Some Mathematical Problems in Quantum Mechanics

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Introduction

The purpose of this article is to make a survey of recent developments in mathematical theory of linear operators pertaining to nonrelativistic quantum mechanics. While there is no doubt that the formalism of quantum mechanics is fundamentally correct in the mathematical sense, unlike that of traditional quantum field theory, it is only during recent years that rigorous proofs were given to basic propositions which physicists have regarded as evident or assumed to be true beyond any doubt. What looks physically evident is often quite difficult to prove mathematically, for physical intuition does not always follow mathematical logic.

The scope of this review is rather limited; we are mostly concerned with *analytical* problems*) related to the Hamiltonian operators of quantum mechanical systems consisting of a finite number of particles. We consider primarily operators of the form

$$H=H_n=-\sum_{i=1}^{n}\frac{1}{2m_i}\Delta_i+\sum_{i<j}^{1,n}V_{ij}(\boldsymbol{r}_i-\boldsymbol{r}_j), \tag{1}$$

where $\boldsymbol{r}_i$ is the 3-dimensional position vector of the i-th particle, Δ_i is the corresponding Laplacian, $m_i>0$ is the mass, and $V_{ij}(\boldsymbol{r})$ are real-valued functions defined on the 3-dimensional space R^3.

(1) is invariant under translation, so that the motion of the center of mass can be separated out. We are also interested in the Hamiltonian describing the resulting internal (relative) motion, which takes place in the $(3n-3)$-dimensional space. There is no unique choice for the $3n-3$ variables. If one chooses an arbitrary particle, call it the n-th particle, and refers other particles to this particular one, the reduced operator takes the form

$$H=H_n'=-\sum_{i,j}^{1,n-1}a_{ij}\mathrm{grad}_i\cdot\mathrm{grad}_j+\sum_{i=1}^{n-1}V_{in}(\boldsymbol{r}_i)+\sum_{i<j}^{1,n-1}V_{ij}(\boldsymbol{r}_i-\boldsymbol{r}_j), \tag{2}$$

where $\mathrm{grad}_i=\partial/\partial\boldsymbol{r}_i$ and (a_{ij}) is a certain positive-definite symmetric matrix

*) We do not go into algebraic problems, such as are related to group theory, for which there is abundant literature. It may be remarked, however, that in group-theoretical treatments of quantum mechanics, it has been assumed without proof that the Hamiltonian operators have eigenvalues (bound states). It is precisely in the question of the existence of eigenvalues, for example, that the analytical theory is interested.

with real constant elements. In many cases, however, one need not choose any particular coordinate system for the internal motion.

(2) can also represent an operator of an $(n-1)$-particle system subjected to a given external force, without being related to a system of the form (1). Of course (1) is formally a special case of (2) with n replaced by $n+1$.

In some mathematical problems, the special form (1) or (2) of the operator is not important and it is more convenient to consider operators of the form

$$H=\sum_{j,k}^{1,N} a_{jk}\left(\frac{1}{i}\frac{\partial}{\partial x_j}-A_j(x)\right)\left(\frac{1}{i}\frac{\partial}{\partial x_k}-A_k(x)\right)+V(x), \tag{3}$$

where $x=(x_1, \cdots, x_N)$ is a variable ranging over the N-dimensional space R^N, $V(x)$ and $A_j(x)$ are given real-valued functions on R^N, and (a_{jk}) is a positive-definite, real symmetric matrix. The functions $A_j(x)$ are included to take into account the external magnetic field. (1) and (2) are special cases of (3) with $N=3n$ and $N=3n-3$, respectively.

§1. Preliminaries

Before going into discussion of the Hamiltonian operators, we collect here some general mathematical notions related to operator theory.

a) Basic definitions

Let $\mathfrak{H}$ be a separable Hilbert space, with the inner product (u, v) and the norm $\|u\|=(u, u)^{1/2}$. A *linear operator* T in $\mathfrak{H}$ is a function defined on a *linear manifold* $\mathfrak{D}=\mathfrak{D}(T)$, called the *domain* of T, and taking values in $\mathfrak{H}$, such that $T(\alpha u+\beta v)=\alpha Tu+\beta Tv$ for every $u, v\in\mathfrak{D}(T)$. T is *bounded* if $\|Tu\|\leq M\|u\|, u\in\mathfrak{D}(T)$, for some constant $M<\infty$. T is *compact* (or *completely continuous*) if $\mathfrak{D}(T)=\mathfrak{H}$ and if, for any bounded sequence $u_n\in\mathfrak{H}$, the sequence Tu_n has a converging subsequence.

The *graph* of T is the subset of the product space $\mathfrak{H}\times\mathfrak{H}$ consisting of all elements of the form $\{u, Tu\}$, $u\in\mathfrak{D}(T)$. T is *closed* if its graph is a closed set.

T is *densely defined* if $\mathfrak{D}(T)$ is dense in $\mathfrak{H}$. If T is densely defined, the *adjoint* T^* of T is defined as the *maximal* operator such that $(Tu, v)=(u, T^*v)$ holds for all $u\in\mathfrak{D}(T)$ and $v\in\mathfrak{D}(T^*)$. T^* is always closed. T is *symmetric* if T^* is an extension of T. T is *selfadjoint* if $T^*=T$ (which implies that T^* and T have the same domain).

