PERTURBED OPERATORS IN HILBERT SPACE *

by

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ABSTRACT

This report reviews the theory of perturbed operators in an abstract Hilbert space and some important applications of the theory to quantum chemistry. It is intended to serve as an introduction to the original papers of Rellich, Sz-Nagy, Kato and others. The theory developed by these authors, which is apparently little known among quantum chemists, rigorously justifies the use of Rayleigh-Schrodinger perturbation theory in many important quantum chemistry problems.

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INTRODUCTION

The purpose of this report is to describe the properties and interpretation of some of the perturbation series used in quantum chemistry. However, since these results can only be obtained through the use of the techniques of abstract[1] Hilbert space it will be necessary to describe these techniques, and explain why they are useful. Details of proofs will not be given since these are available either in standard books, or in the original articles, for which this report is intended to be an introduction.

Any mathematical model for quantum mechanics must provide a unified means for predicting and calculating the results of experiments on atomic phenomena. Heisenberg's matrix mechanics, Schrödinger's differential equation approach, and Dirac's hybrid theory all meet this requirement and have led to highly successful calculation from their first introduction. However, it has always been difficult to justify in rigorous mathematical terms some of the procedures used. In fact,matrix mechanics, differential equations, and Dirac's theory with its strong reliance on the delta function do not lend themselves to precise statement, nor to the proof of highly general theorems. For this reason, von Neumann[16, 2] restated the theory in terms of the theory of operators in abstract Hilbert space which was being developed at the time by mathematicians in order to give a more precise and a more unified treatment to the operators which had been considered in various guises since Newton's time. This formulation made the introduction of rigor comparatively easy.

The questions which von Neuman's formulation answers more easily than others are fairly abstract, but nevertheless important for a complete understanding of the mathematical theory. For instance, because explicit solutions are known, one easily shows that the non-relativistic infinite nuclear mass Schrödinger equation for a one electron atom has infinitely many (bound state) eigenfunctions for any positive nuclear charge Z. What is the case for a two electron atom? Direct study of the Schrödinger differential equation cannot easily establish the existence of even the ground state of helium and certainly can not be expected to give any indication of the existence of other stable states, much less of their number. However, by formulating the problem in abstract Hilbert space, Kato [9] was able to show that for any $Z > 1$ there are infinitely many stable states.

This example is chosen because of the relatively physical nature of the question answered. The many mathematical difficulties avoided by von Neumann's method are discussed at length in his book.[3]

The main advantage of working in Hilbert space is the large number of extremely powerful theorems available in this context. Of course, this does not answer the question of why these theorems are available in this context rather than in that of the classical theory of differential equations, or of infinite matrices[4], etc.

The main advantage of any abstract formulation is that unnecessary details are suppressed, thus focusing attention on the essential elements of the problem. Several illustrations may be helpful. Functions which are not square integrable over the configuration space of a physical

problem are sometimes useful in studying the behavior of a free particle corresponding to the continuous spectrum of some Hamiltonian. However, they are not essential and are omitted from Hilbert space, thus allowing the use of greatly simplified algebraic notation. Furthermore, the square integrable functions are reduced to the status of "elements" which have no internal structure (save their norm or length), only various relations with each other. Finally, these functions even lose their individual identity since all functions which are almost everywhere equal (i.e., which differ only on regions of configuration space which have "volume" or measure zero) are lumped together in the same element of Hilbert space. Again this does no violence to the physical interpretation since an integration over some portion of configuration space is necessary before meaningful information can be extracted from a wave function. In these ways extraneous considerations are eliminated from the theory.

The most important aspect of the superiority of the abstract Hilbert space approach is, however, the insistence of the theory on studying the set of functions on which an operator is defined. If one writes down the Schrödinger Hamiltonian operator for an atom or molecule, it is not at all clear what differentiability conditions should be placed on functions before they are considered to be in the domain of definition of the operator. The natural boundary conditions prescribed by the physical interpretation are that the function should be square integrable over the whole configuration space, and this is just the requirement that the function should represent an element in Hilbert

space. But the question of the proper differentiability or continuity requirements to put on eigenfunctions at points where the potential is singular has given rise to discussion and cannot be solved by the general theory of differential equations.[5]

In abstract Hilbert space, operators with different domains are regarded as different operators, and much of the theory revolves around adjusting the domain of an operator by judicious enlargement, until the extended operator possesses the most convenient properties. Since the theory focuses attention on the problem of the choice of a domain and provides machinery for its successful solution, all of the ambiguity derived from the uncertain differentiability conditions on differential equations is removed at the outset.

II. HILBERT SPACE

Hilbert space[6] $\mathcal{H}$ is an infinite dimensional vector space defined over the complex numbers and satisfying the further requirements described below. Thus elements (which we shall often call functions) φ , $\psi, \cdots$ of $\mathcal{H}$ can be added and multiplied by complex numbers and these processes satisfy the usual rules.

An inner product is defined on $\mathcal{H}$ which associates with each ordered pair of elements φ , ψ a unique complex number, (φ , ψ) which satisfies the following rules

$$(a\varphi, \psi) = a(\varphi, \psi) \quad \text{for every complex number } a .$$

$$(\varphi_1 + \varphi_2, \psi) = (\varphi_1, \psi) + (\varphi_2, \psi)$$

$$(\varphi, \psi) = \overline{(\psi, \varphi)}$$

$$(\varphi, \varphi) > 0 \text{ for } \varphi \neq 0$$

The last property allows the definition of a norm[7] $\|\ \|$ and a distance $\|\varphi - \psi\|$ between φ and ψ which satisfy the rules

$$\|\varphi\| = (\varphi, \varphi)^{1/2}$$

$$\|a\varphi\| = |a|\,\|\varphi\|$$

$$|(\varphi, \psi)| \leq \|\varphi\|\ \|\psi\|$$

$$\|\varphi - \psi\| \leq \|\varphi - \theta\| + \|\theta - \psi\|$$

The most important property of $\mathcal{H}$ is that it is complete in this norm, i.e., if a sequence φ_1 , φ_2 , ... satisfied Cauchy's condition ($\|\varphi_n - \varphi_m\|$ becomes arbitrarily small for sufficiently large n and m) then there is an element φ in $\mathcal{H}$ to which the sequence converges strongly ($\|\varphi_n - \varphi\|$ becomes arbitrarily small for sufficiently large n).

Finally we require that there exist a complete orthonormal set in $\mathcal{H}$ which is countably infinite. By this is meant that there exists at least one (in fact there are infinitely many) infinite sequence φ_1 , φ_2 , ... of elements of $\mathcal{H}$ with (φ_i , φ_j) equal to 1 or 0 depending on whether i = j or i ≠ j and such that for any φ in $\mathcal{H}$ $\varphi = \sum_{n=1}^{\infty} (\varphi, \varphi_n)\varphi_n$.

These requirements completely determine the abstract Hilbert space in which the analysis of this report is carried out. However, to make contact with the usual ideas of quantum mechanics it is necessary to construct $\mathcal{H}$ from more familiar objects of classical analysis. Although one of the advantages of the abstract viewpoint is that the same space $\mathcal{H}$ can be represented in several different

ways, there is one of particular importance. Consider the set of square integrable complex valued functions φ on the configuration space of some physical problem together with the inner product $(\varphi, \psi) = \int \varphi \bar{\psi} \, d\tau$ where $\int \ldots d\tau$ represents Lebesgue integration over the whole space. With the aid of classical theorems of analysis, this set of functions is seen to satisfy all the properties of $\mathcal{H}$ except that 1) (φ, φ) is zero for all functions which are almost everywhere zero rather than just for $\varphi = 0$, and 2) expansion in a complete set of orthonormal functions only represents a function almost everywhere. Both these difficulties are overcome by taking the element of $\mathcal{H}$ to be sets of functions which are almost everywhere equal.

