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I. UNITS AND CONVERSIONS

A. Atomic Units

Throughout these notes we shall use the so-called [Hartree atomic units](#) in which mass is reckoned in units of the electron mass ($m_e = 9.1093826 \times 10^{-31}$ kg) and distance in terms of the Bohr radius ($a_0 = 5.299175 \times 10^{-2}$ nm). In this system of units the numerical values of the following four fundamental physical constants are unity by definition:

- Electron mass m_e
- Elementary charge e
- reduced Planck's constant \hbar
- Coulomb's constant $1/4\pi\epsilon_0$

The replacement of these constants by unity will greatly simplify the notation.

It is easiest to work problems entirely in atomic units, and then convert at the end to SI units, using

- Length (Bohr radius) $1a_0 = 5.299175 \times 10^{-2} \text{ nm} = 0.5291775 \text{ \AA}$
- Energy (Hartree) $1E_h = 4.35974417 \times 10^{-18} \text{ J}$

B. Energy Conversions

Atomic (Hartree) units of energy are commonly used by theoreticians to quantify electronic energy levels in atoms and molecules. From an experimental viewpoint, energy levels are often given in terms of electron volts (eV), wavenumber units, or kilocalories/mole (kcal/mol). From [Planck's relation](#)

$$E = h\nu = \frac{hc}{\lambda}$$

The relation between the Joule and the kilocalorie is

$$1 \text{ kcal} = 4.184 \text{ kJ}$$

Thus, 1 kcal/mole is one kilocalorie per mole of atoms, or $4.184 \times 10^3 \text{ J}$ divided by Avogadro's number (6.022×10^{23}) = $6.9479 \times 10^{-21} \text{ J/molecule}$. The conversions between these (and other) energy units is given in numerous places on the web, for example web.utk.edu/~rcompton/constants.

II. APPROXIMATION METHODS

A. Semiclassical quantization

The Bohr-Sommerfeld quantization condition is

$$S = \oint \vec{p} \cdot d\vec{q} = (n + 1/2)h \tag{1}$$

You may have seen this as

$$S = \oint \vec{p} \cdot d\vec{q} = nh$$

As we will see below, the additional factor of $(1/2)h$ is necessary to ensure the correct zero-point energy. For a one-dimensional system this is

$$S = \oint p_x q_x = (n + 1/2)h \quad (2)$$

Here, the momentum is $p = \{2m[E - V(x)]\}^{1/2}$, so that the classical action S is a function of the total energy E .

Consider a harmonic oscillator with $V(x) = \frac{1}{2}kx^2$. In this case

$$p = \left[2m \left(E - \frac{1}{2}kx^2 \right) \right]$$

The contour integral in Eq. (2) goes from the inner turning point $x_<$ to the outer turning point $x_>$ and then back. These turning points are defined by the values at which $p(x) = 0$, namely $x_<(x_>) = \mp(2E/k)^{1/2}$. Thus

$$S = 2 \int_{x_<}^{x_>} [2m (E - \frac{1}{2}kx^2)]^{1/2} dx = 2(2mE)^{1/2} \int_{x_<}^{x_>} \left[1 - \frac{kx^2}{2E} \right]^{1/2} dx$$

The factor of 2 reflects the identity of the integral from $x_<$ to $x_>$ and its reverse. Because it's a contour integral these add rather than cancel.

If we let $u^2 = kx^2/2E$, then $x = \sqrt{2E/k} u$ and $dx = \sqrt{2E/k} du$. In terms of the new variable u , the turning points are $u_<(u_>) = \mp 1$. The classical action is then

$$S = 4E(m/k)^{1/2} \int_{-1}^1 \sqrt{1 - u^2} du$$

Now, let $u = \cos \vartheta$, so that $\sqrt{1 - u^2} = \sin \vartheta$ and $du = -\sin \vartheta d\vartheta$. The integral becomes

$$S = -4E(m/k)^{1/2} \int_{\pi}^0 \sin^2 \vartheta d\vartheta = -4(m/k)^{1/2} (-\pi/2) = 2\pi E(m/k)^{1/2}$$

The Bohr-Sommerfeld quantization condition then implies that

$$2\pi E(m/k)^{1/2} = (n + 1/2)h$$

or

$$E = (n + 1/2)(k/m)^{1/2}(h/2\pi) = (n + 1/2)(k/m)^{1/2}\hbar$$

Since, for the harmonic oscillator $\omega = \sqrt{k/m}$, we recover the quantization condition

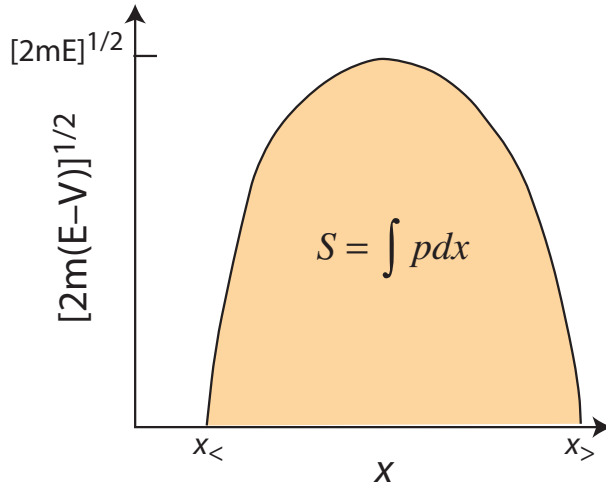


FIG. 1. Dependence on distance of a typical phase integral [Eq. (2)].

$$E = (n + 1/2)\hbar\omega$$

As stated above, without the additional factor of $1/2$, we would not have any zero-point energy, even though the level spacing would be exact.