Let T be closed. The *resolvent set* of T, denoted by $\mathrm{P}(T)$ in this paper, is the set of all complex numbers ζ such that the inverse operator $(T-\zeta)^{-1}$ exists, has domain $\mathfrak{H}$, and is bounded. The complementary set of $\mathrm{P}(T)$ in the complex plane is the *spectrum* of T, denoted by $\Sigma(T)$. The

resolvent $R(\zeta)=(T-\zeta)^{-1}$ is an analytic (operator-valued) function defined for $\zeta\in\mathrm{P}(T)$.

b) The spectra of a selfadjoint operator

Let H be a selfadjoint operator: $H^*=H$. Then its spectrum $\sum(H)$ is a subset of the real axis and its resolvent set $\mathrm{P}(H)$ contains upper and lower open half-planes. The resolvent $R(\zeta)$ is analytic in the two half-planes. In many cases it forms a single analytic function with singularities contained in a half-line on the real axis.

An *eigenvalue* λ of H is a number such that there exists $u\in\mathfrak{H}$, $u\neq 0$ (*eigenvector*) with $Hu=\lambda u$. λ belongs to $\sum(H)$ and hence is necessarily real. The set of all eigenvalues of H is called the *point spectrum* of H, $\sum_p(H)$ in symbol; it is a countable set. (The so-called improper eigenvalues are not considered here.) The collection of all u such that $Tu=\lambda u$ is a subspace (closed linear manifold) of $\mathfrak{H}$, called the *eigenspace* for λ; its dimension is the *multiplicity* of λ. The subspace $\mathfrak{H}_p$ of $\mathfrak{H}$ spanned by the eigenspaces for all eigenvalues of H reduces H; the *part* H_p of H in $\mathfrak{H}_p$ is a selfadjoint operator in $\mathfrak{H}_p$ with a *pure point spectrum*. The orthogonal complement $\mathfrak{H}_c$ of $\mathfrak{H}_p$ in $\mathfrak{H}$ also reduces H; the part H_c of H in $\mathfrak{H}_c$ is again selfadjoint and has no eigenvalues. The spectrum of H_c is called the *continuous spectrum* of H and is denoted by $\sum_c(H)$.

According to these definitions, $\sum_p(H)$ and $\sum_c(H)$ are not necessarily disjoint, and $\sum(H)$ is not necessarily the union of $\sum_p(H)$ and $\sum_c(H)$. For example, it is possible that H has a complete set of eigenvectors with the associated eigenvalues everywhere dense on the real axis; then $\sum_p(H)$ is this dense (but countable) set and $\sum_c(H)$ is empty, while $\sum(H)$ is the whole real axis. (There is another definition of the continuous spectrum, which is not considered here. For the two definitions see e. g. Stone.[1])

An eigenvalue may or may not be an isolated point of $\sum(H)$. Let us collect all isolated eigenvalues with finite multiplicities; the resulting set will be called the *discrete spectrum* (which is not a standard term) and denoted by $\sum_d(H)$. The rest of $\sum(H)$ is called the *essential* (or *limit*) *spectrum*, $\sum_e(H)$ in symbol. Obviously $\sum_d(H)$ and $\sum_e(H)$ are disjoint and add up to $\sum(H)$ by definition. In a certain sense the points of $\sum_d(H)$ would correspond better to the notion of *bound states* than the points of $\sum_p(H)$. Mathematically, the essential spectrum is easier to handle than the continuous spectrum, for it is rather insensitive to perturbation (see Lemma 2 below). But $\sum_e(H)$ and $\sum_c(H)$ coincide in many cases of practical interest.

The following are convenient criteria for a given number λ to belong to various parts of the spectrum. $\lambda\in\sum_p(H)$ if and only if there is $u\in\mathfrak{D}(H)$ with $\|u\|=1$ and $\|(H-\lambda)u\|=0$. $\lambda\in\sum(H)$ if and only if there is a sequence $u_n\in\mathfrak{D}(H)$ such that $\|u_n\|=1$ and $\|(H-\lambda)u_n\|\to 0$. $\lambda\in\sum_e(H)$ if

and only if there is a sequence $u_n \in \mathfrak{D}(H)$ such that $(u_n, u_m) = \delta_{nm}$ and $\|(H-\lambda)u_n\| \to 0$. There is no such simple criterion for $\sum_c(H)$.

H is *bounded from below* if $\sum(H)$ is bounded from below on the real axis. The lower bound $\gamma = \gamma(H)$ of $\sum(H)$ is called the *lower bound* of H. It is also characterized as the largest number γ such that $(Hu, u) \geq \gamma(u, u)$ for all $u \in \mathfrak{D}(H)$. If H is bounded from below, its resolvent $R(\zeta)$ is an analytic function with singularities contained in the interval $[\gamma, +\infty)$ of the real axis.

c) Spectral representation

A selfadjoint operator H admits the *spectral decomposition*

$$H = \int_{-\infty}^{\infty} \lambda dE(\lambda), \tag{4}$$

where $\{E(\lambda)\}$ is the *spectral family* associated with H, consisting of projection operators $E(\lambda)$ monotonically nondecreasing in λ and tending to zero as $\lambda \to -\infty$ and to the identity operator as $\lambda \to +\infty$. Physically, $d(E(\lambda)u,u)$ is the probability distribution for the quantity H measured in the state u, $\|u\| = 1$.

$\{E(\lambda)\}$ is closely related to the behavior of the resolvent $R(\zeta)$ near the real axis; we have namely, if a, b are not eigenvalues,

$$E(b) - E(a) = \frac{1}{2\pi i} \lim_{\varepsilon \downarrow 0} \int_a^b [R(\lambda + i\varepsilon) - R(\lambda - i\varepsilon)]\, d\lambda. \tag{5}$$

Also the various parts of the spectrum are related to $\{E(\lambda)\}$. A real number λ belongs to $\mathrm{P}(H)$ if and only if $E(\lambda+\varepsilon) - E(\lambda-\varepsilon) = 0$ for some $\varepsilon > 0$. $\lambda \in \sum(H)$ if and only if $E(\lambda+\varepsilon) - E(\lambda-\varepsilon) > 0$ for every $\varepsilon > 0$. $\lambda \in \sum_p(H)$ if and only if $E(\lambda)$ is discontinuous at λ.

d) Some perturbation lemmas

We state here some perturbation lemmas in operator theory which are useful in our problems (for the proof see e. g. Kato[2]).

