

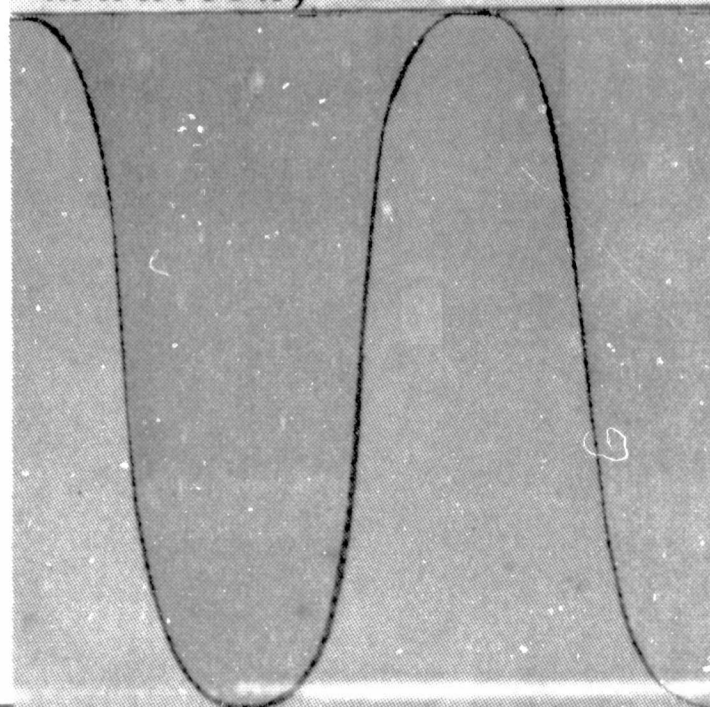
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ON ITERATIVE SOLUTIONS FOR
QUANTUM-MECHANICAL BOUND STATES

Peter D. Robinson

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ABSTRACT

Iterative methods of solving Schrödinger's time-independent wave equation for bound states are considered. The usual differential equation in coordinate space is transformed into an integral equation by means of an appropriate Green's Function. The choice of Green's Function is to some extent arbitrary, but for simplicity the free-particle one is used. Other choices lead to various perturbation theories. Free-particle Green's Functions are discussed for various situations, for both negative and positive energies. The corresponding integral equations are developed in momentum space. The relevant theory of homogeneous linear integral equations is quoted, and its applicability to the iterative solution of the appropriate equations is considered. Two essentially different types of eigenvalue problems arise from Schrödinger's equation; one is relevant for nuclear systems and the other for atomic and molecular systems. The iterative method is better adapted to the former, but in certain circumstances it is suitable for the latter, especially with Coulomb potentials. The work of previous authors is briefly discussed, and possibilities for future progress are suggested.

CONTENTS

1	Introduction	1
2	Perturbation Theories	4
3	Free-particle Green's Functions for negative energy	6
	3.1 Three dimensions	6
	3.2 One dimension $(-\infty, \infty)$	7
	3.3 One dimension $(0, \infty)$	7
	3.4 Higher dimensions	9
4	Free-particle Green's Functions for positive energy	10
5	Momentum Space	12
6	Homogeneous Linear Integral Equations	14
	6.1 Iterative solutions for a symmetric kernel	14
	6.2 Symmetrizable kernels	18
	6.3 Applicability of the iterative scheme	20
7	The different types of eigenvalue problem	23
	7.1 Determination of energy eigenvalues and eigenfunctions	23
	7.2 Coulomb potentials	24
8	Previous work and possible future progress	26
	Acknowledgments	28
	References	29

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ON ITERATIVE SOLUTIONS FOR QUANTUM-MECHANICAL BOUND STATES

Peter D. Robinson*

§ 1. INTRODUCTION

In the vast literature concerning approximate methods of solving the simple Schrödinger equation

$$\left\{ -\frac{1}{2} \nabla^2 + V(\underline{r}) - E \right\} \psi(\underline{r}) = 0, \quad (1)$$

there is relatively little direct mention of iterative solutions for bound (square integrable) states. This is surprising in view of the popularity of such solutions for continuum states in scattering theory, and also of the readiness with which iterative procedures can often be adapted to numerical work. Thus it is perhaps worthwhile to investigate some of the problems involved in obtaining solutions by iteration, to mention briefly some of the work of previous authors, and to indicate avenues for possible future progress.

Integral equations are far more receptive to iteration than are differential equations, and so the first logical step is to convert (1) into an integral equation with the help of an appropriate Green's Function. In principle, this can be done in many different ways. For example, let us suppose that the potential $V(\underline{r})$ may be expressed in the form

$$V(\underline{r}) = u(\underline{r}) + v(\underline{r}), \quad (2)$$

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and that the exact eigenfunctions and eigenvalues of the equation

$$\left\{ -\frac{1}{2}\nabla^2 + u(\underline{r}) - E \right\} \psi(\underline{r}) = 0 \quad (3)$$

are known. Then the Green's Function $G(\underline{r}, \underline{r}')$ of the operator on the left of (3) is known. Thus, writing (1) in the form

$$\left\{ -\frac{1}{2}\nabla^2 + u(\underline{r}) - E \right\} \psi(\underline{r}) = -v(\underline{r}) \psi(\underline{r}), \quad (4)$$

it is evident that bound-state solutions of (1) satisfy the integral equation

$$\psi(\underline{r}) = - \int G(\underline{r}, \underline{r}') v(\underline{r}') \psi(\underline{r}') d\underline{r}'. \quad (5)$$

In this paper we are chiefly concerned with solutions of (5) which can be obtained by iteration according to the scheme

$$\psi_{n+1}(\underline{r}) = - \int G(\underline{r}, \underline{r}') v(\underline{r}') \psi_n(\underline{r}') d\underline{r}'. \quad (6)$$

Reverting back to (4), this means that

$$\left\{ -\frac{1}{2}\nabla^2 + u(\underline{r}) - E \right\} \psi_{n+1}(\underline{r}) + v(\underline{r}) \psi_n(\underline{r}) = 0, \quad (7)$$

and so $\psi_{n+1}(\underline{r})$ is to be a solution of a Schrödinger-type equation with effective potential

$$V_{\text{eff.}}(\underline{r}) = u(\underline{r}) + v(\underline{r}) \frac{\psi_n(\underline{r})}{\psi_{n+1}(\underline{r})}. \quad (8)$$

Thus we shall reach a solution of (1) provided that the sequence $\{\psi_n(\underline{r})\}$

has a limit $\psi(\underline{r})$ as $n \rightarrow \infty$.

