

VARIATIONAL METHODS IN QUANTUM MECHANICS

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Variational methods have been used in quantum mechanics from the very beginning. In the first papers of Schrödinger the problem of finding the energy levels of a particle in a potential field was stated as an eigenvalue problem. A variational principle for problems of this kind had been formulated mathematically long before the appearance of quantum mechanics. So-called direct methods (Ritz method) had also been developed which allowed the approximate calculation of eigenvalues and eigenfunctions by starting from extremal properties.

There exists, however, a large group of quantum mechanical problems where one has to deal with the continuous spectrum of the energy operator and, correspondingly, there exists a variety of variational procedures which may be applied either to the exactly soluble problem of potential scattering or to many-body scattering problems.

In several cases, however, a given quantum mechanical system is in a quasi-stationary state often called as decaying or resonance state where the constituents are bounded for a characteristic time (life-time) then merge into the continuum. One may divide the theoretical methods applied to these non-stationary states into three categories: The first contains theories which treat the problem from the scattering point of view where the relevant quantities are usually found from their relationship to the energy-dependent phase shift. The second contains theories which attempt to solve directly from a complex eigenvalue equation. The third includes methods which, either explicitly or implicitly, treat these states as more or less ordinary bound states.

We construct in this paper a general functional from which several variational methods for the problems mentioned above can be deduced.

For the purposes of illustration we shall consider the one body, one-dimensional symmetric problem, and seek the solution of the equation

$$\mathcal{L}\Psi(r) = 0, \quad (1)$$

where

$$\mathcal{L} \equiv \mathcal{H} - E = -\frac{d^2}{dr^2} + V(r) - k^2. \quad (2)$$

We note in passing that most of our considerations are true for general non-singular operators of the type $\mathfrak{L} = \mathfrak{A} - \lambda$, \mathfrak{A} being a linear but not necessarily selfadjoint operator defined on the Hilbert space L^2 and $\lambda \in C^1$.

Consider the following functional

$$J[\psi; E; \mathfrak{D}_1, \mathfrak{D}_2] = \langle \psi \mathfrak{L} + \mathfrak{D}_1^+, \mathfrak{D}_2 \mathfrak{L} \psi \rangle / (\psi, \psi), \quad (3)$$

where the nominator in the r.h.s. of Eq. (3) is the usual scalar product in the space L^2 with the convention that the adjoint operators \mathfrak{L}^+ and \mathfrak{D}_1^+ act to the left, \mathfrak{D}_1 and \mathfrak{D}_2 are arbitrary non-singular operators, and (ψ, ψ) means a formal norm for the expression (3). It is easy to see that, independently of the actual form of $\mathfrak{D}_1, \mathfrak{D}_2$ and (ψ, ψ) , $J = 0$ if ψ is the exact solution of the Schrödinger equation (1) with energy-eigenvalue E (either from the point spectrum or from the continuous spectrum of the Hamiltonian \mathfrak{H}) when solved subject to the same boundary conditions. The particular choices for $\mathfrak{D}_1, \mathfrak{D}_2$ and (ψ, ψ) , in Eq. (3), result in the following functionals:

$$\text{A. } \mathfrak{D}_1 = \mathfrak{L}^{-1}, \mathfrak{D}_2 = 1$$

A1. Bound states

Choosing $(\psi, \psi) = 1$, with boundary conditions* $\psi(0) = 0$, $\psi(r) \rightarrow 0$ as $r \rightarrow \infty$, we get

$$J[\psi, E] = \langle \psi, \mathfrak{L} \psi \rangle. \quad (4a)$$

It is easy to show that the required stationary values ($\delta J = 0$) of J are all zero and they exist only for a set of eigenvalues of E identical with the eigenvalues of \mathfrak{H} . One can prove that this variational procedure is equivalent to the well-known Rayleigh—Ritz method:

$$\delta E[\psi] = \delta \frac{\langle \psi, \mathfrak{H} \psi \rangle}{\langle \psi, \psi \rangle} = 0. \quad (4b)$$

A2. Scattering states

With the boundary condition $\psi \xrightarrow{r \rightarrow \infty} a_1 \sin kr + a_2 \cos kr$ for any $k > 0$ one obtains the Hulthen functional

$$J[\psi] = \langle \psi, \mathfrak{L} \psi \rangle, \quad (5)$$

from which several variational methods of potential scattering for the phase shift $\eta(k)$ can be deduced [1].

* The boundary condition $\psi(0) = 0$, for any trial function ψ , is always required, so below the behaviour of ψ at infinity will only be indicated.

