Variational Principle for Confined Quantum Systems

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A new variational principle for the energy eigenvalues of a confined quantum system is presented. Whereas the exact wave function Ψ must vanish on the bounding surface of the region, the trial function ψ in this principle need not obey any specific boundary condition. Calculationally, the method is similar to the conventional variational method except that kinetic energy turns out to be a weighted average of $-\int\psi\nabla^2\psi\,d\tau$ and $\int(\nabla\psi)\cdot(\nabla\psi)d\tau$ in the ratio $2:-1$. Although the principle is not a definite (minimum) one, good results are obtained in several examples.

Advances in quantum-well and quantum-well wire devices have stimulated interest in the problem of calculating the energy levels associated with a "confined quantum system," e.g., a hydrogenic impurity state confined to a region of space by impenetrable surfaces. Variational calculations of the binding energies have been done by, e.g., Bastard [1] and Csavinszky and Elabsy [2] for confinement between parallel planes and by Bryant [3], Brown and Spector [4], and Oyoko and Csavinszky [5] for confinement in an infinitely long cylinder (quantum-well wire). In all of these variational calculations, a trial function which vanished on the bounding surfaces was used. The purpose of this Letter is to present a new variational principle for confined systems in which the trial function *need not vanish on the bounding surfaces*. Thus one could use any convenient set of basis functions without having to pay attention to the boundary condition.

Consider a quantum particle which is confined to some region R of space and governed by a Hamiltonian

$$H = -\nabla^2 + V(\mathbf{r}) . \tag{1}$$

Denote one of its exact energy eigenvalues by E and the associated (real) eigenfunction by $\Psi(\mathbf{r})$,

$$(H-E)\Psi(\mathbf{r}) = 0 . \tag{2}$$

The boundary condition for this exact eigenfunction $\Psi(\mathbf{r})$ is

$$\Psi(\mathbf{r}) = 0 \quad \text{for all } \mathbf{r} \in \Sigma , \tag{3}$$

where Σ is the bounding surface of the region R.

Now let $\psi(\mathbf{r})$ be any (real) "trial function" and $y(\mathbf{r})$ be the corresponding error:

$$\psi(\mathbf{r}) = \Psi(\mathbf{r}) + y(\mathbf{r}) . \tag{4}$$

We emphasize that the trial function $\psi(\mathbf{r})$ *need not obey the boundary condition* (3). Using Gauss' theorem, it is easy to show that

$$\int_{\mathbf{R}^-}\psi(H-E)\psi\,d\tau = \int_\Sigma d\mathbf{S}\cdot(y\nabla\psi - \psi\nabla y)$$
$$+ \int_{\mathbf{R}^-}y(H-E)y\,d\tau , \tag{5}$$

where $d\tau$ is an element of the volume R and $d\mathbf{S}$ is a vectorial area element of the surface Σ. [The volume integration is over the region $\mathbf{R}^-$ (up to but not including the surface Σ) and does not include any (imagined) "discontinuity" in $\psi(\mathbf{r})$ at the surface Σ.] Because $\psi = y$ everywhere on the boundary, the surface integral in (5) may be replaced by

$$\int d\mathbf{S}\cdot(y\nabla\psi - \psi\nabla y) = \int d\mathbf{S}\cdot(\psi\nabla\psi - y\nabla y) . \tag{6}$$

Using Gauss' theorem to convert this back into a volume integral, (5) may be written in the symmetric form

$$\int \{-2\psi\nabla^2\psi - (\nabla\psi)\cdot(\nabla\psi) + (V-E)\psi^2\}d\tau$$
$$= \int \{\psi \to y\}d\tau . \tag{7}$$

The right-hand side of (7) is *quadratic* in the error y; therefore the left-hand side is *stationary* about $\psi = \Psi$. Dropping this second order term, we obtain the desired *variational principle* [6] for the energy E,

$$E \approx [E] = \left[\frac{\int\{-2\psi\nabla^2\psi - (\nabla\psi)\cdot(\nabla\psi) + V\psi^2\}d\tau}{\int\psi^2 d\tau} \right] , \tag{8}$$

where the large [ ] brackets denote "stationary value of."

In the conventional (Rayleigh-Ritz) variational principle, one can use for the average kinetic energy either

$$-\int \psi\nabla^2\psi\,d\tau \tag{9}$$

or

$$+\int (\nabla\psi)\cdot(\nabla\psi)d\tau , \tag{10}$$

these two being equivalent by Gauss' theorem *provided that ψ obey the boundary condition* (3). In the present case, with ψ not necessarily obeying the boundary condition, the correct kinetic energy expression turns out to be a weighted average of (9) and (10) in the ratio $2:-1$.

