

3 The Rayleigh-Ritz variational method

3.1 Variational calculation of the ground state energy

In this section: General principles of the Rayleigh-Ritz method; the energy functional; trial functions; variational parameters.

Quantum mechanical systems for which energy levels and wave functions can be obtained analytically are very few in numbers. They are practically limited to the infinite square well, the harmonic oscillator, the atom of hydrogen, and a few other systems of lesser importance. Calculations of energy levels are thus partly or wholly numerical for complex systems, e.g., for systems such as multi-electron atoms, molecules, condensed matter, etc. Most of the methods employed in these calculations are based on an approach generally referred to as the Rayleigh-Ritz variational method. This approach was introduced more than a century ago in a different context and has found applications in many different fields of Physics, Engineering and Mathematics.

The principle of the Rayleigh-Ritz method for the calculation of bound state energies in Quantum Mechanics can be explained in a few words. Suppose that we want to calculate the ground state energy of a system for which we know the Hamiltonian, H . In practice, this system will typically involve many interacting electrons or other particles and be quite complicated. However, to keep things simple we will assume for the time being that there is only one particle in the system and that this particle is confined to the x -axis. The ground state wave function would therefore be a function of x only, the coordinate of the particle. Let us imagine that we do not know the exact ground state wave function. Instead we guess that this function can be approximated by a certain function $\phi(x)$, simple enough that we can carry out the necessary calculations. Then, we define the so-called energy functional, $E[\phi]$:

$$E[\phi] = \frac{\int_{-\infty}^{\infty} \phi^*(x) H \phi(x) dx}{\int_{-\infty}^{\infty} \phi^*(x) \phi(x) dx}. \quad (3.1)$$

The denominator of $E[\phi]$ is simply the square of the norm of $\phi(x)$ and is equal to 1 if $\phi(x)$ is normalized (it is often convenient to work with unnormalized ϕ -functions, for which the denominator is not equal to 1).

It is worth noting that if $\phi(x)$ happens to be the exact ground state wave function, $\psi_{\text{gs}}(x)$, then $E[\phi]$ is nothing else than the exact ground state energy, E_{gs} . Indeed, if $H\psi_{\text{gs}}(x) = E_{\text{gs}}\psi_{\text{gs}}(x)$, then

$$E[\psi_{\text{gs}}] = \frac{\int_{-\infty}^{\infty} \psi_{\text{gs}}^*(x) H \psi_{\text{gs}}(x) dx}{\int_{-\infty}^{\infty} \psi_{\text{gs}}^*(x) \psi_{\text{gs}}(x) dx} = \frac{E_{\text{gs}} \int_{-\infty}^{\infty} \psi_{\text{gs}}^*(x) \psi_{\text{gs}}(x) dx}{\int_{-\infty}^{\infty} \psi_{\text{gs}}^*(x) \psi_{\text{gs}}(x) dx} = E_{\text{gs}}. \quad (3.2)$$

Clearly, one should not expect that $E[\phi] = E_{\text{gs}}$ if $\phi(x)$ is not the exact ground state wave function. However, one can show that the following inequality always hold:

$$E_{\text{gs}} \leq E[\phi] \quad (3.3)$$

whatever the function $\phi(x)$ is. Thus $E[\phi]$ is an upper bound for the ground state energy.

The same also applies to 3D systems and to systems involving more than one particle. Denoting by τ the set of all the coordinates the wave functions depend on, the energy functional can be written more generally as

$$E[\phi] = \frac{\int \phi^*(\tau) H \phi(\tau) d\tau}{\int \phi^*(\tau) \phi(\tau) d\tau}, \quad (3.4)$$

where the integrals are taken over all the coordinates in the problem. (For example, $d\tau \equiv r^2 \sin \theta dr d\theta d\phi$ for a single particle whose position in 3D is described by the usual spherical polar coordinates r, θ, ϕ .) Whatever the number of coordinates, the inequality (3.3) always applies.

Note 1: $E[\phi]$ is a number (the integrals appearing in the numerator and the denominator are both numbers). Clearly, this number depends on the function $\phi(x)$. In Mathematics, a mapping which, like $E[\phi]$, associates a function to a number is called a functional; hence the term “energy functional”. We write the argument of $E[\phi]$ between square brackets, to make it clear that $E[\phi]$ is a functional.

