Solving the vibrational equations using FBR and DVR methods

Problem 1: Try to solve the following Schrödinger equation of one-dimensional harmonic oscillator (in atomic units):

$$(T(x)+V(x))\Psi(x) = E\Psi(x) \tag{1}$$

$$T(x) = -\frac{1}{2\mu}\frac{d^2}{dx^2}, \quad V(x) = \frac{1}{2}kx^2 + bx \tag{2}$$

With k=2000, b=0.05

[Can you find the analytic solution of this equation?]

In fact, this problem is easy to solve. The solutions are:

$$E_n = (n+\frac{1}{2})\omega - \frac{b^2}{2k} \tag{3}$$

$$\Psi_n = N_n e^{-\frac{1}{2}\alpha(x+\frac{b}{k})^2} H_n(\alpha(x+\frac{b}{k})) \tag{4}$$

Where, $\omega = \sqrt{\frac{k}{\mu}}, \alpha = (k\mu)^{\frac{1}{4}}$ \hfill (5)

$$N_n = \sqrt{\frac{\alpha}{\sqrt{\pi}2^n n!}} \tag{6}$$

Exercise 1: Plot the wave functions of the lowest 6 states.

Now, I try to explain you how to use FBR and DVR methods to solve the general one-dimensional Schrödinger equation (eq. 1).

FBR method

FBR: Finite Basis Representation

In quantum chemistry, we have the variational method in which the wave function is expressed by:

$$\psi(x) = \sum_{m=0}^{M-1} C_m \varphi_m(x) \tag{7}$$

Where, M is the number of the basis functions, C_m is the expansion coefficient, $\varphi_m(x)$ the basis function. Substitute eq. (7) into eq. (1), one obtain the following matrix eigenvalue problem:

$$[T+V]C = CE \tag{8}$$

Where the element of the kinetic matrix is: $T_{m'm} = \left\langle \varphi_{m'} / \hat{T} / \varphi_m \right\rangle$ (9)

The elements of the potential matrix is $V_{m'm} = \left\langle \varphi_{m'} / V / \varphi_m \right\rangle$ (10)

Usually, we use harmonic oscillator or Morse oscillator wave functions as the basis set. In this case, the kinetic matrix is diagonal and easy to calculate, while the potential matrix is a full matrix and difficult to calculate (although in the simple case of **Problem 1**, you can find the potential matrix has a simple form). For the purpose of computational efficiency, we often use HEG quardrature [Harris et al, J. Chem. Phys. 43, 1515 (1965)] (which is indeed a type of Gauss quardrature) to calculate the potential matrix. The main steps of this procedure is as follows:

(1) Choose the basis set: $\varphi_0(x), \varphi_1(x), \ldots, \varphi_{M-1}(x)$

(2) Calculate the matrix: $A_{mn} = \left\langle \varphi_m / x / \varphi_m \right\rangle$ (11)

(3) Diagonalize the symmetric matrix A to produce the eigenvalue: $x_0, x_1, \ldots x_{M-1}$ and eigenvector: $B_{ml}(m = 0, M-1, l = 0, M-1)$.

(4) Any integrals of function of x between the basis set can be then easily calculated:

$$F_{m'm} = \left\langle \varphi_{m'} / f(x) / \varphi_m \right\rangle = \sum_{l=0}^{M-1} B_{m'l} f(x_l) B_{ml} \tag{12}$$

In the case of potential matrix,

$$V_{m'm} = \langle \varphi_{m'} / V(x) / \varphi_m \rangle = \sum_{l=0}^{M-1} B_{m'l} V(x_l) B_{ml} \tag{13}$$

Once you obtain the kinetic matrix and potential matrix, use a standard diagonalization method such as TQL method to produce the eigenvalue E_n and the corresponding wave function:

$$\psi_n(x) = \sum_{m=0}^{M-1} C_{mn} \varphi_m(x) \tag{14}$$

Exercise 2: Use FBR method to solve **Problem 1**. The basis functions are:

$\varphi_n = \sqrt{\dfrac{\beta}{\sqrt{\pi} 2^n n!}} e^{-\frac{1}{2}\beta x^2} H_n(\beta x)), n = 0,1,.....,M-1$. The value of β is not necessary

equal to α. I suggest you perform the calculation with M=50 and 100, and $\beta = \alpha, 0.8\alpha, 1.3\alpha.$ Then compare the results with the exact results obtained from eq. (3) and (4).

