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

$$\mathcal{L} = \mathcal{H} - E = -\frac{d^2}{dr^2} + V(r) - k^2. \quad (2)$$
We note in passing that most of our considerations are true for general non-singular operators of the type \( \mathcal{L} = \mathcal{A} - \lambda \), \( \mathcal{A} \) being a linear but not necessarily selfadjoint operator defined on the Hilbert space \( L^2 \) and \( \lambda \in \mathbb{C}^1 \).

Consider the following functional

\[
J[\psi; E; \mathcal{D}_1, \mathcal{D}_2] = \langle \mathcal{L}^{+} \mathcal{D}^{+}_1, \mathcal{D}_2 \mathcal{L}\psi \rangle (\psi, \psi),
\]

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 \( \mathcal{L}^{+} \) and \( \mathcal{D}^{+}_1 \) act to the left, \( \mathcal{D}_1 \) and \( \mathcal{D}_2 \) are arbitrary non-singular operators, and \((\psi, \psi)\) means a formal norm for the expression (3). It is easy to see that, independently of the actual form of \( \mathcal{D}_1, \mathcal{D}_2 \) and \( (\psi, \psi) \), \( J = 0 \) if \( \psi \) 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 \( \mathcal{H} \)) when solved subject to the same boundary conditions. The particular choices for \( \mathcal{D}_1, \mathcal{D}_2 \) and \((\psi, \psi)\), in Eq. (3), result in the following functionals:

\[\text{A. } \mathcal{D}_1 = \mathcal{L}^{-1}, \mathcal{D}_2 = 1\]

\[\text{A1. Bound states}\]

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

\[
J[\psi, E] = \langle \psi, \mathcal{L}\psi \rangle.
\]

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 \( \mathcal{H} \). One can prove that this variational procedure is equivalent to the well-known Rayleigh—Ritz method:

\[
\delta E[\psi] = \delta \frac{\langle \psi, \mathcal{H}\psi \rangle}{\langle \psi, \psi \rangle} = 0.
\]

\[\text{A2. Scattering states}\]

With the boundary condition \( \psi \overset{r \to \infty}{\longrightarrow} a_1 \sin kr + a_2 \cos kr \) for any \( k > 0 \) one obtains the Hultén functional

\[
J[\psi] = \langle \psi, \mathcal{L}\psi \rangle,
\]

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 \( \psi \), is always required, so below the behaviour of \( \psi \) at infinity will only be indicated.
A3. Resonances

a) Expanding the trial function as

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

(6)

where the $\varphi_i$'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].

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

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

$$J[\psi, E] = \langle \mathcal{D}_2 \psi, \mathcal{D}_2 \psi \rangle / \langle \psi, \psi \rangle.$$

(7)

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

$$\langle \omega, \zeta \rangle \approx \sum_i f(x_i) \omega^*(x_i) \zeta(x_i),$$

(8)

for any functions $\omega$ and $\zeta$, 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.


Adopting the expansion (6) for the trial function $\psi$, 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 $\psi$. Of course, the requirement $\delta J[\psi, E] = 0$ also includes variation with respect to $E$.


Taking

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

(9)

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

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 \( \psi \). Note that resonances are not bound states embedded in the continuum, though some connection might be realized between them [7].

\[
C. \, \mathcal{P}_1 = \mathcal{P}_2 = \mathcal{P}_K
\]

where

\[
\mathcal{P}_K = \sum_{i=1}^{K} \langle \zeta_i | \zeta_j \rangle
\]

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

C1. Bound states

The procedure B1. can be applied without modification with the requirement that \( K > N \), \( N \) being the number of basis functions \( \varphi_i \) used in the expansion of \( \psi \). We obtain the method of moments [8] by choosing \( K = N \) and \( \zeta_j = \varphi_j \).

C2. Scattering states [9]

Using the same trial function \( \psi \) 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 \( \Gamma \), 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. \( \psi \xrightarrow{r \to \infty} \exp \{ixr + yr\}, E = (x - iy)^2, y > 0 \). 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 \( \chi_i \) decrease faster than \( \exp \{-yr\} \) for \( r \to \infty \), 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.

References


Dr. Béla GAZDY H-1521 Budapest