For a general potential, an analytic integration of $p dq$ may not be possible. However, it is always possible to evaluate the integral of Eq. (2) numerically, as the area under the curve in Fig. 1

This is easier than numerical integration of the Schroedinger equation. Unfortunately, there is no guarantee that the Bohr-Sommerfeld quantization condition is exact.

B. Time-independent perturbation theory

Suppose the full Hamiltonian can be expanded as

$$H = H_o + \lambda H'$$

where the solutions to the zeroth-order Hamiltonian are known

$$H_o\phi_n^{(0)} = E_n^{(0)}\phi_n^{(0)}.$$

Here the subscript n designates the particular value of the energy. We will then expand the solution to the full Hamiltonian ψ_n as

$$\psi_n = \phi_n^{(0)} + \lambda\phi_n^{(1)} + \lambda^2\phi_n^{(2)}$$

If we substitute this expansion into the Schroedinger equation $H\psi_n = E_n\psi_n$, we obtain

$$H\psi_n = H_o\phi_n^{(0)} + \lambda(H_o\phi_n^{(1)} + H'\phi_n^{(0)}) + \lambda^2(H_o\phi_n^{(2)} + H'\phi_n^{(1)}) + \dots \quad (3)$$

We similarly expand

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

so that

$$E_n\psi_n = E_n^{(0)}\phi_n^{(0)} + \lambda(E_n^{(0)}\phi_n^{(1)} + E_n^{(1)}\phi_n^{(0)}) + \lambda^2(E_n^{(0)}\phi_n^{(2)} + E_n^{(1)}\phi_n^{(1)} + E_n^{(2)}\phi_n^{(0)}) + \dots \quad (4)$$

We assume that the Schroedinger equation is satisfied for all values of the perturbation parameter λ . This means that the terms multiplied by each power of λ in Eq. (3) must equal the terms multiplied by the same power of λ in Eq. (4). In other words

$$H_o\phi_n^{(0)} = E_n^{(0)}\phi_n^{(0)}$$

which is the unperturbed Schroedinger equation, and

$$H'\phi_n^{(0)} + H_o\phi_n^{(1)} = E_n^{(1)}\phi_n^{(0)} + E_n^{(0)}\phi_n^{(1)}. \quad (5)$$

Now, in the last equation, we can expand $\phi_n^{(1)}$ in terms of the solutions to the unperturbed equation, namely

$$\phi_n^{(1)} = \sum_{k \neq n} C_{nk}^{(1)} \phi_k^{(0)} \quad (6)$$

Note that the sum extends over all states except for $k = n$. If we introduce this expansion into Eq. (5) we obtain

$$H' \phi_n^{(0)} + H_o \sum_{k \neq n} C_{nk}^{(1)} \phi_k^{(0)} = E_n^{(1)} \phi_n^{(0)} + \sum_{k \neq n} C_{nk}^{(1)} E_n^{(0)} \phi_k^{(0)} \quad (7)$$

Since $H_o \phi_k^{(0)} = E_k^{(0)} \phi_k^{(0)}$, we can simplify the last equation to

$$H' \phi_n^{(0)} = E_n^{(1)} \phi_n^{(0)} + \sum_{k \neq n} C_{nk}^{(1)} \left(E_n^{(0)} - E_k^{(0)} \right) \phi_k^{(0)} \quad (8)$$

If now, we premultiply the last equation by $\phi_n^{(0)*}$ and integrate over all coordinates, we obtain (we assume that the zeroth order functions are orthonormal, namely $\int \phi_n^{(0)*} \phi_k^{(0)} = \delta_{kn}$)

$$E_n^{(1)} = \int \phi_n^{(0)*} H' \phi_n^{(0)} = \langle \phi_n^{(0)} | H' | \phi_n^{(0)} \rangle$$

Thus, the first-order correction to the energy is just the average, taken over the zeroth-order wavefunction, of the perturbation.

Now, we return to Eq. (8), premultiply by $\phi_k^{(0)*}$ and integrate over all coordinates, we obtain (after taking into account the orthogonality of the $\phi_k^{(0)}$)

$$\langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle = C_{nk}^{(1)} \left(E_n^{(0)} - E_k^{(0)} \right)$$

or

$$C_{nk}^{(1)} = \langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle / \left(E_n^{(0)} - E_k^{(0)} \right) \quad (9)$$

so that Eq. (6) becomes

$$\phi_n^{(1)} = \sum_{k \neq n} \frac{\langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \phi_k^{(0)} \quad (10)$$

Thus, the first-order correction to the wavefunction of state n is obtained by adding a weighted fraction of each of the zeroth-order wavefunctions of state k where the weighting is proportional to the coupling between state k and state n induced by the perturbation, divided by the energy gap between state n and state k . In general, then, significant state mixing occurs if (a) the states are coupled strongly by the perturbation and (b) the states are close in energy.

