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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](#)

$$E = h\nu = \frac{hc}{\lambda} \quad (1)$$

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.

C. Example: vibrational spacings

A good example showing how to work through conversion problems with atomic units are calculations involving molecular vibrational spacings. Typically, transitions between

vibrational levels correspond to wavelengths in the infrared region of the spectrum. The positions of infrared lines is usually designated in wave numbers or cm^{-1} . This is the inverse of the wavelength at which the transition occurs. The abbreviation for wave numbers is $\bar{\lambda}$.

Let's take a simple case, where $\bar{\lambda}=1000 \text{ cm}^{-1}$. Let's say we want to calculate the corresponding vibrational force constant k for an oscillator with vibrational "spacing" of 1000 cm^{-1} and a reduced mass of $16,000 m_e$ (nuclear masses are typically an integer times the mass of the proton, which is $\approx 1800 m_e$). Note that we put the word spacing in quotes, since the units used are those related to the wavelength at which the transition occurs. Conversion from wave numbers to atomic units [1 atomic unit of energy = 219474.6 cm^{-1}] gives the vibrational "spacing" to be $\Delta E = 1000/219474.6 = 4.5563 \times 10^{-3}$ Hartree. Here we have implicitly converted to an energy spacing, saying that the energy spacing at which absorption will occur is governed by the Planck relation [Eq. (1)] Then, if $1/\lambda$ is measured in cm^{-1} , dividing by 219474.6 will give the correct energy spacing in atomic units of energy (Hartree).

For a quantum oscillator of force constant k and reduced mass μ the vibrational spacing is

$$\Delta E = \hbar\omega = \hbar\sqrt{k/\mu}$$

Here ω is the true vibrational frequency (in units of time^{-1}) not the unit related to where the transition occurs. Thus (since $\hbar = 1$ in atomic units)

$$k = \mu(\Delta E)^2$$

Now, equating the ΔE in the last equation with the the observed spacing [Eq. (??)], we obtain

$$k = (4.5563 \times 10^{-3})^2 \times 16000 = 0.3322 \text{ atomic units} \quad (2)$$

The units for force constant are energy \cdot length $^{-2}$, or in atomic units, hartree \cdot bohr $^{-2}$. Since $1 \text{ bohr} = 5.29 \times 10^{-11} \text{ m}$ and $1 \text{ Hartree} = 4.35974417 \times 10^{-18} \text{ J}$, in SI units the value of the force constant k in Eq. (2) is $k = 5.174 \times 10^2 \text{ Joule}\cdot\text{m}^{-2}$.

II. APPROXIMATION METHODS

A. Semiclassical quantization

The Bohr-Sommerfeld quantization condition is

$$S = \oint \vec{p} \cdot d\vec{q} = (n + 1/2)h \quad (3)$$

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

$$S = \oint p_x q_x = (n + 1/2)h \quad (4)$$

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. (4) 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

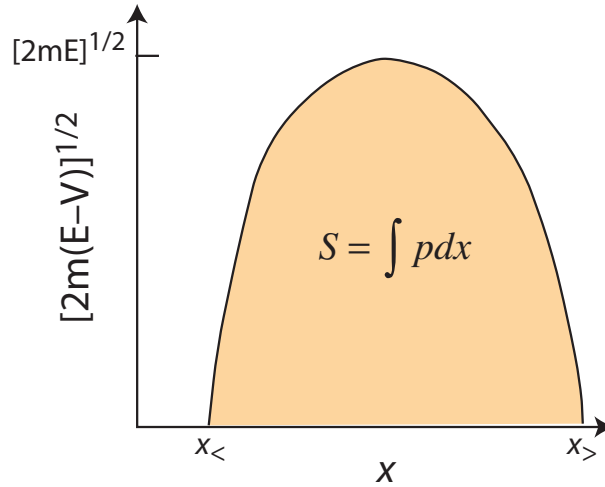


FIG. 1. Dependence on distance of a typical phase integral [Eq. (4)].

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

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. (4) 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

$$H\psi_n = H_o \phi_n^{(0)} + \lambda (H_o \phi_n^{(1)} + H' \phi_n^{(0)}) + \lambda^2 (H_o \phi_n^{(2)} + H' \phi_n^{(1)}) + \dots \quad (5)$$

We similarly expand

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

so that

$$E_n \psi_n = E_n^{(0)} \phi_n^{(0)} + \lambda (E_n^{(0)} \phi_n^{(1)} + E_n^{(1)} \phi_n^{(0)}) + \lambda^2 (E_n^{(0)} \phi_n^{(2)} + E_n^{(1)} \phi_n^{(1)} + E_n^{(2)} \phi_n^{(0)}) + \dots \quad (6)$$

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. (5) must

equal the terms multiplied by the same power of λ in Eq. (6). In other words

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

which is the unperturbed Schroedinger equation, and

$$H'\phi_n^{(0)} + H_o\phi_n^{(1)} = E_n^{(1)}\phi_n^{(0)} + E_n^{(0)}\phi_n^{(1)}. \quad (7)$$

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

$$\phi_n^{(1)} = \sum_{k \neq n} C_{nk}^{(1)} \phi_k^{(0)} \quad (8)$$

Note that the sum extends over all states except for $k = n$. If we introduce this expansion into Eq. (7) we obtain

$$H'\phi_n^{(0)} + H_o \sum_{k \neq n} C_{nk}^{(1)} \phi_k^{(0)} = E_n^{(1)}\phi_n^{(0)} + \sum_{k \neq n} C_{nk}^{(1)} E_n^{(0)} \phi_k^{(0)} \quad (9)$$

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

$$H'\phi_n^{(0)} = E_n^{(1)}\phi_n^{(0)} + \sum_{k \neq n} C_{nk}^{(1)} \left(E_n^{(0)} - E_k^{(0)} \right) \phi_k^{(0)} \quad (10)$$

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. (10), 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

$$C_{nk}^{(1)} = \langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle / (E_n^{(0)} - E_k^{(0)}) \quad (11)$$

so that Eq. (8) becomes

$$\phi_n^{(1)} = \sum_{k \neq n} \frac{\langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} \phi_k^{(0)} \quad (12)$$

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. (5) and (6). We have

$$H_o \phi_n^{(2)} + H' \phi_n^{(1)} = E_n^{(0)} \phi_n^{(2)} + E_n^{(1)} \phi_n^{(1)} + E_n^{(2)} \phi_n^{(0)} \quad (13)$$

Following Eq. (8) we expand $\phi_n^{(2)}$ as

$$\phi_n^{(2)} = \sum_{k \neq n} C_{nk}^{(2)} \phi_k^{(0)} \quad (14)$$

We substitute this equation as well as Eq. (12) into Eq. (13), premultiply by $\phi_n^{(0)}$, and integrate to get (remembering that $\phi_n^{(2)}$ is orthogonal to $\phi_n^{(0)}$)

$$E_n^{(2)} = \langle \phi_n^{(0)} | H' | \phi_n^{(1)} \rangle \quad (15)$$

We can then substitute in Eq. (12) for $\phi_n^{(1)}$ to get

$$E_n^{(2)} = \sum_{k \neq n} \frac{\langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle \langle \phi_n^{(0)} | H' | \phi_k^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} = \sum_{k \neq n} \frac{|\langle \phi_k^{(0)} | H' | \phi_n^{(0)} \rangle|^2}{E_n^{(0)} - E_k^{(0)}} \quad (16)$$

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. (16) is squared, and thus always positive (or zero), the contribution of each term in the summa-

tion will be negative. Thus we conclude that for the lowest energy level, the second-order contribution to the energy will always be negative.

