CLOSED FORM BOUND-STATE PERTURBATION THEORY

OLLIE J. ROSE

SDC Integrated Services, Inc.
Hampton
Virginia 23666

CARL G. ADLER

Physics Department
East Carolina University
Greenville
North Carolina 27834
U. S. A.

ABSTRACT: The perturbed Schrödinger eigenvalue problem for bound states is cast
into integral form using Green's Functions. A systematic algorithm is developed
and applied to the resulting equation giving rise to approximate solutions ex-
pressed as functions of the given perturbation parameter. As a by-product, con-
vergence radii for the traditional Rayleigh-Schrödinger and Brillouin-Wigner
perturbation theories emerge in a natural way.

KEY WORDS AND PHRASES: Closed Form Perturbation Theory.

1980 MATHEMATICS SUBJECT CLASSIFICATION CODES: 81A10

1. INTRODUCTION

The method of Green's Functions is a powerful and widely used tool for obtaining analytical solutions to boundary value problems arising in diverse areas of physics; most notably in potential theory. [1, 2] The Green's Function approach is also extensively used to establish approximation methods in quantum mechanical collision theory. [3] However the use of closed form Green's Functions as a basis for a perturbation treatment of bound state quantal problems has not been exploited. [4, 5] In this paper, we view the notions of Green's Function and integral representations as unifying concepts from which conventional bound-state perturbation theory can be derived. From this approach, we are able to derive various properties such as convergence radii for the different perturbation approximations. In addition, there are obvious advantages to obtaining approximate results for energy and wavefunctions in a closed form (see the Appendix in Section 5 for an example).

Although the arguments in this paper are restricted to bound-state solutions of the time-independent Schrödinger equation, there is generality in two ways. First, the results apply to any number of dimensions and to essentially arbitrary potentials; secondly, there is an easy generalization to almost any linear differential equation of elliptic type.

The general equation we wish to solve is

$$H\psi(r) = E\psi(r) \tag{1.1}$$

where H is defined as usual and $\psi(r)$ is defined on some domain Ω with boundary $\partial\Omega$. We seek a solution to eq. (1.1) defined over Ω and subject to boundary condition $\psi(r) = 0$, for r belonging to $\partial\Omega$. Further we wish to know the allowed values of the unknown parameter E. We assume that Ω is an open, simply connected subset of Euclidean space with piece-wise smooth boundary. We further

suppose that all eigenstates under discussion are non-degenerate. No essential

differences are needed to treat the degenerate case.

The essence of perturbation theory is to suppose that H can be written as

$H_0 + \epsilon H_1$, where ϵ is a small parameter and further that we know the solution to

$$H_0\phi = W\phi. \tag{1.2}$$

We wish to exploit this knowledge to approximate the solutions to eq. (1.1)

written in the form

$$(H_0 + \epsilon H_1)\psi = E\psi. \tag{1.3}$$

We adopt the following notational definitions.

a) ϕ_n - unperturbed wavefunction for the $n\underline{\text{th}}$ eigenstate

b) W_n - energy eigenvalue corresponding to ϕ_n

c) ψ_j - exact wavefunction for the $j\underline{\text{th}}$ eigenstate of the unknown problem

d) E_j - exact energy eigenvalue corresponding to ψ_j

e) $\psi_j^{(k)}$ - $k\underline{\text{th}}$ order approximation to ψ_j

f) $E_j^{(k)}$ - $k\underline{\text{th}}$ order approximation to E_j

2. STATEMENT OF RELEVANT RESULTS FROM ANALYSIS

2.1 GREEN'S IDENTITIES: Let Ω be an open simply connected region of R^ν with

sectionally smooth boundary $\partial\Omega$. Let $L(\overline{x})$ be a differential operator of the form

$$L(\overline{x}) = \nabla_\nu^2 + \eta(\overline{x}); \tag{2.1.1}$$

finally let u and v be differentiable functions defined on the union of Ω and $\partial\Omega$.

The following identities hold.

Green's First Identity:

$$\int_\Omega u*L[u]d\tau = \int_\Omega \{|\nabla u|^2 - |\eta(\overline{x})|^2\}d\tau - \int_{\partial\Omega} (u*\nabla u)\cdot(\hat{n})d\sigma. \tag{2.1.2}$$

Green's Second Identity:

$$\int_{\Omega}\{u*L(v) - v(L[u])*\}d\tau = \int_{\partial\Omega}(u*\nabla v - v\nabla u*)\cdot\hat{n}d\sigma.$$ (2.1.3)

2.2 THE FREDHOLM ALTERNATIVE THEOREM [6]

The Boundary value problem

$$L(\phi) = f(\overline{x}) \text{ for all } \overline{x} \text{ in } \Omega$$

$$\phi(\overline{x}) = 0 \text{ for all } \overline{x} \text{ in } \partial\Omega$$

has a unique solution only if the corresponding homogeneous problem has a non-trivial solution, $u \neq 0$, the inhomogeneous problem will have a solution only if

$(u, f) = \int_{\Omega} u* f \, d\tau = 0$. In this case there is an infinity of solutions of the

form $\phi = cu + \phi_p$, where u satisfies the homogeneous problem and ϕ_p is any parti-

cular solution of the inhomogeneous problem.

2.3 VARIOUS THEOREMS AND PROPOSITIONS

THEOREM 1 [7] Suppose $\delta(\overline{x-y})$ is the Dirac delta function for the specific

n-dimensional coordinate system in use. Let L be a self-adjoint linear differen-

tial operator of the form $L = \nabla_n^2 + \eta(\overline{x})$.

