3

The variational method for the Schrödinger equation

3.1 Variational calculus

Quantum systems are governed by the Schrödinger equation. In particular, the solutions to the stationary form of this equation determine many physical properties of the system at hand. The stationary Schrödinger equation can be solved analytically in a very restricted number of cases – examples include the free particle, the harmonic oscillator and the hydrogen atom. In most cases we must resort to computers to determine the solutions. It is of course possible to integrate the Schrödinger equation using discretisation methods – see the different methods in Appendix A7.2 – but in most realistic electronic structure calculations we would need huge numbers of grid points, leading to high computer time and memory requirements. The variational method on the other hand enables us to solve the Schrödinger equation much more efficiently in many cases. In the next few chapters, which deal with electronic structure calculations, we shall make frequent use of the variational method described in this chapter.

In the variational method, the possible solutions are restricted to a subspace of the Hilbert space, and in this subspace we seek the best possible solution (below we shall define what is to be understood by the 'best' solution). To see how this works, we first show that the stationary Schrödinger equation can be derived by a stationarity condition of the functional:

$$E[\psi] = \frac{\int \mathrm{d}X \psi^*(X) H \psi(X)}{\int \mathrm{d}X \psi^*(X) \psi(X)} = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \tag{3.1}$$

which is recognised as the expectation value of the energy for a stationary state ψ (to keep the analysis general, we are not specific about the form of the generalised coordinate X – it may include the space and spin coordinates of a collection of particles). The stationary states of this energy-functional are defined by postulating that if such a state is changed by an arbitrary but small amount $\delta\psi$, the corresponding

change in E vanishes to first order:

$$\delta E \equiv 0. \tag{3.2}$$

Defining

$$\begin{aligned} P &= \langle \psi | H | \psi \rangle \quad \text{and} \\ Q &= \langle \psi | \psi \rangle, \end{aligned} \tag{3.3}$$

we can write the change δE in the energy to first order in $\delta\psi$ as

$$\begin{aligned} \delta E &= \frac{\langle \psi + \delta\psi | H | \psi + \delta\psi \rangle}{\langle \psi + \delta\psi | \psi + \delta\psi \rangle} - \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} \\ &\approx \frac{\langle \delta\psi | H | \psi \rangle - (P/Q)\langle \delta\psi | \psi \rangle}{Q} + \frac{\langle \psi | H | \delta\psi \rangle - (P/Q)\langle \psi | \delta\psi \rangle}{Q}. \end{aligned} \tag{3.4}$$

As this should vanish for an *arbitrary* but small change in ψ, we find, using $E = P/Q$:

$$H\psi = E\psi, \tag{3.5}$$

together with the Hermitian conjugate of this equation, which is equivalent.

In variational calculus, stationary states of the energy-functional are found *within* a subspace of the Hilbert space. An important example is linear variational calculus, in which the subspace is spanned by a set of basis vectors $|\chi_p\rangle$, $p = 1, \ldots, N$. We take these to be orthonormal at first, that is,

$$\langle \chi_p | \chi_q \rangle = \delta_{pq}, \tag{3.6}$$

where δ_{pq} is the Kronecker delta-function which is 0 unless $p = q$, and in that case, it is 1.

For a state

$$|\psi\rangle = \sum_p C_p |\chi_p\rangle, \tag{3.7}$$

the energy-functional is given by

$$E = \frac{\sum_{p,q=1}^{N} C_p^* C_q H_{pq}}{\sum_{p,q=1}^{N} C_p^* C_q \delta_{pq}} \tag{3.8}$$

with

$$H_{pq} = \langle \chi_p | H | \chi_q \rangle. \tag{3.9}$$

The stationary states follow from the condition that the derivative of this functional with respect to the C_p vanishes, which leads to

$$\sum_{q=1}^{N} (H_{pq} - E\delta_{pq}) C_q = 0 \quad \text{for } p = 1, \ldots, N. \tag{3.10}$$

