Exact Integral Relationship in Quantum Mechanics: Application to the Variational Method*

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An external parameter is, by definition, a quantity which may be varied independently of the coordinate positions and of the momenta of the various particles composing the system. Thus, the Schrödinger equation, for a particular value of the external parameter, belongs to a family of differential equations obtained by varying the numerical value of the external parameter. An explicit example of an external parameter is an imposed magnetic field. The way in which the energy changes throughout the family of Schrödinger equations is given by the Hellmann-Feyman theorem. An exact integral relationship, involving a pair of external parameters, is derived from the Hellmann-Feynman theorem using assumptions which are not unduly restrictive. This relationship is used to arrive at trial (variational) wave functions for quantum mechanical problems which are not exactly soluble. The method is demonstrated in two sample problems. A technique for progressively improving variational calculations is discussed.

I. INTRODUCTION

MANY problems in quantum mechanics involve external parameters. An external parameter is a quantity which may be varied independently of both the position coordinates and the momenta of the various particles composing the system. It may be that a given quantity may be considered as an external parameter only if certain approximations are made. For example, the internuclear distance in a diatomic molecule may be considered as an external parameter if the Born-Oppenheimer approximation is imposed. Other examples of external parameters are electric and magnetic fields, nuclear and ionic charges, and magnetic and electric moments.

The basic problem in quantum mechanics is to solve the Schrödinger equation,

$$\mathcal{H}(\lambda,\mu,\cdots)\Psi_n(\lambda,\mu,\cdots)=E_n(\lambda,\mu,\cdots)\Psi_n(\lambda,\mu,\cdots), \quad (1)$$

where $\lambda,\mu,\cdots$ are several external parameters.

II. AN INTEGRAL RELATIONSHIP

The generalized Hellman-Feynman theorem[1] states that

$$\frac{\partial E_n}{\partial\lambda}=\int\Psi_n^*\frac{\partial\mathcal{H}}{\partial\lambda}\Psi_n d\tau, \quad (2)$$

for each parameter λ. This theorem is consistent with the variational theorem which states that if Ψ is an eigenfunction of $\mathcal{H}$, then a change in E depends only on the change in $\mathcal{H}$ and not on the change in Ψ. Recently, considerable interest has been placed on the importance of choosing trial wave functions which satisfy (2).[2]

If we differentiate (2) with respect to another external parameter, say μ, and assume that derivatives of $\mathcal{H}$ with respect to all external parameters are Hermitian, we obtain

$$\frac{\partial^2 E_n}{\partial\mu\partial\lambda}=\int\Psi_n^*\frac{\partial^2\mathcal{H}}{\partial\mu\partial\lambda}\Psi_n d\tau+2\,\mathrm{Re}\int\Psi_n^*\frac{\partial\mathcal{H}}{\partial\lambda}\frac{\partial\Psi_n}{\partial\mu}d\tau, \quad (3)$$

where Re signifies that the real part of the integral is to be taken.

We will consider only problems in which no discontinuities exist in $\mathcal{H}$ and its derivatives. Then we require that

$$\frac{\partial^2\mathcal{H}}{\partial\lambda\partial\mu}=\frac{\partial^2\mathcal{H}}{\partial\mu\partial\lambda}, \quad \frac{\partial^2 E_n}{\partial\lambda\partial\mu}=\frac{\partial^2 E_n}{\partial\mu\partial\lambda}. \quad (4)$$

An interchange of λ and μ in (3) shows that

$$\mathrm{Re}\int\Psi_n^*\left[\frac{\partial\mathcal{H}}{\partial\lambda}\frac{\partial\Psi_n}{\partial\mu}-\frac{\partial\mathcal{H}}{\partial\mu}\frac{\partial\Psi_n}{\partial\lambda}\right]d\tau=0. \quad (5)$$

Now the phase of Ψ_n is arbitrary and the eigenfunction Φ_n given by

$$\Phi_n=\Psi_n e^{i\gamma(\mu)}e^{i\delta(\lambda)} \quad (6)$$

is just as acceptable as Ψ_n. Suppose that the integral in (5) has the value $i\epsilon(\lambda,\mu)$. We find that

$$\int\Phi_n^*\left[\frac{\partial\mathcal{H}}{\partial\lambda}\frac{\partial\Phi_n}{\partial\mu}-\frac{\partial\mathcal{H}}{\partial\mu}\frac{\partial\Phi_n}{\partial\lambda}\right]d\tau=i\epsilon+i\times\left[\frac{d\gamma}{d\mu}\frac{\partial E_n}{\partial\lambda}-\frac{d\delta}{d\lambda}\frac{\partial E_n}{\partial\mu}\right]. \quad (7)$$

Since $\gamma(\mu)$ and $\delta(\lambda)$ are arbitrary functions, we are free to choose them so that

$$\frac{d\gamma}{d\mu}\frac{\partial E_n}{\partial\lambda}-\frac{d\delta}{d\lambda}\frac{\partial E_n}{\partial\mu}=-\epsilon. \quad (8)$$

It is thus clear that with a proper choice of phase we may write

$$\int\Psi_n^*\frac{\partial\mathcal{H}}{\partial\lambda}\frac{\partial\Psi_n}{\partial\mu}d\tau=\int\Psi_n^*\frac{\partial\mathcal{H}}{\partial\mu}\frac{\partial\Psi_n}{\partial\lambda}d\tau. \quad (9)$$

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[1] H. Hellmann, *Einfuhrung in Die Quantenchemie* (Deuticke, Leipzig, 1937); R. P. Feynman, Phys. Rev. **56**, 340 (1939); T. Berlin, J. Chem. Phys. **19**, 208 (1951).