C. Variational theorem

Suppose you have some function $\psi(x)$ defined on the same domain as the Hamiltonian. For simplicity, we'll consider only one dimension, but this is not necessary. The function $\psi(x)$ can always be expanded in terms of the eigenfunctions of the Hamiltonian $\hat{H}(x)$, namely

$$\psi(x) = \sum_{n=0}^{\infty} C_n \phi_n(x)$$

where

$$\hat{H}(x)\phi_n(x) = \varepsilon_n \phi_n(x)$$

We'll also assume the function $\psi(x)$ is normalized, so that

$$\int \psi^*(x)\psi(x)dx = \sum_m \sum_n C_m^* C_n \int \phi_m^*(x)\phi_n(x)dx = 1$$

The eigenfunctions of \hat{H} form an ortho-normal set ($\int \phi_m^*(x)\phi_n(x)dx = \delta_{mn}$), so that

$$\sum_n |C_n(x)|^2 = 1 \tag{17}$$

Now, consider the expectation value of the Hamiltonian, which we will call E_{var}

$$\begin{aligned} E_{var} &= \langle \psi | \hat{H} | \psi \rangle = \int \psi^*(x) \hat{H}(x) \psi(x) dx = \sum_m \sum_n C_m^* C_n \int \phi_m^*(x) \hat{H}(x) \phi_n(x) dx \\ &= \sum_m \sum_n C_m^* C_n \int \phi_m^*(x) \varepsilon_n \phi_n(x) dx = \sum_n |C_n(x)|^2 \varepsilon_n \end{aligned}$$

We'll assume that $n = 0$ corresponds to the ground state so that $\varepsilon_{n>0} \geq \varepsilon_0$. Thus we can collect the first and last terms in the previous equation, writing

$$E_{var} = \sum_n |C_n(x)|^2 \varepsilon_n \geq \sum_n |C_n(x)|^2 \varepsilon_0 = \varepsilon_0 \sum_n |C_n(x)|^2 = \varepsilon_0$$

We have used Eq. (17) to get rid of the summation in the last term. Note that the inequality

becomes an equality if and only if $\psi(x)$ happens to be identical to the wave function of the ground state ϕ_0 .

This is the variational theorem. In practice, you would construct some function $\psi(x)$ which would depend on a number of parameters α_i , say. The variational energy E_{var} would be a function of these parameters. You could then minimize E_{var} with respect to varying each of these parameters, to obtain the best estimate of the energy of the ground state consistent with your choice of trial wave function.

D. 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

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} \quad (18)$$

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

$$\begin{bmatrix} 1 & S_{12} \\ S_{21} & 1 \end{bmatrix} \quad (19)$$

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

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

The expectation value of the Hamiltonian is then

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

which can be written as

$$\langle\phi|H|\phi\rangle = E_{var}\langle\phi|\phi\rangle \quad (22)$$

Problem 1

Obtain an expression for E_{var} 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

$$|\phi\rangle = C_1|1\rangle + C_2|2\rangle + C_3|3\rangle \quad (23)$$

If we take the derivative of Eq. (22) with respect to the i^{th} coefficient C_i we obtain

$$\frac{\partial\langle\phi|H|\phi\rangle}{\partial C_i} = E_{var} \frac{\partial\langle\phi|\phi\rangle}{\partial C_i} + \langle\phi|\phi\rangle \frac{\partial E_{var}}{\partial C_i} \quad (24)$$

or, explicitly,

$$2C_i H_{ii} + \sum_{j \neq i} C_j (H_{ij} + H_{ji}) = E_{var} \left[2C_i S_{ii} + \sum_{j \neq i} C_j (S_{ij} + S_{ji}) \right] + \frac{\partial E_{var}}{\partial C_i} \langle\phi|\phi\rangle \quad (25)$$

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

$$C_i H_{ii} + \sum_{j \neq i} C_j H_{ij} = E_{var} \left[C_i S_{ii} + \sum_{j \neq i} C_j S_{ij} \right] + \frac{\partial E_{var}}{\partial C_i} \langle\phi|\phi\rangle \quad (26)$$

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 $\partial E / \partial C$ partial derivatives in Eq. (26) by zero, we obtain

$$\mathbf{H} \times \mathbf{c} - E_{var} \mathbf{S} \times \mathbf{c} = \mathbf{0} \quad (27)$$

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

$$[\mathbf{H} - E_{var}\mathbf{I}] \mathbf{c} = \mathbf{0} \quad (28)$$

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 3 particular choices of the \mathbf{c} vector, which *diagonalize* the \mathbf{H} matrix and three different values of the eigenvalue E . 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 and a diagonal matrix $\boldsymbol{\varepsilon}$ with diagonal elements equal to the three different values of E . We can group these three into a single matrix equation

$$\mathbf{H}\mathbf{C} = \mathbf{C}\boldsymbol{\varepsilon} \quad (29)$$

The ordering of the right hand side ensures that the successive columns of \mathbf{C} will be multiplied by the successive values of E . [If the ordering were $\boldsymbol{\varepsilon}\mathbf{C}$, then each *row* of \mathbf{C} would be multiplied by the different values of E , which is not what is implied in Eq. (28)].

Premultiplication of Eq. (29) by \mathbf{C}^T , gives

$$\mathbf{C}^T\mathbf{H}\mathbf{C} = \mathbf{C}^T\mathbf{C}\boldsymbol{\varepsilon} \quad (30)$$

If the overlap matrix \mathbf{S} is diagonal, then the expansion states are orthonormal. The transformation \mathbf{C} preserves this orthonormality and is called an orthogonal transformation, with the property

$$\mathbf{C}^T\mathbf{C} = \mathbf{C}\mathbf{C}^T = \mathbf{I}$$

Consequently, Eq. (30) simplifies to

$$\mathbf{C}^T\mathbf{H}\mathbf{C} = \boldsymbol{\varepsilon} \quad (31)$$

Thus \mathbf{C} defines the diagonalizing transformation of the matrix \mathbf{H} .

Problem 2

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

$$\mathbf{C} = \begin{bmatrix} \cos \vartheta & \sin \vartheta \\ -\sin \vartheta & \cos \vartheta \end{bmatrix} \quad (32)$$

With this expression for \mathbf{C} carry out the orthogonal transformation of Eq. (31) and then require that the off-diagonal elements vanish, since \mathbf{E} is a diagonal matrix. This will allow you to evaluate the value of the angle ϑ in terms of the matrix elements of \mathbf{H} . Then, evaluate the two diagonal matrix elements of \mathbf{E} in terms of ϑ and the matrix elements of \mathbf{H} . Give your answer in terms of $\cos \vartheta$ and $\sin \vartheta$.

Note if you use Matlab to do this problem, and set up the transpose matrix with symbolic variables then know that \mathbf{C}' (with the period) ensures the transpose, while \mathbf{C}^{\dagger} is the Hermitian adjoint.

E. Secular Determinant

Let's say you haven't figured out how to use Matlab or Mathematica and you don't have access to Wolfram Alpha. So, you want to solve for the eigenvalues the old-fashioned way, by finding the roots of the secular determinant.