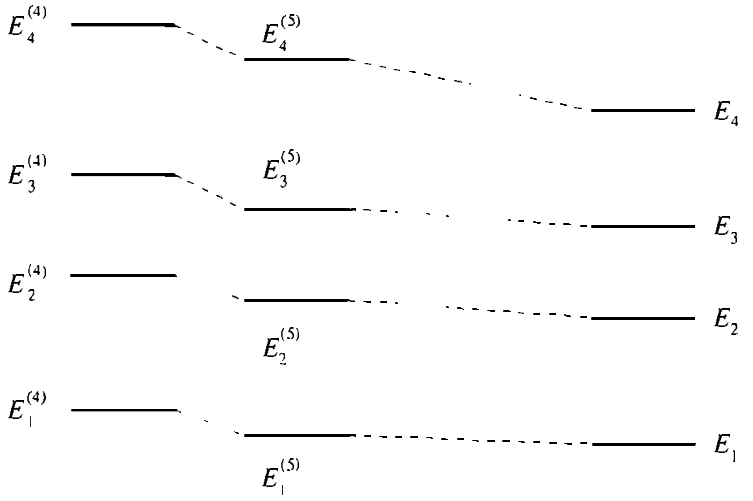

Figure 3.1. The behaviour of the spectrum of Eq. (3.11) with increasing basis set size in linear variational calculus. The upper index is the number of states in the basis set, and the lower index labels the spectral levels.

Equation (3.10) is an eigenvalue problem which can be written in matrix notation:

$$\mathbf{HC} = E\mathbf{C}. \tag{3.11}$$

This is the Schrödinger equation, formulated for a finite, orthonormal basis.

Although in principle it is possible to use nonlinear parametrisations of the wave function, linear parametrisations are used in the large majority of cases because of the simplicity of the resulting method, allowing for numerical matrix diagonalisation techniques, discussed in Appendix A7.2, to be used. The lowest eigenvalue of (3.11) is always higher than or equal to the ground state energy of Eq. (3.5), as the ground state is the minimal value assumed by the energy-functional in the full Hilbert space. If we restrict ourselves to a part of this space, then the minimum value of the energy-functional must always be higher than or equal to the ground state of the full Hilbert space. Including more basis functions into our set, the subspace becomes larger, and consequently the minimum of the energy-functional will decrease (or stay the same). For the specific case of linear variational calculus, this result can be generalised to higher stationary states: they are always higher than the equivalent solution to the full problem, but approximate the latter better with increasing basis set size (see Problem 3.1). The behaviour of the spectrum found by solving (3.11) with increasing basis size is depicted in Figure 3.1.

We note here that it is possible to formulate the standard discretisation methods such as the finite difference method of Appendix A7.2 as linear variational methods with an additional nonvariational approximation caused by the discretised representation of the kinetic energy operator. These methods are usually considered as separate: the term variational calculus implies continuous (and often analytic) basis

functions. Because the computer time needed for matrix diagonalisation scales with the third power of the linear matrix size (it is called a $\mathcal{O}(N^3)$ process), the basis should be kept as small as possible. Therefore, it must be chosen carefully: it should be possible to approximate the solutions to the full problem with a small number of basis states. The fact that the basis in (continuous) variational calculus can be chosen to be so much smaller than the number of grid points in a finite difference approach implies that even though the latter can be solved using special $\mathcal{O}(N)$ methods for sparse systems (see Appendix A8.2), they are still far less efficient than variational methods with continuous basis functions in most cases. This is why, in most electronic structure calculations, variational calculus with continuous basis functions is used to solve the Schrödinger equation; see however Refs. [1] and [2].

An example of a variational calculation with orthonormal basis functions will be considered in Problem 3.4. We now describe how to proceed when the basis consists of nonorthonormal basis functions, as is often the case in practical calculations. In that case, we must reformulate (3.11), taking care of the fact that the *overlap matrix* **S**, whose elements S_{pq} are given by

$$S_{pq} = \langle \chi_p | \chi_q \rangle \tag{3.12}$$

is not the unit matrix. This means that in Eq. (3.8) the matrix elements δ_{pq} of the unit matrix, occurring in the denominator, have to be replaced by S_{pq}, and we obtain

$$\mathbf{HC} = E\mathbf{SC}. \tag{3.13}$$

This looks like an ordinary eigenvalue equation, the only difference being the matrix **S** in the right hand side. It is called a *generalised eigenvalue equation* and there exist computer programs for solving such a problem. The numerical method used in such programs is described in Section 3.3.