Lemma 1 Let H_0 be a selfadjoint operator and V a symmetric operator. Suppose V is "small relative to H_0" in the sense that $\mathfrak{D}(V) \supset \mathfrak{D}(H_0)$ and $\|Vu\| \leq a\|u\| + b\|H_0 u\|$ for all $u \in \mathfrak{D}(H_0)$, where a, b are constants and $b < 1$. Then $H = H_0 + V$ with $\mathfrak{D}(H) = \mathfrak{D}(H_0)$ is selfadjoint. If, in addition, H_0 is bounded from below, the same is true of H.

Lemma 2 Let H_0 be selfadjoint and V symmetric and compact. Then $H = H_0 + V$ is selfadjoint and has the same essential spectrum as H_0.

§2. Definition of the Hamiltonian

The first mathematical problem we have to consider is the exact defi-

nition of the Hamiltonian operator H. The operators (1) to (3) are only *formal differential operators* and, as such, are not useful for the purpose of quantum mechanics. The trouble is that they are only vaguely defined, for one is not sure in advance what degree of singularities are allowed of functions on which they operate.

For the correct definition of the Hamiltonian H, the leading principle is the condition that H should be a selfadjoint operator in the basic Hilbert space $\mathfrak{H}$, which is to be $L^2(R^{3n})$ for (1), $L^2(R^{3n-3})$ for (2), and $L^2(R^N)$ for (3). As was shown by von Neumann,[3] selfadjointness is necessary and sufficient for H to be observable (i. e. for all statistical statements for H to make sense).

Now it may well happen that a given formal differential operator determines a unique selfadjoint operator in a natural way; then it should be chosen as the correct Hamiltonian. For the operator (3) (which includes (1) and (2) as special cases), this situation will occur in the following way. We define the *minimal operator* $H_{\min}$ associated with (3) as the operator in $\mathfrak{H}=L^2(R^N)$ with domain $C_0^\infty(R^N)$ (the set of all infinitely differentiable functions vanishing outside some bounded region, depending on individual functions). $H_{\min}$ is a symmetric operator, as is seen from the fact that (3) is *formally selfadjoint*, at least if the $A_j(x)$ are continuously differentiable and $q(x)$ is locally square integrable. $H_{\min}$ has *closure* (the smallest closed extension), as all symmetric operators do. If the closure is selfadjoint (in which case $H_{\min}$ is said to be *essentially selfadjoint*), it is the unique selfadjoint operator that can be constructed from (1) by a reasonable means.

Fortunately, it has been found that this is the case with (1) to (3) under quite mild conditions. It was shown by Kato[4] (see also Kato[2]) that in (1) and (2) it suffices to assume that each of the $V_{ij}(\boldsymbol{r})$ is the sum of a function in $L^2(R^3)$ and a bounded function. In this case it was also shown that the domain $\mathfrak{D}(H)$ of the correct Hamiltonian is independent of the potentials V_{ij} and is identical with the domain of the operator for the system of free particles. The proof depends on Lemma 1 of §1, using the fact that the potential energy is "small" relative to the kinetic energy.

Later the result was generalized by Ikebe and Kato,[5] in which a more concrete analysis of the differential operator was made. Without going into details, we shall state here a rather special case of the sufficient conditions for the uniqueness deduced there. The uniqueness holds for (3) if

(i) The $A_j(x)$ are continuously differentiable (they may behave arbitrarily as $|x|\to\infty$);

(ii) $V(x)$ can be written as $V(x)=V'(x)+V''(x)$ with V' and V'' satisfying the following conditions: $|V'(x)|\leq\rho(|x|)$, where $\rho(r)$ is a positive, nondecreasing function of $r>0$ such that $\int_1^\infty \rho(r)^{-1/2}dr=\infty$, and V''

$\in Q_\alpha(R^N)$ for some $\alpha>0$.

Here $Q_\alpha(R^N)$ is the class of functions, introduced by Stummel,[6] consisting of all functions $u(x)$ defined on R^N such that

$$\int_{|x-y|\leq 1} |x-y|^{-N+4-\alpha} |u(y)|^2 dy \tag{6}$$

is a bounded function of $x\in R^N$. If $N+\alpha\leq 4$, the factor $|x-y|^{-N+4-\alpha}$ in (6) is not important, and $u\in Q_\alpha(R^N)$ is equivalent to the condition that $\int_{|x-y|\leq 1} |u(y)|^2 dy$ be a bounded function of x.

Obviously $Q_\alpha(R^N)$ is a linear set. Another important property of $Q_\alpha(R^N)$ is that if a function $u(x)=u(x_1, \cdots, x_M)$, depending on $M<N$ coordinates, belongs to $Q_\alpha(R^M)$, then it belongs to $Q_\alpha(R^N)$ when considered a function of N variables (an observation due to Jörgens[7]). Thus if V'' is the sum of several two-particle potentials $V_{ij}(\boldsymbol{r}_i-\boldsymbol{r}_j)$ as in (1) and (2), it suffices to verify that each $V_{ij}(\boldsymbol{r})$ belongs to $Q_\alpha(R^3)$. It is easily seen in this way the earlier result for (1) and (2) stated above follows as a special case of the condition on V''. On the other hand, no singularity for the $V_{ij}(\boldsymbol{r})$ which is not locally square integrable is allowed under these conditions.