III. PROPERTIES OF UNBOUNDED OPERATORS IN HILBERT SPACE

An operator[8] A in $\mathcal{H}$ assigns a unique element $A\varphi$ to each element φ in a linear submanifold $\mathcal{D}_A$ of $\mathcal{H}$ called the domain of A, subject to the restriction that

$$A(a\varphi + b\psi) = aA\varphi + bA\psi$$

for all φ and ψ in $\mathcal{D}_A$ and all complex numbers a and b. The set of all $A\varphi$ for $\varphi \in \mathcal{D}_A$ is called the range of A and is denoted by $A\mathcal{D}_A$.

It is important to note that the domain of an operator is uniquely specified. When A and B are two operators such that $\mathcal{D}_A \subseteq \mathcal{D}_B$ and $A\varphi = B\varphi$ for all φ contained in $\mathcal{D}_A$, then B is called an extension of A and the two operators are

carefully distinguished if $\mathcal{D}_A \neq \mathcal{D}_B$. A physical "operator" must usually be extended until it becomes self-adjoint in the sense to be defined below. If this is impossible, the "operator" is not satisfactory for use in the theory. Before this centrally important concept can be introduced we must define several other terms.

Few operators have the whole of $\mathcal{H}$ for domain. An important exception is furnished by the bounded operators which are usually defined on all of $\mathcal{H}$. An operator A is called <u>bounded</u> iff (if and only if) there exists a real number b such that $\|A\varphi\| \leq b\|\varphi\|$ for all φ in $\mathcal{D}_A$. The least upper bound for all such b is called the bound or norm of A and is denoted by $\|A\|$. Thus for all φ in $\mathcal{D}_A$ $\|A\varphi\| \leq \|A\|\,\|\varphi\|$. Bounded operators have particularly simple properties, but unfortunately few of the operators needed in quantum mechanics are bounded.

Although few operators are defined on all of $\mathcal{H}$ we do insist that the domain of any operator considered in this report be <u>dense</u>. That is, it is assumed that the domain contains arbitrarily good approximations to any element of $\mathcal{H}$. This is not a serious restriction physically since any physical "operator" is easily defined on some suitable dense domain and all subsequent considerations deal with extensions. On the other hand, from the mathematical viewpoint, entirely too little is known about an operator unless its domain is dense.

Consider the equation $(A-z)\varphi = \psi$ where the operator A, the

complex number z, and the element Ψ of $\mathcal{H}$ are given. This equation may have no solution φ. However, if it has more than one, we can choose distinct solutions φ_1 and φ_2 and then $A(\varphi_1-\varphi_2) = z(\varphi_1-\varphi_2)$, so z is an eigenvalue of A. Thus whenever the range $(A-z)\mathcal{D}_A$ of $(A - z)$ is dense in $\mathcal{H}$ and z is not in the point spectrum (set of eigenvalues) of A there is an operator $(A-z)^{-1}$ with domain $(A-z)\mathcal{D}_A$ which is inverse to $A-z$ in the sense that $(A-z)^{-1}(A-z)\varphi = \varphi$. $(A-z)(A-z)^{-1}\psi = \psi$ for any φ in $\mathcal{D}_A$ or any ψ in $(A-z)\mathcal{D}_A$. The set of complex numbers for which $(A-z)^{-1}$ is defined and bounded is called the resolvent set of A. For z in this set $(A-z)^{-1}$ is usually denoted by R_z and this family of operators depending on z is called the resolvent of z. The complex numbers which are not in the resolvent set of A form the spectrum of A which therefore certainly contains the point spectrum. The continuous spectrum is the set where $(A-z)^{-1}$ is defined (i.e. with dense domain) but not bounded.

The resolvent plays a key role in the theory but consideration of most of its properties must be postponed until other concepts are available. However, consider a bounded transformation A defined on all of $\mathcal{H}$ and a complex number z such that $|z| > \|A\|$. Then the series $-\sum_{n=0}^{\infty} z^{-n-1} A^n \psi$ (where $A^0\psi = 1\cdot\psi = \psi$ and A^n means A applied n times in succession) called the Neumann series, converges strongly and its limit φ satisfies $(A-z)\varphi = \psi$ since $(A-z)\left(-\sum_{n=0}^{N-1} z^{-n}A^n\psi\right) = \psi - z^{-N}A^N\psi$. Thus the resolvent set of a bounded transformation contains all sufficiently large z and the resolvent can be expressed by the Neumann series.

The adjoint[9] $A^\dagger$ of an operator A has for domain the set of all elements φ of $\mathcal{H}$ for which there exists an element $\varphi^\dagger$ of $\mathcal{H}$ which satisfies $(A\psi, \varphi) = (\psi, \varphi^\dagger)$ for all ψ in $\mathcal{D}_A$. When this condition is fulfilled, $A^\dagger\varphi$ is defined to be $\varphi^\dagger$ which can be shown to be unique since $\mathcal{D}_A$ is dense. From this definition we see that $(A\varphi, \psi) = (\varphi, A^\dagger\psi)$ whenever the two expressions are defined, and that the domain of $A^\dagger$ is the largest which allows this equation.

Several other important concepts can be defined in terms of the adjoint. Iff $A^\dagger$ is an extension of A then A is called Hermitian (or symmetric). Thus A is Hermitian iff $(\varphi, A\psi) = (A\varphi, \psi)$ for all φ and ψ in $\mathcal{D}_A$, and this implies that its eigenvalues are real. The operators of physics are Hermitian.

Suppose there is a sequence of functions φ_n in the domain of an operator A, and that both of the sequences φ_n and $A\varphi_n$ converge strongly. It is reasonable to expect that the domain of A can be extended to include the limit φ of the sequence φ_n, with $A\varphi$ defined as the limit of $A\varphi_n$. When A is Hermitian this is actually possible and the resulting operator is still Hermitian. If the domain of an operator A is enlarged by the inclusion of all such extensions, then the new operator is called the closure of A. In particular, if A is Hermitian its closure is $A^{\dagger\dagger}$. An operator which is equal to its own closure is called closed.[10] The resolvent of a closed operator is an analytic function of z throughout the resolvent set, and for each z it is a closed bounded operator defined on all of $\mathcal{H}$.

Most closed Hermitian operators can still be extended in infinitely many ways. The various extensions have different eigenvalues and eigenfunctions, and thus correspond to different operators in the physical sense as well as in the strict mathematical sense[11]. Furthermore, it is important that the set of eigenfunctions of an operator should be complete when the continuous spectrum is suitably included. This is not true for arbitrary Hermitian operators, because the appropriate eigenfunctions may not belong to the domain. Here we see very clearly the need to extend an operator. However, if a Hermitian operator is extended too far it loses its Hermitian character. For instance the adjoint of a Hermitian operator A is only Hermitian if it coincides with the original operator A.

IV. SELF-ADJOINT OPERATORS

An operator A is called <u>self-adjoint</u> when $A = A^{\dagger}$. Self-adjoint operators are exactly those for which the set of eigenfunctions is well defined and "complete" in the sense which we now explain.[12]

If we consider the nonrelativistic infinite nuclear mass Hamiltonian operator for hydrogen, a full set of its eigenfunctions is known. However, the set is not complete: to expand an arbitrary function, an integration over the unbound states is also needed. Since the wave functions of these states are not square integrable they do not represent elements of Hilbert space.

In order to express the type of completeness necessary in this situation, the idea of a resolution of the identity is essential.