When you have N homogeneous linear equations, you can show that the condition for non-trivial (non-zero) solutions correspond to values of E_{var} in Eq. (33) for which the determinant of $\mathbf{H} - E_{var}\mathbf{1}$ vanishes. For a 2×2 problem, this determinant is (here we replace E_{var} with E , for brevity].

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = (H_{11} - E)(H_{22} - E) - H_{12}H_{21} = H_{11}H_{22} - E(H_{11} + H_{22}) + H_{11}H_{22} - H_{12}^2 \quad (33)$$

This is a polynomial of order N in E (here a quadratic, since $N = 2$). There are in general

two roots. Consider a 2×2 system defined by the matrix

$$\mathbf{H} = \begin{bmatrix} 0.3 & 0.05 \\ 0.05 & -0.1 \end{bmatrix} \quad (34)$$

Then, solving it as in Eq. (33), we have

$$|\mathbf{H} - E\mathbf{1}| = \begin{vmatrix} 0.3 - E & 0.05 \\ 0.05 & -0.1 - E \end{vmatrix} = (0.3 - E)(-0.1 - E) - 0.05^2 = E^2 - 0.2E - 0.0325 \quad (35)$$

This quadratic equation has the roots, $E = -0.10616$ and $E = 0.30616$. If we take the lowest root, then the homogeneous equation for the expansion coefficients is

$$\begin{aligned} \begin{bmatrix} 0.3 - E & 0.05 \\ 0.05 & -0.1 - E \end{bmatrix} \begin{bmatrix} C_{11} \\ C_{21} \end{bmatrix} &= \begin{bmatrix} 0.3 + 0.10616 & 0.05 \\ 0.05 & -0.1 + 0.10616 \end{bmatrix} \begin{bmatrix} C_{11} \\ C_{21} \end{bmatrix} \\ &= \begin{bmatrix} 0.40616 & 0.05 \\ 0.05 & 0.00616 \end{bmatrix} \begin{bmatrix} C_{11} \\ C_{21} \end{bmatrix} = 0 \end{aligned} \quad (36)$$

Evaluation of the matrix equations leads to two algebraic equations

$$0.40616C_{11} + 0.05C_{21} = 0$$

and

$$0.05C_{11} + 0.00616C_{21} = 0$$

Both of these can be solved to yield C_{21} in terms of C_{11} , giving, in both cases

$$C_{21} = -0.40616C_{11}/0.05$$

or

$$C_{21} = 8.1231C_{11}$$

The values of the coefficients can then be obtained by requiring that the eigenfunction be

normalized, namely

$$C_{11}^2 + C_{21}^2 = 1 = C_{11}^2(1^2 + 8.1231)^2 = 66.985C_{11}^2$$

from which we obtain

$$C_{11} = 66.985^{-1/2} = 0.12219$$

and then

$$C_{21} = -8.1231C_{11} = -0.99251$$

Problem 3

Obtain the expansion coefficients C_{12} and C_{22} for the eigenvector which corresponds to the second eigenvalue, $E = 0.30616$, *without solving again the secular equation for this new value of E .*

In general, for higher dimensions evaluation of the secular determinant, obtaining the roots of $|\mathbf{H} - E\mathbf{1}| = 0$ and then back solving to obtain the eigenvectors is computationally less efficient than just diagonalizing $[\mathbf{H} - E\mathbf{1}]$.

In Matlab, one can obtain the eigenvalues of a symmetric matrix (say it's defined as the variable `hmat`) by the command

```
eig(hmat)
```

or, the eigenvalues and all eigenvectors, by the command

```
[evec, eval] = eig(hmat)
```

If you have a simple 2×2 (or 3×3) problem and you don't want to enter the matrix first, you can just enter a one-line command [say, for example, for the matrix defined by Eq. (34)]

```
[evec eval] = eig([[0.2 0.05]; [0.05 -0.1]])
```

In Wolfram Alpha, you would enter the request

```
"eigenvalues {{0.2,0.05},{0.05,-0.1}}"
```

These two examples illustrate the differing syntax for dealing with arrays in Matlab and in Wolfram Alpha. Note, also, that Matlab returns the eigenvalues (and corresponding

eigenvectors) lowest first, while Wolfram Alpha returns them in the opposite order.

Problem 4

The Hermite polynomials $H_n(u)$ satisfy the two-term recursion relation (*here we are using n rather than n for the quantum number, since n is usually used in mathematics*)

$$H_{n+1}(u) = 2[uH_n(u) - nH_{n-1}(u)]$$

The first two Hermite polynomials ($n = 0$ and 1) are $H_0(u) = 1$ and $H_1(u) = 2u$. Determine expressions for $H_n(u)$ for $n = 2 - 4$. *If you use Matlab, be really careful you program the recursion relation correctly.*

Defining (in atomic units, where $\hbar = 1$) $\alpha = \mu\omega$ and $u = \sqrt{\alpha}x$, the wavefunctions for the Harmonic oscillator are given by

$$\psi_n(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} N_n H_n(u) e^{-u^2/2} \quad (37)$$

where N_n is a normalization constant.

(a) Knowing that $\int e^{-u^2} du = \sqrt{\pi}/\alpha^{1/2}$, $\int u^2 e^{-u^2} du = \sqrt{\pi}/2\alpha^{3/2}$, and $\int u^4 e^{-u^2} du = 3\sqrt{\pi}/4\alpha^{5/2}$, determine N_n for $n = 0$ and 1 . *Remember we want $\int_{-\infty}^{\infty} \psi_n(x)^2 dx$ to equal one; the integration is over x not u .*

(b) The mass of the proton is 1.0073 atomic mass units (1 amu = 1822.9 atomic units). The vibrational frequency of the H_2 molecule is 4400 cm^{-1} . For H_2 determine μ and ω in atomic units.

(c) In a harmonic oscillator model for H_2 , the potential is $\frac{1}{2}kx^2$, where $x = r - r_e$. What is the force constant k (also in atomic units) for H_2 ?

(d) A molecule in vibrational level n oscillates back and forth between its classical turning points, $r_e \pm x_t$, which are defined as the points at which $V(r \pm x_t) = \varepsilon_n = (n + \frac{1}{2})\omega$. For the harmonic oscillator model of the vibrational motion of the H_2 molecule, what is the value of x_t in the lowest ($n = 0$) vibrational level? *Hint: plot $V(x) - \varepsilon_0$ and find graphically the value of x for which the curve goes through zero, as follows:*

```
v=0.5*k*x^2           % k must have a numeric value,
```



```

                                % and x declared symbolic
ezplot(v-omega/2,[-.3 .3]) % omega must have a numeric value
grid                            % put a grid on the graph
[xt,y]=ginput(1)                % place the cursor over the zero intercept
                                % and click to get your answer

```

(e) Suppose you were to use a quartic oscillator $V(x) = \frac{1}{2}k_4x^4$ to approximate the vibrational potential of H_2 . Choose k_4 so that the difference between the harmonic and quartic potentials, integrated over *twice* the classically allowed range of motion, vanishes

$$\int_{-2x_t}^{+2x_t} \frac{1}{2} [k_2x^2 - k_4x^4] = 0.$$

You've already determined the value of k_2 in part (c) above. What is the resulting value of k_4 in terms of x_t and k_2 ? *We integrate over twice the classically allowed range because the very light effective particle ($\mu = 0.5$ atomic mass units) can penetrate significantly into the classical forbidden region.*

