THEORETISCHE CHEMIE

SS 2011

Numerical Methods of Quantum Dynamics Discrete Variable Representation (DVR) Integrators

LECTURE NOTES

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LaTeXversion compiled with the help of Dr. Ying-Chih Chiang

April 2017

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Chapter 1

Introduction

In this lecture we want to study methods for solving the time-dependent Schrödinger equation:

$$i|\dot{\psi}\rangle = H|\psi\rangle \ . \tag{1.1}$$

Here $H = T + V$, where $V = V(x)$ is a local potential (a product operator), and T, the kinetic energy operator (KEO), is a second order differential operator, e.g.:

$$T = -\frac{1}{2m}\frac{d^2}{d^2x} \qquad \text{or} \qquad T = -\frac{1}{2mr_0^2}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \ .$$

For multi-dimensional problems, T may become *very* complicated.

When solving the time-dependent Schrödinger equation numerically, there are two technical difficulties which must be overcome.

Discretisation
: Replace the wavefunction by a *finite* set of *numbers* and explain how operators act on those, i.e. operators must also be represented by a finite set of numbers.

Integration
: Solve the differential equation Eq. (1.1), which is a first order linear ODE with constant coefficients. It is structurally very simple but can be of very large dimension, like $10^5 \cdots 10^{12}$.

First, however, the working equations have to be derived using a *variational principle*. For basis set expansion of the wavefunction Eq. (1.1) holds, when it is interpreted as a vector-matrix equation. More complicated expansions of the wavefunction may lead to much more complicated equations of motion, e.g. to the MCTDH equations of motion.

Chapter 2

Discretization

2.1 Spectral methods

The spectral method is the most familiar approach, well known from all textbooks. One picks a set of basis functions

$$\{\varphi_j(x)\}_{j=1}^{n}$$

which is orthonormal $\langle\varphi_j|\varphi_k\rangle = \delta_{jk}$, and becomes complete for $n \to \infty$, i.e.

$$\sum_{j=1}^{\infty} |\varphi_j\rangle\langle\varphi_j| = 1 \quad \text{or} \quad \sum_{j=1}^{\infty} \varphi_j(x)\varphi_j^*(x') = \delta(x - x') \; .$$

Additionally we require

$$\varphi_j \; , \; x\varphi_j \; , \; \frac{d\varphi_j}{dx} \in \mathcal{L}^2 \; ,$$

and, most importantly, that the matrix element of the KEO are known analytically

$$\langle\varphi_j|\hat{T}|\varphi_k\rangle = T_{jk} \; . \tag{2.1}$$

We then approximate the wavefunction as

$$\psi(x) = \sum_{j=1}^{n} a_j\varphi_j(x) \qquad \text{with} \qquad a_j = \langle\varphi_j|\psi\rangle \tag{2.2}$$

and any operator $\hat{A}$ as

$$\hat{A} = \sum_{j,k=1}^{n} |\varphi_j\rangle A_{jk}\langle\varphi_k| \qquad \text{where} \qquad A_{jk} = \langle\varphi_j|\hat{A}|\varphi_l\rangle \; . \tag{2.3}$$

The discretization reads

$$\hat{A}\psi \to \mathbf{Aa} \; . \tag{2.4}$$

The error admitted when solving the Schrödinger equation by a spectral method can be traced back to the use of a projected Hamiltonian

$$H \to PHP \qquad \text{where} \qquad P = \sum_{j=1}^{n} |\varphi_j\rangle\langle\varphi_j| \; . \tag{2.5}$$

The projection turns an unbounded operator into a bounded one. In a mathematical sense this is a severe modification, which can be justified for bound systems, but continua may need a special treatment. However, it is obvious that as long as $||(1-P)|\psi_{\rm ex}\rangle||$ is small, the error is likely to be be small.

Spectral methods suffer from the integral problem. The computation of the matrix elements of the potential

$$V_{jk} = \langle\varphi_j|V|\varphi_k\rangle = \int \varphi_j^*(x)V(x)\varphi_k(x)\mathrm{d}x \tag{2.6}$$

requires that $n(n+1)/2$ multi-dimensional[1] integrals must be evaluated. This may take more time than the subsequent propagation of the wave packet or diagonalisation of the Hamiltonian. The discrete variable representation (DVR), to be discussed later, offers a solution to the integral problem.

2.2 Grid methods

Pick a set of points $\{x_\alpha\}_{\alpha=1}^n$ and represent the wavefunction by its values on those points

$$\psi(x) \to (\psi(x_1), \psi(x_2), ..., \psi(x_n))^T = \boldsymbol{\psi} \; . \tag{2.7}$$

The operation of a potential on the wavefunction is then very easy

$$[\hat{V}\psi](x) = V(x)\psi(x) \to (V(x_1)\psi(x_1), V(x_2)\psi(x_2), ..., V(x_n)\psi(x_n))^T \; . \tag{2.8}$$

More complicated is the application of the KEO.

The method of finite differences assumes an equally-spaced grid

$$x_{\alpha+1} = x_\alpha + \Delta x$$

[1]For sake of simplicity we discuss most of the time a one dimensional case. But the interest is eventually in treating multi-dimensional systems.

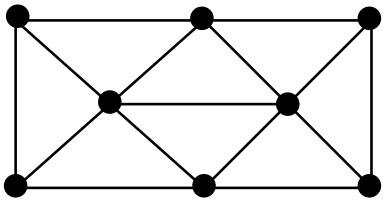


Figure 2.1: Finite elements method (2D problem): partitioning the space into triangles.

and approximate the wavefunction *locally* by a low order polynomial. If it is approximated by a parabola, one arrives at the well known formula

$$\psi''(x_\alpha) = \frac{1}{(\Delta x)^2}\{\psi(x_{\alpha+1}) - 2\psi(x_\alpha) + \psi(x_{\alpha-1})\} \; . \tag{2.9}$$

The finite differences method looks very attractive, in particular because the kinetic energy matrix is tri-diagonal

$$\mathbf{T} = -\frac{1}{2m(\Delta x)^2} \begin{pmatrix} -2 & 1 & 0 & 0 & \\ 1 & -2 & 1 & 0 & \\ 0 & 1 & -2 & 1 & \\ & & \ddots & \ddots & \ddots \end{pmatrix} \; . \tag{2.10}$$

However, the finite differences method is *not* recommended. The step size Δx must be chosen rather small in order to keep the error introduced by the approximate KEO below an acceptable limit.

A better method, very popular among engineers and mathematicians, is the *finite elements method*. It is very successful for partial differential equations in 2 or 3 dimensions, but it was not so successful for quantum problems. The finite elements method represents the wavefunction locally by low-order multi-dimensional polynomials over a small triangular shaped area. See Figure 2.1. There are continuity requirements at the boundaries. Depending on the order of the interpolating polynomial, there may be additional points within the triangles. The differential operators are applied, similar to finite differences, by differentiating the local polynomials. Matrix elements are done by quadrature, e.g.

$$\langle\phi|\psi\rangle = \int \phi^*(\mathbf{x})\psi(\mathbf{x})\mathrm{d}\mathbf{x} = \sum_{\alpha=1}^{n} \phi^*(\mathbf{x}_\alpha)\psi(\mathbf{x}_\alpha)\omega_\alpha \; . \tag{2.11}$$

Numerically one has to solve huge sets of linear equations.

2.3 Pseudo spectral methods

Pseudo-spectral methods make use of both, a global basis set

$$\{\varphi_j(x)\}_{j=1}^n$$

and a set of grid points

$$\{x_\alpha\}_{\alpha=1}^n \ .$$

Pseudo-spectral methods are rather close to spectral methods but look more alike grid methods. For the latter, there is no potential quadrature problem. This makes the pseudo-spectral methods so attractive.

2.3.1 Collocation

Nowadays we are so used to Hilbert-Space methods that one easily overlooks that there is an even easier method for determining the basis set expansion coefficients a_j. One may require that the expansion coincides with the original wavefunction at a set of grid points.This method is called collocation:

$$\psi(x_\alpha) = \sum_{j=1}^{n} a_j \varphi_j(x_\alpha) \ . \tag{2.12}$$

By defining

$$G_{\alpha j} := \varphi_j(x_\alpha) \ , \tag{2.13}$$

one arrives at

$$\boldsymbol{\psi} = \boldsymbol{G}\boldsymbol{a} \qquad \text{or} \qquad \boldsymbol{a} = \boldsymbol{G}^{-1}\boldsymbol{\psi} \ , \tag{2.14}$$

where the vector $\boldsymbol{\psi}$ denotes the grid-representation of $\psi(x)$. Grid points and basis functions must be consistent such that $\boldsymbol{G}$ is regular, i.e. $\det(\boldsymbol{G}) \neq 0$.

The application of the potential operator is – as in any grid method – obvious and trivial

$$\hat{V}\psi \to \{V(x_\alpha)\psi(x_\alpha)\} \ ,$$

i.e. in grid representation, V is a diagonal matrix[2]

$$V_{\alpha\beta}^{(g)} = V(x_\alpha)\delta_{\alpha\beta} \tag{2.15}$$

Let $\hat{T}$ denote a general operator.

$$(\boldsymbol{T}^{(b)})_{jk} := \langle \varphi_j | \hat{T} | \varphi_k \rangle \tag{2.16}$$

$$\boldsymbol{T}^{(g)}\boldsymbol{\psi} = \boldsymbol{G}\boldsymbol{T}^{(b)}\boldsymbol{G}^{-1}\boldsymbol{\psi} = \boldsymbol{G}\boldsymbol{T}^{(b)}\boldsymbol{a} \tag{2.17}$$

[2]We use $(g)/(b)$ to denote any operator under grid/basis representation.

Hence seemingly

$$\boldsymbol{T}^{(g)} = \boldsymbol{G}\boldsymbol{T}^{(b)}\boldsymbol{G}^{-1} \; . \tag{2.18}$$

On the other hand one finds

$$\begin{aligned} \langle\phi|\hat{T}|\psi\rangle &= (\boldsymbol{G}^{-1}\boldsymbol{\phi})^{\dagger}\boldsymbol{T}^{(b)}\boldsymbol{G}^{-1}\boldsymbol{\psi} \\ &= \boldsymbol{\phi}^{\dagger}(\boldsymbol{G}^{\dagger})^{-1}\boldsymbol{T}^{(b)}\boldsymbol{G}^{-1}\boldsymbol{\psi} \; . \end{aligned} \tag{2.19}$$

Hence

$$\boldsymbol{T}^{(g)} = (\boldsymbol{G}^{\dagger})^{-1}\boldsymbol{T}^{(b)}\boldsymbol{G}^{-1} \; . \tag{2.20}$$

The inconsistency between Eqs. (2.17) and (2.20) can be understood easily. It originates from the fact that one derivation contained an integration, the other not. Setting $\hat{T} = \mathbf{1}$, one arrives at

$$\begin{aligned} \langle\phi|\psi\rangle &= \boldsymbol{\phi}^{\dagger}(\boldsymbol{G}\boldsymbol{G}^{\dagger})^{-1}\boldsymbol{\psi} \\ &= \sum_{\alpha,\beta} \phi^{*}(x_{\alpha})(\boldsymbol{G}\boldsymbol{G}^{\dagger})^{-1}_{\alpha\beta}\psi(x_{\beta}) \; . \end{aligned} \tag{2.21}$$

This almost looks like a quadrature rule ($\int f(x)\mathrm{d}x = \sum_{\alpha} w_{\alpha} f(x_{\alpha})$),

$$\langle\phi|\psi\rangle = \sum_{\alpha} w_{\alpha}\phi^{*}(x_{\alpha})\psi(x_{\alpha}) = \boldsymbol{\phi}^{\dagger}\boldsymbol{W}\boldsymbol{\psi} \; . \tag{2.22}$$

