

Construction of a trial function in the variational procedure of quantum mechanics

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A form of variational method for calculating the ground-state energy of a quantum system is considered. The method is based on a prescription for the systematic construction of a trial variational function at each step in the calculation of the ground-state energy; the prescription improves the previous result. In each step of the calculation, it is straightforward to obtain the new variational function. The method is tested in two nontrivial problems. Good agreement between the calculated ground-state energy and its exact value is found. The transformation of the wave function in the transition from one step of the calculation to the next is traced.

It is shown that as the number of steps in the calculation increases the variational wave function reproduces with ever greater accuracy the characteristic features inherent in the exact wave function of the ground state. © 1995 American Institute of Physics.

1. Variational methods are widely used to estimate the ground-state energy of quantum systems.^{1,2} The main problem in the calculation is to make the optimum choice of the trial variational function. Quite generally, this problem comes to the fore if there is a need to make calculations using a given variational function. In this connection, we have the practical problem of constructing a simple procedure for successive “improvement” of a trial function with the aim of obtaining a more accurate approximation to the ground-state energy of the system. As far as possible, this function must reproduce all the characteristic features of the exact wave function, for example, its asymptotic behavior, the presence or absence of periodicity, and the absence of nodes for the ground-state function.

We consider one approach to estimating the energy and constructing the wave function of the ground state of a system described by the Schrödinger equation

$$H\Psi = E\Psi, \quad (1)$$

where H is the Hamiltonian of the system, and Ψ and E are the wave function and energy eigenvalue. It is shown in Ref. 3 that Eq. (1) can be formally solved exactly in the form

$$E = H_{nn} + \sum_{m(\neq n)} \frac{H_{nm}H_{mn}}{E - H_{mm}} + \sum_{\substack{m(\neq pn) \\ p(\neq nm)}} \frac{H_{nm}H_{mp}H_{pn}}{(E - H_{mm})(E - H_{pp})} + \dots, \quad (2)$$

$$\Psi = c_n \left(|n\rangle + \sum_{m(\neq n)} \frac{H_{mn}}{E - H_{mm}} |m\rangle + \sum_{\substack{m(\neq n) \\ p(\neq nm)}} \frac{H_{mp}H_{pn}}{(E - H_{mm})(E - H_{pp})} |m\rangle + \dots \right), \quad (3)$$

where H_{mn} is the matrix element of the operator H on the states $|m\rangle$ and $|n\rangle$ of some arbitrary complete orthonormal basis, and c_n is a normalization constant. If we take $H = H_0 + V$ and as basis functions choose the eigenfunctions of the unperturbed Hamiltonian H_0 , then the expressions (2)

and (3) go over into the well-known Brillouin–Wigner perturbation-theory series. Each successive term of this series is the term of next higher order in the perturbation V relative to the previous term.

We can go over from the expressions (2) and (3) to the expressions

$$E = H_{nn} + \frac{1}{E} \sum_{m(\neq n)} H_{nm}H_{mn} + \frac{1}{E^2} \sum_{mp(\neq n)} H_{nm}H_{mp}H_{pn} + \dots, \quad (4)$$

$$\Psi = c_n \left(|n\rangle + \frac{1}{E} \sum_{m(\neq n)} H_{mn}|m\rangle + \frac{1}{E^2} \sum_{mp(\neq n)} H_{mp}H_{pn}|m\rangle + \dots \right). \quad (5)$$

A characteristic feature of these expressions is that their terms contain the diagonal matrix elements H_{pp} . Therefore, except for the first, all the remaining terms of the series (4) for the energy contain expressions of second order in the perturbation, and this makes it difficult to work with this series. However, this series possesses one characteristic feature. Using the property of completeness of the basis functions, we can express all terms of the series (4) as expectation values of the operators H , H^2 , H^3 , ..., corresponding to a particular state $|n\rangle$. As a result, we have

$$E = \epsilon + \frac{1}{E} \epsilon_2 + \frac{1}{E^2} \epsilon_3 + \dots, \quad (6)$$

where

$$\begin{aligned} \epsilon_1 &= H_{nn}, \quad \epsilon_2 = (H^2)_{nn} - H_{nn}\epsilon_1, \\ \epsilon_3 &= (H^3)_{nn} - (H^2)_{nn}\epsilon_1 - H_{nn}\epsilon_2, \dots \\ \epsilon_p &= (H^p)_{nn} - (H^{p-1})_{nn}\epsilon_1 - (H^{p-2})_{nn}\epsilon_2 - \dots \\ &\quad - H_{nn}\epsilon_{p-1}. \end{aligned} \quad (7)$$

The results (6) and (7) indicate that formally to determine the energy of the system it is sufficient to know only one function in a complete set of orthonormal basis functions, for which, in particular, one can take the wave functions of the zeroth Hamiltonian.