Suppose we choose a trial function with K (real) linear variational parameters C_i,

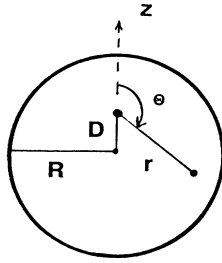$$\psi(\mathbf{r}) = \sum_{i=1}^{K} C_i u_i(\mathbf{r}) . \tag{11}$$

FIG. 1. A hydrogen atom inside a sphere of radius R. Its fixed nucleus is located a distance D along the z axis from the center of the sphere. The basis functions are expressed in terms of the spherical coordinates (r,θ) shown.

Here the $u_i(\mathbf{r})$ are a set of K (real) "basis functions." Again we emphasize that each individual $u_i(\mathbf{r})$, as well as the sum (11), *need not satisfy the boundary condition* (3). Extremalizing (8) with respect to the C_i yields a K-by-K secular determinant for the $[E]$,

$$\det|H_{ij} - [E]S_{ij}| = 0 , \tag{12}$$

where $H_{ij} = T_{ij} + V_{ij}$. The potential energy and overlap matrices are (as usual)

$$V_{ij} = \int u_i V(\mathbf{r}) u_j d\tau , \tag{13}$$

$$S_{ij} = \int u_i u_j d\tau . \tag{14}$$

The kinetic energy matrix,

$$T_{ij} = -\int [u_i \nabla^2 u_j + u_j \nabla^2 u_i + (\nabla u_i) \cdot (\nabla u_j)] d\tau , \tag{15}$$

although symmetric, differs from its conventional form. With the exception of this slight modification in the kinetic energy matrix (15), the entire procedure is calcula-

tionally the same as the usual Rayleigh-Ritz method.

As a simple illustration of the method, we calculate the ground state energy of a hydrogen atom located a distance D from the center of a sphere of radius R; see Fig. 1. Outside the sphere the potential is $V = +\infty$. This system has also recently been studied by Gorecki and Byers Brown [7] and by Diamond, Goodfriend, and Tsonchev [8]. The Hamiltonian (in atomic units) is

$$H = -\tfrac{1}{2}\nabla^2 - r^{-1} . \tag{16}$$

The basis functions we choose are

$$u_{\alpha,\beta}(r,\theta) = e^{-r} r^\alpha \cos^\beta(\theta) , \tag{17}$$

with

$$\alpha = 0,1,2,\ldots,(N-1) ,$$

$$\beta = 0,1,2,\ldots,(M-1) . \tag{18}$$

Each basis function is labeled with two indices (α,β); the number of basis functions is $K = NM$. All integrations over r were done exactly, the upper limit being a function of θ; the integrations over θ were then carried out numerically (200 mesh points proving to be sufficient). Results for several (R,D) with $K = 9$ basis functions ($N = M = 3$; rows a) and with $K = 36$ basis functions ($N = M = 6$; rows b) are shown in Table I. Also shown are results of Gorecki and Byers Brown (rows c) as well as those of, Diamond, Goodfriend, and Tsonchev (rows d). Our results compare favorably with previous calculations, especially those of Diamond, Goodfriend, and Tsonchev. Note the improvement as K is increased from 9 (rows a) to 36 (rows b). The proposed variational principle is *not* a definite (minimum) principle; therefore the results need not *necessarily* improve as K is increased (although many examples, in addition to the one above, show that they almost always *do* improve with increasing K). In this sense, it shares some properties of the Kohn variational method [9,10] for scattering phase shifts. Another aspect of the nondefiniteness of the method is that some roots may occur well below the ground state energy of the system. Table II lists all sixteen roots for $N = M = 4$ (K

TABLE I. Ground state energy of a hydrogen atom. The atom is inside a sphere of radius R; its fixed nucleus is displaced a distance D from the center. (a) Present work, $N = M = 3$. (b) Present work, $N = M = 6$. (c) Gorecki and Byers Brown. (d) Diamond, Goodfriend, and Tsonchev.

R	$D = 0.1$	$D = 0.5$	$D = 1.0$	Source
4.0	−0.489 72	−0.488 48	−0.484 39	a
	−0.483 15	−0.481 02	−0.473 42	b
	−0.483 18	−0.481 05	−0.473 35	c
	−0.483 18	−0.481 07	−0.473 44	d
3.0	−0.458 50	−0.467 51	−0.359 34	a
	−0.423 58	−0.413 92	−0.378 40	b
	−0.423 58	−0.413 73	−0.377 19	c
	−0.423 58	−0.413 89	−0.378 41	d
2.0	−0.183 24	−0.061 13	+0.117 41	a
	−0.122 86	−0.068 89	+0.127 51	b
	−0.122 86	−0.066 07	+0.158 52	c
	−0.122 85	−0.068 89	+0.127 52	d

TABLE II. Hydrogen atom inside a sphere of radius $R = 3$; its fixed nucleus is displaced a distance $D = 0.5$ from the center. The table shows all sixteen roots $[E]$ for $N = M = 4$. The root labeled "*" corresponds to the true ground state. Note the three spurious roots below this one.

