(k)\phi^k \, d^3k$$

with H(k) acting in ℓ^2_k defined

$$H(k) = T(k) + V(k) \tag{2.2}$$

where

$$T(k)\ \phi^k(j) = j^2\ \phi^k(j) \tag{2.3}$$

and

$$V(k)\phi^k(j) = \sum_{q \in \Gamma_k} V_{j-q}\ \phi^k(q) \tag{2.4}$$

T(k) obviously has discrete spectrum which is bounded below, and the resolvent $(z - T(k))^{-1}$ is Hilbert-Schmidt for z in the resolvent set of T(k). Since $(z - T(k))^{-1}$ is also Hilbert-Schmidt, it follows that H(k) has pure discrete spectrum which is also bounded below.

Let $U_k: \ell^2_k \to \ell^2_0$ $k \in B$ be the unitary map defined

$$U_k\ \phi^k(j) = \phi^k(j+k), \qquad j \in \Gamma \ . \tag{2.5}$$

Then we define the operator

$$H^k(0) = U_k H(k) U_k^{-1} = H(0) + 2\underset{\sim}{k}\cdot\underset{\sim}{J} + k^2 \qquad (2\text{-}6)$$

with

$$\underset{\sim}{J}\,\phi(j) = \underset{\sim}{j}\phi(j) \qquad j\varepsilon\Gamma\ . \qquad (2\text{-}7)$$

$H^k(0)$ is thus unitarily equivalent to $H(k)$. Although $H^k(0)$ is defined for $\underset{\sim}{k}\ \varepsilon$ B we can extend its definition to complex values of $\underset{\sim}{k}$ by the rhs of (2-6). Because the domain of the resulting operator family $H^k(0)$ is independent of k, $H^k(0)$ forms a self adjoint type A holomorphic family in each of the components of $\underset{\sim}{k}$. Assume now that the k_3 direction is perpendicular to a Brillouin zone face.

Lemma: Let k_1 and k_2 be held constant and real. Then each eigenvalue $\lambda_n(k)$ of $H^k(0)$ regarded as a function of k_3 may be taken holomorphic in a neighborhood of the real axis. $\lambda_n(k)$ is not constant as a function of k_3.

The holomorphy of the eigenvalues follows from $H^k(0)$ being a self adjoint type A holomorphic family with compact resolvent. Suppose to the contrary that $\lambda_n(k) = \lambda_n$ is constant and define $D = \{k_3\varepsilon\ \mathbb{C}\,|\,(\lambda_n - T^k(0))^{-1}$ is bounded$\}$. (Here, $T^k(0) = T(0) + 2\underset{\sim}{k}\cdot\underset{\sim}{J} + k^2$) Since $(\lambda_n - H^k(0))^{-1} = (\lambda_n - T^k(0))^{-1}(1 - V(0)(\lambda_n - T^k(0))^{-1})^{-1}$ is not bounded for k_3 in a neighborhood N of the real line, 1 must be an eigenvalue of $V(0)(\lambda_n - T^k(0))^{-1}$ in $N \subset D$ and hence throughout D. But this is impossible since by choosing $|\,\mathrm{im}\ k_3|$ sufficiently large and $\mathrm{re}\,k_3$ so that $\inf|\,\mathrm{re}\ k_3 + j_3| > 0$ $\underset{\sim}{j}\varepsilon\Gamma$, the Hilbert-Schmidt norm of this operator may be made arbitrarily small. (The

Hilbert-Schmidt norm of this operator may be conveniently estimated by an integral. See the appendix of [1] for details.)

Lemma: H has no normalizable eigenfunctions.

Suppose ϕ satisfies

$$(H - \lambda)\phi = \int^{\oplus} (H(k) - \lambda)\phi^k \, d^3k = 0$$

and let $B_\lambda = \{k \epsilon B \mid H(k) \text{ has eigenvalue } \lambda\}$. B_λ is closed and the Lebesque measure $\mu(B_\lambda)$ of B_λ in B is zero since B_λ is the zero set of non-constant analytic functions. Thus $\phi^k = 0$ a.e. in the complement of B_λ and since $\mu(B_\lambda) = 0$, ϕ^k is zero a.e.

