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Integral Equations in Quantum Chemistry

Green's functions and integral equations are very useful tools for solving Schrodinger's equation. In making a recent survey of texts on quantum chemistry I was astonished to find the complete neglect of the use of these powerful techniques. They are so fundamental to quantum mechanics that Richard Feynman has completely developed the subject in terms of Green's functions and integral equations *(1)*. His "path integral" approach was the basis for the study of quantum electrodynamics. This is not the only field where these techniques are useful. Most texts on quantum mechanics develop the subjects while introducing scattering theory *(2–4)*. Their power for approximating solutions to the Schrodinger equation via perturbative and iterative techniques is also usually developed along with scattering theory. Although there are a number of specialized texts *(5–7)* which deal with Green's functions and many-body theory, very little is said in current texts on quantum mechanics about many-body theory or the application of Green's functions and integral equations to chemistry. These subjects are playing an important role in current research and will continue to be developed. I feel it important to introduce them in the quantum chemistry course or preferably in the physical chemistry course. After solving the particle in a box problem via differential equations I give my students the following introduction to Green's functions and integral equations.

The Schrodinger equation for a particle bounded with infinite potential to a one dimensional box of unit length is *(8)*

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x) = E\psi(x) \qquad (1)$$

$$V(x) = \begin{cases} 0 & \text{for } 0 \leq x \leq 1 \\ \infty & \text{otherwise} \end{cases}$$

with boundary conditions $\psi(0) = \psi(1) = 0$. This is also the equation for a vibrating string with fixed endpoints.

Since the potential outside of the box is infinite we can set $\psi(x) = 0$ for this region of space and solve eqn. (1) for the interior. Rearranging one has

$$-\psi''(x) = f(x) \qquad (2)$$

where

$$f(x) = \frac{2mE}{\hbar}\psi(x) \qquad (3)$$

Integrating once we obtain

$$\psi'(x) = \alpha - \int_0^x f(\xi)\,d\xi \qquad (4)$$

where

$$\alpha = \psi'(0)$$

A second integration yields

$$\psi(x) = \alpha x - \int_0^x d\eta \int_0^\eta f(\xi)\,d\xi \qquad (5)$$

where the boundary condition $\psi(0) = 0$ has been invoked.

In eqn. (5) we are integrating over a triangular region in the η,ξ plane. Inspection shows that this can be equivalently written as

$$\psi(x) = \alpha x - \int_0^x f(\xi)\,d\xi \int_\xi^x d\eta \qquad (6)$$

As a check the reader should differentiate eqn. (6) twice to yield eqn. (2). Now

$$\psi(x) = \alpha x - \int_0^x (x - \xi)f(\xi)\,d\xi \qquad (7)$$

Since x lies on the closed interval $\{0,1\}$ eqn. (7) can be rewritten as

$$\psi(x) = \alpha x - \int_0^1 (x - \xi)H(x - \xi)f(\xi)d\xi \qquad (8)$$

where $H(t)$ is the Heaviside function

$$H(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0 \end{cases} \qquad (9)$$

Equation (7) can also be obtained by taking the Laplace transform of eqn. (2), solving for the inverse Laplace transform of $\psi(k)$, and introducing any two arbitrary solutions to the homogeneous equation

$$\psi''(x) = 0$$

This method of obtaining eqn. (7) closely resembles the method of solving Schrodinger's equation in momentum space.

We now impose the second boundary condition to solve for α

$$\psi(1) = 0 = \alpha - \int_0^1 (1 - \xi)H(1 - \xi)f(\xi)d\xi \qquad (10)$$

Thus

$$\psi(x) = \int_0^1 \{x(1 - \xi) - (x - \xi)H(x - \xi)\}f(\xi)\,d\xi \qquad (11)$$

$\psi(x)$ has the form

$$\psi(x) = Kf(x)$$

where K is an integral operator defined by

$$Kf(x) = \int_0^1 \{x(1 - \xi) - (x - \xi)H(x - \xi)\}f(\xi)\,d\xi \qquad (12)$$

In eqn. (12) $x(1 - \xi) - (x - \xi)H(x - \xi)$ is the kernal of the integral operator K. When the kernal comes from the solution of an equation with a differential operator, it is called the Green's function of that operator for the appropriate boundary conditions. Thus $G(x,\xi) = x(1 - \xi) - (x - \xi)H(x - \xi)$ is the Green's function of $-d^2/dx^2$ subject to the condition $\psi(0) = \psi(1) = 0$ or

$$G(x,\xi) = \begin{cases} \xi(1 - x) & 0 \leq \xi \leq x \\ x(1 - \xi) & x \leq \xi \leq 1 \end{cases} \qquad (13)$$

Now eqn. (11) may be rewritten

$$\psi(x) = \int_0^1 G(x, \xi)f(\xi)\,d\xi \qquad (14)$$

and using eqn. (3)

$$\psi(x) = \lambda \int_0^1 G(x, \xi)\psi(\xi)\,d\xi \qquad (15)$$

where

$$\lambda = 2mE/\hbar^2 \qquad (16)$$

Equation (14) looks very much like the integral representation of the three dimensional Schrodinger equation which is obtained by applying the Fourier integral theorem to the wave function expressed in momentum space *(9)*.