DVR method

DVR: Discrete Variable Representation

Because the potential matrix in FBR is a full matrix and computational very time-consuming, some researchers find an alternative way (DVR) to solve the eigenvalue problem. One can rewrite eq. (13) in the matrix form:

$$V = B\tilde{V}B^+ \tag{15}$$

Where, $\tilde{V}_{ll'} = v(x_l)\delta_{ll'}$. Substitute eq. (15) into eq. (8),

$$[T + B\tilde{V}B^+]C = CE \tag{16}$$

Multiple the above eq. On the left by B^+, and use the relation $B^+B = I$, leads to:

$$[B^+TB + \tilde{V}]B^+C = B^+CE \tag{17}$$

Set: $B^+TB = \tilde{T}, B^+C = \tilde{C}$, the above eq. becomes:

$$[T + \tilde{V}]\tilde{C} = \tilde{C}E \tag{18}$$

where,

$$T_{l'l} = \sum_{m'=0}^{M-1}\sum_{m=0}^{M-1} B_{m'l'} T_{m'm} B_{ml}, \tilde{V}_{l'l} = V(x_l)\delta_{l'l} \tag{19}$$

Compare eq. (18) and (8), you will find:

(1) the eigenvalue in both DVR and FBR is identical;

(2) the index of matrix (m,m$^{'}$) in FBR is the notation of basis function, whereas the index of matrix(l,l$^{'}$) in DVR is the notation of discretized coordinates;

(3) the eigenvector from the DVR eigenproblem is related to wave function by:

$$C_{mn} = \sum_{l=0}^{M-1} B_{ml}\tilde{C}_{1n}, \psi_n(x) = \sum_{m=0}^{M-1} C_{mn}\varphi_m(x) \tag{20}$$

So you can also see that the DVR points $x_0, x_1, \ldots x_{M-1}$ is dependent on the basis set used.

Exercise 3: Use DVR method to solve **Problem 1.** The basis functions are:

$\varphi_n = \sqrt{\dfrac{\beta}{\sqrt{\pi}2^n n!}}e^{-\frac{1}{2}\beta x^2} H_n(\beta x)), n = 0,1,\ldots, M-1$. M=50 and 100, and $\beta = 0.8\alpha$. The energies and the wave functions should be identical to the results obtained in **Exercise 2** with the same M and β.

There are some other basis sets often used in DVR method. For example, Colbert and Miller (J. Chem. Phys. 96, 1982(1992)) suggested a sinc-DVR points. In this approach, $\varphi_n(x) = (\dfrac{2}{b-a})^{\frac{1}{2}} \sin[\dfrac{n\pi(x-a)}{b-a}]$ n=1,……M

(21)

(a,b) is the integral of the coordinate x of interest. The DVR points is equally spaced:

$$x_l = a + \frac{(b-a)}{M+1} l, l = 1,\ldots\ldots, M \qquad (22)$$

The DVR of the potential energy is simply as:

$$\tilde{V}_{l'l} = V(x_l)\delta_{l'l} \qquad (23)$$

The DVR of the kinetic energy is given by:

$$\tilde{T}_{l'l} = \frac{1}{2\mu} \frac{(-1)^{l'-l} \pi^2}{2(b-a)^2} \left\{ \frac{1}{\sin^2 \dfrac{\pi(l'-l)}{2(M+1)}} - \frac{1}{\sin^2 \dfrac{\pi(l'+l)}{2(M+1)}} \right\}, l' \neq l \qquad (24)$$

$$\tilde{T}_{l'l} = \frac{1}{2\mu} \frac{\pi^2}{2(b-a)^2} \left\{ \frac{(2(M+1)^2+1)}{3} - \frac{1}{\sin^2 \dfrac{\pi l}{(M+1)}} \right\} \qquad (25)$$

One can demonstrate that at the DVR points x_l, the wave function is simply as:

$$\psi_n(x_l) = \tilde{C}_{\ln} \qquad (26)$$

except a normalization factor.

Exercise 4: Use sinc-DVR method to solve **Problem 1.** Compare the energies with the previous exercises. Plot the wave function for the lowest states and compare with **Exercise 1**.

Atomic units

The atomic units are usually in quantum chemical calculations. For convenient, other units are used when read or write. In the atomic units, $\hbar = \dfrac{h}{2\pi} = 1$,

Mass: 1au=1.0/1822.89 amu

For example, the mass of ^{16}O=15.994914 amu =29156.96878 au

Length (bohr): 1au = 0.5291771 Å

Energy (hartree): 1au =27.2114 eV = 219474 cm^{-1} = 2625.50 KJ/mole

Time: 1au = 0.0241890 fs