Note 2: Here is a proof of the important inequality (3.3). Let us represent the function $\phi(\tau)$ by a linear combination of the eigenfunctions of the Hamiltonian H :

$$\phi(\tau) = \sum_n c_n \psi_n(\tau), \quad (3.5)$$

where $\psi_n(\tau)$ are such that $H\psi_n(\tau) = E_n\psi_n(\tau)$. (The coefficients c_n and the functions $\psi_n(\tau)$ are not known in general, but this is not important: the point here is that one can write $\phi(\tau)$ in this way, since the eigenfunctions of the Hamiltonian form a complete basis set.) We will assume that these eigenfunctions are orthonormal:

$$\int \psi_{n'}^*(\tau) \psi_n(\tau) d\tau = \delta_{n'n}. \quad (3.6)$$

Hence

$$\int \phi^*(\tau)\phi(\tau) d\tau = \sum_{n'} \sum_n c_{n'}^* c_n \delta_{n'n} = \sum_n |c_n|^2 \quad (3.7)$$

and

$$\int \phi^*(\tau)H\phi(\tau) d\tau = \sum_{n'} \sum_n c_{n'}^* E_n c_n \delta_{n'n} = \sum_n E_n |c_n|^2. \quad (3.8)$$

Using these two results and subtracting the ground state energy from both sides of Eq. (3.4) gives

$$E[\phi] - E_{\text{gs}} = \frac{\sum_n (E_n - E_{\text{gs}}) |c_n|^2}{\sum_n |c_n|^2}. \quad (3.9)$$

Since by definition the ground state energy E_{gs} is the lowest of the eigenenergies E_n , the right-hand side of this equation is a sum of non-negative numbers. The inequality (3.3) follows.

Note 3: Since the exact ground state energy E_{gs} is the smallest value $E[\phi]$ can take, the difference between $E[\phi]$ and E_{gs} is of second order in the difference between $\phi(\tau)$ and $\psi_{\text{gs}}(\tau)$, the exact ground state wave function. So to speak, $E[\phi]$ is a better approximation to E_{gs} than $\phi(\tau)$ is to $\psi_{\text{gs}}(\tau)$ (unless $\phi(\tau)$ would differ excessively from $\psi_{\text{gs}}(\tau)$).

The inequality (3.3) is of key importance. Suppose indeed that one takes a function $\phi_1(\tau)$ and a function $\phi_2(\tau)$, both representing (perhaps roughly) the ground state wave function, and suppose that $E[\phi_2] < E[\phi_1]$. Then we can be sure that $E[\phi_2]$ is a better approximation to E_{gs} than $E[\phi_1]$, since by virtue of the inequality (3.3) $E_{\text{gs}} \leq E[\phi_2] < E[\phi_1]$. This approximation can be improved by looking for a function $\phi_3(\tau)$ such that $E[\phi_3] < E[\phi_2]$: the lower the value of $E[\phi]$ is, the closer it is to the exact ground state energy.

In practice, one uses functions $\phi(\tau)$ depending on one or several parameters. For instance, in the example discussed in Section 3.2, the function $\phi(\lambda; x)$ defined by Eq. (3.14) depends both on x and on a variable λ . The latter is just a parameter which can be varied independently from x : changing the value of λ changes the way $\phi(\lambda; x)$ varies with x . Thus the value of $E[\phi]$ obtained by plugging $\phi(\lambda; x)$ in Eq. (3.1) is also a function of λ . Let us denote the latter by $E(\lambda)$:

$$E[\phi] \equiv E(\lambda) = \frac{\int_{-\infty}^{\infty} \phi^*(\lambda; x) H \phi(\lambda; x) dx}{\int_{-\infty}^{\infty} \phi^*(\lambda; x) \phi(\lambda; x) dx}. \quad (3.10)$$

In this context, $\phi(\lambda; x)$ is called a trial function and λ is a variational parameter. Finding the best possible approximate value of the exact ground state energy

using a trial function depending on a variational parameter λ thus reduces to finding the minimum value of the function $E(\lambda)$.

More generally, one may work with trial functions depending on several variational parameters, $\lambda_1, \lambda_2, \dots, \lambda_N$. Then the energy functional is a function $E(\lambda_1, \lambda_2, \dots, \lambda_N)$ of these parameters. The minimum of that function is found by finding the values of these parameters at which

$$\frac{\partial E}{\partial \lambda_j} = 0 \quad j = 1, 2, \dots, N. \quad (3.11)$$

As discussed in Section 3.3, this multi-parameter approach is widely used in a formulation where the calculation reduces to computing the eigenvalues of a matrix representing the Hamiltonian.