In actual fact the potentials $u(\underline{r})$ for which the Green's Function $G(\underline{r}, \underline{r}')$ is known are few in number, and these functions can be very complicated.^[1] Furthermore, it may not be sensible to express the true potential $V(\underline{r})$ in the form (3) using one of the tractable u 's. Therefore in the interests of simplicity and uniformity we will concentrate on the situation where $u(\underline{r})$ is identically zero, so that $V(\underline{r}) \equiv v(\underline{r})$, and the Green's Function is that for a free particle.

The outline of the main part of this paper is as follows. In §3, the free-particle Green's Functions are given for negative energy, together with the corresponding integral equations for bound states. The situation for positive energy is discussed in §4. In §5, analogous integral equations are given in momentum space; these arise naturally from the Fourier Transform of the Schrödinger equation. The theory of homogeneous linear integral equations on which the iterative scheme (6) is based follows in §6, together with some discussion of the difficulties in adapting the theory for our purposes. The two essentially different types of eigenvalue problem are discussed in §7. The relationships between the two species of eigenvalue and eigenfunction are investigated, and are shown to be especially close for Coulomb potentials. Finally, in §8 the work of some previous authors is mentioned and possibilities for future progress are suggested.

However, before proceeding with the main discussion in §3, we should remark that (6) is by no means the only iterative scheme which is possible for the integral equation (5). Indeed, (5) is the starting point of the various perturbation theories for bound states, and in §2 we digress for a brief mention of the iterative procedure on which they are based. This digression is perhaps not out of place, as it is instructive to compare the different iterative schemes.

§2. PERTURBATION THEORIES

Let us suppose that equation (3) admits bound-state solutions $\{\phi_j\}$ (assumed orthonormalized) with eigenvalues ϵ_j . Then $G(\underline{r}, \underline{r}')$ is the sum of $G_1(\underline{r}, \underline{r}')$ and $G_2(\underline{r}, \underline{r}')$ where

$$G_1(\underline{r}, \underline{r}') = \sum_j \phi_j(\underline{r}) \phi_j(\underline{r}') (\epsilon_j - E)^{-1} \quad (9)$$

and $G_2(\underline{r}, \underline{r}')$ is the corresponding integral over the continuum states. The bound-state solution of (5) which tends to, say, $\phi_i(\underline{r})$ as $v(\underline{r})$ vanishes is given by removing the ϕ_i term from the integral and then multiplying ψ by a constant so that the coefficient of $\phi_i(\underline{r})$ becomes unity. The effect of this is to impose on $\psi(\underline{r})$ the extra condition

$$E - \epsilon_i = \int \phi_i(\underline{r}') v(\underline{r}') \psi(\underline{r}') d\underline{r}' , \quad (10)$$

and equation (5) then becomes

$$\psi(\underline{r}) = \phi_i(\underline{r}) - \int G_1^\dagger(\underline{r}, \underline{r}') v(\underline{r}') \psi(\underline{r}') d\underline{r}' . \quad (11)$$

The $\dagger$ indicates that the $j = i$ term has been removed from G_1 in (9).

Equations (10) and (11) together define the bound state $\psi(\underline{r})$ and eigenvalue E (if they exist) which tend to ϕ_i and ϵ_i as $v(\underline{r})$ shrinks to zero.

Equation (11) is a non-homogeneous linear integral equation of Fredholm type, whose solution can in principle be obtained by iterating according to the scheme

$$\left. \begin{aligned} \psi_0(\underline{r}) &= \phi_i(\underline{r}) , \\ \psi_{m+1}(\underline{r}) &= \phi_i(\underline{r}) - \int G^+(\underline{r}, \underline{r}') v(\underline{r}') \psi_m(\underline{r}') d\underline{r}' . \end{aligned} \right\} \quad (12)$$

The corresponding iterates to E are defined from (10) by

$$E_m - \epsilon_i = \int \phi_i(\underline{r}') v(\underline{r}') \psi_m(\underline{r}') d\underline{r}' , \quad (13)$$

and the analogue of equation (7) is

$$\left\{ -\frac{1}{2} \nabla^2 + u(\underline{r}) - E \right\} \psi_{m+1}(\underline{r}) + v(\underline{r}) \psi_m(\underline{r}) = (E_m - E) \phi_i(\underline{r}) , \quad (14)$$

showing that we again reach a solution of (1) provided that the sequence $\{\psi_m\}$ has a limit ψ as $m \rightarrow \infty$ (and hence $E_m \rightarrow E$).

This iteration process here is not as simple as that defined by (6), but it is well adapted to situations where $v(\underline{r})$ can be regarded as a small perturbation to a potential $u(\underline{r})$ for which the solutions of the Schrödinger equations are known. The familiar Rayleigh-Schrödinger perturbation theory as well as the Brillouin-Wigner theory can be derived^[2] from (12) and (13), and Fredholm perturbation theory arises from applying Fredholm's iterated kernel method directly to (11). The Rayleigh-Schrödinger theory is one of the most useful tools^[3] in obtaining approximate solutions of (1), but its relation to an iterative procedure is often forgotten. Recently Hirschfelder^[3] has proposed a different kind of iteration for first-order Rayleigh-Schrödinger corrections to eigenfunctions.

