Methods of Electronic-Structure Calculations

From Molecules to Solids

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equation (4.9) is that for an N-particle system, Ψ contains a dependence on $3N$ position coordinates and N spin coordinates,

$$\Psi(\vec{x}) = \Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N, \sigma_1, \sigma_2, \sigma_3, \ldots, \sigma_N) \equiv \Psi(\vec{r}, \vec{\sigma}). \tag{4.12}$$

In this case we may assume that Ψ can be written as a product of a position-dependent part times a spin-dependent one,

$$\Psi(\vec{r}, \vec{\sigma}) = \psi(\vec{r})\Theta(\vec{\sigma}), \tag{4.13}$$

but upon insertion in Eq. (4.9) we obtain no information on the spin-dependent part, but only

$$\hat{H}\psi(\vec{r}) = E\psi(\vec{r}). \tag{4.14}$$

It should finally be stressed once more that the factorization is only an assumption. Through this one may obtain some of the solutions to the Schrödinger equation, but there may be other solutions that cannot be written as a simple product of two factors that depend on different coordinates.

5 Variational Principle; Lagrange Multipliers

5.1 VARIATIONAL PRINCIPLE

In this section we shall describe the variational principle. This principle is the foundation for all the approximate methods that we shall discuss later. We therefore repeat that our ultimate goal is to solve the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi, \tag{5.1}$$

but realize that due to the complexity of this equation, it can only in very few cases be solved exactly. It would, therefore, be desirable to be able to approximate the solutions to Eq. (5.1),

$$\Phi \simeq \Psi. \tag{5.2}$$

The fundamental question is, how do we determine Φ, how accurate is Φ, and how do we compare different approximate Φ?

To address this question we start somewhat more generally. We consider the general eigenvalue problem corresponding to Eq. (5.1),

$$\hat{A}f_n = a_n f_n, \tag{5.3}$$

where $\hat{A}$, as $\hat{H}$, is a Hermitian and linear operator.

Since $\hat{A}$ is Hermitian, all the eigenvalues a_n are real, and we shall assume that there exists a smallest one, so that we can sort the eigenvalues according to

$$a_0 \le a_1 \le a_2 \le a_3 \le \cdots \le a_{n-1} \le a_n \le a_{n+1} \le \cdots. \tag{5.4}$$

This procedure can obviously be carried through when $\hat{A}$ equals the Hamilton operator. Actually, it is one of the basic principles of the (non-relativistic) quantum theory that the system seeks — at least at the absolute temperature zero — that

state that corresponds to the lowest energy, i.e., the eigenvalue of our interest is a_0. On the other hand, when, e.g., $\hat{A}$ equals the position operator, $\hat{x}$, there is no smallest eigenvalue. But in almost all cases where we seek approximate solutions to Eq. (5.3), the operator $\hat{A}$ is the Hamilton operator, and the variational principle works.

We need to repeat one further property of the solutions to Eq. (5.3), i.e., the eigenfunctions can per construction be made orthonormal, and we shall therefore assume (notice, this is no lack of generality) that

$$\langle f_n | f_m \rangle = \delta_{n,m}. \tag{5.5}$$

We stress that we do not explicitly need the eigenfunctions f_n or the eigenvalues a_n. We just need to know that they exist and that the eigenfunctions form a complete set in order to carry the arguments through that lead to the variational principle.

A further fundamental principle of quantum theory is that expectation values of experimental observables for a given system in a given state are calculated as matrix elements of (normalized) eigenfunctions. Therefore, if we knew that the system of our interest occupied the state f_n, then the expectation value for the operator $\hat{O}$ is calculated as

$$\frac{\langle f_n | \hat{O} | f_n \rangle}{\langle f_n | f_n \rangle}. \tag{5.6}$$

A special case is the trivial case that $\hat{O}$ equals $\hat{A}$ and that $n = 0$. Then Eq. (5.6) takes the form

$$\frac{\langle f_n | \hat{O} | f_n \rangle}{\langle f_n | f_n \rangle} = \frac{\langle f_0 | \hat{A} | f_0 \rangle}{\langle f_0 | f_0 \rangle} = \frac{\langle f_0 | a_0 | f_0 \rangle}{\langle f_0 | f_0 \rangle} = \frac{a_0 \langle f_0 | f_0 \rangle}{\langle f_0 | f_0 \rangle} = a_0. \tag{5.7}$$