−4.0	+2.6
−2.0	+3.1
−0.88	+6.5
−0.410 13*	+6.8
+0.15	+11.7
+0.47	+35.9
+1.2	+95.8
+1.3	+174.1

$=16$) with $(R,D)=(3,0.5)$. Note the three "spurious" roots lower than the one corresponding to the ground state. Almost always (in this as well as many other examples), these spurious roots (whose number tends to increase and whose numerical values tend to decrease with increasing K) are so far below the desired value as to make them readily identifiable.

As a second example, which shows that the method can also predict excited states, consider a particle in two dimensions constrained to the interior of a quarter circle of radius $R=1$. Using Cartesian coordinates, this region is described by

$$x^2+y^2 \le R^2, \quad x \ge 0, \quad y \ge 0. \tag{19}$$

The Hamiltonian within this region is

$$H = -\tfrac{1}{2}\nabla^2. \tag{20}$$

As a basis set we choose

$$\psi_{n,m}(x,y) = \sin(n\pi x/R)\sin(m\pi y/R), \tag{21}$$

with

$$n = 1,2,\ldots,N. \tag{22}$$
$$m = 1,2,\ldots,M.$$

These satisfy the boundary condition on the two straight segments ($x=0$ and $y=0$) but certainly not on the curved segment. The integrations over x were done analytically, the upper limit being a function of y; the integrations over y were then done numerically using 200 mesh points. This problem of a particle constrained to the interior of a quarter circle can, of course, be solved exactly. Using plane polar coordinates (ρ,θ), the exact eigenfunctions and eigenvalues are

$$\Psi_{p,k}(\rho,\theta) = J_p(\lambda_{pk}\rho/R)\sin(p\theta), \tag{23}$$

$$E_{p,k} = 2(\lambda_{pk}/R)^2. \tag{24}$$

Here J_p is a (cylindrical) Bessel function of order p $=2,4,6,\ldots$, and λ_{pk} is the kth positive root of $J_p(\lambda)$ $=0$. Table III lists the lowest eleven approximate energies $[E]$ obtained using $N=M=6$ ($K=NM=36$ variational parameters). The lowest three of these $[E]$ are spurious roots; the next eight compare quite favorably with the lowest eight exact energies E.

Although the trial function ψ used in this method need not satisfy any particular boundary condition on the surface Σ, the Dirichlet boundary conditions ($\Psi=0$) on the exact eigenfunction Ψ were inserted into the analysis in going from Eq. (5) to Eq. (6). One could instead consider Neumann boundary conditions ($\hat{n}\cdot\nabla\Psi=0$, where $\hat{n}$ is a unit vector normal to Σ) on the exact eigenfunction Ψ in which case a similar analysis yields

$$E \approx [E] \equiv \left[\frac{\int\{(\nabla\psi)\cdot(\nabla\psi)+V\psi^2\}d\tau}{\int\psi^2 d\tau} \right], \tag{25}$$

TABLE III. Particle inside a quarter circle of radius $R=1$. The integers (p,k) are the (angular, radial) quantum numbers for the exact solution; see Eq. (23). The quantities E are the lowest eight exact eigenvalues; the quantities $[E]$ are the lowest eleven approximate eigenvalues, the first three of which are spurious.

(p,k)	E	$[E]$
		-2578.2
		-514.1
		-240.6
(2,1)	26.4	26.2
(4,1)	57.6	55.6
(2,2)	70.8	70.1
(6,1)	98.7	97.1
(4,2)	122.4	116.5
(2,3)	135.0	133.1
(8,1)	149.5	147.4
(6,2)	184.7	180.5

which happens to be a true minimum principle. In this case (Neumann boundary conditions), the correct kinetic energy expression turns out to be a weighted average of (9) and (10) in the ratio 0:1 (rather than 2: -1). The Neumann boundary conditions emerge as the "natural boundary condition" for this situation, as discussed by Courant and Hilbert [11]. An excellent discussion of variational principles in general can be found in the review article of Gerjoy, Rau, and Spruch [12].

Using similar techniques, one may also obtain variational principles for mixed (Dirichlet along Σ_1 and Neumann along Σ_2 with $\Sigma_1+\Sigma_2=\Sigma$) as well as for "logarithmic derivative" boundary conditions ($\hat{n}\cdot\nabla\Psi/\Psi=\beta$, where β can even be a function of Σ). In all of these, the trial function ψ need not satisfy any particular boundary condition on the surface Σ; the boundary conditions are inserted into the derivation of the particular variational principle [e.g., (8) vs (25)]. [Perhaps here is the major distinction between the standard (Rayleigh-Ritz) method and the proposed method. In the former, one uses the same variational principle but constrains the trial function to obey the appropriate boundary conditions. In the latter, one uses a different variational principle (generated using the boundary conditions) but leaves the trial function unconstrained; thus all parameters in the trial function can be variational parameters and none need be "spent" to invoke the boundary conditions.]

The author is indebted to S. I. Tsonchev for supplying a preliminary version of his results and to P. L. Goodfriend for an illuminating discussion concerning atomic units.

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