(a) If the homogeneous problem

$$L[u] = 0 \text{ in } \Omega$$

$$u = 0 \text{ on } \partial\Omega$$

has only the trivial solution $u \equiv 0$, then there exists a unique solution (in the

sense of generalized functions) to the problem

$$L[g(\overline{x},\overline{y})] = \delta(\overline{x},\overline{y}) \text{ for all } \overline{x} \text{ and } \overline{y} \text{ in } \Omega,$$

$$g(\overline{x},\overline{y}) = 0 \text{ for all } \overline{x} \text{ on } \partial\Omega.$$

The function $g(\overline{x},\overline{y})$ is called the Green's Function for the boundary value problem

and is dependent not only on the operator L, but also on the geometry of Ω and

its boundary.

(b) If the homogeneous problem

$$L[u] = 0 \text{ in } \Omega$$

$$u = 0 \text{ on } \partial\Omega, \quad (u,u) = 1$$

has a non-trivial solution $u(\bar{x}) \neq 0$, then there exists a (non-unique) solution
to the problem

$$L[G(\bar{x},\bar{y})] = \delta(\bar{x}-\bar{y}) - u^*(\bar{y})u(\bar{x}) \text{ for all } \bar{x} \text{ and } \bar{y} \text{ in } \Omega, \text{ and } G(\bar{x},\bar{y}) = 0$$

for all $\bar{x}$ on $\partial\Omega$.

The function $G(\bar{x},\bar{y})$ is called the modified Green's function for the boundary
value problem. It will be noted, that in keeping with the Fredholm Alternative
Theorem, the generalized function $\rho(\bar{x},\bar{y}) = \delta(\bar{x}-\bar{y})-u^*(\bar{y})u(\bar{x})$ is orthogonal to
$u(\bar{x})$. We have

$$(u,\rho) = \int_\Omega u^*(\bar{x})\rho(\bar{x},\bar{y})d^\nu x = \int_\Omega [\delta(\bar{x}-\bar{y})-u^*(\bar{y})u(\bar{x})]u^*(\bar{x})d^\nu x$$

$$= u^*(\bar{y})-u(\bar{y})(u,u) = 0,$$

where we have assumed (as we may) that u is normalized.

PROPOSITION 1 [8]: The Green's function in part (a) of Theorem 1 is
symmetric in the sense that $g^*(\bar{x}_1,\bar{x}_2) = g(\bar{x}_2,\bar{x}_1)$ for every $\bar{x}_1$ and $\bar{x}_2$ lying in Ω.

PROPOSITION 2 [9]: Let u be a solution of the completely homogeneous
system: $L[u] = 0$ for all $\bar{x}$ in Ω, $u = 0$ for all $\bar{x}$ in $\partial\Omega$. If we require that
$(u,g) = 0$, this is sufficient to insure that g will be symmetric.

THEOREM 2 [10]

(a) If the completely homogeneous problem has only the trivial solution,
then the unique solution to

$$L[\phi] = f(\bar{x}) \text{ for all } \bar{x} \text{ in } \Omega,$$

and

$$\phi(\bar{x}) = 0 \text{ for all } \bar{x} \text{ on } \partial\Omega$$

is given by

$$\phi(\overline{x}) = \int_\Omega g*(\overline{y},\overline{x})f(\overline{y})d^\nu y = \int_\Omega g(\overline{x},\overline{y})f(\overline{y})d^\nu y. \qquad (2.3.1)$$

Where $g(\overline{x},\overline{y})$ is the Green's Function defined in part (a) of Theorem 1.

(b) If the completely homogeneous problem has a non-trivial solution (say u), and if $(u,f) = 0$, then all solutions of

$$L\phi = f(\overline{x}) \text{ for all } \overline{x} \text{ in } \Omega,$$

$$\phi(\overline{x}) = 0 \text{ for all } \overline{x} \text{ in } \partial\Omega$$

are given by

$$\phi(\overline{x}) = Cu(\overline{x}) + \int_\Omega G*(\overline{y},\overline{x})f(\overline{y})d^\nu y$$

or   (2.3.2)

$$\phi(\overline{x}) = Cu(\overline{x}) + \int_\Omega G(\overline{x},\overline{y})f(\overline{y})d^\nu y,$$

where C is an arbitrary constant.

3. THE APPROXIMATION THEORY

To begin we recall the basic equation from Section 1

$$H_0 \phi_j = W_j \phi_j; \qquad (3.1)$$

the solution of which is known, and the equation of interest which can be written in two different ways,

$$(H_0 - E_n) \psi_n = -\epsilon H_1 \psi_n, \qquad (3.2)$$

or

$$(H_0 - W_n) \psi_n = (E_n - W_n - \epsilon H_1) \psi_n. \qquad (3.3)$$

3.1 APPROXIMATION THEORY BASED ON EQUATION (3.2)

We shall start with eq. (3.2) and apply Theorem 2 with $L = H_0 - E_n$ and $f(\overline{x}) = -\epsilon H_1 \psi_n$. We first see which part of the alternative will apply. The eq. $(H_0 - E_n)\psi_n = 0$ will have a non-trivial solution only if $E_n = W_s$ for some s. To explore the consequences of this, we use the following equation:

$$(E_n - W_s)(\phi_s, \psi_n) = \epsilon(\phi_s, H_1 \psi_n).$$

If $E_n = W_s$, then either $\varepsilon = 0$ or $(\phi_s, H_1 \psi_n) = 0$. In the case of $\varepsilon = 0$, we are

back to the original unperturbed problem and we have $s = n$, $E_n = W_n$, and $\psi_n = \phi_n$.

