Appendix B

Fourier-basis DVR method

The discrete variable representation (DVR) methods, pioneered by Light and coworkers [44, 45], have established themselves as a powerful tool for solving both time-independent [44], as originally introduced, and time-dependent [161, 162] quantum mechanical problems. In this work these techniques are used for finding eigenvalues and eigenfunctions of the Hamilton operator of the equation (4.22) in Chapter 4. The conventional methods for the solution of eigenvalue problems, for example, the Fourier grid Hamiltonian (FGH) method, require modifications in order to allow the treatment of the first coordinate derivatives, present in the equation (4.22). In this Appendix, a convenient analytical expression for the matrix elements of a first coordinate derivative operator within the Fourier-basis DVR formalism.

All DVR's are based on the expansion of a wave function in an orthonormal basis set $\phi_i(x); i = 1, N$ and utilization of a quadrature rule. Normally, the Gaussian quadrature on a set of points x_i with corresponding weights w_i is used. For example,

$$\Psi(x,t) = \sum_{i}^{N} a_i(t)\phi_i(x), \tag{B.1}$$

where the time-dependent expansion coefficients $a_i(t)$ are given by

$$a_i(t) = \sum_j^N w_j \phi_i^*(x_j)\Psi(x_j, t) \tag{B.2}$$

Combining equations (B.1) and (B.2), we get

$$\begin{aligned}\Psi(x,t) &= \sum_i^N \sum_j^N w_j \phi_i^*(x_j)\Psi(x_j,t)\phi_i(x) \\ &= \sum_j^N \Psi_j \psi_j(x),\end{aligned} \tag{B.3}$$

where the functions

$$\psi_j(x) = \sqrt{w_j} \sum_i^N \phi_i^*(x_j)\phi_i(x) \tag{B.4}$$

form a set of orthonormal coordinate eigenfunctions in the discrete representation, and

$$\Psi_j = \sqrt{w_j}\Psi(x_j, t) \tag{B.5}$$

is the amplitude of the wave function on the j-th basis function. The weight factor $\sqrt{w_j}$ ensures the orthonormality of the basis. The n^{th} order derivatives of the wave function are obtained from

$$\frac{\partial^n \Psi(x,t)}{\partial x^n} = \sum_j^N \Psi_j \frac{\partial^n \psi_j(x)}{\partial x^n}, \tag{B.6}$$

where

$$\frac{\partial^n \psi_j(x)}{\partial x^n} = \sqrt{w_j} \sum_i^N \phi_i^*(x_j) \frac{\partial^n \phi_i(x)}{\partial x^n}, \tag{B.7}$$

So far no assumptions were made on the particular basis functions, the only condition imposed on them was that of orthonormality. In this work the Fourier functions (i.e., the eigenfunctions of a particle in a box) shall be utilized. This choice of basis set makes the technique conceptually similar to the FGH method.

Let's consider a one-dimensional quantum system with coordinate $x \in (a,b)$. The kinetic energy operator is given by

$$\hat{\mathrm{T}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{B.8}$$

It is assumed here, that the wave function vanishes at the endpoints a and b. The grid x_i is equally spaced

$$x_i = a + (b-a)i/N, i = 1, ..., N-1 \tag{B.9}$$

and the associated functions for this grid are Fourier functions

$$\phi_n(x) = \sqrt{\frac{2}{b-a}}\sin\left[\frac{\pi n(x-a)}{b-a}\right] \tag{B.10}$$

The DVR representation of the kinetic energy operator (B.8), according to (B.7) is given by

$$\mathrm{T}_{jk} = -\frac{\hbar^2}{2m}\Delta x\sum_{n=1}^{N-1}\phi_n(x_j)\phi_n''(x_k), \tag{B.11}$$

where $\Delta x = (b-a)/N$ is the grid spacing. Taking into account the above definitions, we obtain

$$\mathrm{T}_{jk} = \frac{\hbar^2}{2m}\left(\frac{\pi}{b-a}\right)^2\frac{2}{N}\sum_{n=1}^{N-1}n^2\sin\left(\frac{\pi nj}{N}\right)\sin\left(\frac{\pi nk}{N}\right). \tag{B.12}$$

This sum can be evaluated analytically. First, we consider the case $j \neq k$. The product of sine functions under the sum can be rewritten as

$$\sin\left(\frac{\pi nj}{N}\right)\sin\left(\frac{\pi nk}{N}\right) = \frac{1}{2}[\cos(nA) - \cos(nB)], \tag{B.13}$$

where $A = \pi(j-k)/N, B = \pi(j+k)/N$. It is to note that

$$\sum_{n=1}^{N-1}n^2\cos(nA) = -\frac{\partial^2}{\partial A^2}\mathrm{Re}\sum_{n=1}^{N-1}\mathrm{e}^{inA} \tag{B.14}$$

The latter sum is a geometric progression, which yields

$$\mathrm{Re}\sum_{n=1}^{N-1}\mathrm{e}^{inA} = -\frac{1}{2} + \frac{1}{2}\frac{\sin(NA - A/2)}{\sin(A/2)} \tag{B.15}$$