Similarly, taking into account the completeness property of the basis functions, we can formally express the wave function Ψ (5) in terms of just the one wave function $|n\rangle$. More precisely, the function Ψ can be expressed in terms of the functions that are the results of applying the operators H, H^2, H^3, \dots to the basis function $|n\rangle$. The coefficients of the given functions can be expressed in terms of the parameters ϵ_m (7). This property of the wave function Ψ (5) can be taken as the basis for constructing a variational scheme that makes it possible to improve successively a trial variational function during the course of the calculation.

2. The wave function (5) is formally the exact solution of the Schrödinger equation (1). Suppose that as variational function we take the function (5), having replaced in it the unknown energy E by corresponding variational parameters G_p :

$$\begin{aligned} \Psi^{(k)} = & c_n \left(|n\rangle + G_1 \sum_{m(\neq n)} H_{mn} |m\rangle \right. \\ & + G_2 \sum_{mp(\neq n)} H_{mp} H_{pn} |m\rangle + \dots \\ & \left. + G_k \sum_{mp1\dots f(\neq n)}^{k \text{ pa } 3} H_{mp} H_{p1} \dots H_{fn} |m\rangle \right). \end{aligned} \quad (8)$$

Retaining two variational parameters in the expression (8) we can obtain

$$\begin{aligned} \Psi^{(2)} = & c_n \{ (1 - G_1 \epsilon_1 - G_2 \epsilon_2) |n\rangle + (G_1 - G_2 \epsilon_1) H |n\rangle \\ & + G_2 H^2 |n\rangle \}. \end{aligned} \quad (9)$$

To determine the parameters G_p , it is necessary to take into account the basic variational formula

$$E = \frac{\langle \Psi^{(k)} | H | \Psi^{(k)} \rangle}{\langle \Psi^{(k)} | \Psi^{(k)} \rangle}, \quad \frac{\partial E}{\partial G_p} = 0, \quad p = 1, 2, \dots, k. \quad (10)$$

In the case $k=1$, i.e., when allowance is made for only one variational parameter in the function (8), we obtain from (10)

$$E = \frac{\epsilon_1 + 2G_1 \epsilon_2 + G_1^2 \epsilon_3}{1 + G_1^2 \epsilon_2}, \quad (11)$$

where the variational parameter G_1 is determined from the equation

$$G_1^2 \epsilon_2^2 - G_1 (\epsilon_3 - \epsilon_1 \epsilon_2) - \epsilon_2 = 0. \quad (12)$$

Hence

$$G_1 = \frac{1}{2\epsilon_2^2} [\epsilon_3 - \epsilon_1 \epsilon_2 \pm \sqrt{(\epsilon_3 - \epsilon_1 \epsilon_2)^2 + 4\epsilon_2^3}], \quad (13)$$

where it is necessary to choose the solution that, when substituted in (11), ensures fulfillment of the inequality $E < \epsilon_1$. This inequality gives the simplest estimate of the energy in the variational scheme.

To obtain a more accurate value of E , it is necessary to include in the calculation the second variational parameter G_2 in the function (8). In this case,

$$E = \frac{\epsilon_1 + 2G_1 \epsilon_2 + (2G_2 + G_1^2) \epsilon_3 + 2G_1 G_2 \epsilon_4 + G_2^2 \epsilon_5}{1 + G_1^2 \epsilon_2 + 2G_1 G_2 \epsilon_3 + G_2^2 \epsilon_4}, \quad (14)$$

and the parameters G_1 and G_2 are determined by solving the system of equations

$$\begin{aligned} G_2^2 [\epsilon_3 \epsilon_4 + G_1 (\epsilon_4^2 - \epsilon_3 \epsilon_5)] - G_2 [\epsilon_5 - \epsilon_1 \epsilon_4 - 2G_1 \epsilon_2 \epsilon_4 \\ + G_1^2 (\epsilon_2 \epsilon_5 - \epsilon_3 \epsilon_4)] - \epsilon_3 - G_1 (\epsilon_4 - \epsilon_1 \epsilon_3) + G_1^2 \epsilon_2 \epsilon_3 \\ + G_1^3 (\epsilon_3^2 - \epsilon_2 \epsilon_4) = 0, \end{aligned} \quad (15)$$

$$\begin{aligned} G_1^2 [\epsilon_2^2 - G_2 (\epsilon_3^2 - \epsilon_2 \epsilon_4)] - G_1 [\epsilon_3 - \epsilon_1 \epsilon_2 - 2G_2 \epsilon_2 \epsilon_3 \\ + G_2^2 (\epsilon_3 \epsilon_4 - \epsilon_2 \epsilon_5)] - \epsilon_2 - G_2 (\epsilon_4 - \epsilon_1 \epsilon_3) \\ - G_2^2 (\epsilon_2 \epsilon_4 - 2\epsilon_3^2) - G_2^3 (\epsilon_4^2 - \epsilon_3 \epsilon_5) = 0. \end{aligned} \quad (16)$$

The expressions (14), (15), and (16) solve the problem when two variational parameters are retained. Following this scheme, we can include in the calculation the following terms of the series (8) that determines the trial wave function. Thus, we calculate both the energy of the ground state and its wave function in each stage of the calculation.