(f) With this value of k_4 , let's do several variational calculation for the quartic oscillator, assuming the value of μ appropriate for H_2 , which you determined in part (b) above. Since the quartic oscillator potential is symmetric, the wavefunction for the lowest state will be symmetric and nodeless. We'll use the the lowest three *symmetric* harmonic oscillator functions [Eq. (37) with $n=0, 2$, and 4] as variational functions. The matrix of the Hamiltonian in this 3×3 basis are

$$\begin{aligned} \langle \psi_n | \hat{H} | \psi_{n'} \rangle &\equiv \langle n | \hat{H} | n' \rangle = \langle n | \hat{T} | n' \rangle + \langle n | \hat{V} | n' \rangle \\ &= \langle n | -\frac{1}{2\mu} \frac{d^2}{dx^2} | n' \rangle + \langle n | \frac{1}{2} k_4 x^4 | n' \rangle \end{aligned}$$

The matrix elements of \hat{T} in the harmonic oscillator basis are all zero, except for the following

$$\langle n | \hat{T} | n \rangle = \frac{(2n+1)\alpha}{4\mu}, \quad \langle 0 | \hat{T} | 2 \rangle = \langle 2 | \hat{T} | 0 \rangle = -\frac{\sqrt{2}\alpha}{4\mu}, \quad \langle 2 | \hat{T} | 4 \rangle = \langle 4 | \hat{T} | 2 \rangle = -\frac{\sqrt{3}\alpha}{2\mu}$$

Similarly, the potential matrix elements are

$$\langle \psi_n | \hat{V} | \psi_{n'} \rangle \equiv \langle n | \hat{V} | n' \rangle = (k_4/\alpha^2)V(n, n')$$

where

$$V(0, 0) = \frac{3}{8}, \quad V(0, 2) = V(2, 0) = \frac{3\sqrt{2}}{4}, \quad V(0, 4) = V(4, 0) = \frac{\sqrt{6}}{4}$$

$$V(2, 2) = \frac{39}{8}, \quad V(2, 4) = V(4, 2) = \frac{7\sqrt{3}}{2}, \quad V(4, 4) = \frac{123}{8}$$

Assume that you use just the $n=0$ harmonic oscillator function of Eq. (37) to approximate the wavefunction for the quartic oscillator, and assume that α is a variable parameter. Determine an expression for the variational energy of the H_2 quartic oscillator, as a function of α . Find the value of α which minimizes this, and obtain the best variational estimate of the ground state energy. *Hint: Your energy should be close to the energy of the $n = 0$ state of H_2 treated as a harmonic oscillator.*

Then, keeping this best value of α determine the 3×3 Hamiltonian matrix (give the numerical matrix, in atomic units. *Hint: To check your results $H_{02} \approx 10^{-6}$) and $H_{24} = 4.4138 \times 10^{-3}$. Diagonalize this matrix, to determine the variational approximation to the energies of the lowest three symmetric levels.*

Problem 5

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

$$V(r) = D_e \{ \exp[-2\beta(r - r_e)] - 2 \exp[-\beta(r - r_e)] \} \quad (38)$$

Here D_e is the dissociation energy, r_e is the equilibrium internuclear bond distance.

(a) Give the relation which relates the exponential factor β to the harmonic vibrational frequency ω , the reduced mass of the oscillator μ and the dissociation energy D_e . For

H₂, the bond dissociation energy is 4.52 eV. What is the value of the Morse parameter β in atomic units for the H₂ molecule?

(b) The exact energy levels of the Morse oscillator are given by the [expression](#)

$$E_n = \hbar\omega(n + 1/2) - \frac{[\hbar\omega(n + 1/2)]^2}{4D_e}$$

or, if all quantities are in atomic units

$$E_n = \omega(n + 1/2) - \frac{[\omega(n + 1/2)]^2}{4D_e}$$

here $\omega = \sqrt{k/\mu}$ with $k = d^2V(r)/dr^2|_{r=r_e}$. As n increases, eventually this expression will give the unphysical result that $E_{n+1} - E_n$ is zero or negative. The value of n at which this occurs is an estimate of the number of bound states of the molecule. Obtain an algebraic expression for the maximum number of bound vibrational levels for the H₂ molecule? (You may also want to see the [Morse Oscillator demonstration](#) on the Wolfram Science webpage. If you put in the correct parameters for H₂, you'll see that the number of bound states is equal to what you predicted).

F. Non-orthogonal functions

In Sec. [II C](#) we assumed the expansion functions ϕ_i were orthonormal. Here we will expand the discussion in Sec. [II C](#) to treat this case. Let's be a bit more rigorous. Suppose each eigenfunction ψ_k is expanded in terms of the basis functions ϕ_i

$$\psi_k = \sum_i C_{ik}\phi_i$$

We'll assume, for simplicity, that the C_{ik} are real. Note that we are ordering the indices so that the expansion coefficients of ψ_i are a column of the matrix \mathbf{C} . Then, for any operator \hat{A} , the matrix of the operator in the ψ basis is

$$\langle \psi_k | \hat{A} | \psi_l \rangle = \sum_i \sum_j C_{ik} C_{jl} \langle \phi_i | \hat{A} | \phi_j \rangle = \sum_i \sum_j C_{ij} C_{jl} A_{ij}$$

In matrix notation, this is

$$\mathbf{A}_\psi = \mathbf{C}^T \mathbf{A} \mathbf{C} \quad (39)$$

For simplicity, the matrix \mathbf{A} with no subscript will designate the matrix of \hat{A} in the ϕ basis, while the matrix of \mathbf{A} in the ψ basis will be distinguished by a subscript.

1. Generalized eigenvalue problem

In Sec. IID, we started with the expression $E_{var} = \langle \psi | \hat{H} | \psi \rangle / \langle \psi | \psi \rangle$, differentiated with respect to each of the expansion coefficients, and set equal to zero, to obtain the linear equations [Eq. (27)]

$$\mathbf{H} \mathbf{c} - E_{var} \mathbf{S} \mathbf{c} = \mathbf{0} \quad (40)$$

The solution \mathbf{c} is a column vector. For an expansion in terms of N functions, there are N such sets of N equations. The solutions define a matrix \mathbf{C} . Each column of \mathbf{C} corresponds to one of the ψ_k , with best variational energy $E_{var} = \varepsilon_k$.

In general, when the overlap matrix is not diagonal, the eigenequations (29) become

$$\mathbf{H} \mathbf{C} = \mathbf{S} \mathbf{C} \boldsymbol{\varepsilon} \quad (41)$$

where $\boldsymbol{\varepsilon}$ is a diagonal matrix. The solution to these homogeneous equations, the eigenvalues \mathbf{C} and eigenvectors $\boldsymbol{\varepsilon}$, can be obtained by solution of the *generalized* eigenvalue problem, invoked by the Matlab commands `eig(hmat,smat)`, which gives just the eigenvalues, or `[evec, eval]=eig(hmat,smat)`, which yields both the eigenvalues and the eigenvectors.

Here, since the ϕ_i basis is not orthogonal (\mathbf{S} not diagonal), the overlap between the eigenfunctions ψ_k is obtained from Eq. (39), namely

$$\mathbf{S}_\psi = \mathbf{C}^T \mathbf{S} \mathbf{C} = \mathbf{1} \quad (42)$$

The set of functions ψ_k , which are solutions to the generalized eigenvalue problem, are orthonormal. Similarly, again from Eq. (39), the matrix of \hat{H} in the

$$\mathbf{H}_\psi = \mathbf{C}^T \mathbf{H} \mathbf{C} = \boldsymbol{\varepsilon} \quad (43)$$

2. *Factorization of a symmetric positive definite overlap matrix*

Solution of the generalized eigenvalue problem involves several steps. These are all “under the hood” if you use the Matlab command `eig(gmat, smat)`, but a full discussion is given here for completeness.