Note 4: As its name suggests, the Rayleigh-Ritz variational method is related to calculus of variation. However, the relationship is not immediately obvious.

Note 5: If the trial function is orthogonal to the exact ground state wave function, then $E[\phi]$ is an approximation to the first excited energy level, E_1 , and $E_1 \leq E[\phi]$. This can be understood easily by looking at the proof that $E_0 \leq E[\phi]$ given above. Let us refer to the ground state by the index $n = 0$, so that E_0 is the exact ground state energy and $\psi_0(\tau)$ is the exact ground state wave function. If $\phi(\tau)$ is orthogonal to $\psi_0(\tau)$, then $c_0 = 0$. In this case

$$E[\phi] = \frac{\sum_{n \geq 1} E_n |c_n|^2}{\sum_{n \geq 1} |c_n|^2} \quad (3.12)$$

and therefore

$$E[\phi] - E_1 = \frac{\sum_{n \geq 1} (E_n - E_1) |c_n|^2}{\sum_{n \geq 1} |c_n|^2}. \quad (3.13)$$

The right-hand side of this equation is non-negative since all the eigenenergies E_n appearing in the sum are larger or equal to E_1 . Hence $E_1 \leq E[\phi]$.

3.2 An example

In this section: An example of variational calculation using a single variational parameter.

To illustrate how the method works, we apply it to the calculation of the ground state energy of a particle trapped in an 1D box. For simplicity, we use a trial function depending on only one variational parameter.

Thus we imagine that a particle of mass m is confined to the region extending from $x = 0$ to $x = L$. We take the case where the particle is free between these

two points, its potential energy being zero everywhere on the interval $0 < x < L$. That the particle is confined means that it has zero probability to be outside this region; hence its wave function must be zero for $x \leq 0$ and for $x \geq L$. This system is treated in detail in Chapter 40 of Young and Freedman, where it is shown that the ground state energy of this particle is $\pi^2 \hbar^2 / (2mL^2)$.

Let us see how the variational method fares for this problem. The first step of a variational calculation is to choose a good trial function (a poor trial function would only produce a poor result). To guide this choice, we look at what we can say about the properties of the exact ground state wave function (supposed to be unknown). Specifically, we recall (1) that this wave function must be zero for $x \leq 0$ and $x \geq L$ since the particle is confined in the box; (2) that, on mathematical grounds, the wave function must be continuous at $x = 0$ and $x = L$; and (3) that it must also be “symmetrical” with respect to $x = L/2$ since there is no reason why the particle should have a different probability to be on the left than on the right of the centre of the box. We therefore choose a trial function which has these three properties. We take the following, to keep the calculation relatively simple:¹

$$\phi(\lambda; x) = \begin{cases} 0 & x \leq 0, \\ x(L-x)[1 + \lambda(x - L/2)^2] & 0 < x < L, \\ 0 & x \geq L. \end{cases} \quad (3.14)$$

Note that $\phi(\lambda; x)$ is a function both of x and of the variational parameter λ .

The second step is to write down and calculate the energy functional, $E[\phi]$, as a function of the variational parameter λ . For this we need the Hamiltonian of the problem, H . Here

$$H = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \quad (3.15)$$

in view of our assumption that the potential energy of the particle is zero everywhere inside the box. Plugging the expressions of $\phi(\lambda; x)$ and of H given by Eqs. (3.14) and (3.15) into Eq. (3.10) yields

$$E(\lambda) = \left(-\frac{\hbar^2}{2m} \right) \times \frac{\int_0^L (x(L-x) [1 + \lambda(x - L/2)^2]) \frac{d^2}{dx^2} (x(L-x) [1 + \lambda(x - L/2)^2]) dx}{\int_0^L (x(L-x) [1 + \lambda(x - L/2)^2])^2 dx}. \quad (3.16)$$

¹This example is also given in Bransden and Joachain, with the difference that these authors take the box to extend from $-L/2$ to $L/2$ rather than from 0 to L as we assume here. Their trial function is identical to ours within a shift of the origin of the x -axis by $L/2$.

Calculating these integrals is straightforward, if a little long. The result is

$$E(\lambda) = \frac{3\hbar^2}{mL^2} \frac{11a^4\lambda^2 + 14a^2\lambda + 35}{a^4\lambda^2 + 6a^2\lambda + 21}, \quad (3.17)$$

with $a = L/2$.