Now, let's consider the terms of order λ^2 in Eqs. (3) and (4). We have

$$H_o\phi_n^{(2)} + H'\phi_n^{(1)} = E_n^{(0)}\phi_n^{(2)} + E_n^{(1)}\phi_n^{(1)} + E_n^{(2)}\phi_n^{(0)} \quad (11)$$

Following Eq. (6) we expand $\phi_n^{(2)}$ as

$$\phi_n^{(2)} = \sum_{k \neq n} C_{nk}^{(2)} \phi_k^{(0)} \quad (12)$$

We substitute this equation as well as Eq. (10) into Eq. (11), premultiply by $\phi_n^{(0)}$, and integrate to get (remembering that $\phi_n^{(2)}$ is orthogonal to $\phi_n^{(0)}$)

$$E_n^{(2)} = \langle \phi_n^{(0)} | H' | \phi_n^{(1)} \rangle \quad (13)$$

We can then substitute in Eq. (10) for $\phi_n^{(1)}$ to get

$$E_n^{(2)} = \sum_{k \neq n} \frac{\langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle \langle \phi_n^{(0)} | H' | \phi_k^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} = \sum_{k \neq n} \frac{\left| \langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} \quad (14)$$

Consider the lowest energy level ($n = 1$, say). Then, $E_n^{(0)} - E_k^{(0)}$ will always be a negative number. Since the matrix element in the numerator on the right-hand-side of Eq. (14) is squared, and thus always positive (or zero), the contribution of each term in the summation will be negative. Thus we conclude that for the lowest energy level, the second-order contribution to the energy will always be negative.

C. Linear variational method

Suppose you have two states $|1\rangle$ and $|2\rangle$, which we assume to be normalized. Let the matrix of the full Hamiltonian be

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \quad (15)$$

We shall designate this matrix \mathbf{H} , which, in general, is Hermetian. For simplicity, we will assume here that the matrix is real, so that $H_{12} = H_{21}$. The corresponding overlap matrix,

\mathbf{S} , is

$$\begin{bmatrix} 1 & S_{12} \\ S_{21} & 1 \end{bmatrix} \quad (16)$$

Now, define a linear combination of states $|1\rangle$ and $|2\rangle$

$$|\phi\rangle = C_1|1\rangle + C_2|2\rangle \quad (17)$$

The expectation value of the Hamiltonian is then

$$E_{var} = \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}, \quad (18)$$

which can be written as

$$\langle\phi|H|\phi\rangle = E_{var}\langle\phi|\phi\rangle \quad (19)$$

Problem 1

Obtain an expression for the variational energy in terms of C_1 , C_2 , H_{11} , H_{12} , H_{22} , S_{11} , S_{12} , and S_{22} .

Suppose we use a three-state expansion of the wave function

$$|\phi\rangle = C_1|1\rangle + C_2|2\rangle + C_3|3\rangle \quad (20)$$

If we take the derivative of Eq. (19) with respect to the i^{th} coefficient C_i we obtain

$$\frac{\partial\langle\phi|H|\phi\rangle}{\partial C_i} = E_{var}\frac{\partial\langle\phi|\phi\rangle}{\partial C_i} + \langle\phi|\phi\rangle\frac{\partial E_{var}}{\partial C_i} \quad (21)$$

or, explicitly,

$$2C_i H_{ii} + \sum_{j \neq i} C_j (H_{ij} + H_{ji}) = E_{var} \left[2C_i S_{ii} + \sum_{j \neq i} C_j (S_{ij} + S_{ji}) \right] + \frac{\partial E_{var}}{\partial C_i} \langle\phi|\phi\rangle \quad (22)$$

Since the Hamiltonian \mathbf{H} and overlap \mathbf{S} matrices are symmetric, this simplifies to

$$C_i H_{ii} + \sum_{j \neq i} C_j H_{ij} = E_{var} \left[C_i S_{ii} + \sum_{j \neq i} C_j S_{ij} \right] + \frac{\partial E_{var}}{\partial C_i} \langle \phi | \phi \rangle \quad (23)$$

Since the variational principle guarantees that E_{var} lies above the true energy of the lowest state for any value of the coefficients C_i , we can minimize E_{var} with respect to varying each one of them separately, or,

$$\partial E_{var} / \partial C_1 = 0 = \partial E_{var} / \partial C_2 = \partial E_{var} / \partial C_3$$

If we replace each of the partial derivatives in Eq. (23), we obtain

$$\mathbf{H} \times \mathbf{c} - E_{var} \mathbf{S} \times \mathbf{c} = \mathbf{0} \quad (24)$$

where \mathbf{c} is a 3×1 column vector with elements C_i , and $\mathbf{0}$ is a 3×1 column vector with elements zero. Here \times designates a matrix-vector product.

A simpler case arises when the overlap matrix is the (diagonal) unit matrix. In this case the set of simultaneous homogeneous equations can be written as

$$[\mathbf{H} - E_{var} \mathbf{1}] \mathbf{c} = \mathbf{0} \quad (25)$$

This set of simultaneous *homogeneous* algebraic equations can always be satisfied by the trivial solution in which all the elements of \mathbf{c} are zero. There are only 3 (or, in general N) solutions in which the elements of \mathbf{c} are non-zero solutions. These correspond to three particular choices of the \mathbf{c} vector, which *diagonalize* the \mathbf{H} matrix. We designate these three particular choices by the matrix \mathbf{C} , where the k^{th} column corresponds to the coefficients C_{ik} for the k^{th} set of coefficients. The matrix \mathbf{C} defines the diagonalizing transformation of the matrix \mathbf{H} , namely

$$\mathbf{C}^T \mathbf{H} \mathbf{C} = \mathbf{E}, \quad (26)$$

where the superscript T denotes the matrix transpose and

$$\mathbf{E} = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} \quad (27)$$

The \mathbf{C} matrix is orthogonal (or, if the elements are complex, unitary), so that

$$\mathbf{C} \mathbf{C}^T = \mathbf{C}^T \mathbf{C} = \mathbf{1} \quad (28)$$

where $\mathbf{1}$ is the unit matrix.