The inclusion of the term $V'(x)$ makes it possible that there is some unbounded potential taking large values for large $|x|$. For example, the presence of a uniform external electrostatic field is permitted (the Stark effect). Also the presence of a uniform magnetic field, or any smooth magnetic field, is allowed by the condition (i) (the Zeeman effect). Thus the uniqueness of the Hamiltonian has been established for a large number of physically interesting cases.

Since only locally square integrable singularities are permitted for the $V_{ij}(\boldsymbol{r})$, however, it is an open question whether the presence of highly singular spin interactions still lead to a unique Hamiltonian operator.

The question of the essential selfadjointness of the minimal differential operators aroused considerable interest in mathematical literature. The reader is referred to Brownell,[8] Hellwig,[9] Jörgens[10] (which contains the strongest results so far obtained), Rohde,[11] Stummel,[6] Wienholtz.[12] Also Babbitt[13] and Nelson[14] contain related results discussed from different points of view (Feynman integrals and semigroup theory).

§3. Semiboundedness

The correct Hamiltonian H defined above is bounded from below for the operators (1) and (2) if each $V_{ij}(\boldsymbol{r})$ is the sum of a function in $L^2(R^3)$ and a bounded function; this follows easily from Lemma 1. More generally, the same is true if we consider (3) under the conditions (i), (ii) given above, provided that $V'(x)$ is bounded from below (cf.[5] where this is not

proved explicitly but follows from the formula (4·4)). For general V', H need not be bounded from below. A typical example is the operator of the Stark effect.

We shall denote by $\gamma(H)$ the lower bound of H when H is bounded from below. $\gamma(H)$ may or may not be an eigenvalue of H. Let us note the simple but important fact that $\gamma(H)$ is the same for the system (1) and for the reduced system (2) if the latter corresponds to the internal motion of (1). $\gamma(H)$ is never an eigenvalue for (1); in fact (1) has no eigenvalue at all.

In the case of semibounded H, it is generally believed that the spectrum $\sum(H)$ consists of a discrete spectrum below a certain value (*threshold*) $\mu=\mu(H)$ and that the spectrum above μ is continuous. This is certainly true for hydrogen-like atoms, for which the eigenvalue problem can be solved explicitly. But it is by no means obvious for many-particle systems. We shall see below how far this physically natural conjecture can be justified mathematically.

§4. The essential spectrum

In this section we consider the essential spectrum $\sum_e(H)$ for the Hamiltonian $H=H_n'$ of the form (2).

First consider the case $n=2$, in which case (2) is actually a one-particle problem with potential $V(\boldsymbol{r})=V_{12}(\boldsymbol{r})$. Assume that $V(\boldsymbol{r})$ is the sum of a function in $L^2(R^3)$ and a bounded function which tends to zero as $|\boldsymbol{r}|\to\infty$. We shall show that $\sum_e(H)$ is the interval $[0, +\infty)$.

Let $R(\zeta)=(H-\zeta)^{-1}$ and $R_0(\zeta)=(H_0-\zeta)^{-1}$ be the resolvents for the given operator H and for the free-particle operator H_0. Then we have the "second resolvent equation"

$$R(\zeta)=R_0(\zeta)-R(\zeta)VR_0(\zeta), \qquad \zeta\in\mathrm{P}(H)\cap\mathrm{P}(H_0). \tag{7}$$

In particular (7) is true for $\zeta=-c$ with sufficiently large positive c. Now it can be proved easily that $VR_0(\zeta)$ is a compact operator. Hence the second term on the right of (7) is compact. It follows from Lemma 2 that the two selfadjoint operators $R(-c)$ and $R_0(-c)$ has the same essential spectrum. But $\sum(R_0(-c))$ is the interval $[0, c^{-1}]$, which is at the same time $\sum_e(R_0(-c))$. Hence $\sum_e(R(-c))$ is the same interval, which in turn means that $\sum_e(H)$ is the interval $[0, +\infty)$. (Here we have used the *spectral mapping theorem*, which asserts that $\sum(R(-c))$ is the image of $\sum(H)$ under the map $\lambda\to(\lambda+c)^{-1}$ and that the same is true for $\sum_e$.)

This simple argument does not work for the many-particle case $n\geq 3$, for $VR_0(\zeta)$ is no longer compact. But if one considers the system (2) corresponding to the internal motion of (1), a similar (but somewhat modified)

argument can be applied to the resolvent equation in a more refined form. In this way Hunziker[15] has given an elegant proof of the fact that $\sum_e(H)$ is an interval of the form $[\mu, +\infty)$ if each $V_{ij}(\boldsymbol{r})$ satisfies the same condition as was stated above for $V(\boldsymbol{r})$.

Let us sketch the proof of Hunziker. The resolvent equation has the form

$$R(\zeta)=S(\zeta)+R(\zeta)I(\zeta), \tag{8}$$

in which $S(\zeta)$ and $I(\zeta)$ are analytic in the complex plane cut along a ray $[\mu, +\infty)$. These operators are given explicitly in terms of the resolvents $R^{(p)}(\zeta)$ of the Hamiltonians $H^{(p)}$ corresponding to the *cluster decompositions* of the given system. In other words, $H^{(p)}$ is obtained from (1) by decomposing the system into two or more subsystems (clusters) and by neglecting the V_{ij} between particles in different subsystems. The end μ of the cut is given by

$$\mu=\mu(H)=\min \gamma\ (H^{(p)}) \tag{9}$$

taken over all possible cluster decompositions (or, equivalently, over all decompositions into two clusters). For the resolvent equation (8) cf. also Weinberg[16] and van Winter.[17]