This last lemma shows that the spectrum of H is pure continuous. The absolute continuity of the spectrum of H follows from the holomorphy of the eigenvalues $\lambda_n(k)$. This completes the outline of proof for the main theorem.

We supplement this section with a theorem regarding scattering theory. Let

$$H_1 = H + W(\underset{\sim}{x}) \tag{2-8}$$

with W a real valued function of $\underset{\sim}{x}$ satisfying the condition of the following theorem.

Theorem 2. Let W be relatively compact with respect to $-\Delta$ and assume $|W|^{\frac{1}{2}}(1 - \Delta)^{-1}$ is Hilbert Schmidt. Then the wave operators $\Omega_\pm = s - \lim_{t \to \pm\infty} e^{itH_1} e^{-itH_0}$ exist and are complete, i.e. the range of $\Omega_\pm$ is the absolutely continuous subspace of $\mathcal{H}$ with respect to H_1. The domain of wave operators is $\mathcal{H}$.

See [4]. $W \in L^1 \cap L^2$ suffices for the conditions of the theorem to be satisfied. Other possible perturbations have been considered in [5].

III. Energy Gap in Finite Crystals

Define the Schrodinger operator

$$H_M(N,a,m) = -\sum_{i}^{m} \frac{\Delta_i}{2m} + \sum_{i<j}^{m} v_R(\underset{\sim}{x}_i - \underset{\sim}{x}_j) - \sum_{i,j}^{M,N} v_A(\underset{\sim}{x}_i - \underset{\sim}{y}_j) \quad (3\text{-}1)$$

for the M electrons. Here N vertices $\{y_i\}_{j=i}^{N}$ of an infinite square lattice with lattice constant a are occupied with a proton. v_A and v_R are continuously differentiable functions on $[0,\infty)$ (we identify $v_A(\underset{\sim}{x}) = v_A(|\underset{\sim}{x}|)$, $v_R(\underset{\sim}{x}) = v_R(|\underset{\sim}{x}|)$) such that

(i) $v_A(r)$, $v_R(r) > 0$ and decrease monotonically in r,

(ii) $v_A(r)$, $v_R(r) < Cr^{-3-\delta}$ for some C, $\delta > 0$.

(iii) $\lim_{r\to\infty} \frac{d}{dr} \ln v_R(r) = 0$

(iv) There exist numbers $r_o > \varepsilon_o > 0$ such that

$$\sup_{x \in \mathbb{R}^3} |v_A(\underset{\sim}{x}) - v_A(\underset{\sim}{x} + r_o\underset{\sim}{e}) + v_R(\underset{\sim}{x} + (r_o + \varepsilon_o)\underset{\sim}{e})| - v_A(\varepsilon_o) < -q < 0$$

where $\underset{\sim}{e}$ is a unit vector.

Potentials satisfying these hypotheses with $v_A = v_R$ may be constructed by the following lemma.

Lemma Let w(r) defined on $[0,\infty)$ be a monotonically decreasing function and let there be $r_2 > r_1 > 0$ such that

a) $w(r) = 0$ iff $r \geq r_2$,

b) $w(r_1) = \frac{1}{3} w(0)$,

c) $w'(0) = 0$

d) $-a < w''(r) < -b < 0$ for $r \leq r_1$ and $2b > a$.

Then there is a $q(w)$, $r_o, \varepsilon_o > 0$ such that

$$|w(\underset{\sim}{x}) - w(\underset{\sim}{x} + r_o\underset{\sim}{e}) + w(\underset{\sim}{x} + (r_o + \varepsilon_o)\underset{\sim}{e})| - v(\varepsilon_o) < -q(w)$$

$v(r) = v_A(r) = v_R(v)$ satisfies hypotheses (i) - (iv) provided $v(r) = w(r) + y(r)$, with $w(r)$ satisfying the hypotheses of the lemma and $y(r)$ satisfies

a) $0 < y(r) < \frac{1}{4} q(w)$

b) $y(r) < Cr^{-3-\delta}$

c) $\lim_{r\to\infty} \frac{d}{dr} (\ln y(r)) = 0$

The main result is the following theorem.

Theorem There are constants a_o, m_o such that for all lattice constants $a \geq a_o$, masses $m \geq m_o$ and positive integers N, $M \leq N$, one has inf spectrum $H_M(N,a,m) \leq$ inf essential spectrum $H_M(N,a,m) - g$ for some $g > 0$.