3. As an example, we first of all consider the simple problem described by the Hamiltonian

$$H = -\frac{d^2}{dx^2} + 4 \cos^2 x. \quad (17)$$

As basis functions, we take plane waves $\exp(ikx)/(2l)^{1/2}$ normalized using the "volume" $2l$. We calculate the parameters ϵ_m (7) using the plane wave with wave vector $k=0$. This function is optimal from the point of view of the variational procedure; it ensures the minimum value of ϵ_1 . As a result, we have $\epsilon_1 = \epsilon_2 = 2$, $\epsilon_3 = 12$, $\epsilon_4 = 74$, $\epsilon_5 = 492$. Substitution of these values in (13) gives $G_1 = -0.224745$. Thus, on the basis of the expression (11) we have $E = 1.550511$. Taking into account the second variational parameter in the wave function, we can obtain from Eqs. (15) and (16) the values $G_1 = -0.3104911$ and $G_2 = 1.382213 \cdot 10^{-2}$, and in conjunction with the expression (14) we then obtain $E = 1.5448707$. This last value agrees excellently with the exact value 1.54486... (Ref. 4) of the ground-state energy eigenvalue corresponding to the Hamiltonian (17).

Using the calculated values of $\epsilon_1, \epsilon_2, G_1$, and G_2 and taking into account the explicit form of the Hamiltonian (17), we can readily recover, on the basis of the expression (9), the explicit form of the trial wave functions corresponding to the calculations retaining one and two variational parameters:

$$\Psi^{(1)} = 1.6506791 \frac{1}{\sqrt{2l}} (1 - 1.632995 \cos^2 x), \quad (18)$$

$$\begin{aligned} \Psi^{(2)} = & 1.363757 \frac{2}{\sqrt{2l}} (1 - 0.7630275 \cos^2 x \\ & + 0.1491501 \cos^4 x). \end{aligned} \quad (19)$$

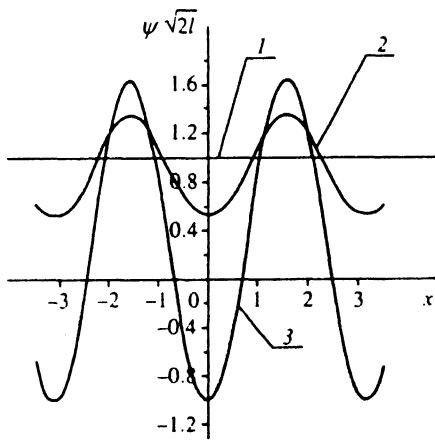


FIG. 1. Variational wave functions: 1—the function of the zeroth approximation; 2—the function (18) of the first approximation; 3—the function (19) of the second approximation.

Plots of these “volume”-normalized functions together with the variational function $\Psi^{(0)}=1/(2l)^{1/2}$ of zeroth order are shown in Fig. 1.

It can be seen from the figure that when the variational parameters are retained the variational function of zeroth order is changed qualitatively. The variational functions $\Psi^{(1)}$ and $\Psi^{(2)}$ are periodic, and their period is equal to the period of the perturbation in the Hamiltonian (17). Thus, these functions are in agreement with Bloch’s theorem.^{5,6} However, there is one important difference between the functions $\Psi^{(1)}$ and $\Psi^{(2)}$. In contrast to the function $\Psi^{(1)}$, the variational function $\Psi^{(2)}$ does not possess nodes. Therefore, retention of the second variational parameter significantly improves the behavior of the wave function. The point is that the ground-state wave function must not have nodes.² From this it may be concluded that the proposed procedure for constructing the variational wave function of the ground state ensures a qualitatively correct behavior of the true wave function.

4. We now consider the more complicated problem described by the Hamiltonian

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \alpha x^4, \quad (20)$$

where α is some constant. This problem is interesting in that standard perturbation theory here gives nothing.