We shall now ask ourselves what happens with the above expectation value (5.7) when we replace f_0 by an approximate function

$$f_0 \simeq \phi. \tag{5.8}$$

The idea is that we can choose ϕ absolutely freely, whereby we also can choose ϕ so that the integrals entering

$$\frac{\langle \phi | \hat{A} | \phi \rangle}{\langle \phi | \phi \rangle} \tag{5.9}$$

can be evaluated. Furthermore, we stress that by evaluating Eq. (5.9) we do not need to know anything about the exact function f_0. However, we immediately arrive at the question: if two persons suggest two different approximate functions ϕ, how do we distinguish between them, and, in particular, how do we determine which one is the better (whatever that may mean). To answer this question partly

we use the completeness of the eigenfunctions f_n so that also any test function ϕ of Eq. (5.8) can be expanded as

$$\phi = \sum_n c_n f_n. \tag{5.10}$$

We only need to know that this expansion in principle is possible; not its precise form. We insert it into Eq. (5.9) and use the fact that the operator $\hat{A}$ is a linear operator. Then

$$\frac{\langle \phi | \hat{A} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \hat{A} \middle| \sum_{n_2} c_{n_2} f_{n_2} \right\rangle}{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} f_{n_2} \right\rangle}$$

$$= \frac{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} \hat{A} f_{n_2} \right\rangle}{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} f_{n_2} \right\rangle}$$

$$= \frac{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} a_{n_2} f_{n_2} \right\rangle}{\left\langle \sum_{n_1} c_{n_1} f_{n_1} \middle| \sum_{n_2} c_{n_2} f_{n_2} \right\rangle}$$

$$= \frac{\sum_{n_1, n_2} \langle c_{n_1} f_{n_1} | c_{n_2} a_{n_2} f_{n_2} \rangle}{\sum_{n_1, n_2} \langle c_{n_1} f_{n_1} | c_{n_2} f_{n_2} \rangle}$$

$$= \frac{\sum_{n_1, n_2} c_{n_1}^* c_{n_2} a_{n_2} \langle f_{n_1} | f_{n_2} \rangle}{\sum_{n_1, n_2} c_{n_1}^* c_{n_2} \langle f_{n_1} | f_{n_2} \rangle}$$

$$= \frac{\sum_{n_1, n_2} c_{n_1}^* c_{n_2} a_{n_2} \delta_{n_1, n_2}}{\sum_{n_1, n_2} c_{n_1}^* c_{n_2} \delta_{n_1, n_2}}$$

$$= \frac{\sum_n c_n^* c_n a_n}{\sum_n c_n^* c_n} = \frac{\sum_n |c_n|^2 a_n}{\sum_n |c_n|^2}$$

$$\geq \frac{\sum_n |c_n|^2 a_0}{\sum_n |c_n|^2} = \frac{a_0 \sum_n |c_n|^2}{\sum_n |c_n|^2} = a_0. \qquad (5.11)$$

At the first step we have inserted the expansion of Eq. (5.10) into Eq. (5.9) and thereby used two different summation variables n_1 and n_2 for clarity. Subsequently, we have used that $\hat{A}$ is a linear operator so that the outcome of letting it act on a linear combination of functions equals the linear combination of the operator acting on the individual functions. Then we use that the functions f_n are eigenfunctions of $\hat{A}$. Afterwards, we move the summations inside the bras and kets to the outside, together with the constant coefficients c_{n_1} and c_{n_2} and the eigenvalues a_{n_2}. By using the orthonormality of the eigenfunctions [Eq. (5.5)], we can reduce the double summations to single summations (and simultaneously change the summation index to n). The crucial step at the unequality is due to the assumption (5.4). This step is valid since every a_n is multiplied by a non-negative real number. Having replaced all a_n by a_0, we can place this constant outside the summation, whereby we easily end up with the final result of Eq. (5.11).

Equation (5.11) tells us that no matter what approximate function ϕ of Eq. (5.8) we suggest, the expectation value (5.9) will always be higher than or identical to the lowest eigenvalue a_0. The identity will only occur when ϕ is an exact eigenfunction for $\hat{A}$ for the lowest eigenvalue a_0.