Hence $\boldsymbol{W}$ is the diagonal weight matrix

$$W_{\alpha\beta} = w_{\alpha}\delta_{\alpha\beta} \tag{2.23}$$

and the w_{α} are the positive weights. To make the collocation scheme consistent with a quadrature rule, we need that $(\boldsymbol{G}\boldsymbol{G}^{\dagger})$ is diagonal, namely

$$(\boldsymbol{G}\boldsymbol{G}^{\dagger})_{\alpha\beta} = w_{\alpha}^{-1}\delta_{\alpha\beta} \; . \tag{2.24}$$

The collocation matrix $\boldsymbol{G}$ hence determines the quadrature weights. The inconsistency between Eqs. (2.17,2.20) is now removed, when we do the final integral by quadrature:

$$\begin{aligned} \langle\phi|\hat{T}|\psi\rangle &= \langle\phi|\hat{T}\psi\rangle \\ &= \boldsymbol{\phi}^{\dagger}\boldsymbol{W}\boldsymbol{G}\boldsymbol{T}^{(b)}\boldsymbol{G}^{-1}\boldsymbol{\psi} \qquad \text{(Eqs.(2.17,2.22))} \\ &= \boldsymbol{\phi}^{\dagger}(\boldsymbol{G}\boldsymbol{G}^{\dagger})^{-1}\boldsymbol{G}\boldsymbol{T}^{(b)}\boldsymbol{G}^{-1}\boldsymbol{\psi} \\ &= \boldsymbol{\phi}^{\dagger}\boldsymbol{G}^{\dagger-1}\boldsymbol{T}^{(b)}\boldsymbol{G}^{-1}\boldsymbol{\psi} = \text{Eq. (2.19)} \end{aligned} \tag{2.25}$$

Hence to lift the inconsistency one needs again Eq. (2.24), i.e.

$$\boldsymbol{G}\boldsymbol{G}^\dagger = \boldsymbol{W}^{-1} \tag{2.26}$$

which can only be satisfied if $\boldsymbol{G}\boldsymbol{G}^\dagger$ is diagonal. Therefore it is our goal to find basis sets and corresponding grid points such that $\boldsymbol{G}\boldsymbol{G}^\dagger$ becomes diagonal. That is,

$$(\boldsymbol{G}\boldsymbol{G}^\dagger)_{\alpha\beta} = \sum_{j=1}^{n} \varphi_j(x_\alpha)\varphi_j^*(x_\beta) = w_\alpha^{-1}\delta_{\alpha\beta} \tag{2.27}$$

Although this equation defines the weights w_α, it is not at all clear that there are basis functions and grid points such that all off-diagonal elements vanish.

We will show below that the *Discrete Variable Representation* (DVR) approach allows us to find such functions and points. But for the time being, we just tactically assume that $\boldsymbol{G}\boldsymbol{G}^\dagger$ is diagonal and investigate the consequences of this assumption.

First we unitarize the transformation matrices

$$\begin{aligned} \boldsymbol{G}\boldsymbol{G}^\dagger = \boldsymbol{W}^{-1} &\Rightarrow \boldsymbol{W}^{1/2}\boldsymbol{G}\boldsymbol{G}^\dagger\boldsymbol{W}^{1/2} = \mathbf{1} \\ &\Rightarrow (\boldsymbol{W}^{1/2}\boldsymbol{G})(\boldsymbol{W}^{1/2}\boldsymbol{G})^\dagger = \mathbf{1} \\ &\Rightarrow \boldsymbol{W}^{1/2}\boldsymbol{G} \text{ is unitary.} \end{aligned} \tag{2.28}$$

We define

$$\begin{aligned} &\boldsymbol{U}^\dagger = \boldsymbol{W}^{1/2}\boldsymbol{G} \quad , \quad \boldsymbol{U} = \boldsymbol{G}^\dagger\boldsymbol{W}^{1/2} \\ &U_{j\alpha} = w_\alpha^{1/2}\varphi_j^*(x_\alpha) \quad \text{(unitary!)} \end{aligned} \tag{2.29}$$

Remember $G_{\alpha j} = \varphi_j(x_\alpha)$. The matrices $\boldsymbol{U}$ and $\boldsymbol{U}^\dagger$ perform a unitary transformation from grid to basis and from basis to grid, respectively. From the unitarity of $\boldsymbol{U}$ there follow two important properties.

Discrete Orthonormality

$$(\boldsymbol{U}\boldsymbol{U}^\dagger)_{jk} = \sum_{\alpha=1}^{n} w_\alpha\varphi_j^*(x_\alpha)\varphi_k(x_\alpha) = \delta_{jk} \tag{2.30}$$

All overlap matrix elements between basis functions are exact by quadrature! This is remarkable as there are $n(n+1)/2$ integrals but only $2n$ free parameters (n grid points and n weights).

Discrete Completeness

$$(\boldsymbol{U}^\dagger \boldsymbol{U})_{\alpha\beta} = \sum_{j=1}^{n} (w_\alpha w_\beta)^{1/2} \varphi_j(x_\alpha) \varphi_j^*(x_\beta) = \delta_{\alpha\beta} \tag{2.31}$$

Remember that the usual completeness relation reads,

$$\sum_{j=1}^{\infty} \varphi_j(x) \varphi_j^*(x') = \delta(x - x') \; , \tag{2.32}$$

or equivalently:

$$\sum_{j=1}^{\infty} |\varphi_j\rangle\langle\varphi_j| = \hat{1} \; , \tag{2.33}$$

whereas the use of a finite basis set leads to a projector

$$\sum_{j=1}^{n} |\varphi_j\rangle\langle\varphi_j| = \hat{P} \; . \tag{2.34}$$

Now it is convenient to redefine the grid representation of the wave function vector by including the weights into the definition of ψ

$$\psi \to (w_1^{1/2}\psi(x_1), \cdots, w_n^{1/2}\psi(x_n))^T = \boldsymbol{\psi} = \{\psi_\alpha\} \; . \tag{2.35}$$

Applying this grid-representation definition to the basis functions φ_j, then Eq.(2.31) states that the vectors $\boldsymbol{\varphi_j}$ are orthonormal and Eq.(2.30) states that these vectors are complete. Hence the vectors $\boldsymbol{\varphi_j}$ form a complete, orthonormal basis of the $\mathcal{C}^n$.

Using Eq.(2.35) a scalar product of two wavefunction vectors yields the overlap integral of the wavefunctions.

$$\boldsymbol{\phi}^\dagger \boldsymbol{\psi} = \sum_{\alpha=1}^{n} w_\alpha \phi^*(x_\alpha) \psi(x_\alpha) = \langle\phi|\psi\rangle \tag{2.36}$$

where the last equal sign is exact, if ϕ and ψ lie entirely in the basis, i.e. $P\phi = \phi$ and $P\psi = \psi$. Otherwise the quadrature is an approximation, but not exact.

Finally we introduce the so called DVR functions

$$|\chi_\alpha\rangle = \sum_{j=1}^{n} |\varphi_j\rangle U_{j_\alpha} \qquad (\Rightarrow \langle\varphi_j|\chi_\alpha\rangle = U_{j\alpha}) \tag{2.37}$$

or

$$\chi_\alpha(x) = \sum_{j=1}^{n} w_\alpha^{1/2} \varphi_j^*(x_\alpha)\varphi_j(x) \; . \tag{2.38}$$

Obviously the DVR functions $\{|\chi\rangle\}$ are orthonormal $\langle\chi_\alpha|\chi_\beta\rangle = \delta_{\alpha\beta}$ as they are obtained from a unitary transformation. Besides that, the DVR functions $\{|\chi\rangle\}$ have a very nice property. Multiplying Eq. (2.38) with $w_\beta^{1/2}$ and setting $x = x_\beta$ one finds [3]

$$w_\beta^{1/2}\chi_\alpha(x_\beta) = \sum_{j=1}^{n} (w_\alpha w_\beta)^{1/2} \varphi_j^*(x_\alpha)\varphi_j(x_\beta) = \delta_{\alpha\beta} \; , \tag{2.39}$$

where the last equal sign follow from Eq. (2.31). In other words, the vectors $\boldsymbol{\chi_\alpha}$ (cf. Eq.(2.35)) are just the Euclidean unit vectors. This property of the DVR-functions is called

Discrete δ-property

$$\begin{aligned} &\chi_\alpha(x_\beta) = w_\alpha^{-1/2}\delta_{\alpha\beta} \\ &\langle\chi_\alpha|\chi_\beta\rangle = \delta_{\alpha\beta} \end{aligned} \tag{2.40}$$

because on the grid the DVR-functions behave similarly like δ functions, see Fig. 2.2. In fact χ is a normalized projection of a δ-function on to the basis. Defining

$$\begin{aligned} \delta_\alpha &= \delta(x - x_\alpha) \\ P &= \sum_{j=1}^{n} |\varphi_j\rangle\langle\varphi_j| \; , \end{aligned}$$

one obtains

$$\begin{aligned} P|\delta_\alpha\rangle &= \sum_{j=1}^{n} |\varphi_j\rangle\varphi_j^*(x_\alpha) \\ \|P|\delta_\alpha\rangle\|^2 &= \sum_{j=1}^{n} |\varphi_j^*(x_\alpha)|^2 = w_\alpha^{-1} \end{aligned}$$

[3] Remember $\delta(x - x_\alpha) = \sum_{j=1}^{\infty} \varphi_j^*(x_\alpha)\varphi_j(x)$ for any complete orthonormal basis $\{\varphi_j\}$.

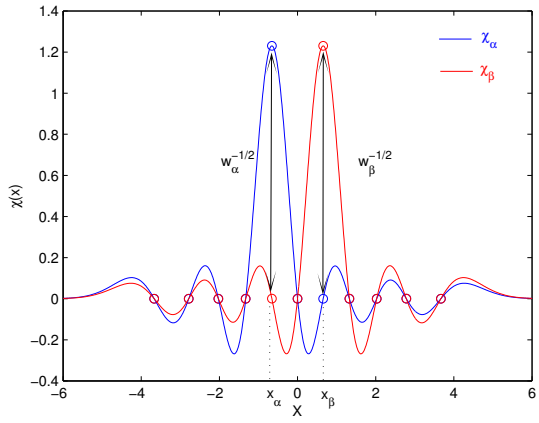


Figure 2.2: Shown are two DVR functions of a harmonic oscillator DVR. The DVR-functions vanish at all grid-points, except the one they refer to. See Eq.(2.40). Note that the grid points are not equally spaced.

where the last equal sign follows from discrete completeness. Therefore,

$$\frac{P|\delta_\alpha\rangle}{\|P|\delta_\alpha\rangle\|} = \sum_{j=1}^{n} |\varphi_j\rangle\varphi_j^*(x_\alpha)w_\alpha^{1/2} = \sum_{j=1}^{n} |\varphi_j\rangle U_{j\alpha} = |\chi_\alpha\rangle \tag{2.41}$$

Hence χ_α is indeed the best approximation to a δ-function, which is possible within a finite basis. (Remember, all these considerations require that $\boldsymbol{GG}^\dagger$ is diagonal.)