The case $E_n = W_s$ with $\varepsilon \neq 0$ and $s \neq n$ involves subtleties that have no

bearing on the present development. [11] We, therefore, assume that ε is such

that $W_n < E_n < W_{n+1}$. With this assumption, $(H_0 - E_n)\psi_n = 0$ has only the trivial

solution $\psi_n = 0$, and by Theorem 2, part (a), ψ_n is given by

$$\psi_n(\overline{x}) = - \varepsilon \int_\Omega g(\overline{x}, \overline{y}) H_1(\overline{y}) \psi_n(\overline{y}) d^\nu y \qquad (3.1.1)$$

The Green's Function, $g(\overline{x}, \overline{y})$, satisfies

$$(H_0 - E_n) g(\overline{x}, \overline{y}) = \delta(\overline{x} - \overline{y}) \text{ for all } \overline{x} \text{ and } \overline{y} \text{ in } \Omega \qquad (3.1.2)$$

and

$$g(\overline{x}, \overline{y}) = 0 \text{ for all } \overline{x} \text{ on } \partial\Omega. \qquad (3.1.3)$$

By standard techniques eq. (2.3.2) can be formed into an equation for E_n

$$E_n = W_n + \varepsilon(\phi_n, H_1 \psi_n) / (\phi_n, \psi_n). \qquad (3.1.4)$$

We begin by supposing that system (3.1.2, 3.1.3) can be solved for $g(\overline{x}, \overline{y})$. Note

that E_n will occur as an unknown parameter, so it is more informative to write

$g(\overline{x}, \overline{y}; E_n)$. We then have the following system for E_n and ψ_n:

$$\psi_n = -\varepsilon \int_\Omega g(\overline{x}, \overline{y}; E_n) H_1(\overline{y}) \psi_n(\overline{y}) d^\nu y, \qquad (3.1.5)$$

$$E_n = W_n + \varepsilon(\phi_n, H_1, \psi_n) / (\phi_n, \psi_n), \qquad (3.1.6)$$

where $H_1(\overline{y})$, $\phi_n(\overline{x})$, W_n, and $g(\overline{x}, \overline{y}; E_n)$ are presumed known. The strategy is to

employ a method of successive approximation and solve the system (3.1.5, 3.1.6)

self-consistently at any order of approximation. To show that this process is

feasible, we prove two crucial results:

(i) $\lim\limits_{\varepsilon \to 0} \psi = \phi_n$.

(This will assure that we can start the iteration and that we can begin with

$\psi_n^{(0)} = \phi_n$).

(ii) The sequence defined by:

$$\psi_n^{(k+1)}(\bar{x}) = \epsilon \int_\Omega g(\bar{x},\bar{y};E_n) H_1(\bar{y}) \psi_n^{(k)}(\bar{y}) d^\nu y \qquad (k \geq 0).$$
$$\tag{3.1.7}$$

will converge for suitably restricted ϵ, thus insuring that we have a valid approximation procedure.

To facilitate these proofs, we want to expand $g(\bar{x},\bar{y};E_n)$ in the complete set of eigenfunctions $\{\phi_k\}_1^\infty$. Let $g = \sum_{n=1}^\infty a_k \phi_k$ where the a_k's are to be determined. Substitute this into eq. (3.1.6) and obtain

$$\sum_{k=1}^\infty a_k(W_k - E_n)\phi_k(\bar{x}) = \delta(\bar{x}-\bar{y}),$$

where we have used $H_0 \phi_k = W_k \phi_k$. Multiply by $\phi_\ell^*(\bar{x})$, integrate and note that $(\phi_\ell,\phi_k) = \delta_{\ell k}$ to obtain

$$a_k = \phi_k^*(\bar{y})/(W_k - E_n),$$

giving the following series for g:

$$g(\bar{x},\bar{y};E_n) = \sum_{k=1}^\infty \phi_k^*(\bar{y})\phi_k(\bar{x})/(W_k-E_n), \text{ with } E_n \neq W_k.$$
$$\tag{3.1.8}$$

Using eq. (3.1.4), we obtain

$$g(\bar{x},\bar{y};E_n) = - (\phi_n,\psi_n)\phi_n^*(\bar{y})\phi_n(\bar{x})/\epsilon(\phi_n,H_1\psi_n)$$

$$+ \sum_{k \neq n} \phi_k^*(\bar{y})\phi_k(\bar{x})/(W_k-E_n)$$
$$\tag{3.1.9}$$

Substitution of eq. (3.1.9) into eq. (3.1.5) produces

$$\psi_n = (\phi_n,\psi_n)\phi_n(\bar{x}) + \epsilon \sum_{k \neq n} (\phi_k,H_1,\psi_n)/(E_n-W_k).$$
$$\tag{3.1.10}$$

Let $\epsilon \to 0$ and get $\psi_n^{(0)} = (\phi_n,\psi_n^{(0)})\phi_n(\bar{x})$, i.e., $\psi_n^{(0)}$ is a multiple of ϕ_n. We shall employ the practice of requiring that $(\phi_n,\psi_n^{(k)}) = 1$ at any stage of approximation, then normalizing at the end. This completes the proof of (i). We note that eqs. (3.1.4, 3.1.10) with $(\phi_n,\psi_n) = 1$ are the standard expressions from which the Brillouin-Wigner Perturbation procedure is developed. [12, 13, 14] The connection between the integral representation of the solution in term of Green's

Functions and the BW equations is thus apparent.