§3. FREE-PARTICLE GREEN'S FUNCTIONS FOR NEGATIVE ENERGY

In this section we give the Green's Functions appropriate to a 'free particle' with negative energy $E = -\frac{1}{2}k^2$, where $k > 0$. When $V \equiv v$, equation (4) can be written as

$$(\nabla^2 - k^2)\psi(\underline{r}) = 2V(\underline{r})\psi(\underline{r}) . \quad (15)$$

For convenience we have removed the factor $-\frac{1}{2}$, and so here the Green's Function $G(\underline{r}, \underline{r}')$ will be $-\frac{1}{2}$ times $G(\underline{r}, \underline{r}')$ with $u \equiv 0$. It is defined as the solution of the equation

$$(\nabla^2 - k^2)G(\underline{r}, \underline{r}') = \delta(\underline{r} - \underline{r}') \quad (16)$$

which is square integrable over $\underline{r}$ -space and finite at $\underline{r} = 0$.

3.1 Three dimensions

Usually the vector $\underline{r}$ refers to the position of a particle in three dimensions, but the equations so far formally apply to any number of dimensions. In three dimensions, we have

$$G(\underline{r}, \underline{r}') = -\frac{1}{4\pi} \frac{e^{-k|\underline{r} - \underline{r}'|}}{|\underline{r} - \underline{r}'|} , \quad (17)$$

so that the integral equation to be solved is

$$\psi(\underline{r}) = -\frac{1}{2\pi} \int \frac{e^{-k|\underline{r} - \underline{r}'|}}{|\underline{r} - \underline{r}'|} V(\underline{r}') \psi(\underline{r}') d\underline{r}' . \quad (18)$$

3.2 One dimension $(-\infty, \infty)$

For one-dimensional systems where a particle is confined to the x-axis $(-\infty < x < \infty)$, the Green's Function is

$$G(x, x') = -(2k)^{-1} e^{-k|x-x'|}, \quad (19)$$

and the integral equation for bound states is

$$\psi(x) = -k^{-1} \int_{-\infty}^{\infty} e^{-k|x-x'|} V(x') \psi(x') dx'. \quad (20)$$

3.3 One dimension $(0, \infty)$

Frequently we are interested in a three-dimensional system where the potential in equation (15) is merely a function $V(r)$ of the radius r . Then the use of spherical polar coordinates (r, θ, ϕ) yields a typical bound state of the form

$$\psi(\underline{r}) = \sum_{m=-\ell}^{\ell} a_m f_{\ell}(r) P_{\ell}^{|m|}(\cos \theta) e^{im\phi}. \quad (21)$$

Here $f_{\ell}(r)$ is a solution of the radial wave equation

$$\left(\frac{d^2}{dr^2} - k^2 \right) (rf_{\ell}) = \{ 2V(r) + \ell(\ell+1)/r^2 \} (rf_{\ell}), \quad (22)$$

or equivalently, of

$$\left\{ \frac{d^2}{dr^2} - k^2 - \ell(\ell+1)/r^2 \right\} (rf_{\ell}) = 2V(r) (rf_{\ell}), \quad (23)$$

which is finite as $r = 0$ and exponentially small as $r \rightarrow \infty$. The appropriate one-dimensional Green's Functions for the operators on the left of (22) and (23) are respectively

$$g(r, r') = -k^{-1} \sinh(kr_{<}) e^{-kr_{>}} = -\frac{1}{2}k^{-1} \{e^{-k|r-r'|} - e^{-k(r+r')}\} \quad (24)$$

and

$$\gamma(r, r') = -(rr')^{\frac{1}{2}} I_{\ell + \frac{1}{2}}(kr_{<}) K_{\ell + \frac{1}{2}}(kr_{>}). \quad (25)$$

Here we have used the customary notation I and K for modified Bessel Functions, and the notation $r_{<}$ and $r_{>}$ for the lesser and greater of r and r' . The Green's Functions yield two different integral equations for $f_{\ell}(r)$, namely

$$rf_{\ell}(r) = \int_0^{\infty} g(r, r') \{2V(r') + \ell(\ell+1)/r'^2\} r' f_{\ell}(r') dr' \quad (26)$$

which corresponds to (22), and

$$rf_{\ell}(r) = 2 \int_0^{\infty} \gamma(r, r') V(r') r' f_{\ell}(r') dr' \quad (27)$$

corresponding to (23). In the situation when $\psi(\underline{r})$ is spherically symmetric and $\ell = 0$, the two Green's Functions are identical and (26) and (27) are the same. But in general we have the two possible approaches.

The integral equation (27) can also be obtained directly from the three-dimensional equation (18). The procedure is first to expand the Green's Function (17) in the form

$$G(\underline{r}, \underline{r}') = \sum_{\ell=0}^{\infty} A_{\ell}(r, r') P_{\ell}(\hat{\underline{r}} \cdot \hat{\underline{r}}'), \quad (28)$$

where the coefficients are actually

$$A_{\ell}(r, r') = -(2\ell+1)(rr')^{-1} \gamma(r, r'). \quad (29)$$

Next we use the expansion theorem for Legendre Polynomials

$$P_{\ell}(\hat{\underline{r}} \cdot \hat{\underline{r}}') = \sum_{m=-\ell}^{\ell} \frac{(\ell-|m|)!}{(\ell+|m|)!} P_{\ell}^{|m|}(\cos \theta) P_{\ell}^{|m|}(\cos \theta') e^{im(\phi-\phi')}, \quad (30)$$

and substitute for (21) and (28) into (18). The orthogonality of the spherical harmonics then leads to equation (27) for $f_{\ell}(r)$.

3.4 Higher dimensions

The Green's Function $G(\underline{r}, \underline{r}')$ in n dimensions is given by Titchmarsh^[1], namely

$$-(2\pi)^{\frac{1}{2}n} k^{\frac{1}{2}n-1} |\underline{r}-\underline{r}'|^{1-\frac{1}{2}n} K_{\frac{1}{2}n-1}(k|\underline{r}-\underline{r}'|). \quad (31)$$

When n is odd, the modified Bessel Function is a spherical one merely involving powers of the argument and negative exponentials (see (17) and (19)), but if n is even a logarithmic term and gamma functions appear.^[4]

In $3n$ dimensions, it is convenient to use n three-dimensional vectors rather than one $3n$ -dimensional vector. For example, if $\underline{r}_1$ and $\underline{r}_2$ describe the positions of the electrons relative to the nucleus in Helium, the integral equation is

$$\psi(\underline{r}_1, \underline{r}_2) = -(k^2/4\pi^3) \iint \rho^{-2} K_2(\rho k) V(\underline{r}'_1, \underline{r}'_2) \psi(\underline{r}'_1, \underline{r}'_2) d\underline{r}'_1 d\underline{r}'_2 \quad (32)$$

where $\rho = |\underline{r}_1 + \underline{r}_2 - \underline{r}'_1 - \underline{r}'_2|$.