The overlap matrix \mathbf{S} is symmetric. In cases where it is positive definite (all elements greater than or equal to zero), you can use [Cholesky decomposition](#) which reduces \mathbf{S} to the product of an upper triangular matrix and its transpose (which is a lower triangular matrix)

$$\mathbf{S} = \mathbf{U}^T \mathbf{U}$$

In Matlab you can invoke this by `U=chol(S)`. Then you can transform Eq. (41) as follows

$$\begin{aligned} \mathbf{H}\mathbf{C} &= \mathbf{S}\mathbf{C}\boldsymbol{\varepsilon} \\ \mathbf{H}\mathbf{C} &= \mathbf{U}^T \mathbf{U}\mathbf{C}\boldsymbol{\varepsilon} \\ (\mathbf{U}^T)^{-1} \mathbf{H}\mathbf{C} &= \mathbf{U}\mathbf{C}\boldsymbol{\varepsilon} \\ (\mathbf{U}^{-1})^T \mathbf{H}\mathbf{U}^{-1} \mathbf{U}\mathbf{C} &= \mathbf{U}\mathbf{C}\boldsymbol{\varepsilon} \\ \tilde{\mathbf{H}}\mathbf{U}\mathbf{C} &= \mathbf{U}\mathbf{C}\boldsymbol{\varepsilon} \\ \tilde{\mathbf{H}}\tilde{\mathbf{C}} &= \tilde{\mathbf{C}}\boldsymbol{\varepsilon} \end{aligned} \tag{44}$$

Here the definition of $\tilde{\mathbf{H}}$ is obvious and we have used the fact that $(\mathbf{A}^T)^{-1} = (\mathbf{A}^{-1})^T$.

Thus, Cholesky factorization can be used to convert a non-orthogonal eigenvalue problem [Eq. (41)] to an orthogonal eigenvalue problem equivalent to Eq. (29). The eigenvalues are unchanged. The eigenvectors $\tilde{\mathbf{C}}$ are directly orthogonal

$$\tilde{\mathbf{C}}^T \tilde{\mathbf{C}} = \mathbf{1}$$

The eigenvectors of the original non-orthogonal problem \mathbf{C} are related to those of Cholesky-factorized orthogonal eigenvalue problem by

$$\mathbf{U}\mathbf{C} = \tilde{\mathbf{C}}$$

which is a set of linear equations. In Matlab, this (or any) set of linear equations can be

solved with the backslash operator `\`, which is also called `mldivide`.

Note that if the \mathbf{S} matrix is positive definite, then it is faster to invoke the generalized eigenvalue routine with the specific `'chol'` flag, namely `[v d]=eig(hmat,smat,'chol')`.

3. Factorization of a symmetric general overlap matrix

If the overlap matrix is not positive definite, then implementation of the generalized eigenvalue routine requires implicit use of the so-called “generalized Schur” or “QZ” decomposition. For more detail the interested reader should consult a more specialized text [Golub, G.H. and Van Loan, C.F. *Matrix Computations* (Johns Hopkins University Press, 3rd ed. 1996) ISBN 0-8018-5414-8. (Section 7.7 at p. 313)].

Problem 6

Let \mathbf{A} be an arbitrary positive definite, symmetric 2×2 matrix. It can be factored as

$$\mathbf{A} = \mathbf{U}^T \mathbf{U}$$

Determine the matrix elements of \mathbf{U} in terms of those of \mathbf{A} .

Then, if you feel adventurous, do the same exercise for a 3×3 matrix. Be sure to use Matlab’s symbolic capabilities to help you here.

4. 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 consider just two non-orthogonal functions ϕ_i with $i = 1, 2$. Assumer, for convenience, that the functions are normalized but not orthogonal, in other words $S_{11} = S_{22} = 1$. Define a new set of functions $\tilde{\phi}_i$, which we will construct to be orthogonal. Let us start by setting $\tilde{\phi}_1$ equal to ϕ_1 . Then, we can take a linear combination of ϕ_1 and ϕ_2 to

construct a second function $\tilde{\phi}_2$ which is orthogonal to $\tilde{\phi}_1$ as well as being normalized

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

We will choose the coefficients A_2 and B_2 to ensure this orthogonality and normalization constraints. Mathematically, we require that $\langle \tilde{\phi}_1 | \tilde{\phi}_2 \rangle = 0$ and $\langle \tilde{\phi}_2 | \tilde{\phi}_2 \rangle = 1$. The first condition implies that

$$0 = \langle \bar{\phi}_1 | \bar{\phi}_2 \rangle = \langle \phi_1 | A_2\phi_1 \rangle + \langle \phi_1 | B_2\phi_2 \rangle = A_2S_{11} + B_2S_{12} = A_2 + B_2S_{12}$$

This leads to the following relation between A_2 and B_2

$$A_2 = -B_2S_{12}$$

The second condition implies that

$$1 = \langle \bar{\phi}_2 | \bar{\phi}_2 \rangle = A_2^2S_{11} + B_2^2S_{22} + 2A_2B_2S_{12} = A_2^2 + B_2^2 + 2A_2B_2S_{12}$$

Substitution from the previous equation gives

$$1 = B_2^2S_{12}^2 + B_2^2 - 2B_2^2S_{12}^2$$

which can be solved to give (taking the positive square root)

$$B_2 = [1 - S_{12}^2]^{-1/2}$$

and then

$$A_2 = -S_{12} [1 - S_{12}^2]^{-1/2}$$

For three states, we start with the two functions $\tilde{\phi}_1$ and $\tilde{\phi}_2$ of the previous paragraph and then orthogonalize the third basis function to these. We write

$$\tilde{\phi}_3 = A_3\tilde{\phi}_1 + B_3\tilde{\phi}_2 + C_3\phi_3 \tag{45}$$

We know that $\tilde{\phi}_1$ and $\tilde{\phi}_2$ are normalized and orthogonal to each other. We need then

$$\langle \tilde{\phi}_1 | \tilde{\phi}_3 \rangle = 0 \quad (46)$$

and

$$\langle \tilde{\phi}_2 | \tilde{\phi}_3 \rangle = 0 \quad (47)$$

and

$$\langle \tilde{\phi}_3 | \tilde{\phi}_3 \rangle = 1 \quad (48)$$

From Eq. (45) we see that the constraint contained in Eq. (46) is equivalent to

$$\begin{aligned} 0 &= A_3 \langle \tilde{\phi}_1 | \tilde{\phi}_1 \rangle + B_3 \langle \tilde{\phi}_1 | \tilde{\phi}_2 \rangle + C_3 \langle \tilde{\phi}_1 | \tilde{\phi}_3 \rangle \\ &= A_3 \times 1 + B_3 \times 0 + C_3 S_{13} \\ &= A_3 + C_3 S_{13} \end{aligned} \quad (49)$$