3.2 Examples of variational calculations

In this section, we describe two quantum mechanical problems and the computer programs that can solve these problems numerically by a variational calculation. In both cases, we must solve a generalised matrix eigenvalue problem (3.13).

You can find a description of the method for diagonalising a symmetric matrix in Appendix A8.2, and the method for solving the generalised eigenvalue problem is considered in Section 3.3; see also problem 3.3. It is not advisable to program the matrix diagonalisation routine yourself; numerous routines can be found on the internet. Solving the generalised eigenvalue problem is not so difficult if you have a matrix diagonalisation routine at your disposal. It is easy to find such a routine on the network (it is part of the LAPACK library, which is part of the ATLAS

numerical library; these can be found in the NETLIB repository). In the following we shall assume that we have such programs available.

3.2.1 The infinitely deep potential well

The potential well with infinite barriers is given by:

$$V(x) = \begin{cases} \infty & \text{for } |x| > |a| \\ 0 & \text{for } |x| \leq |a| \end{cases} \tag{3.14}$$

and it forces the wave function to vanish at the boundaries of the well ($x = \pm a$). The exact solution for this problem is known and treated in every textbook on quantum mechanics [3, 4]. Here we discuss a linear variational approach to be compared with the exact solution. We take $a = 1$ and use natural units such that $\hbar^2/2m = 1$.

As basis functions we take simple polynomials that vanish on the boundaries of the well:

$$\psi_n(x) = x^n(x-1)(x+1), \quad n = 0, 1, 2, \ldots \tag{3.15}$$

The reason for choosing this particular form of basis functions is that the relevant matrix elements can easily be calculated analytically. We start with the matrix elements of the overlap matrix, defined by

$$S_{mn} = \langle \psi_n | \psi_m \rangle = \int_{-1}^{1} \psi_n(x)\psi_m(x)\mathrm{d}x. \tag{3.16}$$

Working out the integral gives

$$S_{mn} = \frac{2}{n+m+5} - \frac{4}{n+m+3} + \frac{2}{n+m+1} \tag{3.17}$$

for $n + m$ even; otherwise $S_{mn} = 0$.

We can also calculate the Hamilton matrix elements, and you can check that they are given by:

$$\begin{aligned} H_{mn} = \langle \psi_n | p^2 | \psi_m \rangle &= \int_{-1}^{1} \psi_n(x) \left(-\frac{\mathrm{d}^2}{\mathrm{d}X^2} \right) \psi_m(x)\mathrm{d}x \\ &= -8 \left[\frac{1 - m - n - 2mn}{(m+n+3)(m+n+1)(m+n-1)} \right] \end{aligned} \tag{3.18}$$

for $m + n$ even, otherwise $H_{mn} = 0$.

PROGRAMMING EXERCISE

Write a computer program in which you fill the overlap and Hamilton matrix for this problem. Use standard software to solve the generalised eigenvalue problem.

Table 3.1. *Energy levels of the infinitely deep potential well.*

$N = 5$	$N = 8$	$N = 12$	$N = 16$	Exact
2.4674	2.4674	2.4674	2.4674	2.4674
9.8754	9.8696	9.8696	9.8696	9.8696
22.2934	22.2074	22.2066	22.2066	22.2066
50.1246	39.4892	39.4784	39.4784	39.4784
87.7392	63.6045	61.6862	61.6850	61.6850

The first four columns show the variational energy levels for various numbers of basis states N. The last column shows the exact values. The exact levels are approached from above as in Figure 3.1.