It is now interesting to inspect the overlap of the DVR-functions with the wave function. We first do it by quadrature

$$\langle\chi_\alpha|\psi\rangle = \sum_{\beta=1}^{n} w_\beta\chi_\alpha(x_\beta)\psi(x_\beta) = w_\alpha^{1/2}\psi(x_\alpha) =: \psi_\alpha \tag{2.42}$$

The Hilbert-space approach, i.e. taking the overlap of the basis function χ_α with the wave function as representing number, and the grid approach, i.e. taking the amplitude of the wave function at a grid point (including the weight) as representing number, are *identical* as long as the quadrature is exact. Additionally, we know from the discrete completeness that the quadrature is exact as long as ψ lies entirely in the basis, i.e. $P\psi = \psi$. In

general we have

$$\begin{aligned}
\langle\chi_\alpha|\psi\rangle &= \langle\sum_{j=1}^{n}\varphi_j U_{j\alpha}|\sum_{k=1}^{\infty}a_k\varphi_k\rangle \\
&= \sum_{j=1}^{n}\sum_{k=1}^{\infty}U^*_{j\alpha}a_k\delta_{jk} \\
&= \sum_{j=1}^{n}a_j U^*_{j\alpha} \\
&= \sum_{j=1}^{n}w_\alpha^{1/2}a_j\varphi_j(x_\alpha) \\
&= w_\alpha^{1/2}(P\psi)(x_\alpha)\ ,
\end{aligned}$$

which leads to

$$w_\alpha^{1/2}\psi(x_\alpha)\equiv\psi_\alpha=\langle\chi_\alpha|\psi\rangle+w_\alpha^{1/2}(Q\psi)(x_\alpha)\ , \tag{2.43}$$

where $Q=1-P$. Again, Hilbert space representation and grid representation are identical as long as $P\psi=\psi$. If ψ has components outside the basis set, we introduce an additional error. This error is usually accepted, because one trades in an efficient way to compute potential matrix elements

$$\langle\chi_\alpha|V|\chi_\beta\rangle=\sum_{\gamma=1}^{n}w_\gamma\chi^*_\alpha(x_\gamma)V(x_\gamma)\chi_\beta(x_\gamma)=V(x_\alpha)\delta_{\alpha\beta}\ . \tag{2.44}$$

Once again the quadrature is exact as long as $V\chi_\beta$ lies within the basis. Within this approach, the application of a potential to a wave function is clear and consistent with the grid approach.

$$\begin{aligned}
&\psi\to\{\psi_\alpha\} \\
&V\psi\to\{V(x_\alpha)\psi_\alpha\}
\end{aligned}$$

We end this section by proving an important theorem.

Theorem The following 5 statements are *equivalent*.

(1) $\boldsymbol{GG}^\dagger$ is diagonal. $(G_{\alpha j}=\varphi_j(x_\alpha))$

(2) $U_{j\alpha}=w_\alpha^{1/2}\varphi_j^*(x_\alpha)$ is unitary.

(3) Discrete orthogonality.
$\sum_{\alpha=1}^{n} w_\alpha \varphi_j^*(x_\alpha)\varphi_k(x_\alpha) = \delta_{jk}$.

(4) Discrete completeness.
$\sum_{j=1}^{n} w_\alpha \varphi_j(x_\alpha)\varphi_j^*(x_\beta) = \delta_{\alpha\beta}$.

(5) Discrete δ-property.
$\chi_\alpha(x_\beta) = w_\alpha^{-1/2}\delta_{\alpha\beta}$ and $\langle\chi_\alpha|\chi_\beta\rangle = \delta_{\alpha\beta}$.

If one of the 5 statements is true, all 5 of them are true and one can construct a DVR. Previously we have already shown (1) $\Leftrightarrow$ (2) $\Leftrightarrow$ (3), (2) $\Leftrightarrow$ (4), and (2) $\Rightarrow$ (5) with the help of (3). We now only need to prove (2) $\Leftarrow$ (5).

The DVR functions in general can be written as a linear combination of basis functions

$$|\chi_\alpha\rangle = \sum_{j=1}^{n} |\varphi_j\rangle U_{j\alpha}$$

with some matrix $\boldsymbol{U}$. From the orthonormality of the DVR- and the basis-functions follows

$$\begin{aligned}\delta_{\alpha\beta} = \langle\chi_\alpha|\chi_\beta\rangle &= \langle\sum_j \varphi_j U_{j\alpha}| \sum_k \varphi_k U_{k\beta}\rangle \\ &= \sum_{j=1}^{n} U_{j\alpha}^* U_{j\beta} = (\boldsymbol{U}^\dagger\boldsymbol{U})_{\alpha\beta} \quad \Rightarrow \ \boldsymbol{U} \text{ is unitary.}\end{aligned} \tag{2.45}$$

The matrix elements of $\boldsymbol{U}$ reads

$$U_{j\alpha} = \langle\varphi_j|\chi_\alpha\rangle = \sum_\beta w_\beta \varphi_j^*(x_\beta)\chi_\alpha(x_\beta) = w_\alpha^{1/2}\varphi_j^*(x_\alpha). \tag{2.46}$$

The quadrature is exact, because the DVR-functions obviously satisfy discrete orthonormality. As the basis functions are just linear combinations of the DVR-functions, they also satisfy discrete orthonormality. Hence all quadratures within the basis set are exact.

2.3.2 Quadrature DVR

Quadrature Rule

Numerical integration is done by a quadrature rule

$$\int_a^b f(x)dx \simeq \sum_{j=1}^{n} w_j f(x_j) \; . \tag{2.47}$$

Numerical mathematicians tried to find weights w_j and nodes x_j to make the integration as accurate as possible. The most obvious way is to take equidistant nodes

$$x_{j+1} = x_j + \Delta x$$

with

$$x_1 = a \; , \;\; x_n = b \; , \;\; \Delta x = \frac{b-a}{n-1} \; .$$

But how to determine the weights w_j? One simply requires that the quadrature rule is exact for all polynomials up to a maximal degree. This yields the so called Newton-Cotes formulas.

For $n = 2$ one obtains the trapezoidal rule

$$\int_a^b f(x)dx \simeq \frac{b-a}{2}(f(a) + f(b)) \tag{2.48}$$

which is exact for linear functions. For $n = 3$ there is Simpson's rule

$$\int_a^b f(x)dx \simeq \frac{b-a}{6}\left((a) + 4f(\frac{a+b}{2}) + f(b)\right) \tag{2.49}$$

which, by chance, is exact for all polynomials up to third order. However, for $n > 6$ the Newton-Cotes formula contains negative weights. This renders them useless. Hence one can use only low-order Newton-Cotes formulas, but, in order to increase the accuracy, one may apply them to smaller intervals.

$$\int_a^b f(x)dx = \int_{a_1}^{a_2} f(x)dx + \int_{a_2}^{a_3} f(x)dx + \cdots + \int_{a_{k-1}}^{a_k} f(x)dx$$

where $a_1 = a$, $b = a_k$. In consequence, the composite trapezoidal rule reads

$$\int_a^b f(x)dx = \frac{\Delta x}{2}\left(f(a) + f(b)\right) + \Delta x \sum_{j=2}^{N-1} f(x_j)$$

where $\Delta x = \frac{b-a}{N-1}$, $x_j = a + (j-1)\Delta x$, i.e. $x_1 = a$ and $x_N = b$. We may also write it as

$$\sum_{j=1}^{N} w_j f(x_j)$$

with

$$w_j = \begin{cases} \frac{\Delta x}{2} & \text{for } j = 1 \text{ and } j = N \\ \Delta x & \text{else} \end{cases}$$

The error can be bounded by $\frac{1}{12(N-1)^2}(b-a)^3 \max_{x\in[a,b]} |f"(x)|$, which vanishes for $N \to \infty$. The error of Simpson's rule vanishes like N^{-4}. These low-order methods can only be applied *locally*. However, we have already learned that it is usually more efficient to use a higher order method, which can be applied globally. This brings us to *Gaussian Integration*. The idea is to vary both weights and nodes, to make the quadrature formula optimal. The quadrature rule is formulated slightly more general.

$$\int \omega(x) f(x) dx = \sum_{\alpha=1}^{n} w_\alpha f(x_\alpha) \tag{2.50}$$

where $\omega(x) \geq 0$ is a polynomial integrable weight function. For example

$$\omega(x) = \begin{cases} 1 & \text{for } a \leq x \leq b \\ 0 & \text{else} \end{cases}$$

which brings us to the standard integral $\int_a^b dx$. Another possible choice of the weights is $\omega(x) = e^{-\alpha x^2}$. To proceed one requires that

$$\int \omega(x) P_j(x) dx = \sum_{j=1}^{n} w_\alpha P_j(x_\alpha) \tag{2.51}$$

holds exactly for all polynomials of degree $j \leq 2n-1$. Gauss has shown that there exists a unique solution with positive weights w_α for all n!

Gaussian quadrature is closely related to orthogonal polynomial. We define

$$P_0(x) = \left[\int \omega(x) dx\right]^{1/2} = \text{const} \tag{2.52}$$

$$\tilde{P}_j(x) = x P_{j-1}(x) \tag{2.53}$$

$$P_j(x) = \tilde{P}_j(x) - \sum_{i=0}^{j-1} a_i P_i(x) \tag{2.54}$$

where the coefficients a_i are defined by Gram-Schmidt orthogonalization to the lower order polynomial with respect to the weight $\omega(x)$. From this follows

$$\int \omega(x) P_j(x) P_k(x) dx = \delta_{jk} \ , \tag{2.55}$$

where P_j is a polynomial of order j. The nodes of the Gaussian quadrature are simply the zeros of the orthogonal polynomial $P_n(x)$, i.e. $P_n(x_\alpha) = 0$ for $\alpha = 1, \cdots, n$. The weights are given by more complicated formula, e.g. $w_\alpha = \frac{2}{(1-x_\alpha^2)(P_n'(x_\alpha))^2}$ for Gauss-Legendre quadrature. Later we will find an easier way to determine weights and nodes. It is important to note, that the orthogonal polynomials given in the literature obey a different normalization than the L^2 one used here. They are normalized such that the coefficient of the highest power is unity. However, we will continue to use L^2 normalized orthogonal polynomials.

Finally, we give an overview of the most standard Gaussian quadratures, their orthogonal polynomials, and their weights

- Legendre Polynomials P_n

$$\omega(x) = \begin{cases} 1 & \text{for} -1 \leq x \leq 1 \\ 0 & \text{else} \end{cases}$$

- Hermite Polynomials H_n

$$\omega(x) = e^{-x^2}$$

- Laguerre Polynomials L_n^α

$$\omega(x) = \begin{cases} x^\alpha e^{-x} & x \geq 0 \\ 0 & \text{else} \end{cases}$$

- Chebyshev Polynomials T_n and U_n

$$\omega(x) = \begin{cases} (1-x^2)^{\mp\frac{1}{2}} & \text{for} -1 \leq x \leq 1 \\ 0 & \text{else} \end{cases}$$

Quadrature DVR

As basis functions we define

$$\varphi_j(x) = \sqrt{\omega(x)} P_{j-1}(x) \tag{2.56}$$

with $j = 1, \cdots, n$. The $\{\varphi\}$ are orthonormal by construction

$$\langle \varphi_j | \varphi_k \rangle = \delta_{jk}$$

and may be generated by a Lanczos recursion

$$\beta_j \varphi_{j+1}(x) = x\varphi_j(x) - \alpha_j \varphi_j(x) - \beta_{j-1}\varphi_{j-1}(x) \tag{2.57}$$

with

$$\varphi_1(x) = \left[\omega(x) / \int \omega(x) dx \right]^{1/2} \tag{2.58}$$

and

$$\alpha_j = \langle \varphi_j | x | \varphi_j \rangle \; ; \qquad \beta_j = \langle \varphi_{j+1} | x | \varphi_j \rangle \; ; \qquad \beta_0 = 0 \tag{2.59}$$

The matrix **Q**

$$Q_{jk} = \langle \varphi_j | x | \varphi_k \rangle \tag{2.60}$$

is built by the Lanczos recursion and hence is tri-diagonal!

