The dynamics of angular degrees of freedom: new basis set and grid representations of Hamiltonian operators

Florian Rupp
TU Muenchen
rupp@ma.tum.de

Clemens Woywod
University of Tromsø
woywod@ch.tum.de
Outline

✓ Part I: Recipe & ingredients for a vibrational calculation
✓ Part II: A new basis set for angular motion & comparison with Legendre functions
✓ Part III: Overview of localized & delocalized representations, construction of localized mixed basis functions, applications
✓ Part IV: Conclusions
Part I

Recipe & ingredients for a vibrational calculation
Vibrational spectrum of H$_2$O

- How to compute very accurately the vibrational levels of H$_2$O in the electronic ground state?

  ✓ Compute potential energy surface on dense grid in (r$_1$, r$_2$, α) – space
  ✓ Make decision: definition of potential energy operator V(r$_1$, r$_2$, α) directly on grid or via analytical model function
  ✓ Select basis functions for description of vibrational wave functions. If V(r$_1$, r$_2$, α) is defined on discrete set of points basis functions are still needed for representation of T operator

- Popular basis functions for radial degrees of freedom:

  \[ \mu_n(x) = \sqrt{\frac{2}{b-a}} \sin\left(\frac{n\pi(x-a)}{(b-a)}\right), \quad n = 1,2,\ldots,N \]

  \[ \nu_n(x) = \sigma \cos\left(\frac{n\pi(x-a)}{(b-a)}\right), \quad n = 0,1,2,\ldots,N-1 \]

  \[ \begin{cases} 
  \sigma = \sqrt{\frac{1}{b-a}}, & n = 0 \\
  \sigma = \sqrt{\frac{2}{b-a}}, & n \neq 0 
  \end{cases} \]

  See e.g. Colbert & Miller, JCP 96, 1982 (1992)
Vibrational basis sets

- Why are the $\mu_n(x)$ and $\nu_n(x)$ functions popular?
  - They yield analytic expressions for $\langle \mu_m|T|\mu_n \rangle$ and $\langle \nu_m|T|\nu_n \rangle$ for finite and infinite definition intervals $[a,b]$.
  - They are associated with an equidistant quadrature grid (relation to Chebychev).
  - The quadrature rule is of Gaussian accuracy (discrete orthogonality).

$$\int_a^b f(x) \, dx = w \sum_{k=1}^{N} f(x_k) \begin{cases} w = \frac{b-a}{N+1}, \text{ for } \mu_n \\ w = \frac{b-a}{N}, \text{ for } \nu_n \end{cases}$$

- Which basis sets are appropriate for bending motion?
  - The bending kinetic energy operator is:

$$\hat{T}_{\text{bend}} = -c_{\text{bend}} \left( \frac{\partial^2}{\partial x^2} + \cot(x) \frac{\partial}{\partial x} \right)$$

$$c_{\text{bend}} = \frac{1}{2\Theta}$$
Legendre basis for bending motion

- In this form, $T_{\text{bend}}$ is hermitian on $[0, \pi]$ with respect to volume element $\sin(x) \, dx$
- $\mu_n(x)$ and $\nu_n(x)$ functions perform badly as basis functions for $T_{\text{bend}}$
- The standard basis functions for $T_{\text{bend}}$ are derived from Legendre polynomials $P_l(x)$:

\[
\begin{align*}
\sigma_0 P_0(\cos(x)) &= \sqrt{\frac{1}{2}} \\
\sigma_2 P_2(\cos(x)) &= \sqrt{\frac{5}{2^5}} (3 \cos(x) + 5 \cos(3x)) \\
\sigma_1 P_1(\cos(x)) &= \sqrt{\frac{3}{2}} \cos(x) \\
\sigma_3 P_3(\cos(x)) &= \sqrt{\frac{9}{2^{13}}} (9 + 20 \cos(2x) + 35 \cos(4x))
\end{align*}
\]

- $P_l(\cos(x))$ are the eigenfunctions of $T_{\text{bend}} \rightarrow$ diagonal analytic representation
- $P_l(\cos(x))$ are associated with quadrature rule of Gaussian accuracy
- Grid point density increases moderately towards interval limits

- $P_l(\cos(x))$ are suitable bending basis functions for harmonic type potential functions $\rightarrow$ performance good because the density of excited state wave functions accumulates at interval borders
Normalized Legendre functions $P_l(\cos(x))$
Part II

A new basis set for angular motion & comparison with Legendre functions
The $\eta_n(x)$ angular basis functions