Let us derive this concept in the simple case of a Hermitian operator A which has a complete set of eigenfunctions $\varphi_1, \varphi_2, \cdots$ in the usual sense. Let the corresponding eigenvalues which are not necessarily all different be $a_1, a_2 \cdots$. Then any function can be written as $\varphi = \sum_{n=1}^{\infty} (\varphi, \varphi_n)\varphi_n$ and $A\varphi = \sum_{n=0}^{\infty} a_n(\varphi, \varphi_n)\varphi_n$. If we consider an operator P_x for each real number x defined by $P_x\varphi = \sum_{a_n \leq x} (\varphi, \varphi_n)\varphi_n$, then in terms of the Stieltjes integral we can write

$$\varphi = \int_{-\infty}^{\infty} dP_x \varphi \qquad A\varphi = \int_{-\infty}^{\infty} x dP_x \varphi \quad \text{for} \quad \varphi \text{ in } \mathfrak{D}_A .$$

The second formula merely expresses the obvious fact that the contribution of each eigenfunction φ_n to φ is multiplied by a_n when A acts on φ. For each real number x P_x will be a <u>projection</u> operator onto the linear submanifold of all functions of the form $\sum_{a_n \leq x} b_n\varphi_n$ with $\sum_{a_n \leq x} |b_n|^2 < \infty$ for arbitrary complex b_n. Any projection operator P is defined on all of $\mathcal{H}$ and satisfies the conditions

$$P \cdot P = P \qquad P^{\dagger} = P \qquad 0 \leq (P\varphi, \varphi) = \|P\varphi\|^2 \leq \|\varphi\|^2 .$$

The range $P\mathcal{H}$ of a projection operator P is always a <u>closed</u> linear submanifold, i.e., if a sequence of elements $\varphi_1, \varphi_2, \cdots$ contained in $P\mathcal{H}$ converges to φ then φ is also contained in $P\mathcal{H}$. Thus projection operators are the simplest and most well behaved of all operators in Hilbert Space.

We have shown how to express any Hermitian operator with complete set of eigenfunctions in terms of a family of these projections. This family P_x can easily be shown to have the following properties as a function of x

$$\lim_{x \to -\infty} P_x \varphi = 0 \quad \text{for all } \varphi$$

$$\lim_{x \to +\infty} P_x \varphi = \varphi \quad \text{for all } \varphi$$

$$\lim_{\substack{x \to x_0 \\ x \geq x_0}} P_x \varphi = P_{x_0} \varphi$$

$$x \geq x_0$$

$$x \leq x' \text{ implies } P_x \cdot P_{x'} = P_{x'} P_x = P_x$$

Such a family of projections is called a resolution of the identity. The central theorem in this subject, the Spectral Theorem,[13] asserts that for any self adjoint operator A there exists exactly one resolution of the identity P_x such that the domain of A is the set of all φ with

$$\int_{-\infty}^{\infty} x^2 d \quad \| P_x \varphi \|^2$$

and such that

$$A \varphi = \int_{-\infty}^{\infty} x \, dP_x \, \varphi$$

for all φ in $\mathcal{D}_A$. It is also true that any operator so defined

is self-adjoint.

This is the property of self-adjoint operators which makes them so important.

In order to show that the concept of a resolution of the identity does replace that of a complete set of eigenfunctions, we must indicate how the discrete eigenvalues and their corresponding eigenfunctions can be derived from the resolution of the identity. Consider again the Hermitian operator A with its complete set of eigenfunctions and P_x defined above. If φ satisfies $A\varphi = a\varphi$, then

$$P_x(\varphi) = \begin{cases} \varphi & x \geq a \\ 0 & x < a \end{cases}$$

and P_x is discontinuous in x at a. Although it is somewhat more difficult to prove in general[14], the situation is the same for any self-adjoint operator, i.e., a real number a is an eigenvalue of A iff the resolution of the identity P_x belonging to A is discontinuous at a, in the sense that $\lim_{\substack{x \to a \\ x < a}} P_x \varphi$ does not equal $P_a \varphi$ for all φ.

Furthermore, φ is an eigenfunction belonging to a iff $P_a \varphi - \lim_{\substack{x \to a \\ x < a}} P_x \varphi = \varphi$.

The spectrum of a self-adjoint operator is completely confined to the real line, and consists exactly of the point spectrum (set of eigenvalues) and the continuous spectrum. A real number b

belongs to the spectrum of a self-adjoint operator A with resolution of the identity P_x iff P_x is not constant throughout any open interval containing b. Thus the continuous spectrum consists of the points at which P_x is continuous but not constant.

If $A = \int_{-\infty}^{\infty} x dP_x$ is a self-adjoint operator, then functions f(A) of A can be expressed by replacing x by f(x) in this expression. For instance $A^2 = AA = \int_{-\infty}^{\infty} x^2 dP_x$ which would be clear if A had a purely point spectrum, since then it merely states that the contribution of each eigenfunction is multiplied twice by its eigenvalue. We shall not develop the more difficult aspects of this highly important operational calculus[15] but only use a few simple expressions of this type. In particular if z is in the resolvent set of A we can express the resolvent R_z as $R_z = \int_{-\infty}^{\infty} \frac{dP_x}{x-z}$. If the distance of z to the nearest point of the spectrum of A is δ then clearly no component of an element acted on by R_z will be multiplied by a factor of magnitude greater than δ^{-1}. Thus $\| R_z \| \leq \delta^{-1}$, and in particular $\| R_z \| \leq |\mathrm{Im}(z)|^{-1}$ where Im(z) is the imaginary part of z. This is an immediate consequence of the fact that the spectrum of a self-adjoint operator is confined to the real axis and that the resolvent set contains at least all nonreal points.

It is of great importance that this fact almost characterizes self-adjoint operators. An operator is called <u>essentially self-adjoint</u> iff its closure is self-adjoint. To prove that a given operator is essentially self-adjoint one usually uses the fact that a Hermitian operator is essentially self-adjoint iff its resolvent

set contains points from both the upper and lower half plane. A self-adjoint operator A is closed since its closure is $A^{++} = A$. Therefore, we can characterize self-adjoint operators as those Hermitian operators A for which there exist points z in both upper and lower half plane with $(A-z)^{-1}$ defined on all of $\mathcal{H}$.

An essentially self-adjoint operator has only one self-adjoint extension which is its closure. Thus essentially self-adjoint operators define a unique resolution of the identity and can be used interchangeably with their self-adjoint closure. However, all Hermitian transformations which are not essentially self-adjoint either have no self-adjoint extensions or have infinitely many.

A Hermitian operator A is said to be bounded below (or half bounded) iff there exists a real number b such that $b(\varphi, \varphi) \leq (A\varphi, \varphi)$ for all φ in $\mathcal{D}_A$. Any such operator has one self-adjoint extension which can be distinguished from all others and which is called the Friedrichs extension.[16]

The method of proving this depends on replacing A by $B=A-b+1$ so that $(\varphi, \varphi) \leq (B\varphi, \varphi)$. Then the quadratic form $(B\varphi, \varphi)$ can be used as a norm for the "incomplete Hilbert space" $\mathcal{D}_A$. By completing this space and identifying its elements with elements of $\mathcal{H}$, the quadratic form is extended to a type called closed which is always defined by a self-adjoint operator. This operator is then the unique Friedrichs extension of $B = A-b-1$.

V. MANY ELECTRON NONRELATIVISTIC HAMILTONIAN

A fundamental problem of quantum chemistry is to find self-adjoint operators corresponding to the various physical observables on atomic and molecular systems. The most important case is that of finding energy operators. The Schrödinger Hamiltonian operator of an N-particle system reacting through Coulomb forces can be written

$$H = -\sum_{i=1}^{N} \frac{1}{2m_i} \nabla_i^2 + \sum_{i>j} \sum \frac{e_i e_j}{r_{ij}} \tag{1}$$

where e_i and m_i are the charge and mass of the i^{th} particle. Thus we wish to investigate whether this operator[17] is essentially self-adjoint on any reasonable domain, or whether great care must be taken to insure this property. A knowledge of the domain on which the operator is self-adjoint will settle all questions concerning the proper differentiability conditions on functions in its domain. Fortunately Kato in an important paper[8] published in 1951 showed that operators of a general type including the operator H of Eq. 1 are essentially self-adjoint when defined on any reasonable domain. The main requirement on the operator is that the potential energy should be the sum of locally square integrable functions in the relative coordinates of each pair of particles. This allows singularities of the form r_{ij}^{-m} if $m < 1.5$.