Let us inspect the integral

$$\langle \varphi_j | x^l | \varphi_k \rangle = \int \omega(x) x^l P^*_{j-1}(x) P_{k-1}(x) dx \; .$$

The integrant is a polynomial of degree j+k+l-2. The Gaussian integral is exact by quadrature for $j + k + l - 2 \leq 2n - 1$, or $j + k + l \leq 2n + 1$. For $l = 0$ or $l = 1$, all matrix element are exact by quadrature! In particular, we satisfy discrete orthogonality

$$\delta_{jk} = \langle \varphi_j | \varphi_k \rangle = \sum_{\alpha=1}^{n} w_\alpha \varphi^*_j(x_\alpha) \varphi_k(x_\alpha) \tag{2.61}$$

and thus have found a DVR!

As discrete orthogonality is satisfied, we also have discrete completeness, and are sure that

$$U_{j\alpha} := w_\alpha^{1/2} \varphi^*_j(x_\alpha)$$

is a unitary matrix. As usual we define DVR functions

$$\chi_\alpha(x) = \sum_{j=1}^{n} U_{j\alpha}\varphi_j(x) = \sum_{j=1}^{n} \varphi_j(x)\varphi_j^*(x_\alpha)w_\alpha^{1/2}$$

and find the discrete δ-property (via discrete completeness)

$$\chi_\alpha(x_\beta) = w_\alpha^{-1/2}\delta_{\alpha\beta} \ .$$

The DVR functions can also be expressed as

$$\chi_\alpha(x) = w_\alpha^{-1/2}\sqrt{\frac{\omega(x)}{\omega(x_\alpha)}}\prod_{\beta=1,\beta\neq\alpha}^{n}\frac{x-x_\beta}{x_\alpha-x_\beta} \ . \tag{2.62}$$

Let us return to a basis set approach using the φ's. One of the problem is to compute the matrix elements of the potential. (VBR: variational basis set)

$$V_{jk}^{\mathrm{VBR}} = \langle\varphi_j|V|\varphi_k\rangle = \int \varphi_j^*(x)V(x)\varphi_k(x)dx \ .$$

Obviously it is convenient to do those integrals by Gaussian quadrature. As this is an approximation, we call the resulting potential matrix V^{FBR}, where FBR stand for *finite basis set representation*.

$$V_{jk}^{\mathrm{FBR}} = \sum_{\alpha=1}^{n} w_\alpha\varphi_j^*(x_\alpha)V(x_\alpha)\varphi_k(x_\alpha) \tag{2.63}$$

$$= \sum_{\alpha=1}^{n} U_{j\alpha}V(x_\alpha)U_{k\alpha}^* \tag{2.64}$$

$$= \left(\mathbf{U}\mathbf{V}^{\mathrm{DVR}}\mathbf{U}^\dagger\right)_{jk} \tag{2.65}$$

where we have introduced $V_{\alpha\beta}^{\mathrm{DVR}} = V(x)\delta_{\alpha\beta}$. We just have shown that the FBR approach is unitarily equivalent to the DVR approximation.

$$\langle\chi_\alpha|x|\chi_\beta\rangle = V(x_\alpha)\delta_{\alpha\beta} = V_{\alpha\beta}^{\mathrm{DVR}} \ .$$

But one must keep in mind that these are approximations. Only if one does the matrix elements exactly[4], as done in the variational basis set representation (VBR), one achieves the variational property that the computed eigenenergies are upper bounds to the exact ones. Using a DVR, this property may be violated.

[4]Using e.g. a harmonic oscillator basis and a polynomial potential, one can do all matrix-elements analytically and hence exact.

In the DVR representation, the potential matrix element are trivial but the matrix elements of the KEO must be obtained by the transformation

$$\mathbf{T}^{\mathrm{DVR}} = \mathbf{U}^{\dagger}\mathbf{T}^{\mathrm{FBR}}\mathbf{U} \tag{2.66}$$

and

$$T^{\mathrm{FBR}}_{jk} = T^{\mathrm{VBR}}_{jk} = \langle\varphi_j|\hat{T}|\varphi_k\rangle \tag{2.67}$$

where the integral is assumed to be known analytically. Hence one may introduce DVR and FBR Hamiltonians

$$\mathbf{H}^{\mathrm{FBR}} = \mathbf{T}^{\mathrm{FBR}} + \mathbf{V}^{\mathrm{FBR}} = \mathbf{T}^{\mathrm{FBR}} + \mathbf{U}\mathbf{V}^{\mathrm{DVR}}\mathbf{U}^{\dagger} \tag{2.68}$$

and

$$\mathbf{H}^{\mathrm{DVR}} = \mathbf{T}^{\mathrm{DVR}} + \mathbf{V}^{\mathrm{DVR}} = \mathbf{U}^{\dagger}\mathbf{T}^{\mathrm{FBR}}\mathbf{U} + \mathbf{V}^{\mathrm{DVR}} \ . \tag{2.69}$$

The two Hamiltonian are, of course, unitarily equivalent:

$$\mathbf{H}^{\mathrm{DVR}} = \mathbf{U}^{\dagger}\mathbf{H}^{\mathrm{FBR}}\mathbf{U} \tag{2.70}$$

$$\mathbf{H}^{\mathrm{FBR}} = \mathbf{U}\mathbf{H}^{\mathrm{DVR}}\mathbf{U}^{\dagger} \ . \tag{2.71}$$

To obtain each of the Hamiltonian matrices one has to do one transformation. It then is not obvious why DVR should be numerically more efficient than FBR, and in fact, for 1D problems, it is not. The situation changes for the multi-dimensional problems because the KEO is usually in tensor form (sum of products form).

Consider a 2D example, with the kinetic energy

$$T = -\frac{1}{2m_x}\frac{\partial^2}{\partial x^2} - \frac{1}{2m_y}\frac{\partial^2}{\partial y^2} - \frac{1}{\mu}\frac{\partial}{\partial x}\frac{\partial}{\partial y} \ . \tag{2.72}$$

The KEO is a sum of product of 1D operators. Let us call the matrices which represent the differential operator by $\mathbf{D}^{nx}$, e.g.

$$D^{1x}_{jk} = \langle\varphi^x_j|\frac{\partial}{\partial x}|\varphi^x_k\rangle \tag{2.73}$$

$$D^{2y}_{j'k'} = \langle\varphi^y_{j'}|\frac{\partial^2}{\partial y^2}|\varphi^y_{k'}\rangle \tag{2.74}$$

Then

$$T^{\mathrm{FBR}}_{jj',kk'} = -\frac{1}{2m_x}D^{(2x)}_{jk}\delta_{j'k'} - \frac{1}{2m_y}D^{(2y)}_{j'k'}\delta_{jk} - \frac{1}{\mu}D^{(1x)}_{jk}D^{(1y)}_{j'k'} \tag{2.75}$$

and

$$T^{\mathrm{DVR}}_{\alpha\alpha',\beta\beta'} = -\frac{1}{2m_x}\left(\mathbf{U}^{(x)\dagger}\mathbf{D}^{(2x)}\mathbf{U}^{(x)}\right)_{\alpha\beta}\delta_{\alpha'\beta'} - \frac{1}{2m_y}\left(\mathbf{U}^{(y)\dagger}\mathbf{D}^{(2y)}\mathbf{U}^{(y)}\right)_{\alpha'\beta'}\delta_{\alpha\beta} - \frac{1}{\mu}\left(\mathbf{U}^{(x)\dagger}\mathbf{D}^{(1x)}\mathbf{U}^{(x)}\right)_{\alpha\beta}\left(\mathbf{U}^{(y)\dagger}\mathbf{D}^{(1y)}\mathbf{U}^{(y)}\right)_{\alpha'\beta'} \ .$$

There are 8 matrix times matrix multiplications ($8n^3$ multiplications) to be made. On the other hand a transformation from DVR to FBR

$$V^{\mathrm{FBR}}_{jj',kk'} = \sum_{\alpha\alpha'=1}^{n} U^{(x)}_{j\alpha}U^{(y)}_{j'\alpha'}V(x_\alpha,y_{\alpha'})U^{(x)*}_{k\alpha}U^{(y)*}_{k'\alpha'}$$

requires $4n^6$ multiplications. In general the DVR transformation effort scales (at most) like $4fn^3$ (there are (at most) f $D^{(1)}$ and f $D^{(2)}$ matrices to be transformed) whereas the FBR one scales like $(2n^3)^f$. Here f denotes the number of degrees of freedom. The gain is therefore

$$\frac{2^{f-2}}{f}n^{3(f-1)}$$

which may be *very* large. For large f it becomes impossible to compute and store V^{FBR}. Note that the storage of V^{DVR} requires n^f data points, whereas V^{FBR} requires n^{2f} points.

We close this section with some remarks on DVRs and their underlying basis sets. First, the Lanczos operator used in the recursion does not need to be simply "x", it may be any monotonic function $f(x)$. In essence one then generates the orthogonal polynomials in f. The orthonormality relation then reads

$$\begin{aligned}\delta_{jk} &= \int \omega(f)\,P_j(f)\,P_k(f)\,df \qquad \Big|\, df = f'dx \\ &= \int |f'(x)|\,\omega(f(x))\,P_j(f(x))\,P_k(f(x))\,dx \ . \end{aligned} \tag{2.76}$$

This allows for new basis functions:

$$\varphi_j(x) = \sqrt{|f'(x)|\,\omega(f(x))}\,P_{j-1}(f(x)) \quad . \tag{2.77}$$

However, the matrix elements of the KEO with respect to these new functions must be analytically known. As an example, take the Legendre polynomials $P_l(\cos\theta)$. Here, however, the weight $|f'(\theta)| = \sin\theta$ is not multiplied to the basis functions, but kept as a weight function in the integral. However, for

the sine-DVR, to be discussed in Section 2.3.5, the just discussed transformation will play an important role.

Second, a DVR (i.e. a basis set) is defined with respect to a certain volume element. Mostly it is simply dq, but it could be e.g. $\sin\theta\, d\theta$ or $r^2 dr$ etc. We return to this point when discussing kinetic energy operators.

Third, a DVR defines the boundary conditions. Examples:
- any value allowed within $[-1, 1]$ (Legendre DVR)
- zero at the boundaries of some interval (Sin-DVR, particle in a box)
- exponential or Gaussian decay (Laguerre DVR, HO-DVR)
- periodic boundary conditions (Exp-DVR, FFT)

2.3.3 Diagonalisation DVR

The numerically most convenient way towards a DVR is provided by a diagonalization of the position operator. Note that the potential operator is a function of the position operator, $\hat{V} = V(\hat{x})$. Let us assume that the matrix elements of the position operator,

$$Q_{jk} = \langle \varphi_j | \hat{x} | \varphi_k \rangle \quad , \tag{2.78}$$

are analytically known. One then could suspect:

$$\hat{V} = V(\hat{x}) \quad \stackrel{?}{\Rightarrow} \quad \boldsymbol{V} = V(\boldsymbol{Q})$$

But this is not exact. In fact,

$$\boldsymbol{V} \simeq PV(\hat{x})P \;\neq\; V(P\hat{x}P) \simeq V(\boldsymbol{Q})$$

where by "$\simeq$" we denote the equivalence between operator and matrix, and where P denotes the projector onto the finite basis set. The equation above holds because

$$\sum_{jk} |\varphi_j\rangle V_{jk} \langle \varphi_k| = P\,\hat{V}\,P$$
$$\sum_{jk} |\varphi_j\rangle \big(V(\boldsymbol{Q})\big)_{jk} \langle \varphi_k| = V(P\hat{x}P) \quad .$$

To give an example,

$$\begin{aligned} V(\hat{x}) &= \hat{x}^2 \\ PV(\hat{x})P &= P\hat{x}^2P \\ V(P\hat{x}P) &= (P\hat{x}P)^2 = P\hat{x}P\hat{x}P \end{aligned}$$