A simple example will illustrate the importance of this theorem. Let us assume that $\hat{A}$ is the Hamilton operator and we seek the lowest energy for some system. We choose one ϕ, calculate the expectation value (5.9), and obtain the number -90 in some (unimportant) units. By choosing another ϕ we obtain -92. We know, from Eq. (5.11), that both results are above or identical to the lowest exact energy. Therefore, the lowest exact energy must be -92 or below. This is what the theorem states. We will now *assume* that the ϕ function that led to the result -92 also is the best approximation to the true eigenfunction of the lowest energy. This is an assumption, although it is in most cases also a good approximation. But it raises also another question: what is meant by a good approximation? Before addressing this through an example in Section 5.4 we shall extend the variational principle slightly.

5.2 AN EXAMPLE

The importance of the variational principle is due the possibility of introducing approximate eigenfunctions to, e.g., the Hamilton operator and to compare

different approximate eigenfunctions. We demonstrated this above for a simple example where two functions were compared. But one may also study a whole class of functions and out of this obtain the 'best' function. Let us illustrate the approach through a simple example.

We study a one-dimensional case with a single particle moving in a potential well. The profile of this well is shown in Fig. 5.1 and is given through

$$V(x) = \begin{cases} -V_0 & \text{for } |x| \leq \ell \\ 0 & \text{for } |x| > \ell. \end{cases} \qquad (5.12)$$

The Schrödinger equation for this particle is given by

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \Psi(x) = E\Psi(x), \qquad (5.13)$$

with $V(x)$ defined above. The Hamilton operator is obviously

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \qquad (5.14)$$

The ground state is the state of the lowest total energy. By looking at the potential of Fig. 5.1 it seems intuitively correct that the particle occupies the potential well as much as possible, i.e., that the wavefunction has the largest amplitude in the region $|x| \leq \ell$. A Gaussian centred at the origin is such a function and we therefore propose the approximate function

$$\phi = \exp(-\alpha x^2). \qquad (5.15)$$

For very small α this function is broad and extends well outside the region of the well, whereby the potential energy goes up. On the other hand, in that case the kinetic energy [the first term on the right-hand side of Eq. (5.14)] is small. For large α the opposite is true: the potential energy is low, but the kinetic energy
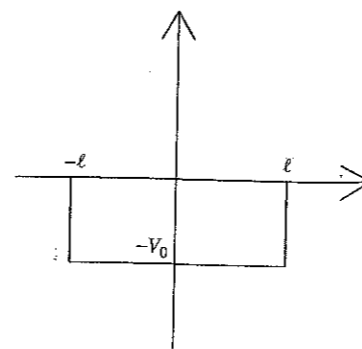

Figure 5.1 The one-dimensional potential well with finite depth

goes up. Thus, the 'best' α will most likely lie somewhere in between. However, we can simply determine it through variation. Thus, the quantity

$$\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \tag{5.16}$$

becomes a function of α,

$$\frac{\langle\phi|\hat{H}|\phi\rangle}{\langle\phi|\phi\rangle} \equiv \tilde{E}(\alpha). \tag{5.17}$$

For any α, $\tilde{E}(\alpha) \geq E_0$ (with E_0 being the ground-state energy), and therefore that α that leads to the lowest $\tilde{E}(\alpha)$ leads to the best estimate for E_0. Accordingly, we determine α by requiring

$$\frac{\partial}{\partial\alpha}\tilde{E}(\alpha) = 0. \tag{5.18}$$

Simultaneously, we will then assume that the resulting function ϕ is the best approximation to the exact ground-state eigenfunction.

We have not carried these calculations through here since they are not important for our general arguments, but hope that the basic ideas are clear.

5.3   VARIATION

In the general case we seek an approximate solution to the lowest eigenvalue and to the corresponding eigenfunction for the eigenvalue equation

$$\hat{A}f_0 = a_0 f_0. \tag{5.19}$$

The eigenfunction (f_0) depends on the coordinates of the system of our interest (in the example above, of the one-dimensional coordinate x), i.e.

$$f_0 = f_0(\vec{x}). \tag{5.20}$$

Equivalently, an approximate solution ϕ will depend on $\vec{x}$. But in addition we may let it depend on further parameters, $p_1, p_2, \ldots, p_{N_p}$ (in the case above of the previous subsection there was only one such parameter, α). Accordingly we write

$$\phi = \phi(p_1, p_2, \ldots, p_{N_p}; \vec{x}). \tag{5.21}$$

As in Eq. (5.17) the expectation value (5.9) becomes a function of these extra parameters,

$$\frac{\langle\phi|\hat{A}|\phi\rangle}{\langle\phi|\phi\rangle} \equiv \tilde{a}(p_1, p_2, \ldots, p_{N_p}), \tag{5.22}$$

and we will determine these parameters by minimizing this function, i.e., by requiring

$$\frac{\partial a(p_1, p_2, \ldots, p_{N_p})}{\partial p_1} = \frac{\partial a(p_1, p_2, \ldots, p_{N_p})}{\partial p_2} = \cdots = \frac{\partial a(p_1, p_2, \ldots, p_{N_p})}{\partial p_{N_p}} = 0. \tag{5.23}$$