It follows from (8) that formally

$$R(\zeta)=S(\zeta)(1-I(\zeta))^{-1}, \tag{10}$$

but this is of little use unless one knows that $(1-I(\zeta))^{-1}$ exists. Hunziker proved that $I(\zeta)$ is compact and $\|I(\zeta)\|\to 0$ as $\zeta\to-\infty$ under the assumptions made and, consequently, the inverse operator in question exists as a *meromorphic function* in the cut plane. It follows that $R(\zeta)$ itself is meromorphic in the same region. Furthermore, it can be shown from the compactness of $I(\zeta)$ that the possible poles of $R(\zeta)$ correspond to eigenvalues of H with finite multiplicities. This proves that only a discrete spectrum exists below $\mu(H)$. On the other hand, it is easy to show that each $\lambda>\mu(H)$ belongs to $\sum(H)$ by constructing a sequence u_n with $\|u_n\|=1$ and $\|(H-\lambda)u_n\|\to 0$ (see §1, b)). It follows that $\sum_e(H)$ is exactly the interval $[\mu(H), +\infty)$.

Under the rather mild assumptions on the V_{ij} made above, it is not clear whether $\sum_e(H)$ is continuous or not (it might consist of a dense point spectrum). Under somewhat stronger conditions, however, one can show that the continuous spectrum $\sum_c(H)$ also coincides with $[\mu(H), +\infty)$. The proof is most conveniently given by considering the *wave operators* (see §5).

The result on $\sum_e(H)$ given above was also proved by van Winter[17),18] under the stronger assumptions that $V_{ij}(\boldsymbol{r})\in L^2(R^3)$; in this case $I(\zeta)$

belongs to the Hilbert-Schmidt class (see also Weinberg[16] and Hunziker[19]). Prior to these authors, Žislin[20] deduced a similar result by a more direct study of the operator H (without using the resolvent equation). The assumptions of Žislin on the V_{ij} are somewhat stronger than Hunziker's and contains the conditions $V_{ij}\geq 0$ for $i<j<n$ and $V_{in}\leq 0$, but he considers the general system (2) in which the matrix (a_{ij}) is arbitrary. In this case it suffices in (9) to consider only the decompositions into two clusters consisting of one and $n-1$ particles. A simplified proof of Žislin's result was also given by Jörgens,[7] in which even the presence of an external vector potential vanishing at infinity is permitted but the matrix (a_{ij}) is assumed to be diagonal.

The result on $\sum_e(H)$ proved above is not necessarily true if there is a strong external electrostatic or magnetic field. For example, the spectrum of the (internal) Hamiltonian for the Stark effect of a hydrogen-like atom is continuous over the whole real axis. The Zeeman effect for the same atom (with infinite nuclear mass) is more interesting; it was proved by Jörgens[21] that here $\sum_e(H)$ is an interval $[\mu, +\infty)$, where $\mu>0$ is proportional to the magnetic field, notwithstanding that it is a one-particle problem with $V(\boldsymbol{r})\to 0$ at infinity.

§5. The wave operators

The study of wave operators belong to scattering theory, which is outside the scope of this article. But we consider the wave operators in so far as they are useful in revealing the structure of the spectrum of the Hamiltonian.

For this limited object, the following mathematical consideration would be sufficient (cf Jauch[22]). Together with the given Hamiltonian H, we consider an auxiliary selfadjoint operator H_0 and the unitary groups $\exp(-itH)$, $\exp(-itH_0)$ generated by them. Let $\mathfrak{M}$ be the set of all $u\in\mathfrak{H}$ such that

$$\lim_{t\to\pm\infty}\exp(itH)\exp(-itH_0)u=W_{\pm}u \tag{11}$$

exist. (11) defines two *isometric operators* $W_{\pm}$ ($\|W_{\pm}u\|=\|u\|$) with domain $\mathfrak{M}$, which is necessarily a subspace of $\mathfrak{H}$. $W_{\pm}$ are extended to the whole of $\mathfrak{H}$ by setting $W_{\pm}u=0$ whenever $u\perp\mathfrak{M}$. The extended operators $W_{\pm}$, called the *wave operators* for the "channel Hamiltonian H_0", are *partially isometric*, with the *initial set* $\mathfrak{M}$ and *final sets* $\mathfrak{N}_{\pm}$ (the images of $\mathfrak{H}$ or, equivalently, of $\mathfrak{M}$ under the maps $W_{\pm}$).

The following results are easy consequences of these definitions. $\mathfrak{M}$ is invariant under $\exp(-itH_0)$ and reduces H_0. $\mathfrak{N}_{\pm}$ are invariant under $\exp(-itH)$ and reduce H. $W_{\pm}$ have the *intertwining property*:

$$\exp(-itH)W_{\pm}=W_{\pm}\exp(-itH_0),\qquad HW_{\pm}\supset W_{\pm}H_0. \tag{12}$$

In particular, the parts of H in $\mathfrak{R}_\pm$ are *unitarily equivalent* to the part of H_0 in $\mathfrak{M}$.

When H is the Hamiltonian for (1), "the channel Hamiltonian" H_0 can be any of the $H^{(p)}$ corresponding to cluster decompositions of the system (see §4). (These are not the correct channel Hamiltonians to be used in scattering theory.) Let $S_1, \cdots, S_p$ be the subsystems (clusters) into which the given system is decomposed, and let

$$H_0=\sum_{k=1}^{p}\left(\frac{1}{2M_k}\mathrm{Grad}_k^2+H_k'\right), \tag{13}$$

where M_k is the total mass of S_k, Grad_k^2 is the sum of the $\mathrm{grad}_i^2=\Delta_i$ for the particles in S_k, and H_k' is the internal Hamiltonian for S_k.