We define, as approximation $\boldsymbol{V}^{\mathrm{VBR}}$, the potential matrix

$$\boldsymbol{V}^{\mathrm{FBR}} = V(\boldsymbol{Q}) \; . \tag{2.79}$$

To evaluate this matrix, one needs to diagonalize $\boldsymbol{Q}$.

$$\boldsymbol{Q} = \boldsymbol{U}\boldsymbol{X}\boldsymbol{U}^{\dagger} \; , \qquad X_{\alpha\beta} = x_\alpha \delta_{\alpha\beta} \tag{2.80}$$

where $\boldsymbol{U}$ denotes the unitary matrix of eigenvectors.

$$\boldsymbol{V}^{\mathrm{FBR}} = V(\boldsymbol{Q}) = V(\boldsymbol{U}\boldsymbol{X}\boldsymbol{U}^{\dagger}) = \boldsymbol{U}V(\boldsymbol{X})\boldsymbol{U}^{\dagger} \tag{2.81}$$

$$V_{jk}^{\mathrm{FBR}} = \sum_{\alpha=1}^{n} U_{j\alpha} V(x_\alpha) U_{k\alpha}^{*} \; . \tag{2.82}$$

Here the acronym FBR denotes an approximate evaluation of potential matrix elements by diagonalization of x (Harris *et al* 1965). Haris introduced his method as an alternative to computing the potential matrix elements by quadrature, but we can go a step further and introduce DVR functions. They are defined as eigenfunctions of $P\hat{x}P$.

$$|\chi_\alpha\rangle = \sum_{j=1}^{n} |\varphi_j\rangle U_{j\alpha} \tag{2.83}$$

$$|\varphi_j\rangle = \sum_{\alpha=1}^{n} U_{j\alpha}^{*} |\chi_\alpha\rangle \tag{2.84}$$

$$\langle\varphi_j|\chi_\alpha\rangle = U_{j\alpha} \tag{2.85}$$

Obviously:

$$\begin{aligned} &\langle\chi_\alpha|\chi_\beta\rangle = \delta_{\alpha\beta} \\ &\langle\chi_\alpha|\hat{x}|\chi_\beta\rangle = x_\alpha\delta_{\alpha\beta} \qquad \text{(Eigenfunctions!)} \; . \end{aligned}$$

Hence

$$x\chi_\alpha(x) = x_\alpha\chi_\alpha(x) + r_\alpha(x) \; . \tag{2.86}$$

with $P\; r_\alpha = 0$, i.e. the rest term r_α is orthogonal to the finite basis. The DVR-functions in Eq. (2.86) is similar to δ-functions,

$$x\delta(x - x_\alpha) = x_\alpha\delta(x - x_\alpha) \; . \tag{2.87}$$

In fact, as already shown (cf. Eq. (2.41)), the DVR-functions χ_α is the best finite basis set representation of the δ-function, $\delta_\alpha(x) = \delta(x - x_\alpha)$, because

$||P\delta_\alpha||^{-1}P\delta_\alpha = \chi_\alpha$. The potential is diagonal with respect to the DVR functions.

$$\begin{aligned} V_{\alpha\beta}^{\mathrm{DVR}} &= \langle\chi_\alpha|\hat{V}|\chi_\beta\rangle = \sum_{jk} U_{\alpha j}^\dagger \langle\varphi_j|\hat{V}|\varphi_k\rangle U_{k\beta} \\ &= \sum_{jk\alpha} U_{\alpha j}^\dagger U_{j\gamma} V(x_\gamma) U_{\gamma k}^\dagger U_{k\beta} = V(x_\alpha)\delta_{\alpha\beta} \ , \end{aligned}$$

where Eq. (2.63) was used in the last step. Hence

$$\boxed{V_{\alpha\beta}^{\mathrm{DVR}} = V(x_\alpha)\delta_{\alpha\beta}} \tag{2.88}$$

Error Analysis

In addition to the basis set truncation error, there is the approximate evaluation of the matrix elements. However, linear potentials are exact in FBR/DVR.

$$\begin{aligned} V &= V_0 + V_1 x \\ \langle\chi_\alpha|\hat{V}|\chi_\beta\rangle &= V_0\langle\chi_\alpha|\chi_\beta\rangle + V_1\langle\chi_\alpha|\hat{x}|\chi_\beta\rangle \\ &= V_0\delta_{\alpha\beta} + V_1 x_\alpha \delta_{\alpha\beta} \\ &= V(x_\alpha)\delta_{\alpha\beta} \qquad \text{(DVR result)} \end{aligned}$$

An error is introduced by x^2 and higher order terms.

$$\begin{aligned} \langle\varphi_j|x^2|\varphi_k\rangle &= \sum_{l=1}^{\infty}\langle\varphi_j|x|\varphi_l\rangle\langle\varphi_l|x|\varphi_k\rangle \\ &= (\boldsymbol{Q}^2)_{jk} + \underbrace{\sum_{l=n+1}^{\infty}\langle\varphi_j|x|\varphi_l\rangle\langle\varphi_l|x|\varphi_k\rangle}_{\text{FBR/DVR error}} \end{aligned}$$

The error would vanish if the matrix $\langle\varphi_j|x|\varphi_l\rangle$ would be diagonal. But this is impossible because it implies φ is a δ function in space. The error is minimized if the matrix $\boldsymbol{Q}$ is tri-diagonal for all n. Then

$$\langle\varphi_j|x^l|\varphi_k\rangle = (\boldsymbol{Q}^l)_{jk} \qquad \text{if} \qquad j+k+l \le 2n+1 \ .$$

(sounds familiar?)
I.e. the FBR/DVR evaluation of the matrix element $\langle\varphi_j|x^l|\varphi_k\rangle$ is *exact* if $j+k+l \le 2n+1$.

Comparing diagonalization FBR to quadrature

$$V_{jk}^{\mathrm{FBR}} = V(\boldsymbol{Q}) = \sum_{\alpha=1}^{n} U_{j\alpha} V(x_\alpha) U_{k\alpha}^*$$
$$\stackrel{!?}{=} \sum_{\alpha=1}^{n} w_\alpha \varphi_j^*(x_\alpha) V(x_\alpha) \varphi_k(x_\alpha)$$

Assigning $w_\alpha^{1/2}$ to each basis function yields by comparison

$$U_{j\alpha} = w_\alpha^{1/2} \varphi_j^*(x_\alpha) \ .$$

The equation looks good and familiar, except that now U and φ are known and we have to evaluate w_α.

$$w_\alpha^{1/2} = U_{k\alpha}^* / \varphi_k(x_\alpha) = U_{j\alpha} / \varphi_j^*(x_\alpha)$$

The right hand side depends on k (or j), and there is no reason why it should be independent of k.
Hence:
The evaluation of $\boldsymbol{V}$ by diagonalization DVR is in general *not* equivalent to evaluation by quadrature. In consequence, there is in general no discrete orthonormality, discrete completeness, or discrete δ-property, simply because there are no weights.
However (Dickinson and Certain, 1968):
If $\boldsymbol{Q}$ is tri-diagonal for all n, then $U_{j\alpha}/\varphi_j^*(x_\alpha)$ is independent of j. The eigenvalues of $\boldsymbol{Q}$, x_α, and the weights $w_\alpha^{1/2} = U_{j\alpha}/\varphi_j^*(x_\alpha)$ constitute a quadrature rule which is of Gaussian quality. The evaluation of the potential matrix via $\boldsymbol{V}^{\mathrm{FBR}} = V(\boldsymbol{Q})$ is then equivalent to evaluating all matrix elements by Gauss quadrature. We then call the (diagonalization) DVR a *proper* DVR. Otherwise, when $\boldsymbol{Q}$ is not tri-diagonal, we call it *improper*. A proper DVR fulfills discrete orthonormality, discrete completeness, etc, because $w^{1/2}\varphi_j^*(x_\alpha)$ is unitary. For an improper DVR, all these nice relations have no meaning because there are no weights.

Finally two technical remarks.

1. It is numerically simpler and more stable to diagonalize x rather than to search for zeros of a polynomial.

2. If $\boldsymbol{Q}$ is not tri-diagonal, one should try to find a monotonic function f so that $F_{jk} = \langle \varphi_j | f(x) | \varphi_k \rangle$ is tri-diagonal. Let f_α denote the eigenvalues of $\boldsymbol{F}$. The grid points are then given by $x_\alpha = f^{-1}(f_\alpha)$. The formula for the weights does not change. This procedure is equivalent to the coordinate change discussed above.

Proper DVR working equations

$$\psi(x) = \sum_{\alpha=1}^{n} \psi_\alpha \chi_\alpha(x)$$

where (with $Q = 1 - P$)

$$\begin{aligned}\psi_\alpha &:= w_\alpha^{1/2} \psi(x_\alpha) \\ &= \langle \chi_\alpha | \psi \rangle + w_\alpha^{1/2} (Q\psi)(x_\alpha)\end{aligned}$$

$$\boldsymbol{\psi} = \begin{pmatrix} \psi_1 \\ \vdots \\ \psi_n \end{pmatrix} = \begin{pmatrix} w_1^{1/2}\psi(x_1) \\ \vdots \\ w_n^{1/2}\psi(x_n) \end{pmatrix}$$

$$\langle \phi | \psi \rangle = \sum_{\alpha=1}^{n} \phi_\alpha^* \psi_\alpha$$

$$\langle \phi | V | \psi \rangle = \sum_{\alpha=1}^{n} \phi_\alpha^* V(x_\alpha) \psi_\alpha$$

One almost never needs the weights w_α explicitly, except for plotting $\psi(x)$ and for defining the initial state.

Summary: Quadrature DVR

A Gaussian Quadrature rule delivers grid-points x_α, weights w_α, and basis functions $\varphi_j(x) = \sqrt{\omega(x)} P_{j-1}(x)$.

$T_{jk} := \langle \varphi_j | \hat{T} | \varphi_k \rangle$ must be known analytically.

$V_{jk}^{\mathrm{VBR}} := \langle \varphi_j | \hat{V} | \varphi_k \rangle$ (exact)

$V_{jk}^{\mathrm{FBR}} := \langle \varphi_j | \hat{V} | \varphi_k \rangle_{\mathrm{quad}} = \sum_{\alpha=1}^{n} w_\alpha \varphi_j^*(x_\alpha) V(x_\alpha) \varphi_k(x_\alpha)$

$V_{\alpha\beta}^{\mathrm{DVR}} := V(x_\alpha)\delta_{\alpha\beta} = \langle \chi_\alpha | \hat{V} | \chi_\beta \rangle_{\mathrm{quad}}$

$\chi_\alpha(x) := \sum_{j=1}^{n} \varphi_j(x)$

$U_{j\alpha} := w_\alpha^{1/2} \varphi_j^*(x_\alpha)$ (uniatry!)

$Q_{jk} := \langle \varphi_j | \hat{x} | \varphi_k \rangle = \langle \varphi_j | \hat{x} | \varphi_k \rangle_{\mathrm{quad}}$, Q_{jk} is tri-diagonal!

Summary: Diagonalisation DVR

Take *any* orthonormal, complete basis set which allows to evaluate

$T_{jk} = \langle\varphi_j|\hat{T}|\varphi_k\rangle$, and $Q_{jk} = \langle\varphi_j|\hat{x}|\varphi_k\rangle$ analytically.