We now prove the second result. Let ψ_n be the hypothetical function to which the $\psi_n^{(j)}$ are supposed to converge. If we can show that $\lim\limits_{j\to\infty} ||\psi_n^{(j)} - \psi_n|| = 0$, with the proper choice of ϵ, then we will have convergence of the iteration procedure. From eq. (3.1.7) we have the following expression:

$$\psi_n^{(j)}(\overline{x}) = -\epsilon \int_\Omega k_1(\overline{x},\overline{y};E_n)\psi_n^{(j-1)}(\overline{y})d^\nu y. \qquad (3.1.11)$$

The kernel, $k_1(\overline{x},\overline{y})$, is defined by

$$k_1(\overline{x},\overline{y};E_n) \equiv g(\overline{x},\overline{y})H_1(\overline{y}). \qquad (3.1.12)$$

We write eq. (3.1.11) in the more convenient form

$$\psi_n^{(j)} = K_1\psi_n^{(j-1)} \qquad (3.1.13)$$

where $K_1[u] \equiv -\epsilon \int g(\overline{x},\overline{y};E_n)H_1(\overline{y})u(\overline{y})d^\nu y$.

It is clear, using eq. (3.1.13) and the linearity of K_1 that

$$K_1\psi_n^{(j-1)} = K_1^2\psi_n^{(j-2)} = K_1^3\psi_n^{(j-3)} = \ldots = K_1^j\psi_n^{(0)} = K_1^j\phi_n. \qquad (3.1.14)$$

Now, since ψ_n is supposed to be a solution for eq. (3.1.1), we have $K_1^p\psi_n = \psi_n$, for all integers $p \geq 0$. We can therefore write

$$||\psi_n^{(j)} - \psi_n|| = ||K_1^j\phi_n - K_1^j\psi_n||. \qquad (3.1.15)$$

Using the linearity of K_1^j and the fact that ϕ_n and ψ_n are fixed functions, we can write

$$||\psi_n^{(j)} - \psi_n|| = ||K_1^j(\phi_n - \psi_n)|| = ||K_1||^j||\phi_n - \psi_n||. \qquad (3.1.16)$$

It is clear from eq. (3.1.16) that $\lim\limits_{j\to\infty}||\psi_n^{(j)} - \psi_n|| = 0$ if and only if $||K_1|| < 1$.

Using the inequality $||K||^2 \leq \iint |k(\overline{x},\overline{y})|^2 d^\nu \overline{x}\, d^\nu \overline{y}$ for Hilbert Schmidt operators [15] and the definition of K_1, we impose the following requirements:

$$||K_1||^2 \leq \epsilon^2 \iint\limits_{\Omega\Omega} |k_1(\overline{x},\overline{y};E_n)|^2 d^\nu x\, d^\nu y < 1. \qquad (3.1.17)$$

We therefore have the following inequality for ε:

$$|\varepsilon| < \{ \int_\Omega \int_\Omega |k_1(\overline{x},\overline{y};E_n)|^2 d^\nu \overline{x} \; d^\nu \overline{y} \}^{-\frac{1}{2}}. \tag{3.1.18}$$

Thus we have shown that for some range of ε, we have a reasonable approximation procedure. Since the inequality (3.1.18) implicitly contains the unknown energy, E_n, on the right side it is not useful as a practical estimate of the convergence radius. However, its use as a demonstration of convergence in principle is not compromised by the occurrence of the unknown E_n provided, as assumed, $E_n \neq W_k$ for any k. This can be seen by a reference to equation (3.1.8) and the definition of $k_1(\overline{x},\overline{y};E_n)$. Whatever the energy E_n is, as long as $E_n \neq W_k$, the integral on the right of inequality (3.1.18) will be a finite number > 0 and thus an ε can be found which will satisfy (3.1.18).

The approximation scheme is summarized below:

$$\psi_n^{(k+1)}(\overline{x}) = -\varepsilon \int_\Omega g(x,y;E_n^{(k)}) H_1(\overline{y}) \psi_n^{(k)}(\overline{y}) d^\nu y \tag{3.1.19}$$

and

$$E_n^{(k+1)} = W_n + (\phi_n, H_1, \psi_n^{(k)}), \text{ with } k = 0, 1, 2, \ldots \tag{3.1.20}$$

The occurrence of E_n as an unknown parameter on the RHS of both equations means that at any given level of approximation the system will have to be solved self-consistently by numerical procedure. Although this makes the calculation more difficult, it has the potential of returning some quite good values for E_n with a fairly low order approximation to ψ_n.

3.2   APPROXIMATION PROCEDURE BASED ON EQUATION (3.3)

We observe that the homogeneous equation, $(H_0 - W_n)\psi_n = 0$, has a non-trivial solution; namely, ϕ_n. Thus Theorem 2, part (b) applies, and we can write the solution to eq. (3.1) as

$$\psi_n = C\phi_n + \int_\Omega G(\overline{x},\overline{y})[E_n - W_n - \varepsilon H_1]\psi_n(\overline{y}) d^\nu y, \tag{3.2.1}$$

Provided that $(\phi_n, [E_n - W_n - \varepsilon H_1]\psi_n) = 0$, which is the same as

$$(E_n - W_n)(\phi_n, \varepsilon H_1 \psi_n). \tag{3.2.2}$$

Equation (3.2.2) is satisfied, as has already been noted.