Equation (15) is a homogeneous Fredholm integral equation of the second kind *(10)*. Introducing $\mu = 1/\lambda$ one can readily see that this is an eigenvalue problem

$$K\psi(x) = \mu\psi(x) \tag{17}$$

Equation (1) was an eigenvalue problem i.e.

$$H\psi = E\psi$$

in fact, μ is just E^{-1} and K is the operator inverse of $-d^2/dx^2$ including boundary conditions.

Since, in eqn. (13) $G(x,\xi) = G(\xi,x)$, the Green's function is symmetric. Because of this symmetry we are assured that the eigenvalues are real and the eigenfunctions corresponding to different eigenvalues are orthogonal *(11)*. At this point, eqn. (17) may be solved using the standard methods for solving a homogeneous Fredholm equation *(12)*. However, we will make use of another property of the Green's function to solve eqn. (17) by inspection.

Let us look at eqn. (2)

$$-d^2\psi(x)/dx^2 = f(x)$$

Suppose $-d^2/dx^2$ possesses a complete orthonormal set of eigenfunctions $\{\phi_n\}$ so that

$$\frac{-d^2\phi_n(x)}{dx^2} = \lambda_n\phi_n(x) \tag{18}$$

We could write

$$\psi(x) = \sum_{n=1}^{\infty} a_n\phi_n(x) \tag{19}$$

$$f(x) = \sum_{n=1}^{\infty} b_n\phi_n(x)$$

Now

$$-\frac{d^2\psi(x)}{dx^2} = -\frac{d^2}{dx^2}\sum_{n=1}^{\infty} a_n\phi_n(x) = -\sum_{n=1}^{\infty}\frac{d^2}{dx^2}a_n\phi_n(x) = -\sum_{n=1}^{\infty} a_n\lambda_n\phi_n(x) = \tag{20}$$

$$f(x) = \sum_{n=1}^{\infty} b_n\phi_n(x)$$

Thus

$$\sum_{n=1}^{\infty}(-a_n\lambda_n - b_n)\phi_n = 0 \tag{21}$$

and

$$a_n = -b_n/\lambda_n \tag{22}$$

We can now write

$$\psi(x) = -\sum_{n=1}^{\infty} 1/\lambda_n b_n\phi_n(x) \tag{23}$$

Because the $\{\phi_n\}$ are orthogonal we can write

$$b_n = \int \phi_n^*(\xi)f(\xi)d\xi \tag{24}$$

Let us write eqn. (23) as

$$\psi(x) = -\sum_{n=1}^{\infty} 1/\lambda_n\phi_n(x) \qquad \int\phi_n^*(\xi)f(\xi)d\xi$$

$$= -\int\sum_{n=1}^{\infty}\frac{\phi_n(x)\phi_n^*(\xi)}{\lambda_n}f(\xi)d\xi \tag{25}$$

Then

$$\psi(x) = \int G(x,\xi)f(\xi)d\xi \tag{26}$$

where

$$G(x,\xi) = -\sum_{n=1}^{\infty}\frac{\phi_n(x)\phi_n^*(\xi)}{\lambda_n} \tag{27}$$

This result is valid for any linear ordinary differential operator and enables one to write the Green's function for an inhomogeneous eqn. (2) in terms of the eigenfunctions and eigenvalues of the corresponding homogeneous eqn. (18).

Our problem is not one of an inhomogeneous equation, however. If we could expand eqn. (13) in an infinite series we could immediately identify $\phi_n(x)$ and λ_n by eqn. (27). These are just the quantities we are after. Since x is bounded on $\{0,1\}$ a Fourier expansion is appropriate.

The Fourier sine series of eqn. (13) can be written

$$G(x,\xi) = \sum_{n=1}^{\infty} b_n \sin n\pi x \tag{28}$$

where

$$b_n = 2\int_0^1 G(x,\xi)\sin n\pi x\,dx \tag{29}$$

Solving for b_n in eqn. (29) one obtains

$$G(x,\xi) = \sum_{n=1}^{\infty}\frac{2\sin n\pi x\sin n\pi\xi}{n^2\pi^2} \tag{30}$$

Therefore

$$\phi_n(x) = (2)^{1/2}\sin n\pi x$$

$$\lambda_n = n^2\pi^2 = 2mE/\hbar^2$$

$$E = n^2h^2/8m$$

One might ask why bother developing the integral equation? Notice the integral operator is bounded whereas the differential operator is not. Theorems about eigenfunction expansion and completeness are thus more easily derived in the integral formalism. The integral equation incorporates the boundary condition. One also has new numerical and variational approximations which complement similar approximations in the differential equation formulation.