Diagonalize: $\mathbf{Q} = \mathbf{U}\mathbf{X}\mathbf{U}^\dagger$, $\mathbf{X}_{\alpha\beta} = x_\alpha\delta_{\alpha\beta}$

$V_{jk}^{\mathrm{FBR}} := V(\boldsymbol{Q}) = \sum_{\alpha=1}^{n} U_{j\alpha}V(x_\alpha)U_{k\alpha}^* = \mathbf{U}\mathbf{V}^{\mathrm{DVR}}\mathbf{U}^\dagger$

$\chi_\alpha(x) := \sum_{j=1}^{n} \varphi_j(x)U_{j\alpha}$

$V_{\alpha\beta}^{\mathrm{DVR}} = V(x_\alpha)\delta_{\alpha\beta} = \langle\chi_\alpha|\hat{V}^{\mathrm{FBR}}|\chi_\beta\rangle \approx \langle\chi_\alpha|\hat{V}|\chi_\beta\rangle$

If $\mathbf{Q}$ is tri-diagonal, then $w_\alpha^{1/2} = U_{1\alpha}/\varphi_1^*(x_\alpha)$
and x_α and w_α constitute a Gaussian quadrature rule.
It is then a proper DVR with Discrete Orthonormality, Discrete Completeness, and Discrete δ-Property.

Otherwise one has an improper DVR without a quadrature rule.

2.3.4 Direct DVR

Define DVR functions $\chi_\alpha(x)$ such that

$$\langle\chi_\alpha|\chi_\beta\rangle = \delta_{\alpha\beta} \tag{2.89}$$

$$w_\alpha^{1/2}\chi_\alpha(x_\beta) = \delta_{\alpha\beta} \tag{2.90}$$

Then we have proven that discrete orthonormality etc. follows, and we have a proper DVR with $\boldsymbol{U} = \mathbf{1}$ and FBR=DVR. Additionally, the matrix elements $\langle\chi_\alpha|\hat{T}|\chi_\beta\rangle = T_{\alpha\beta}^{\mathrm{DVR}}$ must be analytically evaluable.

Example: Universal DVR (Sinc-DVR) by Colbert and Miller (1982)

$$\begin{aligned}
&x_\alpha = x_0 + \alpha\Delta x \quad , \quad \alpha = \ldots, -1, 0, 1, 2, \ldots \\
&\chi_\alpha(x) = \frac{(\Delta x)^{1/2}}{\pi}\frac{\sin\frac{\pi}{\Delta x}(x - x_\alpha)}{x - x_\alpha} \\
&\chi_\alpha(x_\beta) = 0 \quad \text{for } \alpha \neq \beta \\
&\chi_\alpha(x_\alpha) = \frac{(\Delta x)^{1/2}}{\pi}\frac{\pi}{\Delta x} = (\Delta x)^{-1/2} \Rightarrow w_\alpha = \Delta x
\end{aligned}$$

To do the matrix elements, we introduce the Fourier transform $\tilde{\chi}$

$$\chi_\alpha(x) = (2\pi)^{-1/2}\int e^{-ipx}\tilde{\chi}_\alpha(p)dp \tag{2.91}$$

$$\tilde{\chi}_\alpha(p) = \begin{cases} \left(\frac{2\pi}{\Delta x}\right)^{-1/2} e^{i\pi x_\alpha p} & \text{for } |p| \leq \frac{\pi}{\Delta x} \\ 0 & \text{else} \end{cases} \tag{2.92}$$

$$\delta_{\alpha\beta} = \langle\tilde{\chi}_\alpha|\tilde{\chi}_\beta\rangle = \langle\chi_\alpha|\chi_\beta\rangle \tag{2.93}$$

$$\langle\chi_\alpha|\frac{\partial}{\partial x}|\chi_\beta\rangle = \langle\chi_\alpha| - i\hat{p}|\chi_\beta\rangle = \begin{cases} 0 & \text{if } \alpha = \beta \\ \frac{1}{\Delta x}\frac{(-1)^{\alpha-\beta}}{\alpha-\beta} & \text{else} \end{cases} \tag{2.94}$$

$$\langle\chi_\alpha|\frac{\partial^2}{\partial x^2}|\chi_\beta\rangle = \langle\chi_\alpha| - \hat{p}^2|\chi_\beta\rangle = \begin{cases} -\frac{1}{3}\frac{\pi^2}{(\Delta x)^2} & \alpha = \beta \\ -\frac{2}{(\Delta x)^2}\frac{(-1)^{\alpha-\beta}}{(\alpha-\beta)^2} & \alpha \neq \beta \end{cases} \tag{2.95}$$

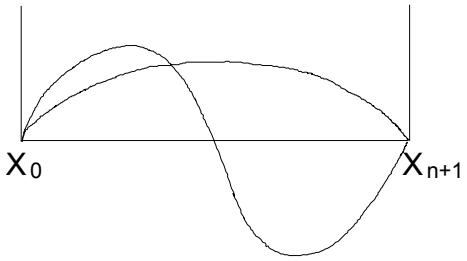
A problematic point of this DVR id that the grid formally runs from $-\infty$ to $+\infty$. However, for regions where the potential is large, one may drop the grid points because the wavefunction (virtually) vanishes there anyway. But because of this additional approximation, the sine-DVR, to be discussed next, should be preferred.

2.3.5 Example: Proper DVR, Sine-DVR

In most cases one cannot derive the DVR grid points, weights, etc. analytically, because it requires the diagonalization of a matrix. For the sine-DVR, however, one can do everything analytically.

The underlining basis functions are the "particle in a box" functions.

$$\varphi_j(x) = \begin{cases} \sqrt{2/L}\sin(j\pi(x-x_0)/L) \text{ for } x_0 \le x \le L \\ 0 \text{ else} \end{cases} \tag{2.96}$$



$L = x_{n+1} - x_0$

The following matrix elements can be done exactly.

$$\langle\varphi_j|\varphi_k\rangle = \delta_{jk} \tag{2.97}$$

$$\langle\varphi_j|\frac{\partial}{\partial x}|\varphi_k\rangle = \mathrm{mod}(j-k,2)\frac{4}{L}\frac{jk}{j^2-k^2} \text{ for } j \neq k \tag{2.98}$$

$$\langle\varphi_j|\frac{\partial^2}{\partial x^2}|\varphi_k\rangle = -\left(\frac{j\pi}{L}\right)^2 \delta_{jk} \tag{2.99}$$

The matrix $\langle\varphi_j|x|\varphi_k\rangle$ is obviously not tri-diagonal. But after transforming the coordinate

$$f(x) = \cos(\pi(x-x_0)/L) \tag{2.100}$$

one finds

$$F_{jk} = \langle\varphi_j|f(x)|\varphi_k\rangle = \frac{1}{2}(\delta_{j,k+1} + \delta_{j,k-1}) = \frac{1}{2}\begin{pmatrix} 0 & 1 & 0 & \cdots \\ 1 & 0 & 1 & \cdots \\ 0 & 1 & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \tag{2.101}$$

This matrix is so simple that it can be diagonalized analytically.

$$U_{j\alpha} = \sqrt{\frac{2}{n+1}}\sin\left(\frac{j\alpha\pi}{n+1}\right) \tag{2.102}$$

with eigenvalues

$$f_\alpha = \cos\left(\frac{\alpha\pi}{n+1}\right) \tag{2.103}$$

This yields the DVR grid-points

$$x_\alpha = f^{-1}(f_\alpha) = x_0 + \frac{L}{\pi}\arccos(f_\alpha) = x_0 + \alpha\frac{L}{n+1} = x_0 + \alpha\Delta x \;\alpha = 1, 2, \ldots, n \tag{2.104}$$

with $\alpha = 1, 2, \ldots, n$ and $\Delta x = \frac{L}{n+1}$. Note that x_0 and x_{n+1} do not belong to the grid! The wavefunction is vanishing there anyway. The weights are constant.

$$w_\alpha^{1/2} = U_{j\alpha}/\varphi_j(x_\alpha) = \sqrt{\frac{L}{n+1}} = \sqrt{\Delta x} \tag{2.105}$$

hence $w_\alpha = \Delta x$ as it is to be expected for an evenly spaced grid.

The FBR derivative matrices are to be transformed to DVR. For the second derivative matrix, this can be done analytically. See MCTDH-review Eq. (B.65). The sum $\chi_\alpha(x) = \sum_{j=1}^{n} \varphi_j(x) U_{j\alpha}$ can also be done analytically:

$$\chi_\alpha(x) = \frac{1}{2\sqrt{L(n+1)}}\left\{\frac{\sin\left[\frac{\pi}{2}(2n+1)\frac{x-x_\alpha}{L}\right]}{\sin\left[\frac{\pi}{2}\frac{x-x_\alpha}{L}\right]} - \frac{\sin\left[\frac{\pi}{2}(2n+1)\frac{x+x_\alpha}{L}\right]}{\sin\left[\frac{\pi}{2}\frac{x+x_\alpha}{L}\right]}\right\}. \tag{2.106}$$

Why does all this work from the quadrature DVR point of view? What is the Gaussian quadrature? The basis functions do not look like $\sqrt{w(x)}$ * polynomial.

We are using a Chebyshev quadrature of second kind.

$$w(x) = (1-x^2)^{1/2} \tag{2.107}$$

$$U_j(x) = \sqrt{\frac{2}{\pi}}\frac{\sin[(j+1)\arccos(x)]}{\sin[\arccos(x)]} \tag{2.108}$$

where U_j is a Chebyshev polynomial of degree j. Now we make a coordinate transformation and replace x by $f(x) = \cos(\pi(x - x0)/L)$. Then

$$\begin{aligned}\varphi_j(x) &= \sqrt{f'(x)w(f(x))}U_{j-1}(f(x)) \\ &= \sqrt{\frac{\pi}{L}\sin\frac{\pi}{L}(x-x_0)\cdot\sin\frac{\pi}{L}(x-x_0)}\frac{\sin[j\pi(x-x_0)/L]}{\sin\frac{\pi}{L}(x-x_0)}\cdot\sqrt{\frac{2}{\pi}} \\ &= \sqrt{\frac{2}{L}}\sin\left(\frac{\pi}{L}j(x-x_0)\right)\end{aligned}$$

i.e. we recover the original definition, Eq.(2.96).

2.3.6 Potential optimized DVR (PODVR)

Large dimensionality (6D or larger) requires small 1D grids for the standard method. One hence needs very adapted basis sets. Let us write the Hamiltonian in the form:

$$H = \sum_{\kappa=1}^{f} h^{(\kappa)} + V^{\mathrm{rst}}(x_1, \ldots, x_f) \tag{2.109}$$

where f denotes the number of degrees of freedom, and $h^{(\kappa)}$ is a 1D Hamiltonian operating on the κ-th degree of freedom. The separation of H into a separable and the non-separable part is not uniquely defined, but one usually can find a separation such that V^{rst} is small.

An obvious choice for a good basis is given by the eigenfunctions of $h^{(\kappa)}$

$$h^{(\kappa)}\varphi_j^{(\kappa)} = \varepsilon_j^{(\kappa)}\varphi_j^{(\kappa)} \tag{2.110}$$

These eigenfunctions can be obtained numerically but accurately by using a very large and fine 1D grid. The full Hamiltonian is then diagonalized in the product basis.

$$\Phi_{j_1\ldots j_f}(x_1, \ldots, x_f) = \varphi_{j_1}^{(1)}(x_1)\cdots\varphi_{j_f}^{(f)}(x_f) \tag{2.111}$$

where on takes only a few lowest eigenfunctions of each degree of freedom. This approach, however, requires to perform the matrix elements

$$V^{\mathrm{rst}}_{j_1\ldots j_f, k_1\ldots k_f} = \langle\Phi_{j_1\ldots j_f}|V^{\mathrm{rst}}|\Phi_{k_1\ldots k_f}\rangle \tag{2.112}$$

which is an f-dimensional integral.

One thus would like to have a DVR which is built on the eigenfunctions $\varphi_j^{(\kappa)}$. There is obviously no related Gaussian quadrature and one has to turn to diagonalization DVR which will be improper.