To begin the analysis Kato requires that the operator be defined on some domain (in the representation of $\mathcal{H}$ corresponding to square integrable functions on the configuration space) which at least includes the dense linear manifold generated by products of Hermite

orthogonal functions of the Cartesian coordinates of configuration space. When H is written as $T+U$ where T is the kinetic energy and U the potential energy operator, then in the momentum space representation of $\mathcal{H}$ T becomes multiplication by a polynomial. This type of operator is known to be essentially self-adjoint and the domain $\mathcal{D}_0$ of its self-adjoint closure T_0 is easy to characterize in the momentum space representation. A Fourier transform translates the definition of $\mathcal{D}_0$ into the configuration space representation again, and by using these two representations and the Fourier transform between them it is shown that any function φ in $\mathcal{D}_0$ when averaged over the space coordinates of all particles but one will be small compared to $\| T_0 \varphi \|$. This fact together with the restrictions on the potential energy operator U proves for any $b' > 0$ and sufficiently large a' the fundamental inequality:

$$\| U \varphi \| \leq a' \| \varphi \| + b' \| T_0 \varphi \| \qquad (2)$$

for all φ in $\mathcal{D}_0$. An easy calculation shows that $(T_0+V \pm ik)^{-1}$ is defined and bounded on all of $\mathcal{H}$ for sufficiently large real k.

From this we conclude the remarkable fact, of great importance in perturbation theory, that the closure of H is defined and self-adjoint on the same domain as its kinetic energy operator. This fact or inequality (2) directly can be taken to mean that despite the $1/r_{ij}$ singularities the kinetic energy operator is "larger" than the potential energy operator.

This is not the place to pursue the generalizations and many important consequences of this paper. The interested reader should

consult the very readable original work,[8] and also [4] [9] [10] [12]. Results which are important for perturbation theory will be mentioned as required.

VI. PERTURBATION THEORY

Perturbation theory calculates approximate solutions to a problem which is too difficult to admit of direct solution, by starting with a solution of a similar but easier problem and then making successively more elaborate attempts to bridge the gap remaining, by the addition of small corrections to the approximate solutions obtained. In the language of quantum mechanics, one usually wishes to find the eigenvalues and eigenfunctions of an operator $H(\lambda) = H_0 + \lambda H_1$ by successive corrections of corresponding eigenvalues and eigenfunctions of $H(0) = H_0$. Here λ is a real variable called the perturbation parameter and the operator λH_1 is considered to be small in comparison to H_0 in some sense. The physically interesting problem may correspond to a single value of λ, to several values, or to all values in some interval containing zero, but in any case it is convenient to retain λ as a bookkeeping device.

The simple assumption that the eigenvalues $E(\lambda)$ and eigenfunctions $\Psi(\lambda)$ of $H(\lambda)$ can be expanded in power series at $\lambda = 0$ leads to equations (4) and (5) by equating the coefficients of powers of λ in equation (3).

$$(H_0 + \lambda H_1)\left(\sum_{n=0}^{\infty} \lambda^n \psi^{(n)}\right) = H(\lambda)\,\psi(\lambda)$$

$$= E(\lambda)\,\psi(\lambda) = \left(\sum_{n=0}^{\infty} \lambda^n E^{(n)}\right)\left(\sum_{n=0}^{\infty} \lambda^n \psi^{(n)}\right) \qquad (3)$$

$$H_0 \psi^{(0)} = E^{(0)} \psi^{(0)} \tag{4}$$

$$(H_0 - E^0)\psi^{(n)} = \sum_{j=1}^{n} E^{(j)} \psi^{(n-j)} - H_1 \psi^{(n-1)} \tag{5}$$

These are the equations of Rayleigh-Schrödinger perturbation theory. Equation (4) which is a special case of (3) with $\lambda = 0$, merely expresses the fact that $\psi^{(0)}$ and $E^{(0)}$ are an eigenfunction and its eigenvalue of the unperturbed operator H_0. Although by themselves these equations usually do not determine unique solutions, we shall not be concerned with methods of removing this ambiguity nor with finding particularly convenient solutions which allow simple formulas for the $E^{(n)}$ in terms of the $\psi^{(n)}$.

The study of perturbed operators $H(\lambda)$ in Hilbert space shows some cases in which it can be proved that the eigenvalues and eigenfunctions of $H(\lambda)$ can be expanded in power series thus justifying the formalism of Rayleigh-Schrödinger perturbation theory and insuring the existence of solutions of (5) for all n. We shall call this situation regular perturbation. In some cases the series converge for the physically meaningful values of the parameter while in others the function defined by the series near $\lambda = 0$ must be analytically continued to the desired value of λ.

There are also perturbation problems in which equation (5) has solutions only for the first n integers or in which other criteria for regular perturbation are not satisfied. In some of these cases

the use of the partial perturbation series can be justified by a theory of asymptotic perturbation. This theory has also been extended to cover the difficult cases when the perturbation causes the spectrum to become completely continuous.

VII. REGULAR PERTURBATION

We wish to study a family of self-adjoint operators $H(\lambda)$ depending on a real parameter λ. We shall follow Kato[18] in calling such a family regular for $|\lambda| < \rho$ iff for some complex number z its resolvent $R_z(\lambda)$ can be expanded in powers of λ for $|\lambda| < \rho$.

There is nothing in this definition to prove that the domain $\mathcal{D}_\lambda$ of $H(\lambda)$ remains constant as λ varies. However, $\mathcal{D}_\lambda$ is constant in most important applications of the theory and in this case a much simpler characterization of regularity is possible. For convenience of later reference we state the relationship in two theorems.

Theorem 1[19] Let H_o be self-adjoint and H_n for $n = 1,2,\ldots$ be Hermitian on a domain $\mathcal{D}$. Let there exist nonnegative constants a,b,c such that

$$\| H_n \varphi \| \leq c^{n-1} \quad (a \| \varphi \| + b \| H_o \varphi \|) \qquad (6)$$

for $n=1,2,\ldots$ and for all φ in $\mathcal{D}$.

Then

$$H(\lambda) = \sum_{n=0}^{\infty} \lambda^n H_n \qquad (7)$$

is defined and self-adjoint on $\mathcal{D}$ for real λ with $|\lambda| < c^{-1}$ and is regular for real λ with $|\lambda| < (b+c)^{-1}$.

Theorem 2:[20] Let $H(\lambda)$ be a Hermitian operator on the domain $\mathcal{D}$ for each real value of λ with $|\lambda| < \rho$ and let $H(0)$ be self-adjoint. Then the following are equivalent:

1) $H(\lambda)$ is regular for $|\lambda| < \rho$

2) For every φ in $\mathcal{D}$ $H(\lambda)\varphi$ can be expanded in a power series about $\lambda = 0$ which converges at least for $|\lambda| < \rho$.

3) $H(\lambda)$ satisfies the hypotheses and therefore the conclusions of Theorem 1.

To prove Theorem 2 we can show 1) implies 2) implies 3) implies 1). Let $R_z(\lambda) = \sum_{n=0}^{\infty} \lambda^n R^{(n)}$ for some z as required by 1). Any element φ in the domain $\mathcal{D}$ of $H(\lambda)$ must be in the range of $R_z(\lambda)$ so we can write $\varphi = R_z(\lambda)\Psi$. Then $H(\lambda)\varphi = [(H(\lambda) - z) + z]R_z(\lambda)\Psi = \Psi + zR_z(\lambda) =$ $(\Psi + zR^{(0)}\Psi) + \sum_{n=1}^{\infty} \lambda^n (zR^{(n)}\Psi)$ which expresses $H(\lambda)\varphi$ as a power series as required by 2).

The H_n of Theorem 1 can be constructed from an $H(\lambda)$ satisfying 2) merely by considering the coefficient of λ^n in the expansion of each $H(\lambda)\varphi$. Since i is in the resolvent set of a self-adjoint operator such as $H(0) = H_o$, it follows that $H(\lambda)R_i(0)$ and $H_n R_i(0)$ are bounded and defined on all of $\mathcal{H}$.

Inequality (6) follows easily.