We then simply need to find the value of λ at which $E(\lambda)$ is a minimum. To this effect, we find the value(s) of λ at which $dE/d\lambda = 0$. Since

$$\frac{dE}{d\lambda} = \frac{12\hbar^2}{mL^2} \frac{13a^6\lambda^2 + 98a^4\lambda + 21a^2}{(a^4\lambda^2 + 6a^2\lambda + 21)^2}, \quad (3.18)$$

the equation for the minimum is simply

$$13a^6\lambda^2 + 98a^4\lambda + 21a^2 = 0. \quad (3.19)$$

This equation has two solutions, namely

$$\lambda_+ = \frac{-49 + \sqrt{2128}}{13a^2} \quad \text{and} \quad \lambda_- = \frac{-49 - \sqrt{2128}}{13a^2}. \quad (3.20)$$

Replacing λ by λ_+ and λ_- in Eq. (3.17) gives the corresponding values of the ground energy, namely

$$E(\lambda_+) = 4.93487 \frac{\hbar^2}{mL^2} \quad \text{and} \quad E(\lambda_-) = 51.0651 \frac{\hbar^2}{mL^2} \quad (3.21)$$

to six significant figures. The first of these values is the lowest of the two. It is therefore the best approximate value of the ground state energy one can find with our trial function. This value is in fact remarkably close to the exact ground state energy, $4.93480\hbar^2/(mL^2)$ (to six significant figures). Note that $E(\lambda_+)$ is larger than the exact value, in agreement with the general inequality (3.3).

3.3 Using basis functions

In this section: Obtaining the energy levels using a finite number of basis functions.

The energy levels of complex quantum systems are often calculated by computing the eigenvalues of a matrix “representing” the Hamiltonian (often an extremely large matrix). This approach is widely used and very powerful. Its principles are not difficult to grasp but are perhaps best explained by way of an example.

Let us consider the following model problem. Suppose that we need to calculate the eigenenergies of the following Hamiltonian,

$$H = H_0 + \frac{\hbar^2}{ma^2} \frac{x}{a}, \quad (3.22)$$

where

$$H_0 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{\hbar^2}{2ma^2} \frac{x^2}{a^2}. \quad (3.23)$$

Here a is a constant with the physical dimensions of a length. As you may have recognized, H_0 is the Hamiltonian of a 1D harmonic oscillator of mass m (you have seen this Hamiltonian in the level 2 Quantum Mechanics course, although perhaps not written exactly in this form). The Hamiltonian H thus describes a perturbed harmonic oscillator. It happens that its eigenenergies (E_n) can be calculated analytically, and the result is extremely simple:

$$E_n = n \frac{\hbar^2}{ma^2}, \quad n = 0, 1, 2, \dots \quad (3.24)$$

Let us pretend that we do not know this result and try instead to calculate these eigenenergies numerically.

To this end, let us proceed in the following way. First, we recall that the eigenfunctions of H_0 , which are known analytically, form a complete orthonormal basis set. We will denote these eigenfunctions by $\chi_n(x)$, $n = 0, 1, 2, \dots$. Thus any eigenfunction $\psi(x)$ of the complete Hamiltonian H can, in principle, be written as an expansion of the form

$$\psi(x) = \sum_{n=0}^{\infty} c_n \chi_n(x), \quad (3.25)$$

where the coefficients c_n are constants. It is not difficult to show (see Note 1 below) that the coefficients c_n and the eigenenergy E satisfy the following system of coupled equations:

$$\sum_{n=0}^{\infty} H_{n'n} c_n = E c_{n'}, \quad n' = 0, 1, 2, \dots, \quad (3.26)$$

with

$$H_{n'n} = \int_{-\infty}^{\infty} \chi_{n'}^*(x) H \chi_n(x) dx. \quad (3.27)$$

Although the matrix elements $H_{n'n}$ can be calculated, the coefficients c_n cannot be worked out using Eq. (3.26) as this system contains an infinite number of coupled equations. We therefore make a key approximation: instead of including all the basis functions $\chi_n(x)$ in the expansion of $\psi(x)$, we restrict n to vary from 0 to a certain maximum value N . Thus we approximate the exact eigenfunction $\psi(x)$ by a linear combination of a finite number of the basis functions $\chi_n(x)$:

$$\psi(x) \approx \sum_{n=0}^N c_n \chi_n(x). \quad (3.28)$$

This approximation can be justified on physical grounds: we can expect that the wave functions of the ground and of the low excited states of H vary much less rapidly with x than the functions $\chi_n(x)$ do for large values of n , and therefore we can expect that the coefficients c_n go to zero for $n \rightarrow \infty$. Making this approximation reduces Eq. (3.34) to a *finite* system of coupled equations:

$$\sum_{n=0}^N H_{n'n} c_n = E c_{n'}, \quad n' = 0, 1, 2, \dots, N. \quad (3.29)$$

The coefficients c_n and the energies E satisfying these coupled equations will not be identical to the exact coefficients and energies, which satisfy Eq. (3.34), but they can be expected to be close to these exact values if N is large enough.