On the very fine grid, one computes

$$Q_{jk}^{(\kappa)} = \langle\varphi_j^{(\kappa)}|x_\kappa|\varphi_k^{(\kappa)}\rangle$$

and diagonalizes $\boldsymbol{Q}$ to obtain grid points and transformation matrices $\boldsymbol{U}^{(\kappa)}$. The 1D Hamiltonians $h^{(\kappa)}$ are then unitarily transformed with the $\boldsymbol{U}^{(\kappa)}$ to DVR-representation. The DVR-representation of V^{rst} is obvious.

Note that in this approach not only the kinetic energy operator, but the whole separable part is done variationally correctly (exact or almost exact integrals; the latter done numerically on the very fine 1D grids). Only V^{rst} is done by the DVR approximation, which however is improper. A DVR representation of the kinetic energy operator (KEO) is not needed, as the KEO is already included when diagonalizing $h^{(\kappa)}$.

2.3.7 Two-dimensional DVR (KLeg and PLeg)

If one uses spherical coordinates[5] θ and ϕ, there will appear operators like

$$\hat{j}^2 = -\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) \tag{2.113}$$

$$\hat{j}_\pm = e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right) . \tag{2.114}$$

These operators are *singular* for $\theta = 0$ *or* π. The singularity appears only in coordinate space, all matrix elements are non-singular when an appropriate basis set, e.g. the spherical harmonics Y_{lm}, are used. In fact,

$$\hat{j}^2 Y_{lm} = l(l+1)Y_{lm} \tag{2.115}$$

$$\hat{j}_\pm Y_{lm} = \sqrt{l(l+1) - m(m\pm 1)}Y_{l,m\pm 1} . \tag{2.116}$$

However, rather than a basis set, we would like to use a DVR. To this end, let us introduce the L^2-normalized associated Legendre functions

$$\tilde{P}_l^m(\cos\theta) = (-1)^m\sqrt{\frac{(2l+1)(l-m)!}{2(l+m)!}}P_l^m(\cos\theta) \tag{2.117}$$

The spherical harmonics are then given by

$$Y_{lm}(\theta,\phi) = \tilde{P}_l^m(\cos\theta)\cdot\frac{e^{im\phi}}{\sqrt{2\pi}} . \tag{2.118}$$

This is *not* a product basis, because $\tilde{P}_l^m$ depends on m.

For $m = 0$, we obtain the usual Legendre functions $P_l^{m=0} = P_l$, which are polynomials in $x = \cos\theta$. The associated functions P_l^m are not polynomials as they contain the factor $(1-x^2)^{|m|/2}$.

For the Legendre polynomials, there exist Gauss-Legendre quadrature and hence a proper DVR for the coordinate θ.

Corry, Tromp, and Lemoine have noticed that Gauss-Legendre quadrature an be used for the $m \neq 0$ case as well. They noticed that

$$\langle\tilde{P}_l^m|\cos^k\theta|\tilde{P}_{l'}^m\rangle = \sum_{\alpha=1}^{n} w_\alpha\tilde{P}_l^m(\cos\theta_\alpha)\cos^k\theta_\alpha\tilde{P}_{l'}^m(\cos\theta_\alpha) \tag{2.119}$$

is exact for $l+l'+k \leq 2n-1$. This is our old result if one recalls that l starts at 0 (not at 1), which replaces $2n+1$ by $2n-1$. We define $l_{\max} = n-1$ and

[5]For semi-rigid and flexible molecules.

restrict l and l' by $0 \leq l \leq l_{\max}$, and we find that all matrix elements are exact by quadrature for $k = 0$ and 1. This looks like a proper DVR. However, for $m \neq 0$, there are fewer basis functions than grid points, because $l \geq |m|$ while we keep using the grid points built from $m = 0$.

Before we proceed, let us change the nomenclature and substitute l, m by j, k, which is the usual nomenclature when dealing with body-fixed coordinates and related KEO.

Furthermore, we exchange ϕ by k via Fourier transform.

$$\psi(\theta, \phi) = \frac{1}{\sqrt{2\pi}} \sum_k \psi(\theta, k) e^{ik\phi} \tag{2.120}$$

$$\psi(\theta, k) = \frac{1}{\sqrt{2\pi}} \int_0^{2\pi} \mathrm{d}\phi \psi(\theta, \phi) e^{-ik\phi} \tag{2.121}$$

The associated operators now read

$$\hat{j}^2 = -\left(\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} - \frac{k^2}{\sin^2\theta} \right) \tag{2.122}$$

$$\hat{j}_\pm = \pm \frac{\partial}{\partial\theta} - k \cot\theta \text{ and } k \to k \pm 1 \tag{2.123}$$

$$\hat{j}^2 \tilde{P}_j^k = j(j+1) \tilde{P}_j^k \tag{2.124}$$

$$\hat{j}_\pm \tilde{P}_j^k = \sqrt{j(j+1) - k(k \pm 1)} \tilde{P}_j^{k\pm1} \,. \tag{2.125}$$

To introduce a DVR, we define transformation matrices U for each value of k individually

$$U_{j\alpha}^k = w_\alpha^{1/2} \tilde{P}_j^k(\cos\theta_\alpha) \tag{2.126}$$

The rows of $U_{j\alpha}^k$ are orthonormal as long as $j \leq j_{\max} \equiv n - 1$. This follows immediately from Eq. (2.119). However, if one restricts j to $j \leq j_{\max}$, there are only $j_{\max} + 1 - |k|$ rows but $n = j_{\max} + 1$ columns. To make $\boldsymbol{U}^k$ square and eventually unitary, we let j run from $|k|$ to $j_{\max} + |k|$ and successively Schmidt-orthogonalize the rows $j_{\max}+1, \ldots, j_{\max}+|k|$ to the lower ones. This ad-hoc procedure for achieving unitary matrices works well, because only the high j-states, which should be only weakly populated, are modified.

Let us analyze what we have done. Schmidt-orthogonalization is equivalent to QR-decomposition, i.e. decomposition of a matrix in a unitary and a tri-angular one. In our case, it reads

$$w_\alpha^{1/2} \tilde{P}_j^k(\cos\theta_\alpha) = \sum_{j'} R_{jj'}^k U_{j'\alpha}^k \tag{2.127}$$

with

$$\boldsymbol{R}^k = \begin{pmatrix} 1 & 0 & 0 & 0 & \cdots & 0 & \cdots \\ 0 & 1 & 0 & 0 & \cdots & 0 & \cdots \\ \vdots & & \ddots & & & \vdots & \\ 0 & \cdots & 0 & 1 & 0 & 0 & \cdots \\ * & * & \cdots & * & 1 & 0 & \cdots \\ * & * & \cdots & * & * & 1 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & & \ddots \end{pmatrix} \tag{2.128}$$

where the stars $*$ denotes (in general small) non-zero entries of R^k. The upper-left $(n-k) \times (n-k)$ corner of R^k is a unit matrix.

Keeping $\tilde{P}_j^k(\cos\theta)$ as basis, we define

$$\chi_\alpha^k(\theta) = \sum_j \tilde{P}_j^k(\cos\theta) U_{j\alpha}^k = w_\alpha^{1/2} \sum_{jj'} \tilde{P}_j^k(\cos\theta) (\boldsymbol{R}^{-1})_{jj'}^k \tilde{P}_{j'}^k(\cos\theta_\alpha) \; . \tag{2.129}$$

The χ's are orthonormal, as they are generated by a unitary transform of the orthonormal $\tilde{P}$, but the χ's are not discrete orthonormal, and they do not obey the discrete δ-property. This introduces an additional error on top of the DVR-approximation. Note, however, that the kinetic energy operators are still exact.

To arrive at working equations for the kinetic energy operators we define the tensors

$$j^2(\alpha,\beta,k) = \sum_{j=|k|}^{j_{\max}+|k|} U_{j\alpha}^k j(j+1) U_{j\beta}^k \tag{2.130}$$

$$j_+(\alpha,\beta,k) = \sum_{j=\max(|k|,|k+1|)}^{j_{\max}+\min(|k|,|k+1|)} U_{j\alpha}^{k+1} \sqrt{j(j+1)-k(k+1)}\, U_{j\beta}^k \tag{2.131}$$

$$j_-(\alpha,\beta,k) = j_+(\beta,\alpha,k-1) \tag{2.132}$$

and the operations of these tensors is given by

$$(j^2\psi)(\theta_\alpha,k) = \sum_{\beta=1}^n j^2(\alpha,\beta,k)\psi(\theta_\beta,k) \tag{2.133}$$

$$(j_\pm\psi)(\theta_\alpha,k\pm1) = \sum_{\beta=1}^n j_\pm(\alpha,\beta,k)\psi(\theta_\beta,k) \; . \tag{2.134}$$

If one works in θ-ϕ space (PLeg), MCTDH uses an exponential DVR to transform $\phi \to k$:

1. $\psi(\theta, k) = \frac{1}{\sqrt{n}} \sum_{\alpha=1}^{n} \psi(\theta, \phi_\alpha) e^{-ik\phi_\alpha}$
2. Apply KLeg operator.
3. $\psi(\theta, \phi_\alpha) = \frac{1}{\sqrt{n}} \sum_{k=k_{\min}}^{k_{\max}} \psi(\theta, k) e^{ik\phi_\alpha}$

where $\phi_\alpha = 2\pi\alpha/n$ and $n = k_{\max} - k_{\min} + 1$.

Chapter 3

Propagation

The time-dependent Schrödinger equation,

$$i\frac{d|\psi(t)\rangle}{dt} = H|\psi(t)\rangle \ , \tag{3.1}$$

has, for time-independent Hamiltonians, the formal solution

$$|\psi(t)\rangle = e^{-iHt}|\psi(0)\rangle \ . \tag{3.2}$$

Once the initial wavefunction $|\psi(0)\rangle$ is known, the behavior of the wavefunction is also known via evaluating the time-evolution operator e^{iHt} operating on $|\psi(0)\rangle$. This procedure of evaluating the time-dependent wavefunction is also known as *propagation*.

In the following sections, we will illustrate different numerical methods which allow us to evaluate $|\psi(t)\rangle$ with a given Hamiltonian and initial condition $|\psi(0)\rangle$.

3.1 Split Operator

The split operator propagator is developed by Feit and Fleck (1982). Its spirit is to separate the kinetic energy operator and the potential operator in the exponential and evaluate them individually, i.e. $e^{iHt} \sim e^{iTt}e^{iVt}$. However, separating the two operators in the exponent introduces errors to the original operator since T and V does not commute. The error can be minimized by dividing a long propagation time t to multi-steps short propagation times. For example, Trotter (1959) proposed

$$e^{-\beta(T+V)} = \left(e^{-\beta(T+V)/n}\right)^n = \lim_{n\to\infty}\left(e^{-\beta T/n}e^{-\beta V/n}\right)^n \ . \tag{3.3}$$

Replacing β by it, we immediately obtain the working equation for propagation. Defining $\tau = t/n$, we would have the propagate wavefunction at time t as the following

$$|\psi(t)\rangle \simeq \left(e^{-iT\tau}e^{-iV\tau}\right)^n |\psi(0)\rangle \ . \tag{3.4}$$

In practice, we cannot take n to infinity, but we can estimate the error which is introduced to the propagation. The Baker-Campbell-Hausdorff formula reads

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]+\frac{1}{12}[A,[A,B]]+\frac{1}{12}[[A,B]B]+\cdots} \ . \tag{3.5}$$

Therefore, the effective time-evolution operator reads

$$e^{-iT\tau}e^{-iV\tau} = e^{-iH_{\text{eff}}\,\tau} = e^{-i(T+V)\tau-\frac{1}{2}\tau^2[T,V]+\tau^3\cdots} \ . \tag{3.6}$$

The first term in the exponent is the system Hamiltonian, and the rest are the errors introduced by split operator propagator. As we already mentioned, the larger the τ, the larger the error.