By introducing more and more parameters it should be possible to obtain very accurate approximations to the exact ground-state eigenfunctions, but, unfortunately, the equations (5.22) very easily become too complicated to be solvable. There is, however, one important exception, the so-called linear variation, which we shall discuss further below. But before this we shall discuss a little further the quality of the approximate eigenfunctions obtained through this variation, by looking at a very simple example.

5.4   THE HYDROGEN ATOM

The Hamilton operator for the single electron of a hydrogen atom is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}, \tag{5.24}$$

where we have assumed that the nucleus is placed at the origin.

In order to avoid having to remember all the fundamental constants, it is useful to work with so-called atomic units. We shall later describe them in more detail but here we just list them. We set

$$\hbar = m = |e| = 4\pi\varepsilon_0 = 1. \tag{5.25}$$

Energies are then given in so-called hartrees (1 hartree $\simeq$ 27.21 eV) and lengths in bohr (1 bohr $\simeq$ 0.5292 Å). With these, the Hamilton operator of Eq. (5.24) becomes

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}. \tag{5.26}$$

The eigenvalue problem

$$\hat{H}\psi_n = e_n\psi_n \tag{5.27}$$

has as its lowest eigenvalue

$$e_0 = -\frac{1}{2} \tag{5.28}$$

and the corresponding eigenfunction is

$$\psi = \frac{1}{\sqrt{\pi}}e^{-r}, \tag{5.29}$$

(this function is normalized) as can be found in most introductory textbooks on quantum theory.

Since we in this case know the exact solution we can directly compare it with results of calculations using the variational method. This is in almost all other cases not possible.

We will apply the variational method for the test function

$$\phi = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha r^2}, \qquad (5.30)$$

i.e., a Gaussian (that furthermore is normalized). In Fig. 5.2 we compare the exact wavefunction [Eq. (5.29)] with that of Eq. (5.30) for different values of α.

Since ϕ of eq. (5.4.7) is normalized, the expectation value of Eq. (5.22) becomes

$$\tilde{E}(\alpha) = \langle \phi | \hat{H} | \phi \rangle, \qquad (5.31)$$

which can be calculated to yield

$$\tilde{E}(\alpha) = \frac{3\alpha}{2} - 2\left(\frac{2\alpha}{\pi}\right)^{1/2}. \qquad (5.32)$$

This function is shown in Fig. 5.3.

Taking the derivative of this with respect to α gives the value of α at the minimum,

$$\alpha = \frac{8}{9\pi} \simeq 0.283, \qquad (5.33)$$

and the expectation value for this value of α is

$$\tilde{E}\left(\alpha = \frac{8}{9\pi}\right) = -\frac{4}{3\pi} \simeq -0.424. \qquad (5.34)$$

By looking at Fig. 5.2 we see that this value of α does appear to give a reasonable (but no more!) description of the exact wavefunction although the agreement between the exact lowest energy [Eq. (5.28)] and the approximate one [Eq. (5.32)] may suggest a better agreement.

However, the application of the variational principle is not restricted to the Hamilton operator. We therefore construct another operator that happens to have the same eigenfunction of the lowest eigenvalue as the Hamilton operator of the hydrogen atom. Please notice that this construction does not result from physical reasons but is used since it may illustrate some few aspects of the variational method.