§ 4. FREE-PARTICLE GREEN'S FUNCTIONS FOR POSITIVE ENERGY

In situations where the energy is positive, the free particle Green's Functions are not square integrable, neither are they uniquely defined. Let us consider the three-dimensional case, and suppose that E has the complex value $\frac{1}{2}(k + i\epsilon)^2$, where k and ϵ are real and positive. The Green's Function $G^{+\epsilon}(\underline{r}, \underline{r}')$ is the square integrable solution of

$$\{\nabla^2 + (k + i\epsilon)^2\} G(\underline{r}, \underline{r}') = \delta(\underline{r} - \underline{r}') \quad (33)$$

which is finite at $\underline{r} = 0$, i. e.

$$G^{+\epsilon}(\underline{r}, \underline{r}') = -\frac{1}{4\pi} \exp\{(-\epsilon + ik)|\underline{r} - \underline{r}'|\} / |\underline{r} - \underline{r}'|. \quad (34)$$

Alternatively when E has the value $\frac{1}{2}(k - i\epsilon)^2$, the Green's Function is

$$G^{-\epsilon}(\underline{r}, \underline{r}') = -\frac{1}{4\pi} \exp\{(-\epsilon - ik)|\underline{r} - \underline{r}'|\} / |\underline{r} - \underline{r}'|. \quad (35)$$

The limits of (34) and (35) as $\epsilon \rightarrow 0$ and E assumes the real positive value $\frac{1}{2}k^2$ are not the same. Neither one is suitable for a bound-state integral equation, since for large r G^{+0} behaves like an outgoing wave and G^{-0} like an incoming wave. G^{+0} and G^{-0} are used to derive scattering solutions when equation (1) describes the scattering by a potential $V(\underline{r})$ of a particle

with unit mass and positive energy.

However, any linear combination of Q^{+0} and Q^{-0} which has the correct singularity at $\underline{r} = \underline{r}'$ is still a solution of the equation

$$(\nabla^2 + k^2) Q(\underline{r}, \underline{r}') = \delta(\underline{r} - \underline{r}') . \quad (36)$$

Such a combination which does not exhibit progressive wave behaviour for large r is

$$-\frac{1}{4\pi} \cos \{k|\underline{r} - \underline{r}'|\} / |\underline{r} - \underline{r}'| + C \sin \{k|\underline{r} - \underline{r}'|\} / |\underline{r} - \underline{r}'| , \quad (37)$$

where C is an arbitrary constant. If C is set equal to zero, so that the Green's Function takes the principal value $\frac{1}{2}(Q^{+0} + Q^{-0})$, the integral equation to be solved for bound states is

$$\psi(\underline{r}) = -\frac{1}{2\pi} \int \frac{\cos \{k|\underline{r} - \underline{r}'|\}}{|\underline{r} - \underline{r}'|} V(\underline{r}') \psi(\underline{r}') d\underline{r}' . \quad (38)$$

If C is not zero, terms involving $J_{\ell + \frac{1}{2}}(kr)$ which are not square integrable are added to the right of (38); this may be seen by using the expansion

$$\frac{\sin k|\underline{r} - \underline{r}'|}{|\underline{r} - \underline{r}'|} = -2\pi^2 \sum_{\ell=0}^{\infty} (2\ell+1) (rr')^{\frac{1}{2}} J_{\ell + \frac{1}{2}}(kr) J_{\ell + \frac{1}{2}}(kr') P_{\ell}(\hat{\underline{r}} \cdot \hat{\underline{r}}') \quad (39)$$

and integrating term by term over $\underline{r}'$. There is no singularity at $\underline{r} = \underline{r}'$, and the $J_{\ell + \frac{1}{2}}(kr)$ terms may be removed directly from the integrals. Thus we must choose C to be zero in order to get an integral equation which describes bound states.

In one dimension, the positive energy integral equation corresponding to (20) is

$$\psi(x) = k^{-1} \int_{-\infty}^{\infty} \sin\{k|x-x'|\} V(x') \psi(x') dx', \quad (40)$$

and equations corresponding to (26) and (27) may be written down using the principal value Green's Functions

$$-k^{-1} \sin(kr_{<}) \cos(kr_{>}) \quad (41)$$

and

$$\frac{1}{2} \pi (rr')^{\frac{1}{2}} J_{\ell + \frac{1}{2}}(kr_{<}) Y_{\ell + \frac{1}{2}}(kr_{>}) \quad (42)$$

respectively. An analogue also exists in n dimensions for (31).

§ 5. MOMENTUM SPACE

With bound states, more attention has been paid in the literature to an integral form of Schrödinger's equation in momentum space than in coordinate space. This is no doubt because an integral equation arises naturally as the Fourier Transform of (1). Let $\Psi(\underline{p})$ be the momentum space wave function, or equivalently let

$$\Psi(\underline{p}) = (2\pi)^{-\frac{1}{2}n} \int e^{i\underline{p} \cdot \underline{r}} \psi(\underline{r}) d\underline{r} \quad (43)$$

be the n -dimensional Fourier Transform of $\psi(\underline{r})$. The number of dimensions, n , will usually be three or one. An application of Green's Theorem shows that the transform of $\nabla^2 \psi(\underline{r})$ is $-p^2 \Psi(\underline{p})$, provided that the resulting surface

integrals at infinity vanish. We assume that $\psi(\underline{r})$, representing a bound state, tends to zero sufficiently fast as $r \rightarrow \infty$ both to ensure this and also to enable the integral (43) to converge (in fact $\psi(\underline{r})$ is nearly always exponentially decreasing). The transform of equation (1) is then

$$(\underline{p}^2 - 2E) \Psi(\underline{p}) = -2(2\pi)^{-\frac{1}{2}n} \int \underline{v}(\underline{p} - \underline{p}') \Psi(\underline{p}') d\underline{p}', \quad (44)$$

where $\underline{v}(\underline{p})$ is the transform of $V(\underline{r})$ and the Convolution Theorem has been used to transform the product $V(\underline{r})\psi(\underline{r})$.