Since 1) is part of the conclusion of Theorem 1 it only remains to prove that theorem. Since $H(0) = H_o$ is self-adjoint we can write $R_{\pm ik}(0) = \int_{-\infty}^{\infty} \frac{1}{x \mp ik}\, dP_x$ where P_x is the resolution of the identity belonging to H_o. The inequality[6] provides a bound for $H_n R_{\pm ik}(0)$. Then for small enough $|\lambda|$ and large enough k we can expand $\left[1 + \sum_{n=1}^{\infty} \lambda^n H_n R_{\pm ik}(0)\right]^{-1}$ in a Neumann series. This proves the regularity since $R_{\pm ik}(\lambda) = R_{\pm ik}(0)\left[1 + \sum_{n=1}^{\infty} \lambda^n H_n R_{\pm ik}(0)\right]^{-1}$. $H(\lambda)$ is also seen to be self-adjoint since $R_{\pm ik}(\lambda)$ is defined on all of $\mathcal{H}$.

It will be seen that this discussion has led to the consideration of operators much more general than $H_o + \lambda H_1$. This greater generality does not complicate the theory and is occasionally helpful in application. The only essential difference when the H_n are all zero beyond a certain point is that the operator $H(\lambda)$ is defined for all real values of λ rather than in a restricted region. Even in the simpler case, however, it need not be regular except in the neighborhood of zero.

There is another criterion for regular operators which can be applied to a family of half bounded operators even when the domain varies with the perturbation parameter.

Theorem 3:[21] Let H_o be bounded below and let all H_n, $n=0,1,2,\cdots$ be Hermitian on the same domain $\mathcal{D}$. Let there be constants a,b,c and b,c, nonnegative such that

$$|(H_n \varphi, \varphi)| \leq c^{n-1}\left[a(\varphi, \varphi) + b\,(H_o \varphi, \varphi)\right] \qquad (8)$$

for every φ in $\mathcal{D}$ and $n=1,2,\ldots$. Then $(\sum_{n=0}^{\infty} \lambda^n H_n \varphi, \varphi)$ is a quadratic form bounded below and defined in $\mathcal{D}$ for $|\lambda| < (b+c)^{-1}$ and the self-adjoint operator $H(\lambda)$ which defines its closure is regular. If the $H_n=0$ for sufficiently large n then $\sum_{n=0}^{\infty} \lambda^n H_n$ is defined on $\mathcal{D}$ and $H(\lambda)$ is its Friedrichs extension.

For the proof, H_o can be replaced by $H = \mathcal{E}^2 + a + bH_o$ which has $\mathcal{E}^2$ for a lower bound by inequality (8). Thus $H^{-1/2}$ and $H^{-1/2} H_n H^{-1/2}$ for all n are bounded Hermitian operators which can be defined on all of $\mathcal{H}$ by using the Friedrichs extension of H. With the help of these operators $H(\lambda)$ can be written explicitly and its resolvent is again expanded in a Neumann series almost as in the proof of Theorem 1.

These two theorems show that on a suitable domain an operator given in the form $\sum_{n=0}^{\infty} \lambda^n H_n$ is self adjoint and regular when H_o satisfies appropriate conditions and the H_n satisfy one or the other of the related inequalities (6) or (8). In particular they remove the necessity of proving directly that the presumably poorly behaved operator $H(\lambda)$ is self-adjoint for nonzero λ .

When the inequalities (6) or (8) can be proved for any values of a,b,c the qualitative parts of this theory follow including in particular the existence of power series expansions near $\lambda = 0$ and thus the formalism of Rayleigh-Schrödinger perturbation theory. However, particularly when dealing with a non-degenerate eigenvalue, it is desirable to obtain small values of a,b,c in order to secure favorable estimates of the various quantities involved.

The specific results which can be obtained are given in the following theorems.

Theorem 4:[22] Let $H(\lambda)$ be self-adjoint and regular in some real neighborhood of $\lambda = 0$. Let E be an eigenvalue of finite multiplicity[23] m of $H(0)$ and let there be a positive number d such that the open interval $(E-d, E+d)$ is free from any other point of the spectrum of $H(0)$. Then there exist power series

$$E_1(\lambda), \cdots, E_m(\lambda)$$

and

$$\Psi_1(\lambda), \cdots, \Psi_m(\lambda)$$

all convergent in some neighborhood of $\lambda = 0$, which satisfy the following conditions:

1) $\Psi_j(\lambda)$ is an eigenfunction of $H(\lambda)$ belonging to the eigenvalue $E_j(\lambda)$ for each $j=1, \cdots, m$

2) $E_j(0) = E$ for each $j = 1, \cdots, m$ and for each real λ for which they are defined the $\Psi_j(\lambda)$ form an orthonormal set.

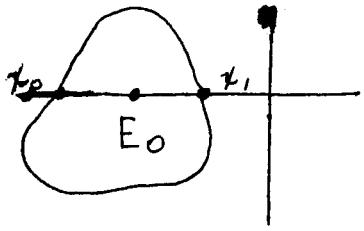
3) For each positive $d' < d$ there exists a positive number $\rho = \rho(d')$ such that the spectrum of $H(\lambda)$ in the interval $(E-d', E+d')$ for real λ with $|\lambda| < \rho$ consists exactly of the points $E_1(\lambda), \cdots, E_m(\lambda)$.

Theorem 5:[24] Let H_n for $n=0,1,2,\cdots$ and $H(\lambda)$ satisfy the hypotheses of Theorem 1. Let E_o be a nondegenerate eigenvalue (be an eigenvalue of finite multiplicity m, which does not split for $\lambda \neq 0$) of H_o and let it be the only point of the spectrum

of H_o in the interval $|E-E_o| < d$ for some positive d. Let $e = (2a/d) + 2b\left[1+(|E_o|/d)\right]$. Then for $|\lambda| < (c+e)^{-1}$ the spectrum of $H(\lambda)$ in the interval $|E-E_o| < d-(d/2)\left[e/(1-|\lambda|c)\right]$ consists of exactly one point eigenvalue $E(\lambda)$ which is nondegenerate (of multiplicity m) and which satisfies the inequality $|E(\lambda)-E_o| < (e/2)\left[e/(1-|\lambda|c)\right]$. Where defined $E(\lambda)$ can be expanded in a convergent power series. For $|\lambda| < (c+e)^{-1}$ there exists a power series $\Psi(\lambda) = \sum_{n=0}^{\infty} \lambda^n \Psi^{(n)}$ which is a normalized eigenfunction of $H(\lambda)$ with eigenvalue $E(\lambda)$. (there exist m power series $\Psi_j(\lambda)$ which for each real λ form a complete orthonormal set of eigenfunctions of $H(\lambda)$ belonging to the eigenvalue $E(\lambda)$).

Theorem 6:[25] Let H_n for n=0,1,2... and $H(\lambda)$ be as described in Theorem 3. Let E_o be the only point of the spectrum of H(0) in the interval (E_o-d, E_o+d). Let E_o be a non-degenerate eigenvalue (an eigenvalue of finite multiplicity which does not split for $\lambda \neq 0$). Then there exists a power series $E(\lambda)$ with $E(0) = E_o$ and a power series $\Psi(\lambda)$ (m orthonormal power series $\Psi_1(\lambda), \cdots, \Psi_m(\lambda)$) all convergent for $|\lambda| < [2a/d + 2b(1+(E_o/d)) + c]^{-1}$ and such that $H(\lambda)\Psi_j(\lambda) = E(\lambda)\Psi_j(\lambda)$.

These theorems are proved by integrating the resolvent $R_z(\lambda)$ of $H(\lambda)$ around a contour in the resolvent set. Let E_o be an isolated eigenvalue of H_o and C be a simple closed curve around E_o which neither includes nor passes through any other point of the spectrum of H_o and let C cross the real axis at $x_o < E_o < x_1$.



Then if the change in order of integration below is justified we get

$$-\frac{1}{2\pi i}\int_C R_z(\lambda)\,dz = -\frac{1}{2\pi i}\int_C \int_{-\infty}^{\infty} \frac{1}{x-z}\, dP_x(\lambda)\,dz \tag{9}$$

$$= \int_{-\infty}^{\infty} \left(-\frac{1}{2\pi i}\int_C \frac{dz}{x-z}\right) dP_x(\lambda) = \int_{x_0}^{x_1} dP_x(\lambda) = P_{x_1}(\lambda) - P_{x_0}(\lambda)$$

since $-\frac{1}{2\pi i}\int_C \frac{dz}{x-z} = \begin{cases} 1 \text{ for } x \text{ inside } C \\ 0 \text{ for } x \text{ outside } C \end{cases}$.