Problem 2

For a two-state problem with a unit overlap matrix, show that the diagonalizing transform can be written in terms of a single angle

$$\mathbf{C} = \begin{bmatrix} \cos(\vartheta) & \sin(\vartheta) \\ -\sin(\vartheta) & \cos(\vartheta) \end{bmatrix} \quad (29)$$

Obtain the value of the angle ϑ in terms of the matrix elements of \mathbf{H} . *Hint:* Use Matlab's symbolic capabilities to carry out the matrix multiplication of Eq. (28), namely

```
syms h11, h12, h22, cs, sn
hmat=[h11 h12;h12 h22];
cmat=[cs sn;-sn cs];
res=cmat'.*hmat*cmat;
simplify(res)
```

Then determine the values of the two energies E_1 and E_2 in terms of the angle ϑ . To check your result, consider the matrix

$$\mathbf{H} = \begin{bmatrix} 0.3 & 0.05 \\ 0.05 & -0.1 \end{bmatrix} \quad (30)$$

The two values of the energy (called the *eigenvalues*) and the corresponding coefficient column vectors (called the *eigenvectors*), can be obtained from Matlab as follows:

```
ham_mat=[0.3 0.05;0.05 -0.1];
[evvec eval]=eig(ham_mat)
```

Problem 3

Check that your answer to problem 2 gives the same eigenvalues and eigenvectors as the solution obtained using the Matlab `eig` command.

D. Orthogonalization

In general, when the overlap matrix is not diagonal, eigenvalues and eigenvectors can be obtained by solution of the *generalized* eigenvalue problem, invoked by the Matlab command `eig(hmat,smat)` which gives the eigenvalues or `[evvec, eval]=eig(hmat,smat)`, which yields both the eigenvalues and the eigenvectors. Note that in this case (\mathbf{S} not diagonal), the eigenvectors are normalized as follows:

$$\mathbf{C}^T \mathbf{S} \mathbf{C} = \mathbf{1} \quad (31)$$

In other words, the Matlab command `eig(hmat)` solves the simultaneous homogeneous equations

$$[\mathbf{H} - E\mathbf{S}]\mathbf{C} = 0$$

under the assumption that the overlap matrix \mathbf{S} is the unit matrix \mathbf{I} . The Matlab command `eig(hmat,smat)` solves the same set of homogeneous equations but with a full (non-diagonal) overlap matrix given by `smat`.

1. Gram-Schmidt orthogonalization

Rather than working with non-orthogonal expansion functions, we can construct an orthonormal set by **Gram-Schmidt** orthogonalization, which proceeds as follows:

Suppose we have two functions ϕ_i with $i = 1, 2$. The functions are normalized but not orthogonal, in other words $\langle \phi_i | \phi_i \rangle = 1$ and $\langle \phi_i | \phi_j \rangle = S_{ij}$. Let us start with function ϕ_i .

Then, we can take a linear combination of ϕ_1 and ϕ_2

$$\tilde{\phi}_2 = A_2\phi_1 + B_2\phi_2$$

We will choose the coefficients A_2 and B_2 so that $\tilde{\phi}_2$ is normalized and orthogonal to ϕ_1 , or, mathematically, we require that $\langle \tilde{\phi}_2 | \tilde{\phi}_2 \rangle = 1$ and $\langle \phi_1 | \tilde{\phi}_2 \rangle = 0$. You can show that the coefficients are given by $A_2 = -S_{12} [1 - S_{12}^2]^{-1/2}$ and $B_2 = [1 - S_{12}^2]^{-1/2}$.

In Gram-Schmidt orthogonalization, one constructs a set of linear combinations of the expansion functions ϕ_i , by taking a linear combination of the functions $1 \dots n$ so that this linear combination is orthogonal to all the preceding linear combinations.

$$\tilde{\phi}_i = \mathbf{D}^{(i)T} \phi_i$$

where, for two states

$$\mathbf{D}^{(2)} = \begin{bmatrix} 1 & A_2 \\ 0 & B_2 \end{bmatrix} \quad (32)$$

and, for three states

$$\mathbf{D}^{(3)} = \begin{bmatrix} 1 & A_2 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & \tilde{A}_3 \\ 0 & 1 & \tilde{B}_3 \\ 0 & 0 & C_3 \end{bmatrix} \quad (33)$$

Problem 4

(a) Assume that you have carried out a Gram-Schmidt normalization for two states, obtaining the coefficients A_2 and B_2 . We label the two orthogonal states $\tilde{\phi}_1$ and $\tilde{\phi}_2$. The overlap matrix between these two states and the third state ϕ_3 is

$$\mathbf{S} = \begin{bmatrix} 1 & 0 & \tilde{S}_{13} \\ 0 & 1 & \tilde{S}_{23} \\ \tilde{S}_{13} & \tilde{S}_{23} & 1 \end{bmatrix}$$

Obtain an expression for the coefficients \tilde{A}_3 , \tilde{B}_3 , and C_3 , in terms of \tilde{S}_{13} and \tilde{S}_{23}

(b) Write down an expression equivalent to Eq. (33) for four states, $\mathbf{D}^{(4)}$. This will involve four new coefficients. Call these \tilde{A}_4 , \tilde{B}_4 , \tilde{C}_4 , and D_4 .