Note 1: To obtain Eq. (3.26), we write the Schrödinger equation satisfied by $\psi(x)$,

$$H\psi(x) = E\psi(x), \quad (3.30)$$

and replace $\psi(x)$ by the right-hand side of Eq. (3.25). This gives

$$\sum_{n=0}^{\infty} c_n H\chi_n(x) = E \sum_{n=0}^{\infty} c_n \chi_n(x). \quad (3.31)$$

Now, we multiply this equation on the left by the complex conjugate of the function $\chi_0(x)$ and integrate the result over x :

$$\sum_{n=0}^{\infty} c_n \int_{-\infty}^{\infty} \chi_0^*(x) H\chi_n(x) dx = E \sum_{n=0}^{\infty} c_n \int_{-\infty}^{\infty} \chi_0^*(x) \chi_n(x) dx. \quad (3.32)$$

The right-hand side of this equation can be simplified by using the orthonormality of the functions $\chi_n(x)$:

$$\sum_{n=0}^{\infty} c_n \int_{-\infty}^{\infty} \chi_0^*(x) \chi_n(x) dx = \sum_{n=0}^{\infty} c_n \delta_{0n} = c_0. \quad (3.33)$$

Eq. (3.32) can thus be written in the following form:

$$\sum_{n=0}^{\infty} H_{0n} c_n = E c_0, \quad (3.34)$$

where

$$H_{0n} = \int_{-\infty}^{\infty} \chi_0^*(x) H\chi_n(x) dx. \quad (3.35)$$

The same operation can be repeated, with Eq. (3.31) now multiplied on the left by $\chi_1^*(x)$ instead of $\chi_0^*(x)$, then $\chi_2^*(x)$ instead of $\chi_1^*(x)$, etc., which yields Eq. (3.26).

Table 3.1: The four lowest eigenvalues of the matrix \mathbf{H} defined in the text, in units of $\hbar^2/(ma^2)$, for increasing basis sizes, and the corresponding exact eigenenergies of the Hamiltonian H of Eq. (3.22). Here N is the largest value taken by the quantum number n in Eq. (3.28).

N	E_0	E_1	E_2	E_3
3	0.00525	1.08726	2.46351	4.44398
5	0.00007	1.00327	2.04446	3.24757
7	0.00000	1.00004	2.00136	3.01900
9	0.00000	1.00000	2.00002	3.00045
Exact	0.00000	1.00000	2.00000	3.00000

Eq. (3.29) can be recast in the more transparent form

$$\mathbf{H} \mathbf{c} = E \mathbf{c} \quad (3.36)$$

by forming a column vector \mathbf{c} with the coefficients c_n and a matrix \mathbf{H} with the matrix elements $H_{n'n}$:

$$\mathbf{c} = \begin{pmatrix} c_0 \\ c_1 \\ \vdots \\ c_N \end{pmatrix}; \quad \mathbf{H} = \begin{pmatrix} H_{00} & H_{01} & \cdots & H_{0N} \\ H_{10} & H_{11} & \cdots & H_{1N} \\ \vdots & \vdots & & \vdots \\ H_{N0} & H_{N1} & \cdots & H_{NN} \end{pmatrix}. \quad (3.37)$$

Comparing Eq. (3.36) to the original Schrödinger equation, Eq. (3.30), we see that the former is an approximate form of the latter in which the eigenfunction $\psi(x)$ and the Hamiltonian operator H are represented by the column vector \mathbf{c} and the matrix \mathbf{H} . Eq. (3.36) shows that the possible values of E are simply the eigenvalues of this matrix. We have thus reduced the problem of finding the eigenenergies of the operator H to finding the eigenvalues of a finite matrix, which is something that can be done readily using standard numerical methods. That this method works very well for our model problem is illustrated by Table 3.1. Clearly, the four lowest eigenvalues of the matrix \mathbf{H} rapidly converge towards the exact eigenvalues of H when N increases.