However, the regularity of $H(\lambda)$ guarantees that $R_z(\lambda)$ can be expressed in a power series in λ at some point z in the resolvent set and it follows that this is possible at every point. On a curve C which remains at a positive distance from the spectrum the radius of convergence of this representation will have a positive minimum which can be calculated when the hypotheses of Theorem 1 or 3 are given. This together with the fact that $R_z(\lambda)$ is also analytic in z can be used to justify the reversal of integration. Then it is easily seen that $P_{x_1}(\lambda) - P_{x_0}(\lambda)$ is a projection onto a finite dimensional space with dimension equal to the multiplicity of E_0, and formula (9) expresses this projection as a power series in λ when $|\lambda|$ is less than the minimum radius of convergence for the series expression of $R_z(\lambda)$ on C. When no splitting occurs under the perturbation then the eigenvalues and eigenfunctions can be obtained from this expression for $R_z(\lambda)$

as power series with the same radius of convergence. The other estimates in the theorem arise from comparing an upper bound of $\| R_z(\lambda) \|$ derived from its power series expansion in λ with its integral representation.

When a degenerate eigenvalue splits under perturbation, the projection operator $P_{x_1}(\lambda) - P_{x_0}(\lambda)$ can be obtained as before, but algebraic singularities may restrict the radius of convergence of series for the individual eigenvalues and eigenfunctions. Nevertheless, some quantitative estimates have been obtained in this case also.[28]

VIII. ASYMPTOTIC PERTURBATION SERIES

The theory of regular perturbation does not include all applications. In particular there are cases when only a finite number of terms of the perturbation series are well defined and finite. Kato[7] has developed a theory of asymptotic perturbation series which provides criteria for the usefulness of perturbation theory in some nonregular cases. For a regular perturbation series the errors divided by λ^N:

$$\left| E(\lambda) - \sum_{n=0}^{N} \lambda^{n} E(n) \right| \Big/ \lambda^N \qquad (10)$$

and

$$\left\| \Psi(\lambda) - \sum_{n=0}^{N} \lambda^{n} \Psi(n) \right\| \Big/ \lambda^N \qquad (11)$$

approach zero as λ approaches zero. We denote this by calling the errors $0(\lambda^N)$. It is this behavior of the partial sums of the perturbation series which Kato generalizes.

The derivation is based on Kato's generalized variational method.[5] If H is self-adjoint and $\|\Psi\| = 1$ is chosen so that $((H\Psi, \Psi)-d, (H\Psi, \Psi) + d)$ contains no eigenvalue of H except E then for some φ belonging to E

$$|E - (H\Psi, \Psi)| < \delta^2 d^{-1}$$

$$\|\varphi - \Psi\| < \delta d_1^{-1}$$

where $\delta = \|H\Psi - (H\Psi, \Psi)\Psi\|$ and d_1 is of the same order of magnitude as d. When the n^{th} partial sum of the perturbation series is used for Ψ then δ becomes formally of order n. The theory consists in justifying this formal application, and Kato summarizes the rather complicated hypotheses and conclusions by saying "roughly speaking, perturbation method gives asymptotic series in ascending powers of the parameter λ which are correct so far as the coefficients can be calculated by means of operations within the Hilbert space".[25]

Kato considers the operator $H_o + \lambda H_1$ defined on the common domain $\mathfrak{D}$ of H_o and H_1 which he assumes Hermitian. The operator H_o restricted to $\mathfrak{D}$ must have a unique self-adjoint extension, but this is <u>not</u> always required for $H_o + \lambda H_1$. The operator $H(\lambda)$ for $\lambda \geq 0$ is chosen as some self-adjoint extension

of $H_o + \lambda H_1$ and as the Friedrichs extension when that is defined. Thus $H(\lambda)$ may be highly discontinuous for $\lambda > 0$, but as λ approaches zero it has the limiting behavior described below.

These conditions must be strengthened before significant conclusions can be drawn. First we assume either that H_o is essentially self-adjoint on $\mathcal{D}$ or that there exist constants a,b,c such that

$$(H_o\Psi, \Psi) \geq c(\Psi, \Psi)$$
$$(H_1\Psi, \Psi) \geq a(\Psi, \Psi) + b(H_o\Psi, \Psi) \tag{12}$$

for all Ψ in $\mathcal{D}$. With these conditions it is possible to show that in any neighborhood of an eigenvalue E of H_o with finite multiplicity m there are at least m points of the spectrum of $H(\lambda)$ (counting multiplicity) for sufficiently small λ. This means that these points of the spectrum are continuous functions of λ at $\lambda = 0^+$. Thus perturbation method is justified to the 0^{th} approximation. Note that the possibility that the spectrum of $H(\lambda)$ may be continuous for $\lambda > 0$ is not ruled out.

If we further assume that $H(\lambda)$ does not have more than m independent functions belonging to points of its spectrum near E then higher approximations are shown to be asymptotic when the coefficients can be calculated within Hilbert space. For instance, if all eigenfunctions with eigenvalue E belong to the domain of H_1 then (in an obvious notation)

$$E_j(\lambda) = E + \lambda E_j^{(1)} + \lambda^2 E_j^{(2)} + o(\lambda^2)$$

$$\varphi_j(\lambda) = \varphi_j + \varphi_j^{(1)} + o(\lambda)$$

It is extremely difficult to establish this last condition on the multiplicity of the perturbed spectrum except in the following cases:

1) $H(\lambda)$ is regular and self-adjoint thus justifying the much more complete theory of the last section.

2) Inequality(12)is satisfied and the spectrum of $H(0)$ below E consists of finitely many points of finite multiplicity.

Thus although this theory of asymptotic perturbation series may apply to important problems where the perturbation is not regular, it is difficult to establish its hypotheses in these cases. One of its chief advantages is that it does facilitate investigation of situations in which the theory of regular perturbation is clearly too demanding, such as perturbation causing the spectrum to become continuous.

When perturbation theory is applied to problems like the Stark effect in which the spectrum of $H(\lambda)$ becomes completely continuous for $\lambda \neq 0$, it is necessary first to consider what the series is approximating. Physically an atom in a weak electric field has almost stable states, and it is the analogue of these which must be described mathematically. Since the objects being approximated are not very clearly defined, it is obvious that the

asymptotic formulation of perturbation theory is more appropriate for their study since it only demands a definition of these objects up to a certain order in λ .

We can expect that almost stable states will have wave functions which make $\| (H-E)\, \varphi \|$ quite small for appropriate E since then the Schrödinger time equation will ensure that the state changes slowly. However, this is not enough to characterize the states which we wish to study, since for any point E of the continuous spectrum of an operator H there are φ which make $\| (H-E)\, \varphi \|$ arbitrarily small. For most points of the continous spectrum though, a function φ chosen to minimize this quantity will become more and more diffuse in space as it approximates a typical non-square integrable "eigenfunction" of the continuous spectrum. We do not wish to study such wave functions which belong to unbound states. Thus we are led to introduce the closed submanifold of $\mathcal{H}$ which consists of functions which are zero outside of some bounded region of configuration space which includes the physical system. Actually the projection P onto this sub-manifold is all that is needed. We wish to study functions Ψ for which $P\Psi$ is (at least approximately) equal to Ψ .

Let E^o be an eigenvalue of H_o of finite multiplicity m and let us assume that solutions to the perturbation equations can be constructed by Hilbert space operations at least through the N^{th} order. If the resulting N^{th} partial sums of the perturbed eigenvalues and eigenfunctions are denoted by $E_1^{(N)}(\lambda), \ldots, E_m^{(N)}(\lambda)$; $\Psi_1^{(N)}(\lambda), \cdots, \Psi_m^{(N)}(\lambda)$ then a calculation shows that

$$\left\| (H(\lambda) - E_j^{(N)}(\lambda))\ \psi_j^{(N)}(\lambda) \right\| = 0(\lambda^N),$$

Thus satisfying one of the criteria for an almost stable state. Under the general hypotheses discussed previously there are at least m independent functions which belong to the spectrum of $H(\lambda)$ near E^o. If it can be shown that those which correspond to almost stable states are exhausted in some sense by those calculated by perturbation theory, then its use as an asymptotic series will be fully justified.