The operator we construct is

$$\hat{G} = \left(\hat{H} + \tfrac{1}{2}\right)^2, \qquad (5.35)$$

where $\hat{H}$ is the operator of Eq. (5.26). This operator has exactly the same eigenfunctions as $\hat{H}$ of Eq. (5.26) (this can be shown by using the completeness of the latter), and the lowest eigenvalue is 0 for the function of Eq. (5.29).
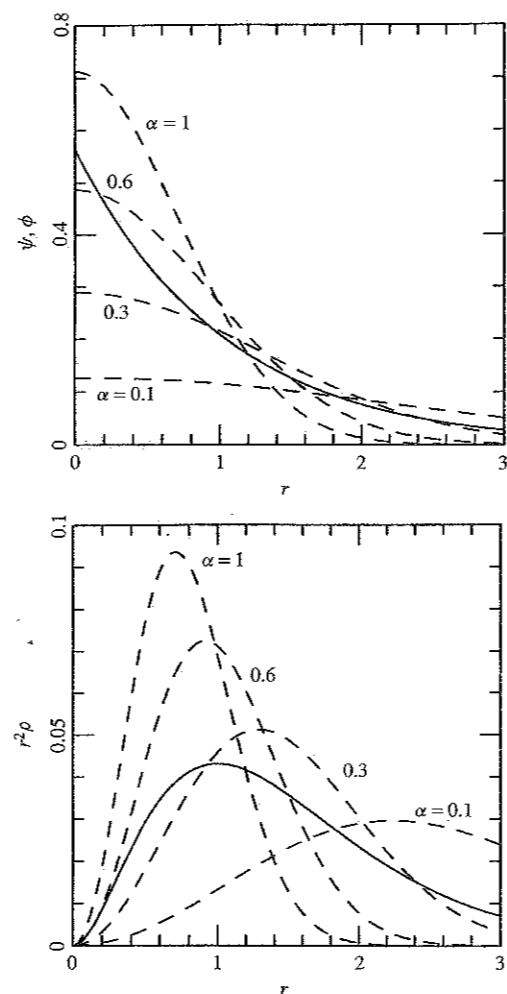
Figure 5.2 The solid line shows the exact hydrogen function of Eq. (5.29), whereas the dashed curves show Gaussians of Eq. (5.30) with $\alpha = 0.1$, 0.3, 0.6, and 1.0. The most compact function is that of the largest α. The upper panel shows the functions themselves, whereas the lower panel shows the functions squared times r^2 (i.e., a radial electron density)

Here we calculate

$$\tilde{G}(\alpha) = \langle \phi | \hat{G} | \phi \rangle, \qquad (5.36)$$

which can be calculated to yield

$$\tilde{G}(\alpha) = \frac{1}{8} + \frac{9}{4}\alpha + \frac{19}{32}\alpha^2 - 2\alpha\sqrt{\frac{2\alpha}{\pi}} - \sqrt{\frac{2\alpha}{\pi}}. \qquad (5.37)$$
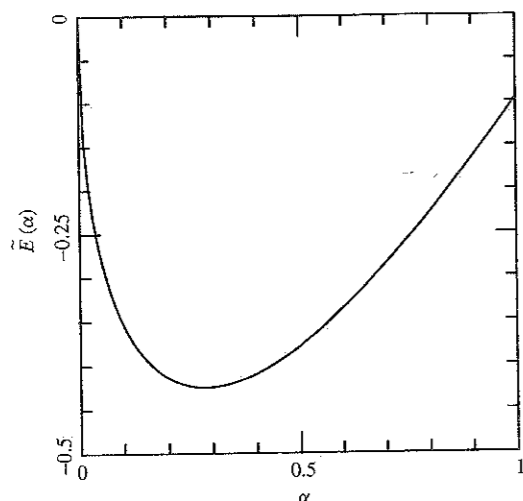
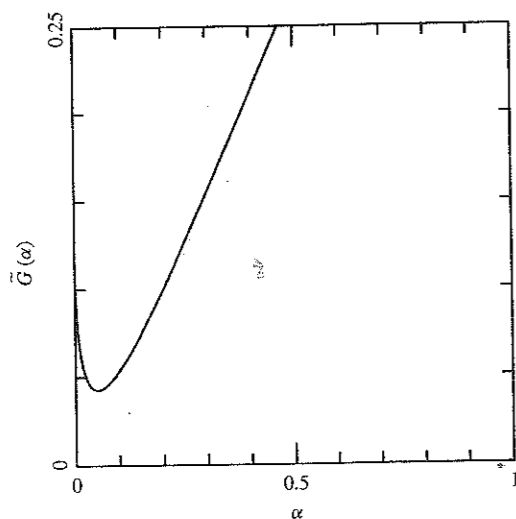**Figure 5.3**   The function $\tilde{E}(\alpha)$ of Eq. (5.32)

Figure 5.4   The function $\tilde{G}(\alpha)$ of Eq. (5.37)

This function is shown in Fig. 5.4.