Recall also, that $G(\overline{x}, \overline{y})$ must satisfy

$$(H_0 - W_n)G(\overline{x} - \overline{y}) = \delta(\overline{x} - \overline{y}) - \phi_n^*(\overline{y})\phi_n(\overline{x}). \tag{3.2.3}$$

Following the convention adopted in Section 3.1., we shall require that

$(\phi_n, \psi_n^{(k)}) = 1$ at each order of the approximation and normalize at the end. With

this convention, we can replace $E_n - W_n$ in Eq. (3.2.1) and obtain

$$\psi_n = C\phi_n + \varepsilon(\phi_n, H_1\psi_n)\int_\Omega G(\overline{x}, \overline{y})\psi_n(\overline{y})d^\nu y - \varepsilon\int_\Omega G(\overline{x}, \overline{y})H_1(y)\psi_n(\overline{y})d^\nu y. \tag{3.2.4}$$

As a preliminary result, we now show that $(\phi_n, \psi_n) = 1$ if and only if $C = 1$.

PROOF: Multiply eq. (3.2.4) by $\phi_n^*(x)$ and integrate to get:

$$(\phi_n, \psi_n) = C + \varepsilon(\phi_n, H_1\psi_n)\int_\Omega\int_\Omega\phi_n^*(\overline{x})G(\overline{x}, \overline{y})\psi_n(\overline{y})d^\nu \overline{y}d^\nu \overline{x}$$

$$- \varepsilon\int_\Omega\int_\Omega\phi_n^*(\overline{x})G(x, y)H_1(\overline{y})\psi_n(\overline{y})d^\nu \overline{y}d^\nu \overline{x}.$$

By Proposition 2, we have $(\phi_n, G) = 0$ for every $\overline{y}$ in Ω, giving $C = (\phi_n, \psi_n)$. We

therefore write

$$\psi_n(\overline{x}) = \phi_n(\overline{x}) + \varepsilon(\phi_n, H_1\psi_n)\int_\Omega G(x, y)\psi_n(y)d^\nu y$$

$$- \varepsilon\int_\Omega G(\overline{x}, \overline{y})H_1(\overline{y})\psi_n(\overline{y})d^\nu \overline{y}. \tag{3.2.5}$$

Equation (3.2.5) will be the basis for a useful approximation procedure.

We begin by proving the following proposition:

PROPOSITION 3: Suppose that $G(\overline{x}, \overline{y})$, $H_1(\overline{y})$ and $\psi_n(x;\varepsilon)$ satisfy the following

hypotheses:

(i) $G(\overline{x}, \overline{y})$ is bounded and continuous on $\Omega X \Omega$

(ii) $\psi_n(x;\varepsilon)$ is well-defined for all ε contained in $N_\delta \equiv \{\varepsilon | 0 \le |\varepsilon| < \delta\}$

       and is bounded and continuous with respect to $\overline{x}$ on Ω

(iii) $H_1(\overline{y}), H_1(\overline{y})G(\overline{x},\overline{y})$, and $H_1(\overline{y})G(\overline{x},\overline{y})\psi_n(x,\epsilon)$ are Reiman Integrable with

respect to $\overline{y}$ for all $\overline{x}$ in Ω and for all ϵ in N_δ.

Then, $\psi_n(x;\epsilon)$ is continuous with respect to ϵ at $\epsilon = 0$, and $\lim_{\epsilon \to 0} \psi_n(\overline{x};\epsilon) = \phi_n(\overline{x})$.

PROOF: Using eq. (3.2.5), we write

$$\psi_n(x;\epsilon) = \phi_n(\overline{x}) + \epsilon(\phi_n,H_1\psi_n)\int_\Omega G(\overline{x},\overline{y})\psi_n(\overline{y};\epsilon)d^\nu\overline{y} - \epsilon\int_\Omega G(\overline{x},\overline{y})H_1(\overline{y})\psi_n(x;\epsilon)d^\nu\overline{y}.$$

Using this and the postulated properties of H_1, G, and ψ_n, it is clear that

$\psi_n(x;0) = \phi_n(\overline{x})$. Next we show that $\lim_{\epsilon \to 0} \psi_n(x;\epsilon) = \phi_n(\overline{x})$, proving continuity. We

have

$$|\psi_n - \phi_n| \leq |\epsilon|\{|\int_\Omega G\psi_n d^\nu\overline{y} - \int_\Omega GH_1\psi_n d^\nu\overline{y}|\}.$$

By hypothesis, there must exist $M < \infty$ such that $|\int_\Omega G\psi_n d^\nu\overline{y} - \int_\Omega GH_1\psi_n d^\nu\overline{y}| \leq M$, and we

get $|\psi_n - \phi_n| \leq |\epsilon M|$, or $\lim_{\epsilon \to 0} \psi_n(x;\epsilon) = \phi_n(\overline{x})$, concluding the proof.

As the next step, we have

PROPOSITION 4: Under the same hypotheses as Proposition 3, $[\partial\psi_n/\partial\epsilon]\big|_{\epsilon=0}$

exists for all $\overline{x}$ in Ω.