The desired criterion can be formulated with the help of several more projection operators. Let $P_x(\lambda)$ be the resolution of the identity belonging to $H(\lambda)$ and let $P^{(N)}(\lambda)$ be the projection onto the closed submanifold generated by $\psi_1^{(N)}(\lambda),\cdots,\psi_m^{(N)}(\lambda)$. Then

$$\left\| (P_{E^o+\varepsilon}(\lambda) - P_{E^o-\varepsilon}(\lambda))\ P - P^{(N)}(\lambda) \right\| = 0(\lambda^N)$$

(where ε is some small positive number) expresses the fact that the functions ψ for which $P\psi = \psi$ and $\left|(H(\lambda)\psi, \psi) - E^o(\psi, \psi)\right| < \varepsilon$ can be expressed up to $0(\lambda^N)$ as linear combinations of the $\psi_j^{(N)}(\lambda)$. This expression can be proved when $\mathcal{D}_{H_1}$ contains the sub-manifold $P\mathcal{H}$ and enough other functions to allow calculation of the N^{th} order perturbed eigenvalues and eigenfunctions.

APPLICATIONS TO QUANTUM-CHEMISTRY

The most important application of the theory outlined above concerns the electron repulsion terms in N-electron atoms, molecules, or ions. The theory shows that these terms can indeed be regarded as perturbations of the non-relativistic independent electron model. The considerations of Section V concerning the Hamiltonian (equation (1)) can easily be altered to show that the hypotheses of Theorem 1 are satisfied for any such perturbation problem. As an example consider an N-electron atom in which for simplicity, although this is not necessary, we shall regard the nucleus as of infinite mass and thus fixed in space. Using atomic coordinates scaled by the atomic number Z we write the Hamiltonian as

$$H = H_o + \frac{1}{Z} H_1 = T_o + W + \frac{1}{Z} H_1$$

where T_o is the closure of $-\frac{1}{2} \sum_{j=1}^{N} \nabla_j^2$

$$W = -\sum_{j=1}^{N} \frac{1}{r_j} \qquad H_1 = \sum_{i>j} \sum \frac{1}{r_{ij}} .$$

The considerations of Section V immediately apply with U replaced by either W or H_1 and so for all φ in $\mathcal{D}_0$ we get

$$\| H_1 \varphi \| \leq a' \| \varphi \| + b' \| T_o \varphi \|$$

$$\| W \varphi \| \leq a'' \| \varphi \| + b'' \| T_o \varphi \|$$

where b' and b'' may both be taken arbitrarily small. However,

$$\| T_o \varphi \| = \| H_o \varphi - W \varphi \| \leq \| H_o \varphi \| + \| W \varphi \|$$

$$\leq \| H_o \varphi \| + a'' \| \varphi \| + b'' \| T_o \varphi \|$$

and therefore

$$\| H_1 \varphi \| \leq \left(a' + \frac{a''}{1-b''} \right) \| \varphi \| + \frac{b'}{1-b''} \| H_o \varphi \|$$

This is obviously a very crude estimate but the coefficient of $\| H_o \varphi \|$ can still be made arbitrarily small. Therefore the perturbation is <u>regular on the whole real axis</u>, even though the radius of convergence at the origin may be very small. Thus for any real number λ_o we may take $H_o' = H_o + \lambda_o H_1$ as an unperturbed operator and apply the theory to $H'(\lambda') = H_o' + \lambda H_1$. If the state under investigation belongs to an isolated eigenvalue of H_o' of finite multiplicity, then it and its eigenfunctions can be expanded in a power series around λ_o. Thus the energy and wave function of any state of a complex atom can be analytically continued in λ along the real axis between atoms of any atomic number ($\lambda = 1/Z$) and an atom with independent electrons, so long as the energy of these states do not enter the continuous

spectrum or cross eigenvalues of infinite multiplicity. In particular no difficulty occurs when the energy of one state crosses that of another. Such crossings certainly occur in the periodic table. This result offers the strongest possible justification for the use of sets of hydrogenic quantum number to describe the states of complex atoms.

When perturbation theory is used to calculate the actual energy of an atomic state the radius of convergence of the series rather than its analytic character is of interest. Because of the great generality of the theory reviewed here, it naturally does not give very close lower bounds on the convergence radius when applied to specific problems. Nevertheless Kato[7], p.172, was able to obtain a radius of convergence of .013 for the perturbation treatment of the ground state of a two electron atom. This ensures that a perturbation calculation of this state converges at least for O^{6+} or atoms of higher atomic number.

Other applications of this theory are to the Stark effect[7], p.204; the diatomic molecule[7], p.194 and to the Zeeman effect[7], p. 195 and[20], p.570. The Stark effect and Zeeman effect pose difficulties because the applied field is not bounded throughout space. Thus the perturbed spectrum in the Stark effect is completely continuous and the theory for weakly quantized states is applied. In the spin-free Zeeman effect for hydrogen a different problem arises. The presence of the magnetic field separates the energy levels of wave functions with different

magnetic quantum number m, and in fact the perturbation energy is λm in suitable units. Thus no matter how small the field strength, infinitely many states with sufficiently high magnetic quantum number will cross any given state of low magnetic quantum number. In other words for any non-zero value of λ there is no interval about an unperturbed energy level which remains free of "foreign" eigenvalues. Thus the perturbation cannot be regular by Theorem 4. However, this difficulty is not serious. Consider the operator L_z for the component of angular momentum in the direction of the applied field. This commutes with both the unperturbed and perturbed Hamiltonian which thus carry functions of magnetic quantum number m into other such functions. Let $\mathcal{H}_m$ be the set of all functions φ with $L_z\varphi = m\varphi$ in the Hilbert space $\mathcal{H}$ of square integrable functions on 3 space (the space of hydrogen wave functions). Then $\mathcal{H}_m$ with the inner product of $\mathcal{H}$ certainly satisfies all the properties of a Hilbert space except that it is possibly not complete. However, any sequence of functions in $\mathcal{H}$ all of which satisfy $L_z\varphi = m\varphi$ converges to a function satisfying this condition and thus converges in $\mathcal{H}_m$ also. Therefore $\mathcal{H}_m$ is another representation of Hilbert space and the operator for the Zeeman effect is defined in $\mathcal{H}_m$ and can be studied there.

A similar procedure can sometimes be used to reduce a particular degenerate eigenvalue to a non-degenerate eigenvalue in a Hilbert space of symmetrized functions thus allowing the use of the more complete theory available for that case. This would be helpful in discussing the excited states of a two electron atom for instance.

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1. I rather pedantically insist on speaking of abstract Hilbert space to emphasize that the rigorous mathematical theory is intended rather than the somewhat informal use of the language of Hilbert space theory which is prevalent in discussions of quantum mechanics.

2. Numbers in square brackets refer to the bibligraphy.

3. [16] see Chapter 1 in particular.

4. See the remarks and reference in [30] p. 98.

5. See Kemble [13] pp. 79 and 197-201. See also the excellent discussion in Kato [8] pp. 195, 196 and 205. Actually if eigenfunctions exist their properties do follow from the general theory of differential equations, but their existence definitely does not.

6. The older literature usually reserves the term Hilbert space for the object defined here which is unique up to isomorphism. However, it is now customary to use the term Hilbert space for any real or complex vector space complete in a norm which comes from an inner product. Thus we should speak of complex separable Hilbert space. Separable is a topological term designating a space with a countable dense subset. The terminology and notation of this report follows the current practice of quantum chemistry whenever convenient. Exceptions are usually noted. Only an introduction to the concepts of Hilbert space can be given. The interested reader should consult one of the many books available in this field for further details. The classical book of Stone [30] is recommended for its completeness and careful development. However, many simplifications of the theory have been introduced

since its publication. A good source for these more recent developments of the basic theory is [27].