We calculate the matrix elements $(H^p)_{mm}$ in the quantities ϵ_n (7) using the oscillator wave function

$$\Psi_0(x) = \left(\sqrt{\frac{\beta}{\pi}} \right)^{1/2} e^{-\beta x^2/2}. \quad (21)$$

This means that as the basis we have taken the wave functions of the harmonic oscillator. It is sensible to determine the parameter β by means of the standard variational procedure. In this case, $\beta=(6\alpha)^{1/3}$. As a result, we have

$$\begin{aligned} \langle H \rangle &= \frac{3}{8} \beta, & \langle H^2 \rangle &= \frac{35}{192} \beta^2, & \langle H^3 \rangle &= \frac{601}{1536} \beta^3, \\ \langle H^4 \rangle &= \frac{40163}{12288} \beta^4, & \langle H^5 \rangle &= \frac{4393865}{98304} \beta^5, \end{aligned} \quad (22)$$

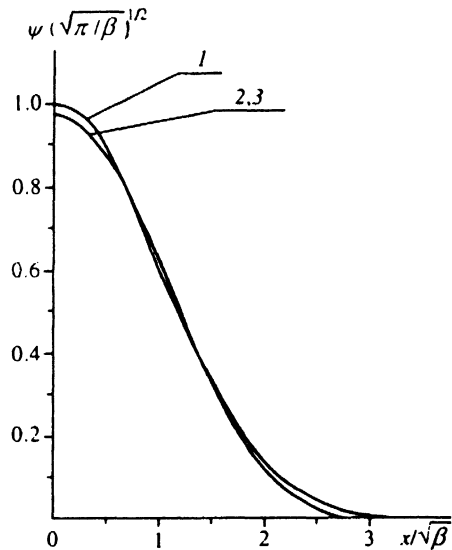


FIG. 2. Variational wave functions: 1—the function of the zeroth approximation (21); 2—the function (24) of the first approximation; 3—the function (25) of the second approximation.

and this enables us to calculate $\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4,$ and ϵ_5 :

$$\begin{aligned} \epsilon_1 &= \frac{3}{8} \beta, & \epsilon_2 &= \frac{1}{24} \beta^2, & \epsilon_3 &= \frac{59}{192} \beta^3, \\ \epsilon_4 &= \frac{13819}{4608} \beta^4, & \epsilon_5 &= \frac{1558393}{36864} \beta^5. \end{aligned} \quad (23)$$

Taking into account now the expressions (11) and (13), we obtain $G_1=-0.142736\beta^{-1}$ and $E=0.678115\alpha^{1/3}$. Note that the dependence of E on α is exact. For $\alpha=1/2$, the energy is $E=0.538220$, and this value differs only slightly from the exact value 0.530181 (Ref. 7). At the same time we find $\langle H \rangle=0.540843$. For a further improvement of the estimate, we must retain the second variational parameter in the calculation. In accordance with (15) and (16) we have $G_1=-0.224443\beta^{-1}$, $G_2=0.0082681\beta^{-2}$, and in conjunction with the expression (14) we then obtain $E=0.669043\alpha^{1/3}$. For $\alpha=1/2$, we have $E=0.531020$. This value exceeds by 0.16% the exact value of the ground-state energy of the system described by the Hamiltonian (20).

Taking into account the calculated variational parameters and the expressions (8), (20), and (21), we obtain

$$\Psi^{(1)} = c_{01}[1 + c_{11}\beta x^2 - c_{21}\beta^2 x^4]\Psi_0(x), \quad (24)$$

$$\begin{aligned} \Psi^{(2)} &= c_{02}[1 + c_{12}\beta x^2 - c_{22}\beta^2 x^4 - c_{32}\beta^3 x^6 \\ &\quad + c_{42}\beta^4 x^8]\Psi_0(x), \end{aligned} \quad (25)$$

where

$$\begin{aligned} c_{01} &= 0.981741, & c_{11} &= 0.0726643, \\ c_{21} &= 0.0242214, & c_{02} &= 0.975683, \\ c_{12} &= 0.0953664, & c_{22} &= 0.0296714, \\ c_{32} &= 0.00141152, & c_{42} &= 0.000235256. \end{aligned} \quad (26)$$

Plots of these functions as well as $\Psi(x)$ (21) are given in Fig. 2. However, on this scale the variational functions $\Psi^{(1)}$

TABLE I. Values of variational wave functions.

$x/\sqrt{\beta}$	Ψ_0	$\Psi^{(1)}$	$\Psi^{(2)}$
2.8	0.020	0.0015	0.0026
3.0	0.011	-0.0033	-0.000328
3.2	0.0060	-0.0046	-0.000371
3.4	0.0031	-0.0042	0.000476
3.6	0.0015	-0.0032	0.0012
3.8	0.000732	-0.0021	0.0015
4.0	0.000335	-0.0013	0.0014

and $\Psi^{(2)}$ can hardly be distinguished. The main difference between them is observed at large $x > 2.8\beta^{1/2}$. The corresponding values of the functions are given in Table I. For $x > 2.85\beta^{1/2}$ we have $\Psi^{(1)} < 0$. In contrast, the wave function $\Psi^{(2)}$ has negative values only in a very narrow range of variation of x , and these values are very small. It is to be

expected that retention of the next variational parameter will make it possible to eliminate altogether the presence of nodes in the wave function that describes the ground state of the system.

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