Similarly, Eq. (47) simplifies to

$$\begin{aligned} 0 &= A_3 \langle \tilde{\phi}_1 | \tilde{\phi}_2 \rangle + B_3 \langle \tilde{\phi}_2 | \tilde{\phi}_2 \rangle + C_3 \langle \tilde{\phi}_2 | \tilde{\phi}_3 \rangle \\ &= A_3 \times 0 + B_3 \times 1 + C_3 \tilde{S}_{23} \\ &= B_3 + C_3 \tilde{S}_{23} \end{aligned} \quad (50)$$

where $\tilde{S}_{23} = \langle \tilde{\phi}_2 | \phi_3 \rangle$. Finally, Eq. (48) simplifies to

$$\begin{aligned} 1 &= A_3^2 \langle \tilde{\phi}_1 | \tilde{\phi}_1 \rangle + B_3^2 \langle \tilde{\phi}_2 | \tilde{\phi}_2 \rangle + C_3^2 \langle \tilde{\phi}_3 | \tilde{\phi}_3 \rangle + 2A_3 B_3 \langle \tilde{\phi}_1 | \tilde{\phi}_2 \rangle + 2A_3 C_3 \langle \tilde{\phi}_1 | \phi_3 \rangle + 2B_3 C_3 \langle \tilde{\phi}_2 | \phi_3 \rangle \\ &= A_3^2 + B_3^2 + C_3^2 + 2A_3 B_3 \times 0 + 2A_3 C_3 S_{13} + 2B_3 C_3 \tilde{S}_{23} \\ &= A_3^2 + B_3^2 + C_3^2 + 2A_3 C_3 S_{13} + 2B_3 C_3 \tilde{S}_{23} \end{aligned} \quad (51)$$

This is complicated, no? You want to use the preceding three equations to solve for the three coefficients A_3 , B_3 , and C_3 . But this is complicated, since Eqs. (50) and (51) involve the overlaps between the orthogonalized $\tilde{\phi}_2$ and the original ϕ_3 . These overlaps are linear combinations of the overlaps S_{13} and S_{23} . It's a real mess to keep track of all this algebra without making mistakes.

In Gram-Schmidt orthogonalization, one is successively constructing a linear combination

of the N^{th} function with all preceding functions ($1 \dots N - 1$) to preserve orthogonality. Let us start with N basis functions, which we will represent by a column vector

$$\mathbf{\Phi}^{(1)} = \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \vdots \\ \phi_N \end{bmatrix}$$

We then orthogonalize ϕ_2 to ϕ_1 , obtaining

$$\mathbf{\Phi}^{(2)} = \begin{bmatrix} \phi_1 \\ \tilde{\phi}_2 \\ \phi_3 \\ \phi_4 \\ \vdots \\ \phi_N \end{bmatrix}$$

We can write this in matrix notation as

$$\mathbf{\Phi}^{(2)} = \mathbf{D}^{(2)T} \mathbf{\Phi}^{(1)}$$

where

$$\mathbf{D}^{(2)} = \begin{bmatrix} 1 & A_2 & 0 & \cdots & 0 \\ 0 & B_2 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix}$$

Then we orthogonalize the third function, getting

$$\Phi^{(3)} = \begin{bmatrix} \phi_1 \\ \tilde{\phi}_2 \\ \tilde{\phi}_3 \\ \phi_4 \\ \vdots \\ \phi_N \end{bmatrix}$$

or

$$\Phi^{(3)} = (\mathbf{D}^{(2)}\mathbf{D}^{(3)})^T \Phi^{(1)} = \mathbf{D}^{(3)T} \mathbf{D}^{(2)T} \Phi^{(1)}$$

where

$$\mathbf{D}^{(3)} = \begin{bmatrix} 1 & 0 & A_3 & \cdots & 0 \\ 0 & 1 & B_3 & \cdots & 0 \\ 0 & 0 & C_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix}$$

The algebra of this procedure, as well as the need to keep rearranging the original overlap matrix, becomes more and more complicated as we proceed to a larger number of basis functions. Ugh!

5. Summary of methods

To summarize, if you chose to expand in a nonorthogonal basis set, there are three alternatives:

(a) Determine the eigenvalues (the diagonal matrix \mathbf{E}) and eigenvectors (\mathbf{C}) of Eq. (41) directly using a generalized eigenvalue call [e.g. `eig(hmat, smat)` in Matlab].

(b) Explicitly use Cholesky factorization as outlined in Sec. IIF 2.

(c) Use Gram-Schmidt orthogonalization to construct N orthonormal states by constructing, successively, the transformation matrices $\mathbf{D}^{(N)}$ defined in the preceding subsection. Then transform the Hamiltonian into the basis of Gram-Schmidt orthogonalized states

$$\mathbf{H}_{\text{GS}} = \mathbf{D}^T \mathbf{H} \mathbf{D} \quad (52)$$

where

$$\mathbf{D} = \mathbf{D}^{(N)} \mathbf{D}^{(N-1)} \dots \mathbf{D}^{(2)} \quad (53)$$

Since the Gram-Schmidt orthogonalized basis states are orthonormal, you can get the eigenvalues and the eigenvectors in the Schmidt orthogonalized basis from a standard diagonalization of the transformed Hamiltonian matrix $\tilde{\mathbf{H}}_{\text{GS}}$.

Now, \mathbf{S} is diagonalized in the Gram-Schmidt basis, so that

$$\mathbf{D}_{\text{GS}}^T \mathbf{S} \mathbf{D}_{\text{GS}} = \mathbf{1}$$

which can be rearranged to

$$\mathbf{S} = (\mathbf{D}_{\text{GS}}^{-1})^T \mathbf{D}_{\text{GS}}^{-1}$$

(Note that the inverse of the matrix \mathbf{D} is not its transpose. The transformation from the non-orthogonal basis to the orthogonal Gram-Schmidt basis is not an orthogonal transformation).

Similarly, Eq. (52) can be rearranged as

$$\mathbf{H} = (\mathbf{D}_{\text{GS}}^{-1})^T \mathbf{H}_{\text{GS}} \mathbf{D}_{\text{GS}}^{-1}$$

In the original basis the eigenequations are

$$\mathbf{H} \mathbf{C} = \mathbf{S} \mathbf{C} \epsilon$$

Substitution here of the two preceding equations (for \mathbf{H} and \mathbf{S}) gives

$$(\mathbf{D}_{\text{GS}}^{-1})^T \mathbf{H}_{\text{GS}} \mathbf{D}_{\text{GS}}^{-1} \mathbf{C} = (\mathbf{D}_{\text{GS}}^{-1})^T \mathbf{D}_{\text{GS}}^{-1} \mathbf{C} \epsilon$$

Multiplication up by $(\mathbf{D}_{\text{GS}})^T$ gives [note that $(\mathbf{D}_{\text{GS}})^T$ is the inverse of $(\mathbf{D}_{\text{GS}}^{-1})^T$].

$$\mathbf{H}_{\text{GS}} \mathbf{D}_{\text{GS}}^{-1} \mathbf{C} = \mathbf{D}_{\text{GS}}^{-1} \mathbf{C} \epsilon$$

In the Gram-Schmidt basis the eigenequations are

$$\mathbf{H}_{\text{GS}}\mathbf{C}_{\text{GS}} = \mathbf{C}_{\text{GS}}\boldsymbol{\epsilon}$$

Comparing these last two equations, we see that the eigenvectors \mathbf{C} in the original basis can be related to the eigenvectors in the Gram-Schmidt basis by

$$\mathbf{C}_{\text{GS}} = \mathbf{D}_{\text{GS}}^{-1}\mathbf{C}$$

or

$$\mathbf{C} = \mathbf{D}_{\text{GS}}\mathbf{C}_{\text{GS}} \tag{54}$$

I have put on the website a [Matlab script](#) which illustrates in detail the linear algebra contained in this section. Download this file and run it!