Check Compare the results with the analytic solutions. These are given by

$$\psi_n(x) = \begin{cases} \cos(k_n x) & n \text{ odd} \\ \sin(k_n x) & n \text{ even and positive} \end{cases} \tag{3.19}$$

with $k_n = n\pi/2$, $n = 1, 2, \ldots$, and the corresponding energies are given by

$$E_n = k_n^2 = \frac{n^2\pi^2}{4}. \tag{3.20}$$

For each eigenvector $\mathbf{C}$, the function $\sum_{p=1}^{N} C_p \chi_p(x)$ should approximate an eigenfunction (3.19). They can be compared by displaying both graphically. Carry out the comparison for various numbers of basis states. The variational levels are shown in Table 3.1, together with the analytical results.

3.2.2 *Variational calculation for the hydrogen atom*

As we shall see in the next two chapters, one of the main problems of electronic structure calculations is the treatment of the electron–electron interactions. Here we develop a program for solving the Schrödinger equation for an electron in a hydrogen atom for which the many-electron problem does not arise, so that a direct variational treatment of the problem is possible which can be compared with the analytical solution [3, 4].

The program described here is the first in a series leading to a program for calculating the electronic structure of the hydrogen molecule. The extension to the H_2^+ ion can be found in the next chapter in Problem 4.8 and a program for the hydrogen molecule is considered in Problem 4.12.

The electronic Schrödinger equation for the hydrogen atom reads:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{1}{r}\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}) \tag{3.21}$$

where the second term in the square brackets is the Coulomb attraction potential of the nucleus. The mass m is the reduced mass of the proton–electron system which is approximately equal to the electron mass. The ground state is found at energy

$$E = -\frac{m}{\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \approx -13.6058 \text{ eV} \tag{3.22}$$

and the wave function is given by

$$\psi(\mathbf{r}) = \frac{2}{a_0^{3/2}} e^{-r/a_0} \tag{3.23}$$

in which a_0 is the Bohr radius,

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 0.529\,18 \text{ Å}. \tag{3.24}$$

In computer programming, it is convenient to use units such that equations take on a simple form, involving only coefficients of order 1. Standard units in electronic structure physics are so-called *atomic units*:the unit of distance is the Bohr radius a_0, masses are expressed in the electron mass m_e and the charge is measured in unit charges (e). The energy is finally given in 'hartrees' (E_H), given by $m_e c^2\alpha^2$ (α is the fine-structure constant and m_e is the electron mass) which is roughly equal to 27.212 eV. In these units, the Schrödinger equation for the hydrogen atom assumes the following simple form:

$$\left[-\frac{1}{2}\nabla^2 - \frac{1}{r}\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}). \tag{3.25}$$

We try to approximate the ground state energy and wave function of the hydrogen atom in a linear variational procedure. We use Gaussian basis functions which will be discussed extensively in the next chapter (Section 4.6.2). For the ground state, we only need angular momentum $l = 0$ functions (s-functions), which have the form:

$$\chi_p(r) = e^{-\alpha_p r^2} \tag{3.26}$$

centred on the nucleus (which is thus placed at the origin). We have to specify the values of the exponents α; these are kept fixed in our program. Optimal values for these exponents have previously been found by solving the *nonlinear* variational problem including the linear coefficients C_p *and* the exponents α [5]. We shall use these values of the exponents in the program:

$$\begin{aligned} \alpha_1 &= 13.007\,73 \\ \alpha_2 &= 1.962\,079 \\ \alpha_3 &= 0.444\,529 \\ \alpha_4 &= 0.121\,949\,2. \end{aligned} \tag{3.27}$$

If the program works correctly, it should yield a value close to the exact ground state energy $-1/2\ E_H$ (which is equal to -13.6058 eV).