2. Diagonalization of the overlap matrix

Another way to construct an orthonormal set of expansion functions is to diagonalize the overlap matrix

$$\mathbf{F}^T \mathbf{S} \mathbf{F} = \boldsymbol{\lambda}$$

where $\boldsymbol{\lambda}$ is a diagonal matrix. The columns of the matrix \mathbf{F} are the linear combinations of the expansion function ϕ_i in which the overlap matrix is diagonal. It is not yet normalized, since the diagonal elements of $\boldsymbol{\lambda}$ are not equal to 1. To impose normalization, we then divide the columns of \mathbf{F} by the square-root of the corresponding diagonal element of the λ matrix. In other words, we define a new matrix \mathbf{G} with

$$G_{ij} = F_{ij} / \lambda_j^{1/2}$$

Then, in the basis defined by the columns of \mathbf{G} the overlap matrix, defined by $\mathbf{G}^T \mathbf{S} \mathbf{G}$ is equal to the unit matrix, as in Eq. (31).

Thus, when expanding in a nonorthogonal basis set, one has three alternatives:

(1). Determining the eigenvalues and eigenvectors directly using a generalized eigenvalue call (e.g. `eig(hmat, smat)` in Matlab).

(2). Using Gram-Schmidt orthogonalization to construct the transformation matrix \mathbf{D} of Eqs. (32) or (33), then diagonalizing, by means of a standard eigenvalue call, the transformed Hamiltonian matrix $\tilde{\mathbf{H}}_2 = \mathbf{D}^T \mathbf{H} \mathbf{D}$. Designate by \mathbf{F}_2 the matrix that diagonalizes $\tilde{\mathbf{H}}_2$ so that

$$\boldsymbol{\varepsilon}_2 = \mathbf{F}_2^T \tilde{\mathbf{H}}_2 \mathbf{F}_2 = \mathbf{F}_2^T \mathbf{D}^T \mathbf{H} \mathbf{D} \mathbf{F}_2 \quad (34)$$

where $\boldsymbol{\varepsilon}_2$ is the diagonal matrix of eigenvalues. Thus, the overall matrix of eigenvectors is

$$\mathbf{C}_2 = \mathbf{D} \mathbf{F}_2 \quad (35)$$

(3). Diagonalizing the overlap matrix, then renormalizing each column, then diagonalizing by means of a standard eigenvalue call, the transformed Hamiltonian matrix $\tilde{\mathbf{H}}_3 = \mathbf{C}^T \mathbf{H} \mathbf{C}$, namely

$$\boldsymbol{\varepsilon}_3 = \mathbf{F}_3^T \tilde{\mathbf{H}}_3 \mathbf{F}_3 = \mathbf{F}_3^T \mathbf{G}^T \mathbf{H} \mathbf{G} \mathbf{F}_3 \quad (36)$$

Thus, the overall matrix of eigenvectors is

$$\mathbf{C}_3 = \mathbf{GF}_3 \quad (37)$$

Problem 5

Suppose that you have a Hamiltonian matrix given by Eq. (30) and an overlap matrix given by

$$\mathbf{S} = \begin{bmatrix} 1 & 0.25 \\ 0.25 & 1 \end{bmatrix} \quad (38)$$

Write a Matlab script that demonstrates that the three alternatives described immediately above result in the same energies.

E. MacDonald's Theorem

In general, non-trivial solutions to Eq. (25) exist only for values of the energy for which the determinant of the matrix $[\mathbf{H} - E_{var}\mathbf{1}]$ vanishes. The determinant will, of course, exist for any arbitrary value of E_{var} . For simplicity, let's use the letter E to stand for E_{var} . The determinant, $f(E)$ will be a polynomial in E of order N . In the case of a set of 3 basis function, the vanishing of the corresponding 3×3 secular determinant can be written as, where we explicitly use the symmetry of the matrix of the Hamiltonian. (We assume real matrix elements).

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} \\ H_{12} & H_{22} - E & H_{23} \\ H_{13} & H_{23} & H_{33} - E \end{vmatrix} \quad (39)$$

With the rules for evaluating a 3×3 determinant, we can express this as

$$(H_{11} - E)(H_{22} - E)(H_{33} - E) + 2H_{12}H_{23}H_{13} - H_{13}^2(H_{22} - E) + \dots = 0 \quad (40)$$

This is a cubic equation, which we can represent schematically in Fig. (2). There will be, in general, three *roots* of the cubic – values of E for which $f(E)=0$.

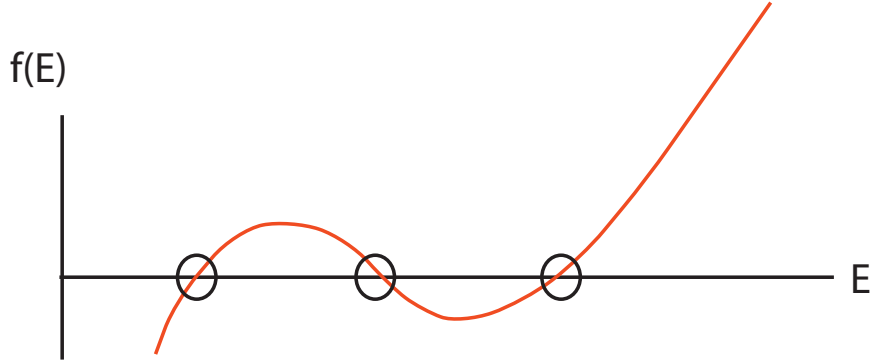


FIG. 2. Dependence on energy of the determinant $|\mathbf{H} - E\mathbf{1}|$ for a 3×3 system.