The minimum of $\tilde{G}(\alpha)$ is found for

$$\alpha \simeq 0.0508, \tag{5.38}$$

i.e., a significantly smaller value than that of Eq. (5.33). By inspecting Fig. 5.2 we see that the larger value of α [Eq. (5.33)] leads to a function that more resembles
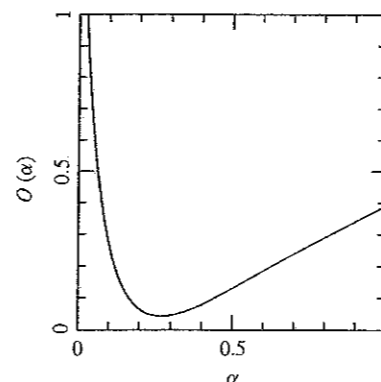
Figure 5.5   The function $O(\alpha)$ of Eq. (5.39)

the true ground-state function, which lends supports to the usual approach of using the Hamilton operator in variationally giving an approximate wavefunction. It does, however, also show that one may occasionally obtain results that are less trustworthy, although the formulas have been applied correctly.

Finally, we may also directly measure the quality of a given approximate wavefunction in the present example by calculating

$$O(\alpha) = \langle \phi - \psi | \phi - \psi \rangle. \tag{5.39}$$

This function is smallest when the difference between the exact and the approximate function is smallest (using the usual norm). $O(\alpha)$ is shown in Fig. 5.5.

The minimum in Fig. 5.5 is found for

$$\alpha \simeq 0.27, \tag{5.40}$$

i.e., for a value close to that of Eq. (5.33).

5.5   LINEAR VARIATION AND LAGRANGE MULTIPLIERS

As mentioned above, the problem of solving the equations (5.23) becomes very easily very complicated also when the number of parameters is not very large. There is, however, one — very important — case, where the equations, although in a slightly modified form, can be solved straightforwardly.

We want to minimize the expectation value

$$\frac{\langle \phi | \hat{A} | \phi \rangle}{\langle \phi | \phi \rangle}. \tag{5.41}$$

We shall now assume that the minimization is done by varying the *coefficients* to some *fixed* so-called basis functions. This means that we will write ϕ as a linear

combination of fixed basis functions,

$$\phi(\vec{x}) = \sum_{i=1}^{N_b} c_i \chi_i(\vec{x}), \qquad (5.42)$$

where N_b is the number of basis functions $\{\chi_i\}$, and where the variation is done by varying the coefficients $\{c_i\}$ but keeping the basis functions $\{\chi_i\}$ fixed.

Equation (5.23) takes then the form

$$\frac{\partial}{\partial c_k} \frac{\langle \phi | \hat{A} | \phi \rangle}{\langle \phi | \phi \rangle} = 0 \qquad (5.43)$$

for all $k = 1, 2, \ldots, N_b$, or by taking the complex conjugate of this equation (this is not really a necessary step, but the equations look simpler!),

$$\frac{\partial}{\partial c_k^*} \frac{\langle \phi | \hat{A} | \phi \rangle}{\langle \phi | \phi \rangle} = 0. \qquad (5.44)$$

We may restate this as requiring that

$$\frac{\partial}{\partial c_k^*} \langle \phi | \hat{A} | \phi \rangle = 0, \qquad k = 1, \ldots, N_b, \qquad (5.45)$$

when we simultaneously require that the function ϕ is normalized:

$$\langle \phi | \phi \rangle = 1. \qquad (5.46)$$

This means that the single equation (5.44) can be replaced by the two equations (5.45) and (5.46).

We shall combine the two equations (5.45) and (5.46) into one by introducing one extra parameter. This is done by considering the quantity

$$K = \langle \phi | \hat{A} | \phi \rangle - \lambda [\langle \phi | \phi \rangle - 1]. \qquad (5.47)$$

The extra parameter λ is a so-called *Lagrange multiplier*, and Eqs. (5.45) and (5.46) then take the form

$$\frac{\partial K}{\partial c_k^*} = \frac{\partial K}{\partial \lambda} = 0. \qquad (5.48)$$

The Lagrange multiplier is a mathematical trick that allows one to incorporate one (or more) extra boundary condition(s) [in this case, that of Eq. (5.46)] into a variation. It is not obvious whether the multiplier has any meaning (although this often is the case), but it is first of all introduced due to its convenience.