[2] J. O. Hirschfelder and C. A. Coulson, J. Chem. Phys. **36**, 941 (1962).

Equation (9) is a criterion for the dependence of Ψ on λ and μ. For each distinct pair of variables, Eq. (9) must be satisfied.

III. APPLICATIONS

So far the theory has been exact in that Ψ_n is an eigenfunction of $\mathcal{H}$ and E_n is the corresponding eigenvalue. Suppose, however, that we cannot solve (1) for Ψ_n; it is then often desirable to approximate E_n by applying a variational procedure in which a trial wave function is used. It is, of course, highly desirable to choose a trial wave function as close as possible to the exact wave function.

If we were to attempt to find a function, by some iterative procedure, which satisfied (9), we might begin with an initial trial wave function which satisfied the following relationship:

$$\frac{\partial \mathcal{H}}{\partial \lambda}\frac{\partial \Psi_n'}{\partial \mu}=\frac{\partial \mathcal{H}}{\partial \mu}\frac{\partial \Psi_n'}{\partial \lambda}. \tag{10}$$

In the present section we will use Eq. (10) in choosing trial wave functions for two sample problems.

First, consider the one-dimensional Hamiltonian,

$$\mathcal{H}=p^2/2m+\mu e^{-\lambda x^2}, \tag{11}$$

with $\mu<0$ and $\lambda>0$. Using (10), we have

$$\partial\Psi'/\partial\lambda=-\mu x^2(\partial\Psi'/\partial\mu), \tag{12}$$

where the prime indicates that Ψ' is to be a trial wave function. Equation (12) is satisfied by

$$\Psi'=\varphi(x)\mu^{g(x)}e^{-\lambda x^2 g(x)}. \tag{13}$$

$\varphi(x)$ and $g(x)$ may be determined by the variational method. However, the symmetry of the Hamiltonian requires that the wave function be even or odd in x. Thus it will be simpler, although less accurate, to replace $\varphi(x)$ and $g(x)$ by the constants A and $\beta/2$, respectively, in the ground state. Then, normalizing Ψ' to unity and applying the variational principle, we obtain

$$E'=-(\hbar^2/2m)\lambda\beta(\beta+\tfrac{1}{2}), \tag{14}$$

$$\Psi'=(\lambda\beta/\pi)^{\frac{1}{4}}e^{-\lambda\beta x^2/2}, \tag{15}$$

where

$$\beta^{\frac{1}{2}}(\beta+1)^{\frac{3}{2}}=-(2m/\hbar^2)(\mu/\lambda). \tag{16}$$

The wave function (15) could be guessed at from other considerations[3]; for example, at small distances, the Hamiltonian (11) approximates that of a harmonic oscillator. In calculations involving nucleons the accuracy of (14) is moderate.

As a second example, we consider the problem of the Yukawa potential. Since the angular momentum is zero in the ground state, we have

$$\mathcal{H}=p^2/2m+(\mu/r)e^{-\lambda r}. \tag{17}$$

The variable r is the distance from the origin. Using (10), we have

$$\partial\Psi'/\partial\lambda=-\mu r(\partial\Psi'/\partial\mu). \tag{18}$$

Equation (18) is satisfied by

$$\Psi'=\varphi(r)\mu^{g(r)}e^{-\lambda r g(r)}. \tag{19}$$

For simplicity we would write

$$\Psi'=A\mu^{\beta}e^{-\lambda\beta r}, \tag{20}$$

where A and β are constants. The function (20) is known to give very good results for large λ.[4] Of course, one would be tempted to use (20) because of the close resemblance of the present problem to that of the Coulomb potential. The example is instructive, nevertheless.

The method outlined above may also be applied to other problems with reasonable success.[5]

IV. DISCUSSION

The solution to the eigenvalue Eq. (1) must satisfy the relationship between pairs of external parameters as shown in Eq. (5). With a proper choice of phase, Eq. (5) reduces to (9). In cases where Ψ cannot be found exactly, it has been shown that the first approximation to (9), namely (10), may often be a good approximation. The quality of a trial wave function, chosen to satisfy (10), must, of course, be decided for each individual problem. If this initial trial function does not give results to the desired accuracy, the energy and wave function may be improved by various iterative procedures.[3] Once an iterative procedure has been chosen, the following criterion might prove useful. Define a quantity I_N as

$$I_N=\int \Psi_N'^{*}\left[\frac{\partial \mathcal{H}}{\partial \mu}\frac{\partial \Psi_N'}{\partial \lambda}-\frac{\partial \mathcal{H}}{\partial \lambda}\frac{\partial \Psi_N'}{\partial \mu}\right]d\tau, \tag{21}$$

$$N\geq 1.$$

Ψ_N' is the trial wave function after the Nth minimization of the energy. Then when $|I_N|\leq\delta$, where δ is a small predetermined number, the iterative process is stopped. After the first minimization of the energy, the trial wave function will no longer satisfy (10), but it is assumed that the iterative procedure converges toward the exact Ψ in which case I_N converges to zero.