If we write (44) as

$$\Psi(\underline{p}) = -2(2\pi)^{-\frac{1}{2}n} (\underline{p}^2 - 2E)^{-1} \int \underline{v}(\underline{p} - \underline{p}') \Psi(\underline{p}') d\underline{p}', \quad (45)$$

and take the inverse transform of both sides, we recover the coordinate space integral equations (18) when $n = 3$, $E = -\frac{1}{2}k^2$, (38) when $n = 3$, $E = +\frac{1}{2}k^2$, (20) when $n = 1$, $E = -\frac{1}{2}k^2$, and (40) when $n = 1$, $E = +\frac{1}{2}k^2$, respectively. In the positive energy cases, the principal value of the integral over $\underline{p}$ -space involving $(\underline{p}^2 - 2E)^{-1}$ must be used.

The integral equation for the Helium atom in momentum space which corresponds to (32) is

$$\Psi(\underline{p}_1, \underline{p}_2) = -2(2\pi)^{-3} (\underline{p}_1^2 + \underline{p}_2^2 + k^2)^{-1} \iint \underline{v}(\underline{p}_1 - \underline{p}'_1, \underline{p}_2 - \underline{p}'_2) \Psi(\underline{p}'_1, \underline{p}'_2) d\underline{p}'_1 d\underline{p}'_2. \quad (46)$$

In momentum space there is also a reduction from three to one dimensions for central potentials, analogous to that discussed in §3.3 for coordinate

space. A central potential $V(r)$ has a Fourier Transform $v(p)$ which is merely a function of the magnitude p of $\underline{p}$. In terms of spherical polar coordinates (p, α, β) a typical bound state has the form

$$\Psi(\underline{p}) = \sum_{M=-L}^L b_M F_L(p) P_L^{|M|}(\cos \alpha) e^{iM\beta}, \quad (47)$$

where $F_L(p)$ is determined from^[5]

$$(p^2 - 2E) F_L(p) = -2(2\pi)^{-\frac{1}{2}} \int_{p'=0}^{\infty} F_L(p') p'^2 dp' \int_{t=-1}^1 v(\sqrt{p^2 + p'^2 - 2pp't}) P_L(t) dt. \quad (48)$$

Equation (48) is obtained by substituting from (47) into (44) and simplifying with the help of the orthogonality of the spherical harmonics.

In the simple case when $L = 0$, it is not difficult to show that (48) reduces to

$$(p^2 - 2E) p F_0(p) = -2(2\pi)^{-\frac{1}{2}} \int_0^{\infty} \{v_c(|p-p'|) - v_c(p+p')\} p' F_0(p') dp', \quad (49)$$

where $v_c(p)$ is the Fourier Cosine Transform of $V(r)$. In this situation, $p F_0(p)$ is the Fourier Sine Transform of $rf_0(r)$, and equation (49) is the Sine Transform of (22) or (23) with $\ell = 0$.

§6. HOMOGENEOUS LINEAR INTEGRAL EQUATIONS

6.1 Iterative Solutions for a Symmetric Kernel

The eigenvalue theory for a homogeneous linear integral equation with a real symmetric kernel is well known,^[6, 7] and we give the relevant results here.

Consider the equation

$$\chi(\underline{x}) = \lambda \int K(\underline{x}, \underline{y}) \chi(\underline{y}) d\underline{y} , \quad (50)$$

where K is real and symmetric in $\underline{x}$ and $\underline{y}$ (which are n -dimensional vectors) and obeys the Hilbert-Schmidt condition

$$\iint K^2(\underline{x}, \underline{y}) d\underline{x} d\underline{y} < \infty . \quad (51)$$

Square integrable solutions χ only exist for discrete, possibly degenerate, real eigenvalues λ_j . These eigenfunctions can be orthonormalized, and we denote them by $\{\theta_j\}$, so that

$$\theta_j(\underline{x}) = \lambda_j \int K(\underline{x}, \underline{y}) \theta_j(\underline{y}) d\underline{y} . \quad (52)$$

For Hilbert-Schmidt kernels, it is known that

$$\sum_j \lambda_j^{-2} < \infty ; \quad (53)$$

consequently there is no finite accumulation point for the eigenvalues, and any eigenvalue has only finite degeneracy. Thus they can be numbered in order of ascending magnitude

$$|\lambda_1| \leq |\lambda_2| \leq |\lambda_3| \leq \dots \quad (54)$$

and we suppose that this is done. Generally some eigenvalues are positive and some negative, and there are an infinite number of them. If there should in fact be only a finite number N of eigenvalues, then

$$K(\underline{x}, \underline{y}) = \sum_{j=1}^N \theta_j(\underline{x}) \theta_j(\underline{y}) \lambda_j^{-1} . \quad (55)$$

According to the Hilbert-Schmidt expansion theory, any function $\chi_1(\underline{x})$ which is expressible as

$$\chi_1(\underline{x}) = \int K(\underline{x}, \underline{y}) \chi_0(\underline{y}) d\underline{y} \quad (56)$$

(χ_0 being square integrable) may be expanded in the form

$$\chi_1(\underline{x}) = \sum_j c_j \theta_j(\underline{x}) \lambda_j^{-1}. \quad (57)$$

The coefficients c_j are defined by the relation

$$c_j = \int \chi_0(\underline{x}) \theta_j(\underline{x}) d\underline{x}, \quad (58)$$

and it should be noted that the orthonormal set $\{\theta_j\}$ is not in general complete.

