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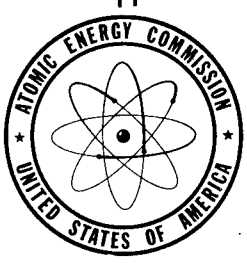

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Variational Principles and the Virial Theorem in Problems of Continuous Spectra in Quantum Mechanics

Yu. N. Demkov

Let us examine the equation for the radial function that determines the S-scattering by a center of force

$$\left[\frac{d^2}{dr^2} + k^2 - V(r)\right]\psi_k(r) = 0, \quad \psi_k(0) = 0, \quad r \geqslant 0, \qquad k^2 = \frac{2mE}{\hbar^2}, \quad V(r) = \frac{2m}{\hbar^2}U(r), \tag{1}$$

where k is the wave number, $U(r)$ is the potential energy, and E is the total energy. We assume that $V(r)$ decreases at infinity more rapidly than $1/r$ and has at zero a pole not higher than of the second order. For large r the solution will then have the asymptotic form

$$\psi_k(r) \sim A \sin(kr + \eta_0), \tag{2}$$

where η_0 depends on k. If we form the functional

$$I_k(\varphi) = \int_0^\infty \varphi(r)\left[\frac{d^2}{dr^2} + k^2 - V(r)\right]\varphi(r)\,dr, \tag{3}$$

where

$$\varphi(0) = 0, \quad \varphi(r) \sim B \sin(kr + \eta), \tag{4}$$

then its variation, under the conditions

$$\varphi(r) = \psi_k(r), \quad \delta\psi_k(0) = 0, \quad \psi_k + \delta\psi_k \sim (A + \delta A)\sin(kr + \eta_0 + \delta\eta) \tag{5}$$

will be[1]

$$\delta I_k(\psi_k) = -A^2 k \delta\eta. \tag{6}$$

Formula (6) enables us to use direct methods for determining ψ_k and η_0. For example, let us set

$$\varphi = \sum_{i=1}^{n} c_i \varphi_i, \tag{7}$$

where

$$\varphi_i(0) = 0, \quad i = 1, 2, \ldots, n; \qquad \varphi_1 \sim \sin kr, \quad \varphi_2 \sim \cos kr, \qquad \varphi_j(r) = 0 \text{ when } r \to \infty, \quad j = 3, 4, \ldots, n. \tag{8}$$

The functional (3) will then be a quadratic form relative to c_i

$$I_k(\varphi) = \sum_{i,j=1}^{n} I_{ij} c_i c_j, \tag{9}$$

where

$$I_{ij} = \int_0^\infty \varphi_i \left(\frac{d^2}{dr^2} + k^2 - V \right) \varphi_j dr. \tag{10}$$

In the subspace of the functions (7), Eq. (6) then reduces to the system

$$\begin{gathered} \sum_{j=1}^{n} I_{1j} c_j = \frac{kc_2}{2}, \quad \sum_{j=1}^{n} I_{2j} c_j = -\frac{kc_1}{2}, \\ \sum_{j=1}^{n} I_{ij}\, c_j = 0, \quad i = 3,\ 4,\ \ldots,\ n. \end{gathered} \tag{11}$$

The condition for the existence of nonzero solutions of this system, namely,

$$\begin{vmatrix} I_{11} & I_{12} - {}^1/_2 k & \ldots & I_{1n} \\ I_{21} + {}^1/_2 k & I_{22} & \ldots & I_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ I_{n1} & I_{n2} & \ldots & I_{nn} \end{vmatrix} = 0, \tag{12}$$

is, generally speaking, not satisfied. Ignoring one of the Eqs. (11), we make the system solvable and arrive at various formulations of the variational method.

In Hulthén's method[1] one sets $\delta\eta = 0$ and introduces the additional condition $I_k = 0$ in order to obtain a sufficient number of equations for the determination of the arbitrary parameters. This condition follows directly from the stationary character of the functional I_k relative to the variation of the normalizing coefficient of the wave function. Such a variation is possible when the function φ is chosen in the form (7), and, correspondingly, the condition $I_k = 0$ follows from Eqs. (11).

Let us now vary the scale of the length in formula (6), i.e., let us replace $\psi_k(r)$ by $\psi_k(r + \varepsilon r)$. The asymptotic form of the function then changes:

$$\psi_k(r + \varepsilon r) \sim A \sin\left[(k + \varepsilon r)\, r + \eta_0(k)\right]. \tag{13}$$

In order that the functional may have a finite value, we must replace k by $k + \varepsilon k$. Then

$$I' = \int_0^\infty \psi_k(r + \varepsilon r) \left[\frac{d^2}{dr^2} + (k + \varepsilon k)^2 - V(r) \right] \psi_k(r + \varepsilon r)\, dr; \tag{14}$$

replacing $r + \varepsilon r$ by ρ and using (1), we have

$$I' = \int_0^\infty \psi_k^2(\rho) \left[(1 + \varepsilon)\, V(\rho) - \frac{1}{1 + \varepsilon} V\left(\frac{\rho}{1 + \varepsilon} \right) \right] d\rho. \tag{15}$$