Now it can be shown that the wave operators $W_\pm$ exist for the pair H, H_0, with the initial set $\mathfrak{M}$ identical with the whole space $\mathfrak{H}$, under certain conditions on the V_{ij}. To this end, consider functions of the form

$$u(x)=v(\boldsymbol{R}_1, \cdots, \boldsymbol{R}_p)\phi_1(x_1')\cdots\phi_p(x'_p), \tag{14}$$

where $\boldsymbol{R}_k$ is the coordinate of the center of mass of S_k, x_k' is the aggregate of the internal coordinates of S_k, ϕ_k is an L^2-function in its variables, and v is in $L^2(R^{3p})$. The proof that the limits (11) exist for (14) is implicitly contained in Kuroda[23] and Hack,[24] who gave the proof explicitly for some special cases of (14). (cf. also van Winter,[18] Hunziker.[15]) Since the set of all linear combinations of functions of the form (14) is dense in $\mathfrak{H}$, it follows that the limit (11) exist for all $u\in\mathfrak{H}$. The conditions on the V_{ij} assumed by van Winter are that for some $\varepsilon>0$

$$\int_{R^3}|V_{ij}(\boldsymbol{r}')|^2(1+|\boldsymbol{r}'-\boldsymbol{r}|)^{-1+\varepsilon}d\boldsymbol{r}'\leq\text{const.} \tag{15}$$

If one is interested in the internal Hamiltonian H obtained from (1) by separation of the motion of the center of mass, the corresponding "channel Hamiltonian" can be obtained by a similar separation applied to the above $H_0=H^{(p)}$.

Now $H_0=H^{(p)}$ has a pure continuous spectrum extending over the interval $[\gamma(H_0), +\infty)$; this is clear since it is translation invariant. Even if we consider the reduced H_0 for the internal motion, it still includes the relative translation of at least two clusters and hence its spectrum is purely continuous. Since the parts of H in $\mathfrak{R}_\pm$ are unitarily equivalent to H_0 (note that $\mathfrak{M}=\mathfrak{H}$), it follows that $\Sigma(H)$ contains a continuous part extending over $[\gamma(H_0), +\infty)$. Since this is true for all $H_0=H^{(p)}$, $\Sigma_c(H)$ contains the interval $[\mu, +\infty)$ where μ is given by (9). Combined with the results of §4, this shows that $\Sigma_c(H)=\Sigma_e(H)=[\mu, +\infty)$.

§6. The discrete spectrum

The fact that $\sum_e(H)$ is an interval $[\mu(H), +\infty)$ proved above implies that the part of $\sum(H)$ below $\mu(H)$ is at most discrete, but it does not necessarily mean that there actually exist eigenvalues below $\mu(H)$. But Zislin[20] was able to prove that there do exist an infinite number of eigenvalues below $\mu(H)$ for all neutral atoms and molecules and for positive ions. More precisely, he proved it for (2) under the following assumptions.

$$\begin{aligned} &V_{ij}(\boldsymbol{r}) = c_{ij}|\boldsymbol{r}|^{-1},\ i<j<n,\ c_{ij}>0, \\ &V_{in}(\boldsymbol{r}) = -\sum_h b_{ih}|\boldsymbol{r}-\boldsymbol{a}_h|,\ b_{ih}>0, \\ &\sum_h b_{ih} > \sum_{\substack{j=1 \\ j\neq i}}^{n} c_{ij}\ (c_{ji}=c_{ij}). \end{aligned} \tag{16}$$

It follows automatically that all these eigenvalues have finite multiplicities and converge to the threshold $\mu(H)$.

It should be remarked that the matrix (a_{ij}) in (2) considered by Zislin may be any positive-definite matrix. In particular, this implies that the atomic nuclei may have any (finite or infinite) mass. Thus his result is a great improvement on the older result due to Kato,[25] in which the existence of an infinite number of eigenvalues was proved for helium atom with infinite nuclear mass but in which only a finite number of eigenvalues were shown to exist for a finite nuclear mass. Cf. also Putnam,[26] in which the existence of at least one eigenvalue was concluded for a positive atomic ion with n electrons and with nuclear charge number $Z \geq 5n(n-1)/8$.

Negative ions are not included in the theorem of Zislin. To prove the existence of bound states for negative ions, one would need special investigations for each ion.

In addition to the works cited above, there are a number of papers dealing with the spectra of Schrödinger-type operators, but some of them are of physical interest only for one-particle systems. See Balslev,[27] Brownell,[28] Molcanov,[29] Ramm,[30] Rejto.[31] [Added in proof: For a generalization of Zislin's results see Uchiyama.[32]]

§7. Symmetry with respect to permutations

So far we have considered the Hamiltonian without taking into account the identity of particles. In this sense the results stated above would seem rather unrealistic.

In some problems this is not a serious matter. If some particles are identical, the Hamiltonian H defined above without symmetry consideration is invariant under the group of all permutations of these particles, so that H is decomposed into the *direct sum* of several parts acting in the mutually

orthogonal subspaces characterized by various symmetry properties. The fact that some of these parts need not be physically realizable is not important here. If H is selfadjoint, as is the case with the Hamiltonians considered above, each of these parts is automatically selfadjoint. Thus there is no difficulty at all about the question of unique determination of the Hamiltonian even when the identity of particles is taken into account.

The situation is changed, however, if one wants to give more detailed description of the spectrum of H. For example, the result on the existence of eigenvalues is not interesting unless the corresponding bound states are physically realizable. The smallest eigenvalue of the (internal) 3-particle problem with 3 identical particles (like lithium atom) has an eigenfunction symmetric with respect to the 3 particles, but such a state is not physically realizable.