By inserting K of Eq. (5.47) into the last identity of Eq. (5.48) we recover immediately the boundary condition (5.46),

$$\langle \phi | \phi \rangle - 1 = 0. \qquad (5.49)$$

From the first equations of Eq. (5.48) we obtain, upon inserting Eq. (5.42),

$$\frac{\partial}{\partial c_k^*} \left[\left\langle \sum_i c_i \chi_i \middle| \hat{A} \middle| \sum_j c_j \chi_j \right\rangle - \lambda \left(\left\langle \sum_i c_i \chi_i \middle| \sum_j c_j \chi_j \right\rangle - 1 \right) \right]$$

$$= \frac{\partial}{\partial c_k^*} \left(\left\langle \sum_i c_i \chi_i \middle| \hat{A} \middle| \sum_j c_j \chi_j \right\rangle - \lambda \left\langle \sum_i c_i \chi_i \middle| \sum_j c_j \chi_j \right\rangle \right)$$

$$= \frac{\partial}{\partial c_k^*} \sum_{i,j} c_i^* c_j [\langle \chi_i | \hat{A} | \chi_j \rangle - \lambda \langle \chi_i | \chi_j \rangle]$$

$$= \sum_j c_j [\langle \chi_k | \hat{A} | \chi_j \rangle - \lambda \langle \chi_k | \chi_j \rangle] \equiv 0. \qquad (5.50)$$

This gives immediately the following eigenvalue equation,

$$\sum_j c_j \langle \chi_k | \hat{A} | \chi_j \rangle = \lambda \sum_j c_j \langle \chi_k | \chi_j \rangle, \qquad (5.51)$$

where we have as many equations ($k = 1, 2, \ldots, N_b$) as we have basis functions, i.e.

$$k = 1, 2, \ldots, N_b. \qquad (5.52)$$

In Eq. (5.50) we recognize matrix elements of the type $\langle \chi_k | \hat{A} | \chi_j \rangle$ and of the type $\langle \chi_k | \chi_j \rangle$. It is useful to define two matrices containing these, i.e.,

$$\underline{\underline{A}}_{kj} = \langle \chi_k | \hat{A} | \chi_j \rangle \qquad (5.53)$$

and

$$\underline{\underline{O}}_{kj} = \langle \chi_k | \chi_j \rangle. \qquad (5.54)$$

The equations (5.51) are then easily rewritten as the generalized matrix eigenvalue equation

$$\underline{\underline{A}} \cdot \underline{c} = \lambda \cdot \underline{\underline{O}} \cdot \underline{c}, \qquad (5.55)$$

where $\underline{c}$ is a column vector containing the sought coefficients $\{c_j\}$. Eq. (5.55) is called the secular equation.

That Eqs. (5.55) and (5.51) are equivalent can easily be shown by writing out the matrix equations (5.55) and inserting the definitions of Eqs. (5.53) and (5.54).

The *very* important point is that the matrix eigenvalue equation (5.55) easily can be solved using standard computer routines. The results will contain the coefficients c_j and the eigenvalue λ. However, the coefficients c_j may have to be multiplied by a common constant in order to satisfy the normalization condition (5.46). Actually, there will not be only one solution, but N_b solutions. One question is thus, which one do we choose.

Once the coefficients are known, the sought expectation value

$$\frac{\langle \phi | \hat{A} | \phi \rangle}{\langle \phi | \phi \rangle} = \frac{\sum_{i,j} c_i^* c_j \langle \chi_i | \hat{A} | \chi_j \rangle}{\sum_{i,j} c_i^* c_j \langle \chi_i | \chi_j \rangle} \tag{5.56}$$

can be calculated. But in our case the Lagrange multiplier has a very simple interpretation that makes this step unnecessary and that furthermore allows us to choose the correct eigenvalue and eigenfunction immediately.

To realize this we multiply Eq. (5.51) by c_k^* and sum all the different equations for the different k, which gives

$$\sum_{j,k} c_k^* c_j \langle \chi_k | \hat{A} | \chi_j \rangle = \lambda \sum_{j,k} c_k^* c_j \langle \chi_k | \chi_j \rangle, \tag{5.57}$$

or

$$\lambda = \frac{\sum_{j,k} c_k^* c_j \langle \chi_k | \hat{A} | \chi_j \rangle}{\sum_{j,k} c_k^* c_j \langle \chi_k | \chi_j \rangle}, \tag{5.58}$$

i.e., the eigenvalue (or Lagrange multiplier) *is* the sought expectation value! Furthermore, out of the N_b eigenvalues and eigenfunctions, we shall choose that corresponding to the smallest eigenvalue.