It remains to determine the linear coefficients C_p in a computer program which solves the generalised eigenvalue problem, just as in Section 3.2.1:

$$\mathbf{HC} = E\mathbf{SC}. \tag{3.28}$$

It is not so difficult to show that the elements of the overlap matrix **S**, the kinetic energy matrix **T** and the Coulomb matrix **A** are given by:

$$\begin{aligned} S_{pq} &= \int \mathrm{d}^3 r\, \mathrm{e}^{-\alpha_p r^2} \mathrm{e}^{-\alpha_q r^2} = \left(\frac{\pi}{\alpha_p + \alpha_q}\right)^{3/2}; \\ T_{pq} &= -\frac{1}{2} \int \mathrm{d}^3 r\, \mathrm{e}^{-\alpha_p r^2} \nabla^2 \mathrm{e}^{-\alpha_q r^2} = 3 \frac{\alpha_p \alpha_q \pi^{3/2}}{(\alpha_p + \alpha_q)^{5/2}}; \\ A_{pq} &= -\int \mathrm{d}^3 r\, \mathrm{e}^{-\alpha_p r^2} \frac{1}{r} \mathrm{e}^{-\alpha_q r^2} = -\frac{2\pi}{\alpha_p + \alpha_q}. \end{aligned} \tag{3.29}$$

See also Section 4.8. Using these expressions, you can fill the overlap and the Hamilton matrix. Since both matrices are symmetric, it is clear that only the upper (or the lower) triangular part (including the diagonal) has to be calculated; the other elements follow from the symmetry.

PROGRAMMING EXERCISE

Write a program in which the relevant matrices are filled and which solves the generalised eigenvalue problem for the variational calculation.

Check 1 Fortunately, we again have an exact answer for the ground state energy: this should be equal to -0.5 hartree $= 13.6058$ eV, and, if your program contains no errors, you should find $-0.499\,278$ hartree, which is amazingly good if you realise that only four functions have been taken into account.

Check 2 The solution of the eigenvalue problem not only yields the eigenvalues (energies) but also the eigenvectors. Use these to draw the variational ground state wave function and compare with the exact form (3.23). (See also Figure 4.3.)

*3.3 Solution of the generalised eigenvalue problem

It is possible to transform (3.13) into an ordinary eigenvalue equation by performing a basis transformation which brings **S** to unit form. Suppose we have found a matrix **V** which transforms **S** to the unit matrix:

$$\mathbf{V}^\dagger \mathbf{S} \mathbf{V} = \mathbf{I}. \tag{3.30}$$

Then we can rewrite (3.13) as

$$\mathbf{V}^{\dagger}\mathbf{H}\mathbf{V}\mathbf{V}^{-1}\mathbf{C} = E\mathbf{V}^{\dagger}\mathbf{S}\mathbf{V}\mathbf{V}^{-1}\mathbf{C} \tag{3.31}$$

and, defining

$$\mathbf{C}' = \mathbf{V}^{-1}\mathbf{C} \tag{3.32}$$

and

$$\mathbf{H}' = \mathbf{V}^{\dagger}\mathbf{H}\mathbf{V}, \tag{3.33}$$

we obtain

$$\mathbf{H}'\mathbf{C}' = E\mathbf{C}'. \tag{3.34}$$

This is an ordinary eigenvalue problem which we can solve for $\mathbf{C}'$ and E, and then we can find the eigenvector $\mathbf{C}$ of the original problem as $\mathbf{V}\mathbf{C}'$.

The problem remains of finding a matrix $\mathbf{V}$ which brings $\mathbf{S}$ to unit form according to (3.30). This matrix can be found if we have a unitary matrix $\mathbf{U}$ which diagonalises $\mathbf{S}$:

$$\mathbf{U}^{\dagger}\mathbf{S}\mathbf{U} = \mathbf{s} \tag{3.35}$$

with $\mathbf{s}$ the diagonalised form of $\mathbf{S}$. In fact, the matrix $\mathbf{U}$ is automatically generated when diagonalising $\mathbf{S}$ by a Givens–Householder QR procedure (see Appendix A8.2). From the fact that $\mathbf{S}$ is an overlap matrix, defined by (3.12), it follows directly that the eigenvalues of $\mathbf{S}$ are positive (see Problem 3.2). Therefore, it is possible to define the inverse square root of $\mathbf{s}$: it is the matrix containing the inverse of the square root of the eigenvalues of $\mathbf{S}$ on the diagonal. Choosing the matrix $\mathbf{V}$ as $\mathbf{U}\mathbf{s}^{-1/2}$, we obtain

$$\mathbf{V}^{\dagger}\mathbf{S}\mathbf{V} = \mathbf{s}^{-1/2}\mathbf{U}^{\dagger}\mathbf{S}\mathbf{U}\mathbf{s}^{-1/2} = \mathbf{I} \tag{3.36}$$

so the matrix $\mathbf{V}$ indeed has the desired property.