Thus the question arises: do there exist eigenvalues of the physically realizable parts of H, and what are the essential or continuous spectra of these parts? These questions have been answered by Žislin and Sigalov.[33]

Let us consider the internal n-particle system (replace $n-1$ by n in (2)) in which all particles are identical and subjected to Coulomb interaction and in which (a_{ij}) is a constant multiple of the identity matrix:

$$a_{ij}=a\delta_{ij},\ a>0;\ V_{ij}(\boldsymbol{r})=c|\boldsymbol{r}|^{-1},\ i<j\leq n,\ c>0;$$
$$V_{i,n+1}(\boldsymbol{r})=-b|\boldsymbol{r}|^{-1},\ b>0. \tag{17}$$

The Hamiltonian $H=H_n$ of this system can be decomposed into the direct sum of several parts, some of which are physically realizable and some are not. The realizable parts are characterized by the irreducible representations $\overline{D}^{(k)}$, $k=0,1,\cdots,[n/2]$, of the symmetric group of degree n (see Wigner [34]). The corresponding parts of H_n will be denoted by $\overline{H}_n^{(k)}$. More precisely, $\overline{H}_n^{(k)}$ is the part of H_n in the reducing subspace $\overline{\mathfrak{H}}(k)$ of $\mathfrak{H}=L^2(R^{3n})$ with the orthogonal projections

$$\overline{P}^{(k)}=\frac{l^{(k)}}{n!}\sum_R\bar{\chi}^{(k)}(R)T_R, \tag{18}$$

where R varies over all permutations of n objects, T_R is the corresponding operator permuting the variables of functions, $\bar{\chi}^{(k)}(R)$ is the character of the representation $\overline{D}^{(k)}$, and $l^{(k)}$ is the dimension of $\overline{D}(k)$.

Let $\overline{H}_{n-1}^{(k)}$, $k=0,1,\cdots,[(n-1)/2]$, be the corresponding operators for the $(n-1)$-particle system *with the same constants* a,b,c as in (17). Then the result of Žislin and Sigalov asserts that the essential spectrum of $\overline{H}_n^{(k)}$ is again an interval of the form $[\mu,+\infty)$, where

$$\mu=\mu(\overline{H}_n^{(k)})=\min[\tau(\overline{H}_{n-1}^{(k)}),\tau(\overline{H}_{n-1}^{(k-1)})],\ 0<k\leq\left[\frac{n}{2}\right], \tag{19}$$

except for $k=n/2$ with even n, and

$$\mu(\bar{H}_n^{(0)})=\gamma(\bar{H}_{n-1}^{(0)}),\ \mu(\bar{H}_n^{(n/2)})=\gamma(\bar{H}_{n-1}^{(n/2-1)}), \tag{20}$$

$\gamma(H)$ denoting as before the lower bound of H.

If, in addition, $b>(n-1)c$, then there are an infinite number of eigenvalues of $\bar{H}_n^{(k)}$ below $\mu(\bar{H}_n^{(k)})$ (again these eigenvalues have finite multiplicities and converge to $\mu(\bar{H}_n^{(k)})$). Note that all the conditions are satisfied by neutral atoms and positive atomic ions.*)

These results show that there are infinitely many eigenvalues of the real physical system (with electron spins taken into account but without spin interactions), and indeed infinitely many isolated ones. Not all eigenvalues are isolated in the whole system, however, for some isolated eigenvalues of $\bar{H}_n^{(k)}$ for some k are larger than $\mu(\bar{H}_n^{(j)})$ for some $j\neq k$ and, consequently, are contained in $\sum_e(\bar{H}_n^{(j)})$. For more details we refer the reader to their papers.

§8. Non-existence of positive eigenvalues

We have seen above that under rather general conditions the essential spectrum $\sum_e(H)$ is an interval $[\mu(H), +\infty)$, and that it is even identical with the continuous spectrum $\sum_c(H)$ in many cases. But this does not exclude the possibility that there are (finitely or infinitely many or even densely distributed) eigenvalues contained in that interval. Thus it is desirable to show that there do not exist too many eigenvalues.

The possibility of eigenvalues being "immersed" in the continuous spectrum is not excluded even in a one-particle problem, though it might appear to contradict physical intuition. An example of a spherically symmetric potential which tends to zero at infinity and for which there exists a positive eigenvalue was given by von Neumann and Wigner.[36] (The potential given by them goes to zero like $|\boldsymbol{r}|^{-2}$, but there was a computational error involved and the correct behavior is like $|\boldsymbol{r}|^{-1}$. In fact there can be no positive eigenvalue for a potential falling off like $|\boldsymbol{r}|^{-2}$.)

Thus it is of interest to ask under what conditions one can exclude the appearance of positive eigenvalues.

For a one-particle problem with a not necessarily spherically symmetric potential $V(\boldsymbol{r})$, it was shown by Kato[37] that no positive eigenvalues exist if $|\boldsymbol{r}|^{1+\varepsilon}|V(\boldsymbol{r})|\to 0$ as $|\boldsymbol{r}|\to\infty$ for some $\varepsilon>0$. Odeh[38] proved that the same is true if $\partial V(\boldsymbol{r})/\partial|\boldsymbol{r}|\leq 0$ for sufficiently large $|\boldsymbol{r}|$ and $V(\boldsymbol{r})\to 0$ as $|\boldsymbol{r}|\to\infty$. The proofs are fairly complicated for the seemingly simple problem.

*) Recently Zislin and Sigalov[35] extended these results by taking into account the rotation and inversion groups together with the permutation group.