Thus iteration according to the scheme

$$\chi_{n+1}(\underline{x}) = \int K(\underline{x}, \underline{y}) \chi_n(\underline{y}) d\underline{y}, \quad n = 0, 1, 2, \dots \quad (59)$$

yields

$$\chi_n(\underline{x}) = \sum_j c_j \theta_j(\underline{x}) \lambda_j^{-n}. \quad (60)$$

Hence if N is large we have

$$\lambda_1^N \chi_n(\underline{x}) \sim c_1 \theta_1(\underline{x}), \quad (61)$$

and

$$\chi_N / \chi_{N+1} \rightarrow \lambda_1 \text{ as } N \rightarrow \infty. \quad (62)$$

If λ_1 should be degenerate, the right of (61) must be replaced by the appropriate linear combination of eigenfunctions. The rate of convergence of

the iteration depends on the ratio of λ_1 to the next biggest eigenvalue.

If K is positive-definite (so that all the eigenvalues are positive), successive bounds to λ_1 are available. [2, 8] If

$$I_{n,m} = \int \chi_n(\underline{x}) \chi_m(\underline{x}) d\underline{x}, \quad (63)$$

then it can be shown that

$$\lambda_1^{(n)} \geq \lambda_1^{(n+1/2)} \geq \lambda_1^{(n+1)} \geq \dots \geq \lambda_1, \quad (64)$$

where $\lambda_1^{(n)} = I_{n,n-1}/I_{n,n}$ and $\lambda_1^{(n+1/2)} = I_{n,n}/I_{n,n+1}$, etc. The sequence (64) actually converges to λ_1 . Lower bounds can also be found for λ_1 , but unfortunately these usually demand a knowledge of the next biggest eigenvalue. If K is neither positive- nor negative-definite, then (64) weakens to

$$|\lambda_1^{(n+1/2)}| \geq |\lambda_1^{(n+3/2)}| \geq \dots \geq |\lambda_1|. \quad (65)$$

Iterative schemes converging to θ_2, θ_3 , etc. can be constructed. The idea is that if χ_0 is orthogonal to $\theta_1, \theta_2 \dots \theta_{t-1}$ (i.e. if $c_1 = c_2 = \dots = c_{t-1} = 0$) then $\lambda_t^N \chi_N(\underline{x})$ will converge to $c_t \theta_t(\underline{x})$. Temple [8] gives a device which ensures such orthogonality even if $\theta_1, \theta_2 \dots \theta_{t-1}$ are unknown.

The extremal properties of the eigenfunctions and eigenvalues are straightforward. The magnitude of

$$\iint K(\underline{x}, \underline{y}) f(\underline{x}) f(\underline{y}) d\underline{x} d\underline{y} \quad (66)$$

has a maximum equal to $|\lambda_1|^{-1}$ on the set of normalized functions, which it attains when $f = \theta_1$. More generally, the maximum is equal to $|\lambda_t|^{-1}$ on

the set which is orthonormalized to $\theta_1, \theta_2 \dots \theta_{t-1}$. Individual properties for the sets of positive and negative eigenvalues are also available.

6.2 Symmetrizable kernels

The kernels of the integral equations which we have derived for bound states are not symmetric, but in many cases they are symmetrizable. In coordinate space, the typical equation is

$$\psi(\underline{r}) = \int 2G(\underline{r}, \underline{r}'; E) V(\underline{r}') \psi(\underline{r}') d\underline{r}' . \quad (67)$$

The free-particle Green's Function $G(\underline{r}, \underline{r}'; E)$ is real and symmetric in $\underline{r}$ and $\underline{r}'$. It is negative-definite for negative E , being the inverse of the negative-definite differential operator $(\nabla^2 - k^2)$, but it loses this property for positive E .

Let us suppose that we are dealing with negative energies, and consider the favourable situation when $V(\underline{r})$ is never positive ($V(\underline{r})$ must of course be negative somewhere for negative-energy bound states). Then we may write (67) in the symmetric form (50), where

$$\chi(\underline{r}) = \{-V(\underline{r})\}^{1/2} \psi(\underline{r}) \quad (68)$$

and

$$K(\underline{r}, \underline{r}'; E) = -2\{-V(\underline{r})\}^{1/2} \{-V(\underline{r}')\}^{1/2} G(\underline{r}, \underline{r}'; E) \quad (69)$$

provided that

$$\lambda = 1 . \quad (70)$$

The theory of §6.1 is now formally applicable to equation (67). The iterative procedure (59) is equivalent to

$$\psi_{n+1}(\underline{r}) = \int 2G(\underline{r}, \underline{r}'; E) V(\underline{r}') \psi_n(\underline{r}') d\underline{r}' . \quad (71)$$

If $\{\theta_j\}$ are now the eigenfunctions for ψ , they are orthonormalized with respect to a weighting factor $-V(\underline{r})$, i.e.

$$\int -V(\underline{r}) \theta_i(\underline{r}) \theta_j(\underline{r}) d\underline{r} = \delta_{ij} . \quad (72)$$

The kernel $K(\underline{r}, \underline{r}'; E)$ given by (69) is positive-definite, and so the stronger bounding sequence (64) is available.