PROOF: Consider the difference $\psi_n(x;h) - \psi_n(x;0)$ and use Proposition 3 to

obtain

$$\psi_n(\overline{x};h) - \psi_n(\overline{x};0) = h\{[(\phi_n,H_1\psi_n(\overline{s};h))]\int_\Omega G(\overline{x},\overline{y})\psi_n(\overline{y};h)d^\nu y$$

$$-\int_\Omega G(\overline{x},\overline{y})H_1\psi_n(\overline{y};h)d^\nu y\}. \qquad (3.2.6)$$

The equation being valid and well-defined for $0 \leq h \leq \delta$. We now divide both sides of

eq. (3.2.6) by h, and consider the limit of the RHS as $h \to 0$. We obtain

$$\lim_{h \to 0}[(\phi_n,H_1\psi_n)\int_\Omega G\psi_n d^\nu y - \int_\Omega GH_1\psi_n d^\nu y] = -(G,H_1\phi_n)(\overline{x})$$

since using Proposition 2 and 3

$$\int_\Omega G(\overline{x},\overline{y})\phi_n(\overline{y})d^\nu y = 0.$$

Since the limit as $h \to 0$ of the RHS/h of eq. (3.2.6) exists, so also must limit of

LHS/h as h→0, implying that $[\partial\Psi_n(x;\epsilon)/\partial\epsilon]\Big|_{\epsilon=0}$ exists and is in fact given by

$$\partial\psi_n(\overline{x};\epsilon)/\partial\epsilon\Big|_{\epsilon=0} = -\int_\Omega G(\overline{x},\overline{y})H_1(\overline{y})\phi_n(\overline{y})d^\nu y.$$

We now prove the following proposition:

PROPOSITION 5: The derivative, $[\partial^k\psi_n(\overline{x};\epsilon)/\partial\epsilon^k]\Big|_{\epsilon=0}$ exists for all $k \geq 0$, under the same assumptions as Propositions 3 and 4.

PROOF: We shall prove this by induction: Proposition 3 and 4 are the cases $k = 0$ and $k = 1$. We write eq. (3.2.6) as follows:

$$\psi_n(\overline{x}) = \phi_n(\overline{x}) + \epsilon F(\overline{x};\epsilon),$$

where F is defined as

$$F(\overline{x},\epsilon) \equiv (\phi_n, H_1\psi_n)\int_\Omega G(\overline{x},\overline{y})\psi_n(\overline{y})d^\nu y - \int_\Omega G(\overline{x},\overline{y})H_1(\overline{y})\psi_n(\overline{y})d^\nu y \qquad (3.2.7)$$

We assume that $[\partial^k\psi_n/\partial\epsilon^k]\Big|_{\epsilon=0}$ exists for $k = 0, 1, 2, \ldots, \ell$ and show the existence for $\ell + 1$. The existence of $[\partial^\ell\psi_n/\partial\epsilon^\ell]\Big|_{\epsilon=0}$ implies the existence of $[\partial^\ell F/\partial\epsilon^\ell]\Big|_{\epsilon=0}$. In fact we have, using Liebnitz' Rule for the derivative of a product [16]

$$\partial^\ell F/\partial\epsilon^\ell = \{\sum_{j=0}^{\ell} C_{\ell,j}(\phi_n, H_1\partial^{\ell-j}\psi_n/\partial\epsilon^{\ell-j})\int_\Omega G(\overline{x},\overline{y})(\partial^j\psi_n/\partial\epsilon^j)d^\nu y$$

$$- \int_\Omega G(\overline{x},\overline{y})H_1(\overline{y})(\partial^\ell\psi_n/\partial\epsilon^\ell)d^\nu y\}\Big|_{\epsilon=0}. \qquad (3.2.8)$$

Clearly, the RHS of eq. (3.2.8) depends only on the existence of $[\partial^k\psi_n/\partial\epsilon^k]\Big|_{\epsilon=0}$, for $k = 0, 2, \ldots, \ell$. Next, observe that

$$\partial^\ell\psi_n/\partial\epsilon^\ell\Big|_{\epsilon=0} = (\partial^\ell/\partial\epsilon^\ell)[\epsilon F(\overline{x};\epsilon)]\Big|_{\epsilon=0} = \ell\partial^{\ell-1}F/\partial\epsilon^\ell\Big|_{\epsilon=0} + \epsilon\partial^\ell F/\partial\epsilon^\ell\Big|_{\epsilon=0}$$

$$= \ell\partial^{\ell-1}F/\partial\epsilon^{\ell-1}\Big|_{\epsilon=0}. \qquad (3.2.9)$$

Finally, we show that eq. (3.2.9) holds for $\ell + 1$.

Consider

$$\partial^{\ell}\psi_n(\overline{x};h)/\partial\epsilon^{\ell}-\partial^{\ell}\psi_n(\overline{x};0)/\partial\epsilon^{\ell} =$$

$$\ell\partial^{\ell-1}F(\overline{x};h)/\partial\epsilon^{\ell} + h\partial^{\ell}F(\overline{x};0)/\partial\epsilon^{\ell}\ell\partial^{\ell-1}F(\overline{x};h)/\partial\epsilon^{\ell}. \qquad (3.2.10)$$

Divide eq. (3.2.10) by h and consider the limit of the RHS as h→0 (presuming

$\partial^{\ell}F(\overline{x};0)/\partial^{\ell}$ to exist) we have

$$\partial^{\ell+1}\psi_n(\overline{x};0)/\partial\epsilon^{\ell+1} \equiv \lim_{h\to 0}(1/h)[\partial^{\ell}\psi_n(\overline{x};h) - \partial^{\ell}\psi_n(\overline{x};0)/\partial\epsilon^{\ell}]$$

$$= (\ell+1)\partial^{\ell}F(\overline{x};0)/\partial\epsilon^{\ell}.$$

This concludes the proof of Proposition 5. We have shown that the function

$\psi_n(\overline{x};\epsilon)$ is C^{∞} with respect to ϵ at $\epsilon = 0$. Although this is a remarkable result,

it does not prove that $\psi_n(\overline{x};\epsilon)$ is analytic in ϵ.