For a many-particle problem of the form (2) with a diagonal matrix (a_{ij}), Weidmann[39] proved that no positive eigenvalues exist if all the $V_{ij}(\boldsymbol{r})$, $i<j\leq n$, are homogeneous of degree $-\alpha$ with $0<\alpha\leq 1$ (i.e. $V_{ij}(t\boldsymbol{r})=t^{-\alpha}V_{ij}(\boldsymbol{r})$ for any $t>0$). The conditions are satisfied by Coulomb potentials. Later Weidmann improved the result by showing that it suffices to assume $0<\alpha<2$ (unpublished). The result is closely related to the *virial theorem*, which asserts that $((2K+\alpha V)u,u)=0$ if u is an eigenfunction of H, where $H=K+V$ is the decomposition of H into the kinetic and potential energy parts (see e.g. Schiff[40]). Since $Hu=(K+V)u=\lambda u$, where λ is the eigenvalue, it follows that $((2-\alpha)K+\alpha\lambda)u,u)=0$, which is impossible if $0<\alpha<2$ and $\lambda\geq 0$. Although this proof looks almost trivial, the proof of the virial theorem is not at all simple when the eigenvalue is not an isolated point of the spectrum. Also it is not clear whether homogeneous potentials with $\alpha\geq 3/2$ are permitted for the uniqueness of the Hamiltonian.

If there are no positive eigenvalues, the interval $[0,+\infty)$ consists of a pure continuous spectrum. But the nature of the part of the spectrum in the interval $[\mu(H),0]$ is still not clarified by the arguments presented above. In general the interval will contain at least some eigenvalues, for this is true if $b>0$ and $c=0$ in (8).

§9. Properties of eigenfunctions and wave packets

Since the Hamiltonian H is defined as the *closure* of the minimal operator $H_{\min}$ (see §1) in the Hilbert space, it is not a differential operator in the classical sense. If u is an eigenfunction of H, for example, it satisfies the *abstract* equation

$$Hu=\lambda u, \tag{21}$$

but it is not at all obvious that (11) is identical with the Schrödinger equation regarded as a differential equation. It can be proved, however, that this is actually the case; the proof depends essentially on the ellipticity of the differential operator. The eigenfunction u can be shown to be a smooth function at each point where the potentials $V_{ij}(\boldsymbol{r}_i-\boldsymbol{r}_j)$ (or the coefficients $A_j(x)$ and $q(x)$, if one considers (3)) are smooth. More generally, the same is true with any function u representing a *wave packet*. Here we mean by a wave packet any function u belonging to a subspace $[E(b)-E(a)]\mathfrak{H}$, $-\infty<a<b<\infty$, of the Hilbert space $\mathfrak{H}$. An important property of such u is that $u\in\mathfrak{D}(H^m)$ for any positive integer m.

Naturally an eigenfunction or a wave packet u will have a singularity at a point where some of the V_{ij} is singular. The singularity of u is not too strong, however. In any case u is square integrable since it belongs to $\mathfrak{H}=L^2$. Furthermore, it was shown (see Kato[41]) that in the case (1) or

(2), u is everywhere continuous with locally bounded (though not necessarily continuous) first derivatives, provided that the singularities of $V_{ij}(\boldsymbol{r})$ are at most of the Coulomb type. Thus one may safely exclude any locally unbounded function from the family of eigenfunctions and wave packets. (For more detailed behavior of wave packets see loc. cit.; cf. also Rohde[42] for discussions of the regularity of wave packets for general differential operators.)

§10. The Green function and eigenfunction expansions

The *Green function* $G(x, y; \zeta)$ is the kernel of the integral operator representing the resolvent $R(\zeta)=(H-\zeta)^{-1}$. (Here and in what follows x denotes the total coordinates $\boldsymbol{r}_1, \cdots, \boldsymbol{r}_n$ for (1) or $\boldsymbol{r}_1, \cdots, \boldsymbol{r}_{n-1}$ for (2).) There is no general theorem which shows that $R(\zeta)$ is an integral operator, but this can be proved under certain assumptions on the V_{ij}. For one-particle problems, the Green function was constructed by Povzner[43] and Ikebe[44] (see also Faddeev[45]). Making use of the resolvent equation (8), van Winter[17] was able to construct, step by step, the Green function $G_n(x, y; \zeta)$ for the n-particle system. Under the assumption that the $V_{ij}(\boldsymbol{r}) \in L^2(R^3)$, G_n is obtained by solving an integral equation with a Hilbert-Schmidt kernel, which can be computed by using G_{n-1}. $G_n(x, y; \zeta)$ turns out to be meromorphic in ζ in the plane cut along $[\mu(H), \infty)$.

In the abstract form, this process is already given by (10), in which the operator $I(\zeta)$ is of Hilbert-Schmidt class under the stated assumption (see also Weinberg[16] and Hunziker[19]). The construction of the Green function can also be carried out in the momentum representation, although the kernel is then not a proper function.

Since the spectral family $\{E(\lambda)\}$ for a given selfadjoint operator is related by (5) to the resolvent $R(\zeta)$, it is expected that one can obtain a concrete expression for $E(\lambda)$ if one is well-informed of the behavior of the Green function in the immediate neighborhood of the real axis. The *eigenfunction expansion theorem* was obtained in this way for ordinary differential operators (see e. g. Titchmarsh[46]). Similar methods were used by Povzner[47] and Ikebe[44] to prove the expansion theorem for the Hamiltonian of a one-particle system. Here an arbitrary function $u \in L^2(R^3)$ is expressed as the sum of a series in discrete eigenfunctions and an integral, over the space R^3 of wave number vectors, of improper eigenfunctions representing distorted plane waves (cf. also Faddeev,[45] Ikebe,[48] Shizuta[49]).

The problem of eigenfunction expansion seems to be extremely difficult for many-particle problems. So far the only case in which a mathematical proof is known is the 3-particle problem (1) (or, equivalently, 2-particle internal problem (2)) studied by Faddeev,[50] in which the expansion is

given explicitly in the momentum representation.

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