For example most students of quantum chemistry are introduced to the Rayleigh-Ritz variational procedure for the Schrodinger equation. For the Hamiltonian operator and an appropriate trial ket *(13)*

$$\frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} \geq E \tag{31}$$

and for the integral operator or inverse Hamiltonian *(14)*

$$\frac{\langle\phi|K|\phi\rangle}{\langle\phi|\phi\rangle} \leq \mu \tag{32}$$

Expanding the ket $|\phi>$ in terms of a linearly independent basis $|i>$ gives

$$R(C_1, C_2, \ldots C_n) = \frac{\langle\phi|L|\phi\rangle}{\langle\phi|\phi\rangle} = \sum_{i,j=1}^{n} C_i^*C_j\langle i|L|j\rangle\Big/\sum_{i,j=1}^{n}\langle i|j\rangle C_i^*C_j \tag{33}$$

If we choose the coefficients C_i so that R is as small as possible (eqn. (31)) or as large as possible (eqn. (32)) we can expect a close approximation to the eigenvalues. In either case we obtain the extremum by differentiating R with respect to each C_i and equating the result to zero.

This can be summarized by the secular equation

$$\det\{L - R^*\Delta\} = 0 \tag{34}$$

where L_{ij} is $\langle i|L|j\rangle$, L is either H or K, R^* is the extremal value of R and $\Delta_{ij} = \langle i|j\rangle$.

The n roots R_k are approximations to the first n eigenvalues *(15)*. The C_i^k determine the trial wave function corresponding to the kth eigenvalue $|\phi_k> = \Sigma\, C_i^k|i>$.

Let us use a trial wave function to get an approximation to the ground state energy of the particle in a box. First we use the differential equation

$$H\phi = \lambda\phi$$

where $H = -d^2/dx^2$ and $\lambda = 2mE/\hbar^2$. Let

$$\phi = \begin{cases} \sum_i C_i|i> = C_1 x(1-x) & \text{for } 0 \le x \le 1 \\ 0 \text{ otherwise} \end{cases}$$

This is a simple trial function satisfying the boundary condition $\phi(0) = \phi(1) = 0$. Now

$$H|1> = -\mathrm{d}^2/\mathrm{d}x^2(x)(1-x) = 2 \tag{35}$$

and

$$\langle 1|H|1\rangle = H_{11} = \int_0^1 2x(1-x) = 1/3 \tag{36}$$

$$\langle 1|1\rangle = \Delta_{11} = \int_0^1 x^2(1-x)^2\mathrm{d}x = 1/30 \tag{37}$$

$$H_{11} - R_1^*\Delta_{11} = 0 \tag{38}$$

$$R_1^* = 10 \tag{39}$$

For the integral operator

$$K\psi = \mu\psi \tag{40}$$

Using the same trial function

$$K|1> = \int_0^1 G(x,\xi)\xi(1-\xi)\mathrm{d}\xi = 1/12\,x - 1/6\,x^3 + 1/12\,x^4 \tag{41}$$

$$\langle 1|K|1\rangle = 3.373 \times 10^{-3} \tag{42}$$

$$K_{11} - R_1^*\Delta_{11} = 0 \tag{43}$$

$$R_1^* = 0.1012 \tag{44}$$

Notice that $\mu = 1/\lambda$. Comparing we see

$$\lambda(\text{exact}) = \pi^2 \simeq 9.870$$
$$\lambda(\text{diff.}) = 10$$
$$\lambda(\text{integ}) = 9.881$$

This simple example shows how the integral and differential forms of Schrodinger's equation can be used to complement one another in a variational calculation. The reader should note that the trial wave function for the differential operator must satisfy the boundary conditions of the problem. In the integral case the Green's function forces the proper boundary conditions for any trial wave function. In fact, one can choose the trial function

$$\phi = 1$$

for the integral variational procedure and obtain an upper bound of twelve to the lowest eigenvalue.

The solution of the particle in a box problem using Green's functions and integral equations is somewhat like breaking peanuts with a sledge hammer. However, now that an introduction has been given much more difficult problems can be handled using these powerful techniques. In our physical chemistry course we use this approach to solve diffusion problems and also to give an introduction to scattering theory. This paper has shown how the integral formulation can complement the differential formulation in a variational calculation. The two formulations also strongly complement one another as iterative tools. The reader interested in further study should consult the fine book by Greenberg *(16)*.

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