This method can be improved by symmetrization. If we separate the exponent by $H = V/2 + T + V/2$, applying the Baker-Campbell-Hausdorff formula gives the effective time-evolution operator under symmetrization.

$$e^{-iV\tau/2}e^{-iT\tau}e^{-iV\tau/2} = e^{-iH_{\text{eff}}\,\tau} = e^{-iH\tau+\frac{i\tau^3}{24}[H,[T,V]]+\tau^4\cdots} \ . \tag{3.7}$$

In this case, the error starts with the third order of τ. We obtain one order more by symmetrization and we will always refer to the symmetrized form when mentioning the split operator propagator hereafter. The effective Hamiltonian reads

$$H_{\text{eff}} = H - \frac{\tau^2}{24}\left[H,[T,V]\right] + O\left(\tau^3\right) \ . \tag{3.8}$$

It is Hermitian and hence secures the norm conservation. However, the effective Hamiltonian does not commute with the original system Hamiltonian The energy is not conserved. To understand how to estimate the error term for the SPO propagator, we discuss in the following three examples.

One Dimensional Problem

Given a kinetic energy operator $T = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ and a general potential $V(x)$, the leading error term can be estimated by evaluating $[H,[T,V]]$. First we evaluate $[T,V]$.

$$[T,V] = TV - VT = -\frac{\hbar^2}{2m}\left(V'' + 2V'\frac{d}{dx}\right) \tag{3.9}$$

Then we continue to evaluate the following commutators.

$$\begin{aligned} [V,[T,V]] &= -\frac{\hbar^2}{m}(V')^2 \; ; \\ [T,[T,V]] &= \frac{\hbar^4}{4m^2}\left(V''\frac{d^2}{dx^2} + 2\frac{d}{dx}V''\frac{d}{dx} + \frac{d^2}{dx^2}V''\right) \end{aligned} \tag{3.10}$$

The error term $[H,[T,V]]$ is just the sum of these two terms. From these equations follows that, when $\frac{\hbar^2}{m} \to 0$, the propagation by SPO will be exact ($H_{\text{eff}} = H$). Thus the SPO exhibits some semi-classical behavior, although it is not exact for hermonic Hamiltonians. However, in a quantum system, $\frac{\hbar^2}{m} \neq 0$, the propagation is in error and the $\langle E \rangle$ is not conserved ($[H_{\text{eff}}, H] \neq 0$).

Harmonic Oscillator

Given a harmonic oscillator potential $V(x) = \frac{1}{2}m\omega^2 x^2$. Based on Eq. 3.10 and Eq. 3.7, the leading error term of the propagator reads

$$[H,[T,V]] = 2\hbar^2\omega^2\left(\frac{1}{2}m\omega^2x^2\right) + 2\hbar^2\omega^2\left(\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\right) = 2\hbar^2\omega^2\left(V - T\right) \; . \tag{3.11}$$

In addition, we have $|\langle V - T\rangle| < \langle H\rangle = \left(n + \frac{1}{2}\right)\hbar\omega$. Thus, if we choose the atomic units, the SPO error term can be bounded by:

$$\text{Err(SPO)} < \frac{\left(n + \frac{1}{2}\right)}{12}\omega^3\tau^3 \; . \tag{3.12}$$

In contrast, the error introduced when using a Taylor expansion of the exponential till second order reads

$$\frac{\tau^3 H^3}{3!\hbar^3} = \frac{\left(n + \frac{1}{2}\right)^3\omega^3\tau^3}{6} \; , \tag{3.13}$$

which is much larger than the SPO error, when $n > 1$.

Centrifugal Potential

Given a centrifugal potential $V(r) = \frac{l(l+1)}{2mr^2}$, please estimate the leading error term. The spirit is similar to the last two sections, however, we will only estimate $[V,[T,V]]$ for simplicity. The commutator of kinetic energy operator and a r-dependent potential reads

$$[T,V] = -\frac{1}{2mr^2}\left(2rV' + r^2V'' + 2r^2V'\frac{d}{dr}\right) \; , \tag{3.14}$$

and our goal commutator reads

$$[V,[T,V]] = \frac{1}{2mr^2} 2r^2 V'V' = \frac{l^2(l+1)^2}{m^3 r^6} \ . \tag{3.15}$$

Numerical Detail

The SPO propagator is usually combined with Fast Fourier Transform (FFT) in computation. The idea is to obtain both potential and momentum under their own space so that both are diagonal. The procedure is like the following: one first obtain $\left(e^{-iV(x)\tau/2}\psi(x,t)\right)$ in the x-space and than do a Fourier transform to the k-space, multiply with $e^{-i\frac{P^2}{2m}\tau}$ and than do the inverse Fourier transform and multiply with $e^{-iV(x)\tau/2}$.

$$\psi(x,t+\tau) = e^{-iV(x)\tau/2} F^{-1}\left(e^{-i\frac{P^2}{2m}\tau} F\left(e^{-iV(x)\tau/2}\psi(x,t)\right)\right) \tag{3.16}$$

The propagator is relatively stable even in the region where the potential is high or the wavefunction is highly oscillated, compared to other energy based propagators. On the other hand, SPO requires doing $e^{-iV\tau/2}$ and $e^{-iT\tau}$ exactly, so it will fail in efficient when the degrees of freedoms are inseparable.

3.2 Approximant de Padé

Padé approximation states that a function can be written in a *rational* form as an approximation of itself. For instance, with the Padé approximation and the first order Taylor expansion, the propagator for a time step τ reads

$$e^{-iH\tau} = \frac{e^{-iH\tau/2}}{e^{iH\tau/2}} \approx \frac{1-iH\tau/2}{1+iH\tau/2} \ . \tag{3.17}$$

Applying this propagator to the wavefunction at time t, we found that $|\psi(t+\tau)\rangle$ reads

$$|\psi(t+\tau)\rangle = \frac{1-iH\tau/2}{1+iH\tau/2}|\psi(t)\rangle \ . \tag{3.18}$$

As one can see, the propagator posses the form $\frac{1-x}{1+x}$, which is known as *Cayley transform*. Hence this method is sometimes called Cayley integrator. Eq. 3.18 can be further rearranged and gives a working equation as a system of linear equations:

$$(1+iH\tau/2)|\psi(t+\tau)\rangle = (1-iH\tau/2)|\psi(t)\rangle \ . \tag{3.19}$$

Note that at each step, $|\psi(t)\rangle$ is known, and so are the Hamiltonian and τ. Therefore, finding $|\psi(t+\tau)\rangle$ is equal to solving the unknown $\mathbf{x}$ in the following equation $\mathbf{Ax} = \mathbf{b}$, where $\mathbf{A}$ is a matrix and $\mathbf{x}$, $\mathbf{b}$ are vectors. Gauss elimination and default subroutines from the LAPACK can be easily applied to solve the equation. This method is also numerically stable. Unfortunately, it will be extremely numerically expensive when the Hamiltonian becomes larger.

The effective Hamiltonian H_{eff} can be found by the following relation

$$e^{-iH\tau} \approx \frac{1 - iH\tau/2}{1 + iH\tau/2} = e^{-iH_{\text{eff}}\tau} \ . \tag{3.20}$$

Thus H_{eff} reads

$$H_{\text{eff}} = \frac{i}{\tau} ln \frac{1 - iH\tau/2}{1 + iH\tau/2} \ . \tag{3.21}$$

Here we quickly review the properties of functions $ln(1-ix)$ and $ln(1+ix)$. First, the combination of the two functions gives arctan function.

$$\frac{i}{2}\left[ln(1-ix) - ln(1+ix)\right] = \text{arctan}x \tag{3.22}$$

Besides, the power series reads

$$ln(1+ix) = ix + \frac{1}{2}x^2 - \frac{i}{3}x^3 - \frac{1}{4}x^4 + \frac{i}{5}x^5 + \cdots \ , \tag{3.23}$$

and

$$ln(1-ix) = -ix + \frac{1}{2}x^2 + \frac{i}{3}x^3 - \frac{1}{4}x^4 - \frac{i}{5}x^5 + \cdots \ . \tag{3.24}$$

Defining $\tilde{\tau} = \tau/2$ and set $x = H\tilde{\tau}$, we can rewrite the effective Hamiltonian based on Eq. 3.22, 3.23, 3.24. Finally we have

$$H_{\text{eff}} = \frac{1}{\tilde{\tau}}\text{arctan}H\tilde{\tau} = H\left(1 - \frac{\tilde{\tau}^2}{3}H^2 + \frac{\tilde{\tau}^4}{5}H^4 + \cdots\right) \ . \tag{3.25}$$

According to Eq. 3.25, the effective Hamiltonian is Hermitian. As a consequence, the norm of $|\psi(t)\rangle$ is conserved all the time. More important, $[H_{\text{eff}}\ , H^n] = 0$ for all $n \geq 0$. Therefore, there is no probability error during the propagation but only the phase error. For example, Eq. 3.26 shows that the error only appear in the phase during the propagation of an eigenfunction of H.

$$e^{-iH_{\text{eff}}\tau}\phi_n = e^{-iE_n\tau} \cdot e^{i\left(\frac{2}{3}E_n^3\tilde{\tau}^3 - \frac{2}{5}E_n^5\tilde{\tau}^{5\cdots}\right)}\phi_n \tag{3.26}$$

3.3 Second Order Difference (SOD)

Previously we illustrate the propagators which involve only single time step, i.e. evaluating $|\psi(t+\tau)\rangle$ based only on $|\psi(t)\rangle$. There are also methods to propagate a wave function by using wave functions of different time steps. Second order difference (SOD) is one of those multi-step integrators. Suppose we have the wave functions $|\psi(t-\tau)\rangle$,$|\psi(t)\rangle$, and $|\psi(t+\tau)\rangle$. They are

$$\begin{aligned} |\psi_+\rangle &:= |\psi(t+\tau)\rangle = e^{-iH\tau}|\psi(t)\rangle \\ |\psi_0\rangle &:= |\psi(t)\rangle \\ |\psi_-\rangle &:= |\psi(t-\tau)\rangle = e^{iH\tau}|\psi(t)\rangle \ . \end{aligned} \tag{3.27}$$

The wave function difference is given by

$$|\psi_+\rangle - |\psi_-\rangle = (e^{-iH\tau} - e^{iH\tau})|\psi_0\rangle = -2i\sin(H\tau)|\psi_0\rangle \ . \tag{3.28}$$

The exact propagation is given by multi-steps, i.e. $|\psi_+\rangle$ depends on $|\psi_-\rangle$ and $|\psi_0\rangle$.

$$|\psi_+\rangle = |\psi_-\rangle - 2i\sin(H\tau)|\psi_0\rangle \tag{3.29}$$

However, when performing the propagation, one usually use an approximated form by linearizing the sine function.

$$|\psi_+\rangle = |\psi_-\rangle - 2iH\tau|\psi_0\rangle \tag{3.30}$$

This working equation, Eq. 3.30, can be viewed as we use an effective Hamiltonian H_{eff} in Eq. 3.29. Therefore, we have the effective Hamiltonian as the following:

$$\begin{aligned} \sin(H_{\text{eff}}\tau) &= H\tau \\ H_{\text{eff}} &= \frac{1}{\tau}\arcsin(H\tau) \ . \end{aligned} \tag{3.31}$$

Although the H_{eff} is Hermitian, the norm of the wave function is only *conditionally stable*, i.e. for all Hilbert space $\|H\tau\|_H < 1$, due to the fact that the arcsin function becomes complex and H_{eff} hence non-hermitian, if the argument is not within [-1,1]. It can be shown that the norm of wave function will explode suddenly when $\|H\tau\|_H > 1$.