Collecting together equations (B.13),(B.14), and (B.15), we obtain[1]

$$\mathrm{T}_{jk} = \frac{\hbar^2}{2m}\frac{(-1)^{j-k}}{(b-a)^2}\frac{\pi^2}{2}\left[\csc\left(\frac{\pi(j-k)}{2N}\right)^2 - \csc\left(\frac{\pi(j+k)}{2N}\right)^2\right] \tag{B.16}$$

for $j \neq k$. In the case $j = k$, the sum (B.14) becomes

$$\sum_{n=1}^{N-1} n^2 \sin^2\left(\frac{\pi n j}{N}\right) = \frac{1}{2}\sum_{n=1}^{N-1} n^2\left[1-\cos\left(\frac{2\pi n j}{N}\right)\right] = \frac{1}{2}\left[\sum_{n=1}^{N-1} n^2 - \sum_{n=1}^{N-1} n^2\cos\left(\frac{2\pi n j}{N}\right)\right]. \tag{B.17}$$

The first sum in (B.17) is equal to $\frac{1}{6}(N-1)N(2N-1)$, and the second sum has been calculated previously. We obtain

$$\mathrm{T}_{jj} = \frac{\hbar^2}{2m}\frac{1}{(b-a)^2}\frac{\pi^2}{2}\left[\frac{2N^2+1}{3} - \csc^2\left(\frac{\pi j}{N}\right)\right] \tag{B.18}$$

for the diagonal elements of the kinetic energy DVR matrix ($j = k$).

Now we consider the following operator

$$\hat{\mathrm{K}} = \frac{d}{dx}, \tag{B.19}$$

which, with the appropriate multiplier, represents the momentum conjugate to the coordinate x. The DVR expression for this operator is

$$\mathrm{K}_{jk} = \Delta x \sum_{n=1}^{N-1} \phi_n(x_j)\phi_n'(x_k). \tag{B.20}$$

Substituting the Fourier basis functions (B.10) into (B.20), we obtain

$$\mathrm{T}_{jk} = \frac{2\pi}{N(b-a)}\sum_{n=1}^{N-1} n \sin\left(\frac{\pi n j}{N}\right)\cos\left(\frac{\pi n k}{N}\right). \tag{B.21}$$

Rewriting the product of sine and cosine functions using trigonometric relations,

$$\sin\left(\frac{\pi n j}{N}\right)\cos\left(\frac{\pi n k}{N}\right) = \frac{1}{2}\left[\sin(nA) + \sin(nB)\right], \tag{B.22}$$

[1] $\csc x = 1/\sin x$

where A and B have been defined previously. Using the same reasoning as in equation (B.14),

$$\sum_{n=1}^{N-1} n\sin(nA) = -\frac{\partial}{\partial A}\mathrm{Re}\sum_{n=1}^{N-1}\mathrm{e}^{inA}. \tag{B.23}$$

Further calculation is straightforward. Finally, we obtain

$$\mathrm{K}_{jk} = -\frac{(-1)^{j-k}\pi}{2(b-a)}\left[\cot\left(\frac{\pi(j-k)}{2N}\right)+\cot\left(\frac{\pi(j+k)}{2N}\right)\right], j\neq k, \tag{B.24}$$

for non-diagonal, and

$$\mathrm{K}_{jj} = -\frac{\pi}{2(b-a)}\cot\left(\frac{\pi j}{N}\right), j=k \tag{B.25}$$

for the diagonal matrix elements of the $\hat{\mathrm{K}}$ operator in the DVR basis. The potential energy operator $\hat{\mathrm{V}}$ is diagonal in this representation.

To demonstrate, how the DVR technique described above is applied in practice, let us consider the formulation of the DVR matrix elements of the zeroth-order bending molecular Hamiltonian (4.22). It is defined as:

$$\begin{aligned}\hat{\mathrm{H}}^0_\alpha = &-\left(\frac{\hbar^2}{2\mu_1 r_1^2}+\frac{\hbar^2}{2\mu_2 r_2^2}-\frac{\hbar^2\cos\alpha}{m_2 r_1 r_2}\right)\frac{\partial^2}{\partial\alpha^2}-\frac{\hbar^2\sin\alpha}{2m_2 r_1 r_2}\frac{\partial}{\partial\alpha}\\ &-\frac{\hbar^2\cos\alpha}{4m_2 r_1 r_2}-\frac{\hbar^2}{8\mu_1 r_1^2}-\frac{\hbar^2}{8\mu_2 r_2^2},\end{aligned} \tag{B.26}$$

where r_1, r_2 are assumed fixed at their equilibrium values. The matrix elements of this Hamiltonian are then written as:

$$(\mathrm{H}_\alpha)_{jk} = -c_1\mathrm{T}_{jk}+c_2\left[(\mathrm{CT})_{jk}-(\mathrm{SK})_{jk}-\frac{1}{4}\mathrm{C}_{jk}\right]+\left(\frac{1}{8}c_1+\mathrm{V}(\alpha_j)\right)\delta_{jk}, \tag{B.27}$$

where

$$c_1 = \frac{\hbar^2}{2}\left(\frac{1}{\mu_1 r_1^2}+\frac{1}{\mu_2 r_2^2}\right),\quad c_2 = \frac{\hbar^2}{m_2 r_1 r_2},\quad \mathrm{C}_{jk} = \cos(\alpha_j)\delta_{jk},\quad \mathrm{S}_{jk} = \sin(\alpha_j)\delta_{jk}. \tag{B.28}$$

To obtain the eigenenergies and eigenfunctions of the Hamilton operator (B.26) the following matrix equation is solved:

$$\left[(\mathrm{H}_\alpha)_{jk} - E_j\delta_{jk}\right]\chi^0_j(\alpha_k) = 0. \tag{B.29}$$