For the application of the theory to quantum mechanics von Neumann [16] is an indispensible source.

7. In books on physics the term norm is sometimes applied to (φ,φ) itself. [13] p. 116. However, the usage given here is standard among mathematicians. The inner product is sometimes also slightly altered so that $(a\varphi, \psi) = (\varphi, \bar{a}\psi) = \bar{a}(\varphi,\psi)$. We use a bar to denote complex conjugate.

8. The objects called operators here are more properly linear operators on linear transformations.

9. Von Neumann defines adjoint differently p. 92, but the definition given here is more useful for our purposes and is quite standard. R.N. p. 299.

10. A helpful and illuminating discussion of these ideas in terms of the graph of an operator is given in R.N. pp. 303-307.

11. A very illuminating example of the relation between Hermitian operators and their self-adjoint extensions is given in [27] p. 309-311.

12. Von Neumann [16] pp. 102-170, gives a very thorough discussion of the ideas we outline here.

13. See for instance [27] p. 313.

14. For this and related matters see von Neumann [16] p. 103-131.

15. A complete but difficult discussion is in [30] p. 128-154.

16. See [27] pp. 329-335 for this beautiful proof.

17. Both because this operator can be shown to be half bounded and because it is real it can be shown that any domain on which it is Hermitian does have at least one extension on which it is self-adjoint.[27] p. 329.

18. [7] p. 154. This is equivalent to Rellich's original definition. [20] p.559. Definition 1,2, Satz 1. A good discussion of the idea behind these definitions is given in[24] pp. 94-99.

19. [20] p. 562. Satz 5 also[7] p. 163.

20. This theorem is essentially due to Rellich[22] p. 476, Hilfsatz 4.

21. [7] p. 164.

22. [20] p. 560. Satz 3.

23. We allow m=0 which is interpreted to mean the absence of any point of the spectrum from the various intervals.

24. This theorem is essentially Theoreme II of Sz. Nagy [15]. However, a refinement of the proof by Kato[7] p. 157-162 allows an improvement in the convergence radii. The main points of the theorem were first proved by Rellich[21], p. 360, Satz 1.

25. [7] pp. 164, 169.

X. REMARKS ON THE BIBLIOGRAPHY

The most complete general survey of regular perturbation is still the five papers of Rellich [18], .. [23] published between 1936 and 1942. The first and second papers deal mainly with bounded operators and with continuous perturbation respectively. The bulk of the theory for unbounded operators is contained in [20] and [21] while [22] chiefly studies operators with completely discrete spectra all points of which are regular. However, all five papers contain illuminating examples and counter examples. Some of this material appears in English in [24].

The methods of proof used by Rellich are greatly simplified in [15] which gives the clearest and most direct proofs of the main theorems. Some further improvements have been made by Kato and appear together with his theory of asymptotic perturbation in his excellent paper [7], a summary of which is published in [6].

The forthcoming book by Friedrichs [2] promises to be of great interest when it is published in 1964. Schröder [28] and Speisman [29] contain different estimates of the convergence radii for operators of the form $H_o + \lambda H_1$ which may be superior in some cases. Titchmarsh [30], Murray, [14] and Primas [17] all use different mathematical techniques to study perturbation problems.

Other papers in the bibliography extend the theory in various ways.

BIBLIOGRAPHY

1 . Friedrichs, K. O. On the Perturbation of Continuous Spectra, Comm. on Applied Math. Vol. 1 (1948), pp. 361-406.

2 . ---, Perturbation of Spectra in Hilbert Space, AMS Lecture in Applied Math. 1964.

3 . Heinz, E., Beiträge zur Störungstheorie der Spektralzerlegung, Math. Ann., 123, pp. 415-438, 1951.

4 . Ikebe, T. and Kato, T., Uniqueness of the Self-Adjoint Extension of Singular Elliptic Differential Operators, Arch. for Rat. Mech. Anal., 9, pp. 77-92, 1962.

5. . Kato, T., On the Upper and Lower Bounds of Eigenvalues, J. Phys. Soc., Japan, 4, pp. 334-339, 1949.a

6. . --- , On the Convergence of the Perturbation Method I. Prog. of Theoret. Phys. vol. 4, pp. 514-523, 1949.b II. Prog. of Theoret. Phys. vol. 5, pp. 95-101, 207-212, 1950.

7 . --- On the Convergence of the Perturbation Method. Journ. Faculty of Sci., University of Tokyo, vol. 6, pp. 145-226, 1951.

8. --- Fundamental Properties of Hamiltonian Operators of Schrödinger type, Trans. Amer. Math. Soc., 70, pp. 195-211, 1951.

9. --- On the Existence of Solutions of the Helium Wave Equation, Trans. Amer. Soc., 70, pp. 212-218, 1951.

10. --- Notes on Some Inequalities for Linear Operators, Math. Ann. 125, pp. 208-212, 1952.

11 . --- Perturbation Theory of Semi-Bounded Operators, Math. Ann., 125, pp. 435-447, 1953.

12 . --- On the Eigenfunctions of Many Particle Systems in Quantum Mechanics, Div. of Electromagnetic Res. N.Y.U. Inst. of Math. Sci., Res. Report No. CX 25, 1956.

13 . --- Kemble, E.C., The Fundamental Principles of Quantum Mechanics with Elementary Applications, N.Y. 1958, Dover.

14 . Murray, F. J., Perturbation Theory and Lie Algebras, J. Math. Phys., 3, pp. 451-468, 1962.

15 . Sz. Nagy, B. Perturbations des transformations auto-adjointes dans l'espace de Hilbert, Commentarii Math. Helv., 19, pp. 347-366, 1947.

16 . Neumann, J. von, Mathematical Foundations of Quantum Mechanics, Tr. by R. T. Beyer, Princeton, 1955, (Princeton U. Press.)

17 . Primas, H., Eine verallgemeinerte Störungstheorie fur Quantenmechanische Mehrteilchenprobleme, Helv. Phys. Acta, 34, pp. 331-351, 1961.

18 . Rellich, F., Storungstheorie der Spektralzerlegung, I. Math. Ann., 113, pp. 600-619, 1936.

19 . " II. Math. Ann., 113, pp. 677-685, 1936.

20 . " III. Math. Ann.,116, pp. 555-570, 1939.

21 . " IV. Math. Ann., 117, pp. 356-382, 1940.

22 . " V. Math. Ann., 118, pp. 462-484, 1942.

23 . --- Störungstheorie der Spektralzerlegung, in Proc. of the International Congress of Mathematicians, Cambridge,

Mass., 1950, (A.M.S., Providence, R.I., pp. 606-613, 1952).

24 . --- Perturbation Theory of Eigenvalue Problems, N.Y. 1953, (N.Y.U. Institute of Math. Sci.) 1953 a.

25 . --- New Results in the Perturbation Theory of Eigenvalue Problems, in Simultaneous Linear Equations and Determination of Eigenvalues, N.B.S. publ. No. 29, Washington, D.C., 1953 b.

26 . --- Linearly Perturbed Operators, in Report of an International Conference on Operator Theory and Group Representations, pp. 30-36, Washington, D.C., 1955, (Publ. 387, Nat. Acad. of Sci., Nat. Res. Council.).

27 . Riesz, F., and Sz.-Nagy, B., Functional Analysis, Tr. by L.F. Boron, Ungar, New York, 1955.

28 . Schröder, J., Fehlerabschätzungen zur Störungsrechnung bei linearen Eigenwertproblemen mit Operatoren eines Hilbertschen Raumes, Math. Nachr., 10, pp. 113-128, 1953.

29 . Speisman, G., Convergent Schrödinger Perturbation Theory Phys. Rev. 107, pp. 1180-1192, 1957.

30 . Titchmarsh, E. C., Eigenfunction Expansions Associated with Second Order Differential Equations, 2 vols., Oxford, 1946, 1958.

. Stone, M. H., Linear Transformations in Hilbert Space, New York, 1932 (Amer. Math. Soc.).