*3.4 Perturbation theory and variational calculus

In 1951, Löwdin [6] devised a method in which, in addition to a standard basis set A, a number of extra basis states (B) is taken into account in a perturbative manner, thus allowing for huge basis sets to be used without excessive demands on computer time and memory. The size of the matrix to be diagonalised in this method is equal to the number of basis states in the restricted set A; the remaining states are taken into account in constructing this matrix. A disadvantage is that the latter depends on the energy (which is obviously not known at the beginning), but, as we shall see, this does not prevent the method from being useful in many cases.

We start with an orthonormal basis, which could be a set of plane waves. The basis is partitioned into the two sets A and B, and for the plane wave example, A will contain the slowly varying waves and B those with shorter wavelength. We

shall use the following notation: n and m label the states in A, α and β label the states in B, and p and q label the states in both sets. Furthermore we define

$$H'_{pq} = H_{pq}(1 - \delta_{pq}), \tag{3.37}$$

that is, H' is H with the diagonal elements set to 0. Now we can write Eq. (3.11) as

$$(E - H_{pp})C_p = \sum_{n\epsilon A} H'_{pn}C_n + \sum_{\alpha\epsilon B} H'_{p\alpha}C_\alpha. \tag{3.38}$$

If we define

$$h'_{pn} = H'_{pn}/(E - H_{pp}), \tag{3.39}$$

and similarly for $h'_{p\alpha}$, then we can write Eq. (3.38) as

$$C_p = \sum_{n\epsilon A} h'_{pn}C_n + \sum_{\alpha\epsilon B} h'_{p\alpha}C_\alpha. \tag{3.40}$$

Using this expression to rewrite C_α in the second term of the right hand side, we obtain

$$\begin{aligned} C_p &= \sum_{n\epsilon A} h'_{pn}C_n + \sum_{\alpha\epsilon B} h'_{p\alpha}\left(\sum_{n\epsilon A} h'_{\alpha n}C_n + \sum_{\beta\epsilon B} h'_{\alpha\beta}C_\beta\right) \\ &= \sum_{n\epsilon A}\left(h'_{pn} + \sum_{\alpha\epsilon B} h'_{p\alpha}h'_{\alpha n}\right)C_n + \sum_{\alpha\epsilon B}\sum_{\beta\epsilon B} h'_{p\alpha}h'_{\alpha\beta}C_\beta. \end{aligned} \tag{3.41}$$

After using (3.40) again to re-express C_β and repeating this procedure over and over, we arrive at

$$C_p = \sum_{n\epsilon A}\left(h'_{pn} + \sum_{\alpha\epsilon B} h'_{p\alpha}h'_{\alpha n} + \sum_{\alpha,\beta\epsilon B} h'_{p\alpha}h'_{\alpha\beta}h'_{\beta n} + \cdots\right)C_n. \tag{3.42}$$

We now introduce the following notation:

$$U^A_{pn} = H_{pn} + \sum_{\alpha\epsilon B}\frac{H'_{p\alpha}H'_{\alpha n}}{E - H_{\alpha\alpha}} + \sum_{\alpha\beta\epsilon B}\frac{H'_{p\alpha}H'_{\alpha\beta}H'_{\beta n}}{(E - H_{\alpha\alpha})(E - H_{\beta\beta})} + \cdots \tag{3.43}$$

Then (3.42) transforms into

$$C_p = \sum_{n\epsilon A}\frac{U^A_{pn} - H_{pn}\delta_{pn}}{E - H_{pp}}C_n. \tag{3.44}$$