This method works very well in many other cases, too, and has been used in innumerable calculations across all fields of Physics. Although the basis functions adopted in practical applications differ from the functions $\chi_n(x)$ used in the example above, the general idea is always the same: the eigenfunctions of the Hamiltonian are represented by finite linear combinations of well chosen basis functions, and the energy levels are calculated by computing eigenvalues of a matrix representing the Hamiltonian on this basis.

Note 2: Computing energy levels in this way amounts, in fact, to a variational calculation. To see this, let us come back to the example above, specifically to Eq. (3.28), and derive Eq. (3.29) starting from Eq. (3.1). We chose the right-hand side of Eq. (3.28) as trial function, taking the coefficients c_0, c_1, \dots, c_N to be variational parameters. Thus we define

$$\phi(c_0, c_1, \dots, c_N; x) \equiv \sum_{n=0}^N c_n \chi_n(x). \quad (3.38)$$

For simplicity, we take the coefficients c_n and the functions $\chi_n(x)$ to be real; thus $c_n^* \equiv c_n$ and $H_{n'n} \equiv H_{nn'}$ here. (The latter identity follows from the Hermiticity of the Hamiltonian.) Inserting this trial function in Eq. (3.1) and using the orthonormality properties of the functions $\chi_n(x)$ yields

$$E[\phi] = \frac{\sum_{n'=0}^N \sum_{n=0}^N c_{n'} c_n H_{n'n}}{\sum_{n'=0}^N \sum_{n=0}^N c_{n'} c_n \delta_{n'n}}. \quad (3.39)$$

It is useful for the sake of the argument to rewrite this last equation in the following form:

$$\sum_{n'=0}^N \sum_{n=0}^N c_{n'} c_n H_{n'n} = E \sum_{n=0}^N c_n^2 \quad (3.40)$$

with $E \equiv E(c_0, c_1, \dots, c_N)$. We now differentiate this equation with respect to c_0 :

$$\sum_{n=0}^N c_n H_{0n} + \sum_{n'=0}^N c_{n'} H_{n'0} = \frac{\partial E}{\partial c_0} \sum_{n=0}^N c_n^2 + 2E c_0. \quad (3.41)$$

The condition that the energy functional is stationary with respect to changes in the variational parameters means here that the parameters c_n must be such that

$$\frac{\partial E}{\partial c_n} = 0, \quad n = 0, 1, \dots, N. \quad (3.42)$$

Setting the partial derivative equal to zero in Eq. (3.41), using the identity $H_{n'n} \equiv H_{nn'}$ and simplifying the result gives

$$\sum_{n=0}^N c_n H_{0n} = E c_0, \quad (3.43)$$

which is Eq. (3.29) for $n' = 0$. The corresponding equations for the other values of n' are obtained similarly.

The upshot is that the energies E obtained by solving Eq. (3.29) are as close to the exact eigenenergies of the system as can be achieved with the basis functions used in the calculation.

Note 3: Mathematical note: One can show that the right-hand side of Eq. (3.25) converges uniformly if $\psi(x)$ is a well behaved function and the functions $\chi_n(x)$ are the eigenfunctions of H_0 . The convergence being uniform, it is mathematically justified to neglect the large- n terms in this expansion.

Note 4: Non-orthonormal basis sets are sometimes used, in which case the resulting system of coupled equations takes on the slightly more complicated form

$$\sum_{n=0}^N H_{n'n} c_n = E \sum_{n=0}^N S_{n'n} c_n, \quad n' = 0, 1, 2, \dots, N, \quad (3.44)$$

where $S_{n'n}$ is the “overlap integral” of the n -th and n' -th basis functions. In general,

$$S_{n'n} = \int \chi_{n'}^*(\tau) \chi_n(\tau) d\tau \quad (3.45)$$

and

$$H_{n'n} = \int \chi_{n'}^*(\tau) H \chi_n(\tau) d\tau \quad (3.46)$$

if the functions $\chi_n(\tau)$ form part of a basis set and one sets

$$\psi(\tau) = \sum_{n=0}^N c_n \chi_n(\tau). \quad (3.47)$$

In terms of matrices, Eq. (3.44) reads

$$\mathbf{H} \mathbf{c} = E \mathbf{S} \mathbf{c}. \quad (3.48)$$

Solving this equation is a “generalized eigenvalue problem”, which can be tackled numerically using ready-made programs.