Suppose we use N ortho-normal functions, $\{\phi_1, \phi_2, \dots, \phi_N\}$, in our expansion of the wavefunction. Diagonalization of the matrix of the Hamiltonian gives

$$\mathbf{C}^T \mathbf{H} \mathbf{C} = \begin{bmatrix} E_1 & \cdots & 0 \\ \vdots & \ddots & \vdots \\ 0 & \vdots & E_N \end{bmatrix} \quad (41)$$

Each column of the \mathbf{C} matrix defines a variational solution, which we will designate ψ_n .

We will prove here that root n (the n^{th} eigenvalue) is an upper bound to the energy of the n^{th} state. To do so we define a new set of basis functions, of order $N + 1$, namely $\{\psi_1, \psi_2, \dots, \psi_N, \phi_{N+1}\}$. In this new $N + 1 \times N + 1$ basis, the matrix of the Hamiltonian is

$$\mathbf{H} = \begin{bmatrix} E_1^{(N)} & \cdots & 0 & h_1 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & E_N^{(N)} & h_N \\ h_1 & \cdots & h_N & h_{N+1} \end{bmatrix} \quad (42)$$

where $h_i = \langle \psi_i | H | \phi_{N+1} \rangle$ for $i \leq N$ and $h_{N+1} = \langle \phi_{N+1} | H | \phi_{N+1} \rangle$. Here the superscript (N) indicates that the energies were obtained in a basis of N functions. To obtain the new

energies, in the $N + 1 \times N + 1$ basis, we need to find the roots of the secular determinant

$$\begin{vmatrix} E_1^{(N)} - E & \cdots & 0 & h_1 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & E_N^{(N)} - E & h_N \\ h_1 & \cdots & h_N & h_{N+1} - E \end{vmatrix} = 0 \quad (43)$$

Applying the rules for expansion of a determinant, you can show that Eq. (43) is equivalent to

$$(h_{N+1} - E) \prod_{i=1}^N (E_i^{(N)} - E) - \sum_{i=1}^N h_i^2 \prod_{\substack{j=1 \\ j \neq i}}^N (E_j^{(N)} - E) = 0 \quad (44)$$

Consider the simplest case ($N = 2$). We will assume that $E_1^{(2)}$ is less than (lower than) $E_2^{(2)}$. The $N + 1 = 3$ secular determinant is

$$\begin{vmatrix} E_1^{(2)} - E & 0 & h_1 \\ 0 & E_2^{(2)} - E & h_2 \\ h_1 & h_2 & h_3 - E \end{vmatrix} = (E_1^{(2)} - E)(E_2^{(2)} - E)(h_3 - E) - h_2^2(E_1^{(2)} - E) - h_1^2(E_2^{(2)} - E) = f(E) \quad (45)$$

Now, if $E = E_1^{(2)}$, then $f(E = E_1^{(2)}) = -h_1^2 [E_2^{(2)} - E_1^{(2)}]$ (all the other terms vanish). This has to be negative, since $E_1^{(2)} \leq E_2^{(2)}$. If, however, $E = E_2^{(2)}$, then $f(E = E_2^{(2)}) = -h_2^2 [E_1^{(2)} - E_2^{(2)}]$, which has to be positive (by the same reasoning).

Thus, $f(E)$ changes sign between $E = E_1^{(2)}$ and $E = E_2^{(2)}$, so that there will be one root between $E_1^{(2)}$ and $E = E_2^{(2)}$. Now, if E goes to negative infinity, then, Eq. (45) shows that

$$\lim_{E \rightarrow -\infty} f(E) = -E^3, \quad (46)$$

which is positive (E is large and negative). Thus, since $f(E)$ is negative at $E = E_1^{(2)}$, one more root will occur at an energy less than $E_1^{(2)}$.

Problem 6

Show that $f(E)$ also changes sign between $E = E_2^{(2)}$ and $E = +\infty$.

Thus the two roots for $N = 2$ are interleaved between the three roots for $N = 3$, and so on as N increases, as shown schematically in Fig. (3). Consequently, we see that

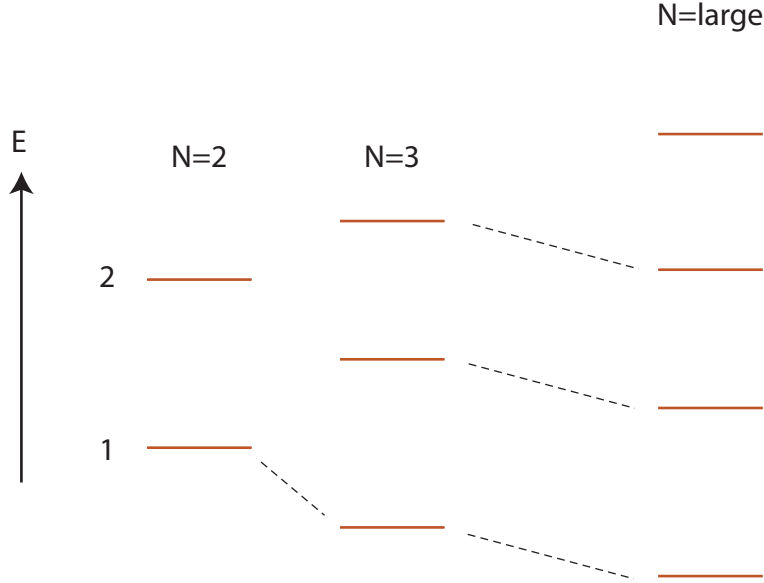


FIG. 3. Illustration of the placement of the linear variational roots as N , the size of the basis set, increases.

the n^{th} eigenvalue obtained from a linear variational treatment is an upper bound to the n^{th} true energy. This is known as the Hylleraas-Undheim-MacDonald theorem, discovered independently by Hylleraas and Undheim [1] and MacDonald [2].