Choosing p in A (and calling it m), (3.44) becomes

$$(E - H_{mm})C_m = \sum_{n\epsilon A} U^A_{mn}C_n - H_{mm}C_m, \tag{3.45}$$

so

$$\mathbf{UC} = E\mathbf{C}. \tag{3.46}$$

This equation is similar to (3.11), except that **H** is replaced by **U**. Notice that **U** depends on the energy which remains to be calculated, which makes Eq. (3.46) rather difficult to solve. In practice, a fixed value for E is chosen somewhere in the region for which we want accurate results. For electrons in a solid, this might be the region around the Fermi energy, since the states with these energies determine many physical properties.

The convergence of the expansion for **U**, Eq. (3.44), depends on the matrix elements $h'_{p\alpha}$ and $h'_{\alpha\beta}$, which should be small. Cutting off after the first term yields

$$U^A_{mn} = H_{mn} + \sum_{\alpha \epsilon B} \frac{H'_{m\alpha} H'_{\alpha n}}{E - H_{\alpha\alpha}}. \tag{3.47}$$

Löwdin perturbation theory is used mostly in this form.

It is not a priori clear that the elements $h'_{p\alpha}$ and $h'_{\alpha\beta}$ are small. However, keeping in mind a plane wave basis set, if we have a potential that varies substantially slower than the states in set B, these numbers will indeed be small as the H'_{pn} are small, so in that case the method will improve the efficiency of the diagonalisation process. The Löwdin method is frequently used in pseudopotential methods for electrons in solids which will be discussed in Chapter 6.

Exercises

3.1 MacDonald's theorem states that, in linear variational calculus, not only the variational ground state but also the higher variational eigenvectors have eigenvalues that are higher than the corresponding eigenvalues of the full problem.

Consider an Hermitian operator $\mathcal{H}$ and its variational matrix representation **H** defined by

$$H_{pq} = \langle \chi_p | \mathcal{H} | \chi_q \rangle.$$

χ_p are the basis vectors of the linear variational calculus. They form a finite set.

We shall denote the eigenvectors of $\mathcal{H}$ by ϕ_k and the corresponding eigenvalues by λ_k; Φ_k are the eigenvectors of **H** with eigenvalues Λ_k. They are all ordered, i.e. ϕ_0 corresponds to the lowest eigenvalue and so on, and similarly for the Φ_k.

(a) Write Φ_0 as an expansion in the complete set ϕ_k in order to show that

$$\frac{\langle \Phi_0 | \mathcal{H} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} = \Lambda_0 \geq \lambda_0.$$

(b) Suppose Φ'_1 is a vector perpendicular to ϕ_0. Show that

$$\frac{\langle \Phi'_1 | \mathcal{H} | \Phi'_1 \rangle}{\langle \Phi'_1 | \Phi'_1 \rangle} \geq \lambda_1.$$

(Note that, in general, the lowest-but-one variational eigenstate Φ_1 is not perpendicular to ϕ_0 so this result does not guarantee $\Lambda_1 \geq \lambda_1$.)

(c) Consider a vector $\Phi_1' = \alpha\Phi_0 + \beta\Phi_1$ which is perpendicular to ϕ_0. From (b) it is clear that $\langle\Phi_1'|H|\Phi_1'\rangle/\langle\Phi_1'|\Phi_1'\rangle \geq \lambda_1$. Show that

$$\frac{\langle\Phi_1'|\mathcal{H}|\Phi_1'\rangle}{\langle\Phi_1'|\Phi_1'\rangle} = \frac{|\alpha|^2\Lambda_0 + |\beta|^2\Lambda_1}{|\alpha|^2 + |\beta|^2}$$

and that from this it follows that $\Lambda_1 \geq \lambda_1$. This result can be generalised for higher states.