A3. Resonances

a) Expanding the trial function as

$$\psi = \sum_{i=1}^N a_i \varphi_i, \tag{6}$$

where the φ_i 's are elements of a complete set in the space L^2 , Eq. (4b) reduces to a real symmetrical matrix-eigenvalue problem, as in the case of bound states. The positive roots which are stable when varying the basis size N , approximate the resonance position E_r [2].

b) Applying the co-ordinate rotation $r \rightarrow r \exp [i\theta]$ to the Hamiltonian $\mathcal{H} \rightarrow \mathcal{H}(\theta)$, the stable eigenvalues $E = E_r - i\Gamma/2$ of the complex Hamiltonian matrix will correspond to complex resonance energies [3].

$$\mathbf{B.} \mathfrak{D}_1 = f(r) \times, \mathfrak{D}_2 = 1$$

i.e. \mathfrak{D}_1 means multiplication by a suitably chosen positive definite weight-function, and \mathfrak{D}_2 is the unit operator in the Hilbert space L^2 . We then have the least-squares or variance functional

$$J[\psi, E] = \langle \psi \mathfrak{L}^+ f, \mathfrak{L} \psi \rangle / (\psi, \psi). \tag{7}$$

A more simplified version of (7) arises by approximating the integrals in (7) by summation

$$\langle \omega, \zeta \rangle \approx \sum_i f(x_i) \omega^*(x_i) \zeta(x_i), \tag{8}$$

for any functions ω and ζ , where the summation is taken over specific points x_i in the space of the system, and f has been chosen to make the best approximation.

B1. Bound states [4]

Adopting the expansion (6) for the trial function ψ , the most simple normalization for the expression (7) is $|a_1|^2 = 1$, where a_1 is the leading linear parameter in the decomposition of ψ . Of course, the requirement $\delta J[\psi, E] = 0$ also includes variation with respect to E .

B2. Scattering states [5]

Taking

$$\psi = \sum_{i=-1}^N a_i \varphi_i, \tag{9}$$

with $\varphi_{-1} = \sin kr$, $\varphi_0 = g(r) \cos kr$, where $g(0) = 0$, $g(r) \xrightarrow[r \rightarrow \infty]{} 1$ and $k = +\sqrt{E}$ is fixed, it can be normalized as $(\psi, \psi) = |a_{-1}|^2 + |a_0|^2$. After optimizing (7), the approximate s -wave phase shift η_0 is given by $\text{tg } \eta_0 = a_0/a_{-1}$.

B3. Resonances [6]

Taking $(\psi, \psi) = \langle \psi, \psi \rangle$, the procedure B1. can be applied to determine the real part of the complex resonance energy E . This method makes use of the fact that the wave function at the positive energy E_r is highly localized in the region of interaction, i.e. $J[\psi, E]$ has a well-defined minimum at E_r with square-integrable ψ . Note that resonances are not bound states embedded in the continuum, though some connection might be realized between them [7].

$$\text{C. } \mathfrak{D}_1 = \mathfrak{D}_2 = \mathfrak{S}_K$$

where

$$\mathfrak{S}_K = \sum_{i=1}^K \chi_i \langle \chi_j, \chi_i \rangle \quad (10)$$

is a projection operator projecting onto a K -dimensional subspace of the Hilbert space L^2 , spanned by the functions χ_i . The operator \mathfrak{S}_K has been used in order not to calculate matrix elements of $(\mathfrak{H} - E)^2$.

C1. Bound states

The procedure B1. can be applied without modification with the requirement that $K > N$, N being the number of basis functions φ_i used in the expansion of ψ . We obtain the method of moments [8] by choosing $K = N$ and $\chi_j \neq \varphi_j$.

C2. Scattering states [9]

Using the same trial function ψ as in Eq. (8) with the normalization described in B2., the variational problem leads to an algebraic eigenvalue problem for the coefficients a_i .

C3. Resonances

a) Applying the co-ordinate rotation indicated in A3.b the procedure C1. can be repeated to calculate the complex resonance eigenvalues $E = E_r - i\Gamma/2$ [10]. Here an additional optimization is needed with respect to E_r and Γ , simultaneously.

b) Let us define the resonance energy as complex eigenvalue of the Schrödinger equation (1) with purely outgoing-wave boundary condition at infinity, i.e. $\psi \xrightarrow{r \rightarrow \infty} \exp[ixr + \gamma r]$, $E = (\alpha - i\gamma)^2$, $\gamma > 0$. Usually, variational methods cannot cope with this boundary condition because of the divergent integrals appearing in the variational functional. This method, however, does not fail provided all of the χ_i 's decrease faster than $\exp[-\gamma r]$ for $r \rightarrow \infty$, ensuring finite matrix elements [11].

Summary

A formal variational functional is constructed for general operator-eigenvalue problems. Specific choices for the two non-singular operators, which are contained in the functional, lead to the well-known variational methods applied to quantum mechanical bound state, scattering state and resonance problems.

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