Problem 7

Suppose that you have a Hamiltonian matrix given by

$$\mathbf{H} = \begin{bmatrix} 0.29 & -0.44 \\ -0.44 & -0.39 \end{bmatrix}$$

and an overlap matrix given by

$$\mathbf{S} = \begin{bmatrix} 1 & 0.68 \\ 0.68 & 1 \end{bmatrix}$$

Use method (c) above (Gram-Schmidt orthogonalization) to obtain (i) the eigenvalues, (ii) the eigenvectors (\mathbf{C}_{gs}) in the basis of the Gram-Schmidt orthogonalized states, and, (iii), from Eq. (54), the eigenvectors in the original basis (\mathbf{C})

Check your results by comparing with the result of a generalized eigenvalue call `[C,epsilon]=eig(H,S)` which will yield the eigenvalues and the eigenvectors in the original basis.

G. MacDonald's Theorem

As discussed in subsection II E, the determinant of the matrix $[\mathbf{H} - E_{var}\mathbf{1}]$ is a polynomial in E_{var} , which we will call $f(E)$, of order equal to the number of basis functions N . Non-trivial solutions exist only for values of the energy for which this determinant vanishes. These values correspond to the “roots” of this polynomial function of E .

Let's assume we're using 3 basis functions. Let's further assume that the matrix elements of the Hamiltonian are all real. We know, in addition, that the matrix is symmetric, so that $H_{ij} = H_{ji}$. We can use the rules for evaluating a 3×3 determinant, so that, similarly to Eq. (35), the secular determinant is

$$\begin{vmatrix} H_{11} - E & H_{12} & H_{13} \\ H_{12} & H_{22} - E & H_{23} \\ H_{13} & H_{23} & H_{33} - E \end{vmatrix} \\ = (H_{11} - E)(H_{22} - E)(H_{33} - E) + 2H_{12}H_{23}H_{13} - H_{13}^2(H_{22} - E) + \dots \quad (55)$$

The qualitative dependence on E of this cubic function is depicted in Fig. (2). There will be, in general, three values of E for which $f(E)=0$. These are shown as small circles in Fig. (2). Diagonalization of the matrix H will yield 3 eigenvalues and

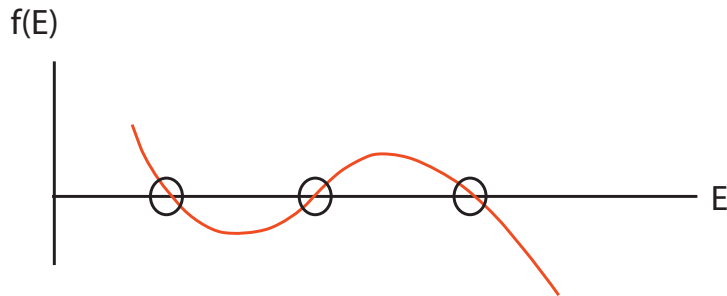


FIG. 2. Dependence on energy of the determinant $|\mathbf{H} - E\mathbf{1}|$ for a 3×3 system.

3 eigenvectors, which we 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 of the system. 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 other words we replace the first N basis functions by the linear combination of these functions that diagonalize the $N \times N$ matrix of the Hamiltonian, and then add on the original basis functions ϕ_{N+1} . In this

new $(N + 1) \times (N + 1)$ basis, the matrix of the Hamiltonian is

$$\mathbf{H}^{(N+1)} = \begin{bmatrix} E_1^{(N)} & \cdots & 0 & h_1 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & E_N^{(N)} & h_N \\ h_1 & \cdots & h_N & h_{N+1} \end{bmatrix} \quad (56)$$

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 $E_i^{(N)}$ denotes the i^{th} linear variational energy in the basis of N functions. To obtain the energies in the $N + 1 \times N + 1$ basis, we need to find the roots of the determinant of $[\mathbf{H}^{(N+1)} - \mathbf{E}\mathbf{I}]$. Explicitly, this is

$$\begin{vmatrix} E_1^{(N)} - E & \cdots & 0 & h_1 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & E_N^{(N)} - E & h_N \\ h_1 & \cdots & h_N & h_{N+1} - E \end{vmatrix} = 0 \quad (57)$$

Applying the rules for expansion of a determinant, you expand out Eq. (57) to give

$$(h_{N+1} - E) \prod_{i=1}^N (E_i^{(N)} - E) - \sum_{i=1}^N h_i^2 \prod_{\substack{j=1 \\ j \neq i}}^N (E_j^{(N)} - E) = 0 \quad (58)$$

For an explicit example, 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

$$\begin{vmatrix} E_1^{(2)} - E & 0 & h_1 \\ 0 & E_2^{(2)} - E & h_2 \\ h_1 & h_2 & h_3 - E \end{vmatrix} = (E_1^{(2)} - E)(E_2^{(2)} - E)(h_3 - E) - h_2^2(E_1^{(2)} - E) - h_1^2(E_2^{(2)} - E) = f(E) \quad (59)$$

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, $f(E)$ goes from negative to positive at E increases from $E_1^{(2)}$ to $E_2^{(2)}$. In other words there will be one root between $E_1^{(2)}$ and $E = E_2^{(2)}$. Now, if E goes to negative infinity,

then, Eq. (59) shows that

$$\lim_{E \rightarrow -\infty} f(E) = -E^3, \quad (60)$$

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

Problem 8

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 $N = 3$. This interleaving will continue as N increases, as shown schematically in Fig. (3). Consequently,

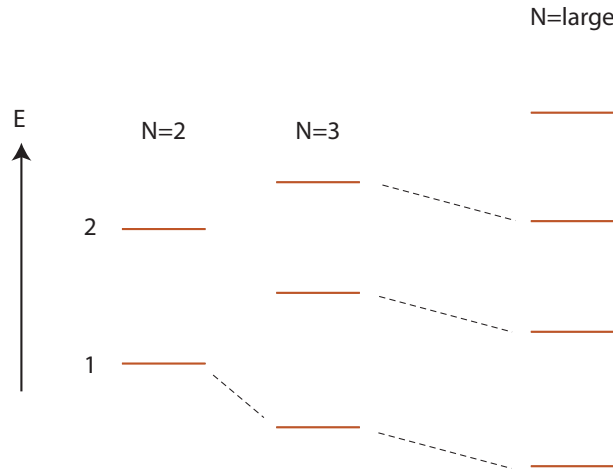


FIG. 3. Illustration of the placement of the linear variational roots as N , the size of the basis set, increases.

we see that 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 [E. Hylleraas and B. Undheim, *Z. Phys.*, **65**, 759 (1930)] and MacDonald [J. K. L. MacDonald, *Phys. Rev.*, **43**, 830 (1933)].