F. DVR method for bound state energies

Many phenomena are interpreted by one-dimensional models. The Discrete Variable Representation (DVR) method is a straightforward, accurate way to determine the energies and wavefunctions of bound states for any arbitrary one-dimensional potential.

Consider a one-dimensional Hamiltonian in Cartesian coordinates

$$H(x) = V(x) - \frac{1}{2m} \frac{d^2}{dx^2} \quad (47)$$

We will designate the true wavefunctions for this Hamiltonian as $\phi_i(x)$, where i denotes the cardinal number of the energy ($i=1$ is the lowest energy, $i = 2$ is the energy of the first excited state, etc). These wavefunctions are assumed to be orthonormal, so that

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad (48)$$

Also, since the ϕ_i are solutions to the Schrodinger equation, the matrix of \hat{H} is diagonal in the $\{\phi_i\}$ basis, namely

$$\langle \phi_i | H | \phi_j \rangle = \delta_{ij} E_j \quad (49)$$

Now, suppose that we wanted to evaluate the $\langle \phi_i | H | \phi_j \rangle$ matrix element by numerical integration. To do so we divide the range of x over which the wavefunction is appreciably greater than zero into N sectors of equal width h . The initial and final values of x are denoted x_0 and x_N . We'll use a repeated trapezoidal rule for integration. [3] The repeated trapezoidal rule is

$$\int_{x_0}^{x_N} f(x) dx \cong h \left[\frac{1}{2} f(x = x_0) + f(x = x_1) + \cdots + f(x = x_{N-1}) + \frac{1}{2} f(x_N) \right] \quad (50)$$

Thus, the matrix element of \hat{H} is given by

$$\langle \phi_i | H | \phi_j \rangle \cong h \sum_{k=0}^N \phi_i(x_k) \left[V(x_k) - \frac{1}{2m} \frac{d^2}{dx^2} \right] \phi_j(x_k) \quad (51)$$

Note that we have ignored the factors of $\frac{1}{2}$ which appear in Eq. (50) because we assume that the range of integration is large enough that the wavefunctions ϕ_i all vanish at the end points. Thus $\phi_i(x_0) = \phi_j(x_0) = \phi_i(x_N) = \phi_j(x_N) = 0$

To evaluate the second derivative term, we use a 3-point finite difference approximation for the 2nd derivative. [3] This is

$$\left. \frac{d^2 f}{dx^2} \right|_{x=x_k} \cong \frac{f(x = x_{k+1}) - 2f(x = x_k) + f(x = x_{k-1}))}{h^2} = \frac{f_{k+1} + f_{k-1} - 2f_k}{h^2} \quad (52)$$

Thus, the expression for the matrix elements of H is

$$\langle \phi_i | H | \phi_j \rangle \cong \sum_{k=0}^N h \phi_i(x_k) \left\{ V(x_k) \phi_j(x_k) - \frac{1}{2m} [\phi_j(x_{k+1}) - 2\phi_j(x_k) + \phi_j(x_{k-1}))] \right\} \quad (53)$$

To simplify the notation we will define $c_{ki} \equiv \phi_i(x_k)$ (in other words: c_{ki} is the value of the i^{th} wavefunction at $x = x_k$), so that Eq. (53) can be written as

$$\langle \phi_i | H | \phi_j \rangle \cong h \sum_{k=0}^N c_{ki} \left\{ V(x_k) c_{kj} - \frac{1}{2m} [c_{k+1,j} - 2c_{k,j} + c_{k-1,j}] \right\} \quad (54)$$

This last equation can be written, formally, as a matrix equation

$$\langle \phi_i | H | \phi_j \rangle \cong h \mathbf{c}_i^T [\mathbf{V} + \mathbf{T}] \mathbf{c}_j \quad (55)$$

where \mathbf{c}_i is a column vector ($\mathbf{c}_i = [c_{1i} \ c_{2i} \ \dots]$), \mathbf{V} is a diagonal matrix with elements $V_{kl} = \delta_{kl} V(x = x_k)$ and \mathbf{T} is a tri-diagonal matrix with elements $T_{kk} = 1/mh^2$ and $T_{k,k\pm 1} = -1/(2mh^2)$. (Remember that h here is the spacing of the numerical integration grid *not* Planck's constant.)

The matrix of the Hamiltonian, with matrix elements $\langle \phi_i | H | \phi_j \rangle$, can then be written in matrix notation as

$$\mathbf{H} = h \mathbf{C}^T [\mathbf{V} + \mathbf{T}] \mathbf{C} \quad (56)$$

where each column of the matrix \mathbf{C} is given by \mathbf{c}_i . But we know that $\langle \phi_i | H | \phi_j \rangle = \delta_{ij} E_j$. This is equivalent to saying, in matrix notation, $\mathbf{H} = \mathbf{E}$, where \mathbf{E} is a diagonal matrix with elements E_i . Thus $\mathbf{H} = \mathbf{E} = h \mathbf{C}^T [\mathbf{V} + \mathbf{T}] \mathbf{C}$.

Consequently, since $h \mathbf{C}^T [\mathbf{V} + \mathbf{T}] \mathbf{C}$ is a diagonal matrix, and the matrices \mathbf{V} and \mathbf{T} are symmetric, the matrix \mathbf{C} is non other than the matrix of eigenvectors which diagonalize the matrix $h [\mathbf{V} + \mathbf{T}]$. The eigenvectors are proportional to the values of the true wavefunctions at the points $x = x_k$, and thus are the *discrete variable representations* (hence the name, DVR) of these wavefunctions. The eigenvalues are proportional to the true energies. We discuss this proportionality next.