5.6   AN EXAMPLE

As an example we consider the potential of Fig. 5.6, given by

$$V(x) = (x^2 - 1)^2, \tag{5.59}$$

which is shown in Fig. 5.

The corresponding one-dimensional Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi(x) \equiv \hat{H}\psi = E \cdot \psi(x), \tag{5.60}$$

cannot be solved directly and instead we seek an approximate solution. To this end we *choose* some fixed basis functions $\{\chi_j\}$ for which we can calculate the matrix elements $\langle \chi_k | \hat{H} | \chi_l \rangle$ and $\langle \chi_k | \chi_l \rangle$. These functions could, e.g., be

$$\chi_1(x) = e^{-(x-1)^2}$$

$$\chi_2(x) = e^{-(x+1)^2}$$

$$\chi_3(x) = (x - 1)e^{-(x-1)^2}$$

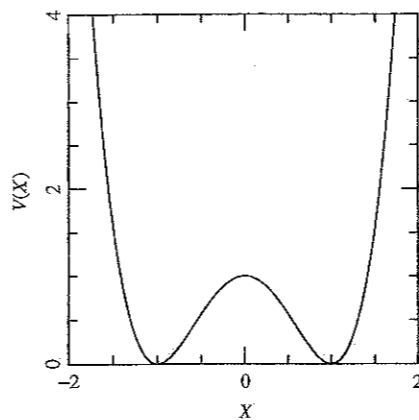$$\chi_4(x) = (x + 1)e^{-(x+1)^2} \tag{5.61}$$

Figure 5.6   The potential $V(x)$ of Eq. (5.59)

and, consequently, we approximate the ground-state eigenfunction to Eq. (5.60) as

$$\psi(x) \simeq \phi(x) = c_1 \chi_1(x) + c_2 \chi_2(x) + c_3 \chi_3(x) + c_4 \chi_4(x), \tag{5.62}$$

where the coefficients c_i are sought.

Applying the method of the previous subsection, these coefficients can be found through the following 4×4 generalized eigenvalue problem (the secular equation),

$$
\begin{pmatrix}
\langle \chi_1 | \hat{H} | \chi_1 \rangle & \langle \chi_1 | \hat{H} | \chi_2 \rangle & \langle \chi_1 | \hat{H} | \chi_3 \rangle & \langle \chi_1 | \hat{H} | \chi_4 \rangle \\
\langle \chi_2 | \hat{H} | \chi_1 \rangle & \langle \chi_2 | \hat{H} | \chi_2 \rangle & \langle \chi_2 | \hat{H} | \chi_3 \rangle & \langle \chi_2 | \hat{H} | \chi_4 \rangle \\
\langle \chi_3 | \hat{H} | \chi_1 \rangle & \langle \chi_3 | \hat{H} | \chi_2 \rangle & \langle \chi_3 | \hat{H} | \chi_3 \rangle & \langle \chi_3 | \hat{H} | \chi_4 \rangle \\
\langle \chi_4 | \hat{H} | \chi_1 \rangle & \langle \chi_4 | \hat{H} | \chi_2 \rangle & \langle \chi_4 | \hat{H} | \chi_3 \rangle & \langle \chi_4 | \hat{H} | \chi_4 \rangle
\end{pmatrix}
\cdot
\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}
$$

$$
= E \cdot
\begin{pmatrix}
\langle \chi_1 | \chi_1 \rangle & \langle \chi_1 | \chi_2 \rangle & \langle \chi_1 | \chi_3 \rangle & \langle \chi_1 | \chi_4 \rangle \\
\langle \chi_2 | \chi_1 \rangle & \langle \chi_2 | \chi_2 \rangle & \langle \chi_2 | \chi_3 \rangle & \langle \chi_2 | \chi_4 \rangle \\
\langle \chi_3 | \chi_1 \rangle & \langle \chi_3 | \chi_2 \rangle & \langle \chi_3 | \chi_3 \rangle & \langle \chi_3 | \chi_4 \rangle \\
\langle \chi_4 | \chi_1 \rangle & \langle \chi_4 | \chi_2 \rangle & \langle \chi_4 | \chi_3 \rangle & \langle \chi_4 | \chi_4 \rangle
\end{pmatrix}
\cdot
\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix}. \tag{5.63}
$$

The solution sought is the one that corresponds to the lowest eigenvalue E.