In momentum space, the typical equation (45) may also be symmetrized when E is negative (so that $(p^2 - 2E)$ is positive). This time to recover equation (50) we must set

$$\chi(\underline{p}; E) = (p^2 - 2E)^{1/2} \Psi(\underline{p}) , \quad (74)$$

$$K(\underline{p}, \underline{p}') = -2(2\pi)^{-\frac{1}{2}n} \nu(\underline{p} - \underline{p}') (p^2 - 2E)^{-\frac{1}{2}} (p'^2 - 2E)^{-\frac{1}{2}} , \quad (75)$$

and again

$$\lambda = 1 . \quad (70)$$

For real potentials $V(\underline{r})$, the Fourier Transform $\nu(\underline{p} - \underline{p}')$ is actually Hermitian symmetric in $\underline{p}$ and $\underline{p}'$ whenever it has a non-zero complex part, otherwise it is symmetric (the theory of real symmetric kernels immediately extends to complex Hermitian symmetric ones). It should be noted that the

iterative step

$$\Psi_{n+1}(\underline{p}) = -2(2\pi)^{-\frac{1}{2}n} (p^2 - 2E)^{-1} \int V(\underline{p} - \underline{p}') \Psi_n(\underline{p}') d\underline{p}' \quad (76)$$

is actually the Fourier Transform of the corresponding step (71) in coordinate space (the 'n' in the power of (2π) on the right of (76) is the number of dimensions, and has nothing to do with the iteration.) The potential $V(\underline{r})$ does not have to be of one sign in order to establish the symmetric kernel (74) in momentum space, and this kernel $K(\underline{p}, \underline{p}')$ is not necessarily positive-definite.

The formal eigenvalue and expansion theory for symmetrizable kernels is given by Zaanen^[7] in several cases, two of which are possibly relevant here. In the first (appropriate to coordinate space), the kernel is $A(\underline{x}, \underline{y})h(\underline{y})$ where (i) $A(\underline{x}, \underline{y})$ has finite double-norm (ii) $h(\underline{x})$ is bounded and non-negative (iii) $h(\underline{x})A(\underline{x}, \underline{y})h(\underline{y})$ is Hermitian symmetric. In the second case (appropriate to momentum space), the kernel is $A(\underline{x})H(\underline{x}, \underline{y})$ where (i) $H(\underline{x}, \underline{y})$ is positive-definite and has finite double-norm (ii) $A(\underline{x})$ is real, measurable and bounded.

6.3 Applicability of the iterative scheme

First of all, it is clear that this particular iterative method is not going to work at all for bound states with positive energy. There the free-particle Green's Functions are not even square integrable (their norm is infinite). Thus a fortiori they cannot possibly satisfy the Hilbert-Schmidt condition (51) (i. e. have finite double-norm). Furthermore, in order to get positive-energy states at all, the potential $V(\underline{r})$ must tend to $+\infty$ as $r \rightarrow \infty$.^[1] This would

make the situation worse as far as the double-norm of a symmetrized kernel like (69) (but using $+V$ instead of $-V$) is concerned. If we try to iterate with a suitable square integrable ψ_0 in (71), the ψ_1 obtained is itself not square integrable, unless ψ_0 happens to be an exact eigenfunction; in this lucky event, the factor multiplying the unpleasantly large contribution to ψ_1 is zero. A simple illustration of this phenomenon is furnished using $V = ax^2$ and $\psi_0 = e^{-bx^2}$ to start an iteration based on equation (40) for the harmonic oscillator.

The picture is far brighter for negative-energy bound states, where there are excellent prospects for applying this iterative method, and subsequently we consider only such states. The Green's Functions themselves are certainly square integrable, but unfortunately do not have finite double-norms. For instance, in three dimensions, (17) shows that, for any value of $\underline{r}'$,

$$\int \{G(\underline{r}, \underline{r}')\}^2 d\underline{r} = (8\pi k)^{-1}, \quad (77)$$

and the integral of $(8\pi k)^{-1}$ over $\underline{r}'$ -space is infinite. Thus Zaanen's formal theory is not immediately applicable as far as coordinate space is concerned. Whether it is applicable in momentum space will depend on the nature of $v(\underline{p} - \underline{p}')$.

Even though $G(\underline{r}, \underline{r}')$ itself does not have finite double-norm, in cases where $V(\underline{r})$ is never positive it is quite likely that the symmetrized kernel (69) will have, and in such cases the theory of §6.1 is applicable. For this to happen in three dimensions, it is necessary that $V(\underline{r})$ should tend to zero faster than $1/r$ as $r \rightarrow \infty$. However the iterative method seems to work

perfectly well for the hydrogen atom where the potential is just $-1/r$ and so it is possible that the Hilbert-Schmidt condition is not strictly necessary. Alternatively this difficulty might be avoided by first inserting a convergence factor $e^{-\alpha r}$ into V , and then letting α tend to zero.

To sum up then, this iterative method is not applicable to positive-energy bound states. It is certainly applicable to negative-energy bound states for which $V(\underline{r})$ is never positive and for which the symmetrized kernel has finite double-norm. In this favourable situation, the symmetrized kernel is positive-definite, and a stronger bounding sequence is available for the eigenvalues. The method may be applicable to negative-energy bound states for other potentials; this will depend on the precise nature of $V(\underline{r})$ or its Fourier Transform. There seems no reason why one should not apply the method in any negative-energy case and hope for the best!

§7. THE DIFFERENT TYPES OF EIGENVALUE PROBLEM

7.1 Determination of energy eigenvalues and eigenfunctions

Even when the iterative scheme is applicable to the typical integral forms (67) and (45) of the Schrödinger equation (1), there is still a possible drawback when the object is to find energy eigenvalues and eigenfunctions of the operator $\{-\frac{1}{2}\nabla^2 + V(\underline{r})\}$. We will discuss what happens only in coordinate space, but there is a parallel situation in momentum space.

Iteration according to (71) leads to eigenvalues $\lambda_j(E)$ and eigenfunctions $\varphi_j(E)$ of the integral equation

$$\psi(\underline{r}) = \lambda \int G(\underline{r}, \underline{r}'; E) V(\underline{r}') \psi(\underline{r}') d\underline{r}', \quad (67a)$$

or equivalently of the Schrödinger-type differential equation

$$\{-\frac{1}{2}\nabla^2 + \lambda V(\underline{r}) - E\} \psi(\underline{r}) = 0. \quad (1a)$$

The energy E plays the role of a fixed parameter. Thus essentially this iterative method is most suitable for problems in which the energy E is known and the corresponding 'potential strengths' λ_j must be found, together with the appropriate eigenfunctions φ_j . Such situations arise naturally in nuclear systems where E is the known binding energy of a nucleon and the nature of the potential in which the nucleon moves is uncertain.