Most computer diagonalization routines give orthogonal eigenvectors, so that $\mathbf{C}^T \mathbf{C} = \mathbf{1}$, or, in terms of the individual eigenvectors

$$1 = \sum_{k=0}^N c_{ki} c_{ki} = \mathbf{c}_i^T \mathbf{c}_i \quad (57)$$

However, we want the wavefunctions to be normalized, so that $\langle \phi_i | \phi_j \rangle = \delta_{ij}$. If we were to evaluate this overlap matrix element by a trapezoidal integration equivalent to Eq. (50), using the \mathbf{c}_i eigenvectors, we would obtain

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \sum_{k=0}^N h c_{kj} c_{ki} = h \mathbf{c}_j^T \mathbf{c}_i = h \quad (58)$$

which is equal to h , not unity. Consequently, we have to renormalize the eigenvector matrix \mathbf{C} by dividing every element by $h^{1/2}$. Let us define these renormalized eigenvectors as $\mathbf{d}_i = h^{-1/2}\mathbf{c}_i$. In other words, the value of the normalized wavefunction of the i^{th} state at $x = x_k$ is $d_{ki} = c_{ki}h^{-1/2}$. With this renormalization, Eq. (59) becomes

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} h \sum_{k=0}^N d_{kj} d_{ki} = h \mathbf{c}_i^T \mathbf{c}_i / (h^{1/2})^2 = \mathbf{c}_i^T \mathbf{c}_i = 1 \quad (59)$$

which is now correctly normalized.

Since the value of the i^{th} normalized eigenvector at $x = x_k$ is d_{ki} , the energy of the i^{th} state is given by [see Eq. (55)]

$$E_i = \langle \phi_i | H | \phi_i \rangle = h \mathbf{d}_i^T [\mathbf{V} + \mathbf{T}] \mathbf{d}_i \quad (60)$$

which is also equal to

$$E_i = \langle \phi_i | H | \phi_i \rangle = \mathbf{c}_i^T [\mathbf{V} + \mathbf{T}] \mathbf{c}_i \quad (61)$$

Thus, the simplest DVR approach is diagonalization of the matrix $[\mathbf{V} + \mathbf{T}]$. The eigenvalues are then equal to (no longer proportional to) the true energies of the system. The discrete approximation to the wavefunction is still given by $d_{ki} = c_{ki}h^{-1/2}$, because, regardless of whether we diagonalize $[\mathbf{V} + \mathbf{T}]$ or $h[\mathbf{V} + \mathbf{T}]$ any computer program will automatically give eigenvectors which satisfy $\mathbf{1} = \mathbf{C}^T \mathbf{C}$.

The DVR method is only as accurate as the underlying numerical integration. Increasing the number of points increases the size of the \mathbf{V} and \mathbf{T} matrices but (presumably) improves the accuracy.

In actual practice, a slightly better approximation is obtained by a 5-point approximation [3] to the 2^{nd} derivative, namely

$$\left. \frac{d^2 f}{dx^2} \right|_{x=x_k} = \frac{-f_{k+2} + 16f_{k+1} - 30f_k + 16f_{k-1} - f_{k-2}}{12h^2} \quad (62)$$

which implies that the matrix T has five non-zero bands.

Problem 7

The three-parameter [Morse potential](#) is a good approximation to many potential curves for

diatomic molecules.

$$V(r) = D_e [1 - e^{-a(r-r_e)}]^2 \quad (63)$$

Here D_e is the dissociation energy, r_e is the equilibrium internuclear bond distance. Give the relation which relates a to the harmonic vibrational frequency ($\omega = (k/m)^{1/2}$) and the dissociation energy D_e .

The energies of the first 3 vibrational levels of the H^{35}Cl molecule are listed in Table I. The equilibrium bond length of HCl is $r_e = 2.587$ bohr and the dissociation energy is

TABLE I. Energies of the first three vibrational levels of the H^{35}Cl molecule.

n	$E(\text{cm}^{-1})$
0	1482.30
1	4368.33
2	7150.75

$D_e = 4.61$ eV. The atomic masses of H and ^{35}Cl are 1.007825 and 34.968852 atomic mass units respectively. Use this data to estimate the value of a .

Then, modify the Matlab script [dvr_quartic.m](#) to determine using the DVR method the value of a which gives the Morse potential with the energies of the first three vibrational levels which best fits the experimental energies (Table I) of HCl. The best fit will minimize the root mean square error

$$\Delta(a) = \left\{ \frac{1}{N-1} \sum_{i=0}^N [\varepsilon_i(a) - E_i]^2 \right\}^{1/2},$$

where E_i is the experimental energy of the i^{th} level and $\varepsilon_i(a)$ is the energy of the i^{th} vibrational level as predicted by the Morse potential with parameter a .

To check your Matlab script, you can compare your DVR results with the analytical formulas in the [Wolfram Science](#) and [Wikipedia](#) webpages for the Morse oscillator.

[1] E. Hylleraas and B. Undheim, Z. Phys., **65** 759 (1930).

[2] J. K. L. MacDonald, Phys. Rev., **43**, 830 (1933).

- [3] [M. Abramowitz and I. Stegun](#), in Natl. Bur. Stand. Appl. Math. Ser. (1965), Vol. 55, Chap. 25.