It is often true that the energy, as obtained from the variational principle, is somewhat insensitive to the

[3] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953).

[4] R. G. Sachs and M. G. Mayer, Phys. Rev. **53**, 991 (1938).

[5] This method, applied to the problem of the shielding of a nuclear magnetic moment by an electron, leads to a trial wave function of the form used successfully by M. J. Stephen, Proc. Roy. Soc. (London) **A243**, 264 (1957).

form of the approximate wave function. In that case, the relative accuracy of two or more approximate wave functions, which give comparable energy values, could be determined by the ratios of the corresponding I_N values.

It should be noted that a trial wave function which minimizes the energy, with respect to some variational parameter, satisfies the Hellmann-Feynman theorem.[2,6]

[6] G. G. Hall, Phil. Mag. (London) **6**, 249 (1961).

One further point is in order. Equation (9) implies the phase relationship (8). Care must be taken not to make simultaneous use of formulas which presuppose another choice of phase.

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Singularities in Angular Momentum of the Scattering Amplitude for a Class of Soluble Potentials*

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The analyticity of the scattering amplitude in the variables, energy, and angular momentum is explicitly studied for square well and a class of continuous potentials having a $1/r^2$ type of core or tail. The trajectories of the poles in the l plane and their residues have been determined numerically.

I. INTRODUCTION

THE conjectures about the existence and properties of poles of the relativistic S matrix in complex angular momentum in the theory of strong interactions are based on the corresponding situation in potential scattering. The analyticity in the variables momentum k and angular momentum l in the case of potential scattering has been discussed by Regge[1] and by Froissart.[2]

The purpose of the present work is to study explicitly the trajectories of the poles and their residues for a class of soluble potentials. In Sec. II we discuss the analyticity of the S matrix in terms of the logarithmic derivative of the wave functions. The conclusions of this section are valid for all cutoff potentials. The contours in the l plane for the Watson-Sommerfeld transformation are discussed in Sec. III and the determination of the singularities in Sec. IV. In the following sections the potentials are considered explicitly and the numerical results and their interpretations are given.

II. ANALYTIC CONTINUATION OF THE S MATRIX IN l AND k

We consider the radial Schrödinger equation with complex k and complex $\lambda=l+\frac{1}{2}$ in units $\hbar^2=2m=1$,

$$\left(\frac{d^2}{dr^2}+k^2-\frac{\lambda^2-\frac{1}{4}}{r^2}-V(r)\right)\varphi(k,\lambda,r)=0. \quad (1)$$

The potential $V(r)$ is assumed to vanish outside a sphere of radius r_0, or behave as $1/r^2$ for $r>r_0$

$$V(r)=V_0(r)\theta(r_0-r)+\frac{\Lambda}{r^2}\theta(r-r_0).$$

The tail of the potential could be eliminated by writing

$$V(r)=\left(V_0(r)-\frac{\Lambda}{r^2}\right)\theta(r_0-r)+\frac{\Lambda}{r^2},$$

and absorbing the last part into the centrifugal term in Eq. (1). The effective λ in Eq. (1) would be then $(\lambda^2-\Lambda)^{\frac{1}{2}}$. However, it is more convenient to treat the tail of the potential separately. Inside the region $r<r_0$, the potential is arbitrary as long as the logarithmic derivative of φ exists at $r=r_0$. The solution of Eq. (1) in the region $r>r_0$ may be written as

$$\varphi(k,\nu,r)=B_1(k,\nu)(kr)^{1/2}J_\nu(kr)+B_2(k,\nu)(kr)^{1/2}J_{-\nu}(kr), \quad r>r_0, \quad (2)$$

where

$$\nu=\lambda=l+\tfrac{1}{2} \quad \text{if} \quad V=0 \quad \text{for} \quad r>r_0, \quad (3a)$$

$$\nu=[(l+\tfrac{1}{2})^2-\Lambda]^{1/2} \quad \text{if} \quad V=\Lambda/r^2 \quad \text{for} \quad r>r_0. \quad (3b)$$

Here $J_\nu(z)$ and $J_{-\nu}(z)$ are the usual Bessel functions which are linearly independent except when ν is an integer. They are entire functions of ν in the product domain of the whole ν plane and the z plane except for a possible branch point at $z=0$. The circuit relation at

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[1] T. Regge, Nuovo cimento **14**, 951 (1959); **18**, 947 (1960); A. Bottino, A. M. Longoni, and T. Regge, *ibid.* **23**, 954 (1962).
[2] M. Froissart (to be published).