On the other hand, I' can be considered as the functional $I_{k + \varepsilon k}$, in which the following variational function has been substituted:

$$\psi_k(r + \varepsilon r) = \psi_{k + \varepsilon k}(r) + \delta\psi; \tag{16}$$

the variation of the phase will then be

$$\delta\eta = \eta_0(k) - \eta_0(k + \varepsilon k). \tag{17}$$

Expanding (15), (16), and (17) in powers of ε, ignoring the terms in ε^2 and higher, and using (6), we obtain

$$\int_0^\infty \psi_k^2(r)\left[2V(r)+r\frac{dV}{dr}\right]dr = A^2k^2\,\frac{d\eta_0}{dk}. \tag{18}$$

The case $l \neq 0$ differs only through the addition of the term $l(l+1)/r^2$ to $V(r)$. This term does not appear in (18), and, consequently,

$$\int_0^\infty \psi_{kl}^2(r)\left(2V+r\,\frac{dV}{dr}\right)dr = A^2k^2\frac{d\eta_l}{dk}, \quad l=0,\ 1,\ 2,\ \ldots \tag{19}$$

A similar formula can also be obtained in the three-dimensional case if one begins with the method proposed by Kohn.[2] In this case one considers the equation

$$[\nabla^2 + k^2 - V(\mathbf{r})]\,\psi(\mathbf{r}) = 0 \tag{20}$$

and the functional

$$I(\psi_1, \psi_2) = \int \psi_1(\mathbf{r})\,[\nabla^2 + k^2 - V(\mathbf{r})]\,\psi_2(\mathbf{r})\,d\tau, \tag{21}$$

where ψ_1 and ψ_2 satisfy Eq. (20) and have at infinity the asymptotic form:

$$\begin{gathered}\psi_i \sim e^{i\mathbf{k}_i\mathbf{r}} + f_k(\mathbf{k}_i^0,\ \mathbf{r}^0)\frac{e^{ikr}}{kr}, \quad i=1,\ 2,\\ |\mathbf{k}_i| = k, \quad \mathbf{k}_i^0 = \frac{\mathbf{k}}{k}, \quad \mathbf{r}^0 = \frac{\mathbf{r}}{r}.\end{gathered} \tag{22}$$

If we vary ψ_1 and ψ_2 in such a way that

$$\psi_i + \delta\psi_i \sim e^{i\mathbf{k}_i\mathbf{r}} + [f_k(\mathbf{k}_i^0,\ \mathbf{r}^0) + \delta f_k(\mathbf{k}_i^0,\ \mathbf{r}^0)]\,\frac{e^{ikr}}{kr}, \tag{23}$$

then the variation of I can be written as

$$\delta I(\psi_1,\ \psi_2) = -\,4\pi\delta f_k(\mathbf{k}_1^0,\ -\mathbf{k}_2^0). \tag{24}$$

The variation of the scale of length in (24) leads to the formula

$$\int \psi_1(\mathbf{r})\,[2V(\mathbf{r}) + \mathbf{r}\nabla V(\mathbf{r})]\,\psi_2(\mathbf{r})\,d\tau = 4\pi\,\frac{\partial f_k(\mathbf{k}_1^0,\ -\mathbf{k}_2^0)}{\partial k}. \tag{25}$$

If we take $V(\mathbf{r})$ to be spherically symmetric, substitute into (25) the expansions of ψ_1, ψ_2, and f_k in spherical harmonies, and integrate with respect to the angles, then we obtain a system of equations (19) for the phases and the radial functions. Eq. (6) can be obtained from (24) in the same way.

In case of a discrete spectrum the variation of the scale of length leads to a virial theorem,[3] which can be written in a similar form, namely,

$$\int \psi^2(\mathbf{r})\,[2V(\mathbf{r}) + \mathbf{r}\,\nabla V(\mathbf{r})]\,d\tau = 2\mathcal{E}; \tag{26}$$

here ψ is normalized, and $\mathcal{E} = \frac{2mE}{\hbar^2}$.

The formulas (19) and (25) are generalizations of the virial theorem for the case of a continuous spectrum and may have useful applications in problems of collision theory that are described by Eq. (19), i.e., in the process of diffraction of a plane wave by a spatial nonhomogeneity of finite size.

The derivation of these formulas has a certain similarity with the derivation of the virial theorem for molecules. Here, when varying the scale, one has to change the wave number, and therefore the derivative of the phase relative to the wave number appears in the final formula. In the case of a molecule, the variation of the scale changes the distance between the nuclei, and the final formula contains the derivative of the total energy with respect to the distance between the nuclei (for the equilibrium position of the molecule this derivative becomes zero).

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