From a practical point of view, however, Proposition 5 amply justifies trying

the following power series expansion as a representation for $\psi_n(\overline{x};\epsilon)$:

$$\psi_n(\overline{x};\epsilon)=\phi_n(\overline{x})+\epsilon[\partial\psi_n/\partial\epsilon]\big| + (\epsilon^2/2!)[\partial^2\psi_n/\partial\epsilon^2]\big| + \ldots \qquad (3.2.11)$$
$$\qquad\qquad\qquad\qquad\quad \epsilon=0 \qquad\qquad\qquad\qquad \epsilon=0$$

We next estimate the range of values of ϵ for which the series (3.2.11) can be

expected to converge. A dominating series is the following:

$$s(\epsilon) = ||\phi_n|| + |\epsilon|\{||\partial\psi_n(\overline{x};0)/\partial\epsilon||\} + \ldots \qquad (3.2.12)$$

We can write the series (3.2.12) in the simpler form

$$s(\epsilon) = \alpha_0 + |\epsilon|\alpha_1 + |\epsilon^2/2!|\alpha_2 + \ldots \qquad (3.2.13)$$

where the definition of the α_k's is obvious. By the ratio test, if

$\lim_{p\to\infty}|\epsilon^{p+1}\alpha_{p+1}p!/\epsilon^p\alpha_p(p+1)!| < 1$, then the series $s(\epsilon)$ will be convergent, implying

that the series (3.2.11) is absolutely and uniformly convergent for $\overline{x}$ in Ω. Thus,

let $L \equiv \lim_{p\to\infty} |\alpha_{p+1}/(p+1)\alpha_p|$ and convergence will be assured if $|\epsilon| < 1/L$. In

practice, the limit L is hard to compute, so we will estimate it using the first

two terms of the series, i.e., $p = 0$. If we define

$$K_2[u] = \int_\Omega G(\overline{x},\overline{y})H_1(\overline{y})u(\overline{y})d^\nu y,$$

then we have

$$L = \alpha_1/\alpha_0 = ||K_2[\phi_n]||/||\phi_n|| = ||K_2||.$$

Our estimate, therefore, becomes

$$|\epsilon| < \{\int_\Omega\int_\Omega |G(\overline{x},\overline{y})H_1(\overline{y})|^2 d^\nu x\ d^\nu y\}^{-\frac{1}{2}}. \qquad (3.2.14)$$

Inequality (3.2.14) should be compared with the estimate (3.1.18) which per-

tained to the BW theory.

Our next task will be to show the connection of this procedure to the

Rayleigh-Schrödinger theory. To do this, we expand $G(\overline{x},\overline{y})$ in the ortho-

normal set $\{\phi_k\}^\infty_1$.

Recall eq. (3.2.3)

$$(H_0 - W_n)G(\overline{x},\overline{y}) = \delta(\overline{x}-\overline{y}) - \phi_n^*(\overline{y})\phi_n(\overline{x}).$$

Substitution of $G = \sum_{k=1} a_k^{(n)}\phi_k(\overline{x})$, and multiplication by $\phi_p^*(\overline{x})$ followed by

integration gives

$$\sum_{k=1}^\infty (W_k-W_n)a_k^{(n)}\delta_{pk} = \phi_p^*(\overline{y}) - \phi_n^*(\overline{y})\delta_{pn}, \qquad (3.2.15)$$

for calculating $a_k^{(n)}$.

We, therefore, write

$$G(\overline{x},\overline{y}) = \sum_{s\neq n} \phi_s^*(\overline{y})\phi_s(\overline{x})/(W_s-W_n). \qquad (3.2.16)$$

Substitution of eq. (3.2.16) into eq. (3.2.10) gives

$$\psi_n(\overline{x}) = \phi_n(\overline{x}) + \epsilon(\phi_n,H_1\psi_n) \sum_{s\neq n} (\phi_s,\psi_n)\phi_s(\overline{x})/(W_s-W_n)$$

$$- \epsilon \sum_{s\neq n} (\phi_s,H_1\psi_n)\phi_s(\overline{x})/(W_s-W_n). \qquad (3.2.17)$$

Let $\psi_n \rightarrow \phi_n$ on the RHS of eq. (3.2.17) producing

$$\psi_n(1) = \phi_n + \epsilon \sum_{s \neq n} (\phi_s, H_1 \psi_n) \phi_s(\overline{x})/(W_n - W_s),$$

which is the defining equation for Rayleigh-Schrödinger Perturbation Theory [13, 14]. Resubstitution of $\psi_n^{(1)}$, $\psi_n^{(1)}$, $\psi_n^{(3)}$, . . ., $\psi_n^{(k)}$ will produce the RS theory.

4. SUMMARY

4.1 WAVE FUNCTION (EXACT - GREEN'S FUNCTION KERNELS)

(BW) $\psi_n(\overline{x}) = -\epsilon \int_\Omega g_{BW}(\overline{x}, \overline{y}) H_1(\overline{y}) \psi_n(\overline{y}) d^\nu y$

(RS) $\psi_n(\overline{x}) = \phi_n + \int_\Omega [E_n - W_n - \epsilon H_1(\overline{y})] g_{RS}(\overline{x}, \overline{y}) \psi_n(\overline{y}) d^\nu y$

The Green's Functions satisfy the following equations:

(BW) $(H_0 - E_n) g_{BW}(\overline{x}, \overline{y}) = \delta(\overline{x} - \overline{y}),$

(RS) $(H_0 - W_n) g_{RS}(\overline{x}, \overline{y}) = \delta(\overline{x} - \overline{y}) - \phi_n^*(\overline{y}) \phi_n(\overline{x}),$