H. 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

$$H(x) = V(x) - \frac{1}{2m} \frac{d^2}{dx^2} \quad (61)$$

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

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} \quad (62)$$

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

$$\langle \phi_i | H | \phi_j \rangle = \delta_{ij} E_j \quad (63)$$

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, [M. Abramowitz and I. Stegun, *Handbook of Mathematical Functions*, Chap. 25, p. 885], namely

$$\int_{x_0}^{x_N} f(x) dx \cong h \left[\frac{1}{2} f(x = x_0) + f(x = x_1) + \cdots + f(x = x_{N-1}) + \frac{1}{2} f(x_N) \right] \quad (64)$$

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

$$\langle \phi_i | H | \phi_j \rangle \cong h \sum_{k=0}^N \phi_i(x_k) \left[V(x_k) - \frac{1}{2m} \frac{d^2}{dx^2} \right] \phi_j(x_k) \quad (65)$$

Note that we have ignored the factors of $\frac{1}{2}$ which appear in Eq. (64) because we assume that the range of integration is large enough that the wavefunctions ϕ_i vanish at the end points for all values of i . In other words, $\phi_i(x_0) = \phi_j(x_0) = \phi_i(x_N) = \phi_j(x_N) = 0$

To evaluate the second derivative term, we use a 3-point finite difference approximation

for the 2nd derivative. [3] This is

$$\left. \frac{d^2 f}{dx^2} \right|_{x=x_k} \cong \frac{f(x=x_{k+1}) - 2f(x=x_k) + f(x=x_{k-1}))}{h^2} = \frac{f_{k+1} + f_{k-1} - 2f_k}{h^2} \quad (66)$$

Thus, the expression for the ij^{th} matrix element of H is

$$\langle \phi_i | H | \phi_j \rangle \cong \sum_{k=0}^N h \phi_i(x_k) \left\{ V(x_k) \phi_j(x_k) - \frac{1}{2m} [\phi_j(x_{k+1}) - 2\phi_j(x_k) + \phi_j(x_{k-1}))] \right\} \quad (67)$$

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. (67) can be written as

$$\langle \phi_i | H | \phi_j \rangle \cong h \sum_{k=0}^N c_{ki} \left\{ V(x_k) c_{kj} - \frac{1}{2m} [c_{k+1,j} - 2c_{kj} + c_{k-1,j}] \right\} \quad (68)$$

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

$$\langle \phi_i | H | \phi_j \rangle \cong h \mathbf{c}_i^T [\mathbf{V} + \mathbf{T}] \mathbf{c}_j \quad (69)$$

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.)

Let us now divide the column vectors by $h^{-1/2}$ to get a new column vector

$$\mathbf{d}_i = h^{-1/2} \mathbf{c}_i \quad (70)$$

so that Eq. (69) becomes

$$\langle \phi_i | H | \phi_j \rangle \cong \mathbf{d}_i^T [\mathbf{V} + \mathbf{T}] \mathbf{d}_j \quad (71)$$

The full matrix of the Hamiltonian, with matrix elements $\langle \phi_i | H | \phi_j \rangle$ given by Eq. (69), can then be written in matrix notation as

$$\mathbf{H} = \mathbf{D}^T [\mathbf{V} + \mathbf{T}] \mathbf{D} \quad (72)$$

where each column of the matrix \mathbf{D} is given by \mathbf{d}_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 $\mathbf{H} = \mathbf{E} = \mathbf{D}^T [\mathbf{V} + \mathbf{T}] \mathbf{D}$.

Consequently, since $\mathbf{D}^T [\mathbf{V} + \mathbf{T}] \mathbf{D}$ is equal to a diagonal matrix, and the matrices \mathbf{V} and \mathbf{T} are symmetric, the matrix \mathbf{D} is non other than the matrix of eigenvectors which diagonalize the matrix $[\mathbf{V} + \mathbf{T}]$. The eigenvalues are, in the limit $h \rightarrow 0$, the true energies.

The eigenvectors \mathbf{d}_i arising from this diagonalization are proportional [Eq. (70)] to the values of the wave functions at the points $x = x_k$. To check that everything is consistent, remember that these wave functions should be orthonormal, as expressed in Eq. (62). If we were to evaluate the overlap matrix elements by trapezoidal integration equivalent to Eq. (64), using the \mathbf{c}_i eigenvectors, we would obtain

$$\langle \phi_i | \phi_j \rangle = \delta_{ij} = \sum_{k=0}^N h c_{kj} c_{ki} = h \mathbf{c}_j^T \mathbf{c}_i = \mathbf{d}_j^T \mathbf{d}_i \quad (73)$$

The matrix \mathbf{D} arising from computer diagonalization of the matrix of the Hamiltonian [Eq. (72)] will be orthogonal, so that $\mathbf{D}^T \mathbf{D} = \mathbf{1}$, or, element-by-element, $\mathbf{d}_i^T \mathbf{d}_j = \delta_{ij}$. Consequently, we conclude from Eq. (73) that the ϕ_i eigenvectors are orthogonal. The values of the wavefunctions at the points $x = x_k$ are thus given by the c_{ki} coefficients. This method then provides discrete representations (more often called *discrete variable representations*, hence the name, DVR) of the wavefunctions. As the step size h goes to zero, these DVR functions become the true wave functions.

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

$$\left. \frac{d^2 f}{dx^2} \right|_{x=x_k} = \frac{-f_{k+2} + 16f_{k+1} - 30f_k + 16f_{k-1} - f_{k-2}}{12h^2} \quad (74)$$

which implies that the matrix \mathbf{T} has five non-zero bands.

Problem 9

The Matlab script `dvr_quartic.m` carries out the DVR procedure for a quartic oscillator approximation to the H_2 harmonic oscillator with $k_4 = 11.3173 \text{ bohr}^{-4}$. The script is set up to use a three-point approximation to the \mathbf{T} matrix. Input parameters are the mass in atomic units μ (for H_2 $\mu=0.5036$ atomic mass units = 918.58 atomic units) the value of the range `delr` with $|r - r_e| \leq \text{delr}$ bohr, and the approximate spacing `hh`. The number of points is then determined as $M = \text{floor}(2 * \text{delr} / \text{hh}) + 1$ (we want M to be an integer, which is ensured by the `floor` function, which reduces its argument to the nearest integer). Finally, the exact spacing is determined as $h = (\text{rmax} - \text{rmin}) / (M - 1)$.

(a) Keeping the range fixed at `delr` = 0.6, and decreasing the spacing, determine the maximum value of h for which you can converge the energies of the first two levels to within $1e-5$ hartree ($10 \mu\text{hartree}$).

(b) For a harmonic oscillator, the frequency varies inversely as the square root of the mass. Assuming a quartic potential with the same value of k_4 , determine the dependence on the reduced mass of the energy of the lowest level for H_2 , HD , and D_2 . Do these three energies show the same $E \sim \mu^{-1/2}$ dependence as the harmonic oscillator?

Problem 10

Consider a double-well potential

$$V(x) = E_o(Cx^4 - x^2)$$

(a) Plot the potential for the following choice of parameters: $E_o = 2 \times 10^{-4}$ hartree/bohr² and $C = 0.045 \text{ bohr}^{-2}$.

(b) Model each of the two equivalent wells as a harmonic oscillator. Determine the effective force constant and obtain the energy as $\varepsilon = V_{min} + \frac{1}{2} \sqrt{k/\mu}$, where V_{min} is the

energy of the minimum of each of the wells. Assume the mass is that of a proton (mass $\mu = 1$ atomic mass unit = 1837 atomic units).

(c) rewrite the script `dvr_quartic.m` to obtain the energies for the first 6 levels of this double-well potential for a proton (mass $\mu = 1$ atomic mass unit = 1837 atomic units). The energy of the lowest state should be close to what you obtained in part (b). Superimpose the position of these levels on your plot of the potential.

(d) Plot on one plot the wavefunctions of the first two states.