3.2 The overlap matrix **S** is defined as

$$S_{pq} = \langle\chi_p|\chi_q\rangle.$$

Consider a vector ψ that can be expanded in the basis χ_p as:

$$\psi = \sum_p C_p\chi_p.$$

(a) Suppose ψ is normalised. Show that **C** then satisfies:

$$\sum_{pq} C_p^* S_{pq} C_q = 1.$$

(b) Show that the eigenvalues of **S** are positive.

3.3 [**C**] In this problem, it is assumed that a routine for diagonalising a real, symmetric matrix is available.

(a) [**C**] Using a library routine for diagonalising a real, symmetric matrix, write a routine which, given the overlap matrix **S**, generates a matrix **V** which brings **S** to unit form:

$$\mathbf{V}^\dagger\mathbf{S}\mathbf{V} = \mathbf{I}.$$

(b) [**C**] Write a routine which uses the matrix **V** to produce the solutions (eigenvectors and eigenvalues) to the generalised eigenvalue problem:

$$\mathbf{H}\mathbf{C} = E\mathbf{S}\mathbf{C}.$$

The resulting routines can be used in the programs of Sections 3.2.1 and 3.2.2.

3.4 [**C**] The potential for a finite well is given by

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

In this problem, we determine the bound solutions to the Schrödinger equation using plane waves on the interval $(-L, +L)$ as basis functions:

$$\psi_n(x) = 1/\sqrt{2L}\, e^{ik_n x}$$

with

$$k_n = \pm\frac{n\pi}{L}, \quad n = 0, 1, \ldots$$

It is important to note that, apart from the approximation involved in having a finite basis set, there is another one connected with the periodicity imposed by the specific form of the basis functions on the finite interval $(-L,L)$. In this problem, we use units such that the factor $\hbar^2/2m$ assumes the value 1.

(a) Show that the relevant matrix elements are given by

$$\begin{aligned} S_{mn} &= \delta_{mn} \\ \langle\psi_n|p^2|\psi_m\rangle &= -k_n^2\delta_{nm} \quad \text{and} \\ \langle\psi_n|V|\psi_m\rangle &= -\frac{V_0}{L}\frac{\sin(k_m-k_n)a}{k_m-k_n} \quad \text{for } n \neq m \\ \langle\psi_n|V|\psi_n\rangle &= -\frac{V_0}{L}a \end{aligned}$$

The stationary states in an even potential (i.e. $V(x) = V(-x)$) have either positive or negative parity [3]. From this it follows that if we use a basis $1/\sqrt{L}\cos k_n x$ (and $1/\sqrt{2L}$ for $n = 0$), we shall find the even stationary states, and if we take the basis functions $1/\sqrt{L}\sin k_n x$, only the odd states. It is of course less time-consuming to diagonalise two $N \times N$ matrices than a single $2N \times 2N$, knowing that matrix diagonalisation scales with N^3.

(b) Show that the matrix elements with the cosine basis read

$$\begin{aligned} S_{mn} &= \delta_{mn} \\ \langle\psi_n|p^2|\psi_m\rangle &= -k_n^2\delta_{nm} \quad \text{and} \\ \langle\psi_n|V|\psi_m\rangle &= -\frac{V_0}{L}\left[\frac{\sin(k_m-k_n)a}{k_m-k_n}+\frac{\sin(k_m+k_n)a}{k_m+k_n}\right] \\ & \qquad \text{for } n \neq m \\ \langle\psi_n|V|\psi_n\rangle &= -\frac{V_0}{L}\left[a+\frac{\sin(2k_n a)}{2k_n}\right] \quad \text{for } n \neq 0 \\ \langle\psi_0|V|\psi_0\rangle &= -\frac{V_0}{L}a \quad \text{for } n = 0 \end{aligned}$$

In the sine-basis, the last terms in the third and fourth expressions occur with a minus sign.

(c) [**C**] Write a computer program for determining the spectrum. Compare the results with those of the direct calculation (which, for $V_0 = 1$ and $a = 1$, yields a ground state energy $E \approx -0.4538$).

As you will note, for many values of A, V_0, L and N, the variational ground state energy lies below the exact ground state energy number. Explain why this happens.

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