Let us outline the strategy of the proof. By Hunziker's theorem, the infimum of the essential spectrum for $H_M(N,a,m)$ lies at $\inf_{M'< M} \{\text{inf spec } H_{M'}(N,a,m)\}$. We make the inductive hypothesis that the infimum is actually $\lambda_{M-1,N}$, i.e. the ground state for the Hamiltonian with one less electron. It is therefore natural to consider the tensor product of the corresponding ground state eigenfunction $\psi_{M-1,N}$ with a one particle trial function ϕ and try to show that the energy expectation value for the tensor product is bounded above by $\lambda_{M-1,N} - g$. This would establish the existence of discrete spectrum for $H_M(N,a,m)$ below $\lambda_{M-1,N} - g$ and thus the existence of a ground state ψ_{MN} corresponding to $\lambda_{MN} = \text{inf spec } H_M(N,a,m)$. The induction then proceeds to $M \leq N$. However, two modifications

to this strategy are required.

In the case of the electrons obeying Fermi statistics, the tensor product of $\psi_{M-1,N}$ and ϕ should be antisymmetrized. In order to avoid difficulties arising from matrix elements complicated by the antisymmetrization, we first multiply $\psi_{M-1,N}$ by a symmetric factor $N(\underset{\sim}{x}_1,\underset{\sim}{x}_2,\ldots,\underset{\sim}{x}_{M-1})$ so that the resulting function vanishes whenever any of its variables lies in the support of ϕ . N is constructive so that the norm of $N\psi_{M-1,N}$ is nearly one.

The function $\psi_{M-1,N}$ is further modified by a unitary operator which shifts the variables of $\psi_{M-1,N}$ a small amount in a lattice site where the one particle density

$$\rho(\underset{\sim}{x}) = \int dx_2 \ldots dx_{M-1} \left| \psi_{M-1,N}(\underset{\sim}{x},\underset{\sim}{x}_2,\ldots,\underset{\sim}{x}_{M-1}) \right|^2$$

is small. The reason for the shift can be seen by the following heuristic argument: In the limit as $a,m \to \infty$, we expect $\rho(\underset{\sim}{x})$ to become highly concentrated about each proton site with weight about $1/N$. If M is approximately equal to N, the potential seen by an additional electron situated at $\underset{\sim}{x}$ near one of these positions (say $\underset{\sim}{y}_i$) is

$$-v_A(\underset{\sim}{x}-\underset{\sim}{y}_i)+(M-1)\int v_R(\underset{\sim}{x}-\underset{\sim}{x}^1)\rho(\underset{\sim}{x}^1)d\underset{\sim}{x}^1 \sim -v_A(\underset{\sim}{x}-\underset{\sim}{y}_i)+\frac{(M-1)}{N}v_R(\underset{\sim}{x}-\underset{\sim}{y}_i)$$

which may be insufficient to bind the additional electron for $M \tilde{\sim} N \to \infty$ (i.e. the attraction is cancelled by the repulsion.) We find however that if $\psi_{M-1,N}$ and hence ρ are shifted slightly in the site of the additional electron, it will bind with an overall decrease in energy. (The site is selected according to

the change in the kinetic, attractive and repulsive potential caused by the shift being small.) This local shift approximates the polarization of the M-1 electrons due to the introduction of an additional electron. This shifting gives an intuitive idea of why hypothesis (iv) regarding the potentials is included.

Finally we note that some local singular behavior of the potentials can be accommodated. If v_A, v_R satisfy the hypotheses of the theorem and the lattice spacing and electron mass imply that there is a uniform gap, then there is also a uniform gap under the perturbation $v_A \to v_A + v_A^{sing}, v_R \to v_R + v_R^{sing}$ provided the $L^{3/2}(\mathbb{R}^3)$ -norms of v_A^{sing}, v_r^{sing} are sufficiently small. The proof of this remark is effected by use of a Sobolev inequality estimating the expectation value for a contribution to the potential energy in terms of the kinetic energy expectation value. Somewhat curiously, we do not know of a decomposition of $v_A = v_R$ = Yukawa potential into continuous and singular parts for which a uniform gap can be shown.

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