4.2 WAVE FUNCTIONS (EXACT - EIGENFUNCTION EXPANSION)

(BW) $\psi_n(\overline{x}) = \phi_n(\overline{x}) - \epsilon \sum_{k \neq n} (\phi_n, H_1 \psi_n)/(W_k - E_n)$

(RS) $\psi_n(\overline{x}) = \phi_n(\overline{x}) - \epsilon(\phi_n, H_1 \psi_n) \sum_{k \neq n} (\phi_k, \psi_n) \phi_k(\overline{x})/(W_k - W_n)$

$$- \epsilon \sum_{k \neq n} (\phi_n, H_1 \psi_n) \phi_k(\overline{x})/(W_k - W_n)$$

4.3 WAVE FUNCTIONS (FIRST ORDER - GREEN'S FUNCTION KERNELS)

(BW) $\psi_n(1) = \phi_n - \epsilon \int_\Omega g_{BW}(x, y; E_n^{(1)}) H_1(\overline{y}) \phi_n(\overline{y}) d^\nu y$

(RS) $\psi_n^{(1)} = \phi_n - \epsilon \int_\Omega g_{RS}(\overline{x}, \overline{y}) H_1(\overline{y}) \phi_n(\overline{y}) d^\nu y$

4.4 WAVE FUNCTIONS (FIRST ORDER - EIGENFUNCTION EXPANSIONS)

(BW) $\psi_n(1) = \phi_n - \epsilon \sum_{k \neq n} (\phi_k, H_1 \phi_n) \phi_k(\overline{x})/(W_k - E_n)$

(RS) $\psi_n(1) = \phi_n - \epsilon \sum_{k \neq n} (\phi_k, H_1 \phi_n) \phi_k(\overline{x})/(W_k - W_n)$

4.5 ENERGY FORMULAS (EXACT)

(BW, RS) $E_n = W_n + \varepsilon(\phi_n, H_1\psi_n)$

5. APPENDIX--THE PERTURBED INFINITE SQUARE WELL IN CLOSED FORM PERTURBATION

THEORY. [8]

Consider the infinite square well of width L with a perturbation "V_o"

added to the right half of the well. The unperturbed solutions are

$$\phi_n(x) = \sqrt{2/L} \, \sin(n\pi x/L)$$

and

$$W_n = n^2 h^2/8mL^2.$$

The standard (RS) perturbation theory approach to this problem produces the

following results for the ground state

$$E_1^{(2)} = W_1 + V_0/2 - (rV_0^2/\pi^2 W_1) \sum_{k=1}^{\infty} \frac{4k^2}{k^2-1,} \qquad (5.1)$$

and

$$\psi_1^{(1)}(x) = \phi_1(x) - (4V_0/W_1\pi) \sum_{k=1}^{\infty} (-1)^k k\phi_{2k}/(4k^2-1)^2. \qquad (5.2)$$

The closed form modified Green's Function obtained by standard techniques is

$$G(x,y) = (\mu/\lambda_n L)[(L-y) \, \cos(\lambda_n y)\sin(\lambda_n x)$$

$$- x \, \sin(\lambda_n y)\cos(\lambda_n x)] \quad \text{for } x < y$$

and

$$G(x,y) = (\mu/\lambda_n L)[(L-x) \, \cos(\lambda_n x)\sin(\lambda_n y)$$

$$- y \, \sin(\lambda_n x)\cos(\lambda_n y)] \quad \text{for } x > y$$

where $\lambda_n \equiv n\pi/L$ and $\mu = 2m/h^2$. For the ground state, n = 1, the use of this

Green's Function in the appropriate equations yields

$$E_1^{(2)} = W_1 + V_0/2 - V_0/16W_1$$

and

$$\psi_1^{(1)}(x) = \phi_1(x) + (\mu V_0/4\pi_1) \sqrt{2/L} \begin{cases} x \cos(\lambda_1 x) & (x < L/2) \\ \\ (L-x)\cos(\lambda_1 x) & (x \geq L/2). \end{cases}$$

These equations are equivalent [8] to equations (5.1) and (5.2) and in many cases would be more useful.

REFERENCES

1. Jackson, J. D., _Classical Electrodynamics_, John Wiley, New York, 1962.

2. Arfken, G., _Mathematical Methods for Physicists_, Academic Press, New York, 1970, 748-766.

3. Merzbacher, E., _Quantum Mechanics_, John Wiley, New York, 1970, Chapter 19.

4. Kato, T., _Perturbation Theory for Linear Operators_, Springer-Verlag, New York, 1976.

5. Rellich, F., _Perturbation Theory of Eigenvalue Problems_, Gordon and Breach, New York, 1969.

6. Korn, G. A. and T. M. Korn, _Mathematical Handbook for Scientists and Engineers_, McGraw-Hill, New York, 1968, 506.

7. Ibid., 515-516.

8. Rose, O. J., _A Study of Various Perturbation Methods for Solving the Time Independent Schrödinger Equation_, M S Thesis, East Carolina University, 1975, 18-20.

9. Ibid.

10. Ibid.

11. Ibid, 104.

12. Merzbacher, op cit.

13. Davydov, A. A., _Quantum Mechanics_, Neo Press, Ann Arbor, 1966, 171-173.

14. Silvert, W., Comparison of Rayleigh-Schrödinger and Brillouin-Wigner Perturbation Theories, _American Journal of Physics_, 40(1972).

15. Statgold, I., _Boundary Value Problems of Mathematical Physics_, Vol. I, MacMillan, New York, 1967.

16. Neilsen, K. L., _Differential Equations_, Barnes & Noble, New York, 1962, 11.