In atomic and molecular systems, the potential is usually known and energy eigenvalues E_j and eigenfunctions θ_j are required. In

order to find these from $\lambda_j(E)$ and $\varphi_j(E)$, we must satisfy the appropriate condition (70). Thus E_j is defined so that

$$\lambda_j(E_j) = 1, \quad (70a)$$

which makes equation (1a) reduce to (1) as required. The corresponding eigenfunction is

$$\theta_j = \varphi_j(E_j). \quad (78)$$

Even in quite simple problems when some iteration is possible analytically, it may well be necessary to determine E_j numerically. This could be an unfortunate feature of the method.

Happily we are often concerned with a simpler type of situation, where the energy of some state (usually the ground state) is known with sufficient accuracy either from experiment or by calculation from a variational method. The potential is known, λ is unity, and the problem is merely to find successive improvements in an approximate eigenfunction. The iterative method can then be applied directly, and consequent improvements in the expectation values of operators obtained.

7.2 Coulomb potentials.

When the potential $V(\underline{r})$ is a homogeneous function of the radial distances, the two types of eigenvalue problem are closely related. The energy eigenvalues and eigenfunctions can be deduced from those for λ merely by considering a change of scale in equation (1a). This device will work for atomic and molecular systems in the absence of any external

fields, in which case the potential merely consists of the Coulombic interactions between the various particles.

Let us consider the motion of the electron in a hydrogen atom. V is $-1/r$, and equations (1) and (1a) become

$$\left\{ -\frac{1}{2} \nabla^2 - \frac{1}{r} - E \right\} \psi(\underline{r}) = 0 \quad (79)$$

and

$$\left\{ -\frac{1}{2} \nabla^2 - \frac{\lambda}{r} - E \right\} \psi(\underline{r}) = 0 . \quad (79a)$$

If we set $s = r\lambda$ in (79a) and divide through by λ^2 , we obtain

$$\left\{ -\frac{1}{2} \nabla_s^2 - \frac{1}{s} - \frac{E}{\lambda^2} \right\} \psi(s/\lambda) = 0 . \quad (79b)$$

Thus if $\lambda_j(E)$ and $\varphi_j(E, \underline{r})$ are a typical λ -eigenvalue and eigenfunction of (79a) for a fixed E , it follows by comparison of (79) and (79b) that the energy eigenvalues E_j and eigenfunctions $\theta_j(\underline{r})$ of (79) are given by

$$E_j = E \{ \lambda_j(E) \}^{-2} \quad (80)$$

and

$$\theta_j(\underline{r}) = \varphi_j(E, \underline{r}/\lambda_j(E)) . \quad (81)$$

To preserve the consistency of (70a) and (80), we must take the positive square root if we use (80) to give λ_j in terms of E_j , i.e.

$$\lambda_j(E) = + \sqrt{E/E_j} . \quad (82)$$

For calculation purposes, the E in (1a) may be set equal to any convenient

value. The obvious choice is $E = -\frac{1}{2}$, to make the k in the Green's function equal to unity. (As is well known, we have $E_j = -1/2j^2$, $j=1,2,3,\dots$ for the hydrogen atom, and so it follows from (82) that when $E = -\frac{1}{2}$ the eigenvalues for λ in (79a) are given by $\lambda_j = j$).

The relations (80) and (81) will hold for any atom. In the case of a molecule with a typical internuclear vector distance $\underline{R}$, we should find that

$$E_j(\underline{R}) = E\{\lambda_j(E, \underline{R}/\mu_j)\}^{-2} \quad (83)$$

and

$$\theta_j(\underline{r}, \underline{R}) = \varphi_j(E, \underline{r}/\mu_j, \underline{R}/\mu_j) \quad (84)$$

where

$$\mu_j = \lambda_j(E, \underline{R}) \quad (85)$$

§8. PREVIOUS WORK and POSSIBLE FUTURE PROGRESS

The first applications of these iterative methods for bound states appear to have been in classical mechanics by Temple [8, 9] and his collaborator Bickley [9]. The possibility of iteration for discrete quantum states was first mentioned by Thomas [10]; he gave two elementary examples, one (with zero energy) in coordinate space and the other in momentum space. Subsequent work seems to have been entirely in momentum space, motivated by the determination of momentum wave functions and by the way in which an integral equation arises naturally in momentum space as the Fourier Transform of Schrödinger's equation. The iterative techniques were rediscovered by

Svartholm [11], who used them to calculate binding energies of light atomic nuclei. Further progress with some nuclear problems was made by McWeeny [12], Salpeter [13, 14], and Goldstein [14].

The principal attempts at tackling bound-state atomic and molecular problems by iteration are those by McWeeny [15, 16] and Coulson [15]. These authors studied the ground states of the helium atom and the hydrogen molecule ion (again in momentum space) and were able to calculate accurately the momentum distribution functions. Difficulties were anticipated in extending their procedures to more complex systems. A recent suggestion for simplification by employing Fock's projective momentum space is made by Shibuya and Wulfman [17]. This device was explored earlier by Lévy [18], who also considered the Dirac equations in momentum space.

There would seem to be appreciable scope for future progress with bound-state atomic and molecular problems on two fronts. Firstly, using sensible approximate wave functions as a starting point, it would sometimes be possible to make one or two iterations analytically for simple systems. It would be interesting to compare these corrected wave functions with those obtained by conventional perturbation theory, and to see which method gives the more accurate expectation values for certain operators. Secondly, when analytical iteration is not feasible, it should be fairly simple to compute the various iterates to the wave function. The computation would be quite straightforward for one-dimensional problems, and the procedure should be more economical on machine time than other methods which

solve a differential rather than an integral equation. Even when the numerical integrations are many-dimensional, the iterative method may well prove to be more efficient than the much-used variation and perturbation methods.

Preliminary calculations starting with e^{-2r} and e^{-ar^2} (where $a = 8/9\pi$) as approximations to the true hydrogen ground state e^{-r} are very encouraging. Three or four iterations lead to a very accurate wave function in each case. Further work is beginning along the lines indicated above.

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