- Can we formulate basis functions for bending motion that are analog to the $\mu_n(x)$ and $\nu_n(x)$ functions?
  - How about:
    \[
    \eta_n(x) = \sqrt{\frac{2}{\pi}} \frac{\sin(nx)}{\sqrt{\sin(x)}}, \ n = 1, 2, ..., N
    \]

- Properties of $\eta_n(x)$ functions:
  - they are orthonormal on $[0, \pi]$ wrt to volume element $\sin(x)\,dx$
  - the matrix elements $\langle \eta_m | T_{bend} | \eta_n \rangle$ have simple analytic solutions
  - they are related to an equidistant quadrature grid
  - the quadrature rule
    \[
    \int_0^\pi f(x) \sin(x) \, dx = \sum_{k=1}^N w_k f(x_k) \quad \text{with} \quad w_k = \sqrt{\frac{\pi}{N+1}} \sin\left(\frac{\pi k}{N+1}\right)
    \]
    is of Gaussian accuracy
\( \eta_n(x) \) functions
Definition of model Hamiltonian

- We compare the performance of $\eta_n(x)$ and $P_l(\cos(x))$ basis functions
- Model system: pure bending motion of $\text{H}_2\text{O}$

$$\hat{H} = \hat{T}_{bend} + c_0 + c_1(\cos(x)) + c_2(\cos(x))^2 + c_3(\cos(x))^3 + c_4(\cos(x))^4$$

relatively harmonic potential $\rightarrow$ well suited for Legendre basis

- Variational Basis Representation (VBR) for $H$

$$\langle \varphi_m(x) | \hat{O} | \varphi_n(x) \rangle = \int_a^b \varphi_m(x) \left[ \hat{O} \varphi_n(x) \right] w(x) \, dx$$

✓ For a true VBR, all matrix elements must be evaluated exactly
Legendre VBR for $\text{H}_2\text{O}$ bending
ηₙ(x) VBR for H₂O bending
How to improve performance of $\eta_n(x)$?

- Obviously, a basis formed exclusively by $\eta_n(x)$ functions is incomplete.
- Can we use the complementary functions?

$$\sigma_n \frac{\cos(nx)}{\sqrt{\sin(x)}}, n = 0,1,2..., N-1$$

- Can we supplement the $\eta_n(x)$ functions? For example:

$$s_r(x) = \exp(-r \sin(x)) \quad s_t(x) = \exp(-t \sin(x))$$

$$\{\eta_m(x)(1 - s_r(x)), P_n(\cos(x))s_t(x)\}$$

- Switching functions $(1-s_r(x))$, $s_t(x)$ keep basis orthogonal.
- Evaluation of matrix elements tedious.
Supplementation of $\eta_n(x)$ functions

- Is direct basis extension an option? For example:

$$\begin{align*}
\left\{ \eta_1(x), \eta_2(x), \ldots, \eta_N(x), \\
\sigma_0 P_0(\cos(x)), \sigma_1 P_1(\cos(x)), \ldots, \sigma_M P_M(\cos(x)) \right\}
\end{align*}$$

- We construct representation of $H$ in this mixed basis $\rightarrow$ symmetric matrix $A$
- Loewdin (symmetric) orthogonalization of mixed basis:
  - Diagonalization of overlap matrix yields eigenvector matrix $U$ and the matrix $X=\text{diag}(1/\sqrt{\epsilon_1}, 1/\sqrt{\epsilon_2}, \ldots, 1/\sqrt{\epsilon_N})$
  - Orthogonalization of mixed basis according to:

$$\left( UXU^T \right) A \left( UXU^T \right) = H$$

- $H$ is the desired representation of $H$ in orthonormal mixed basis
Mixed basis (+ $P_0, P_1$) VBR H$_2$O bending
Part III

Overview of localized & delocalized representations, construction of localized mixed basis functions, applications
Overview: representations

- We differentiate between infinitely localized, nearly localized and delocalized basis functions.
- Discrete representations are only possible for local operators.
- Discrete Variable Representation (DVR) of local operator $O$ is a matrix diagonal over the grid points $x_k$.
- If the grid is related to orthogonal basis functions $\varphi_m(x)$ through a quadrature rule of the form:

$$\int_{a}^{b} f(x) w(x) dx = \sum_{k=1}^{N} w_k f(x_k)$$

then we can define a Finite Basis Representation (FBR):

$$\int_{a}^{b} \varphi_m(x) \left[ \hat{O} \varphi_n(x) \right] w(x) dx \approx \sum_{k=1}^{N} \varphi_m(x_k) \left[ \hat{O} \varphi_n(x_k) \right] w_k$$
FBR matrix is an approximation to the VBR matrix

FBR and DVR are equivalent:

In analogy we can define:

NDVR matrix is an approximation to the DVR matrix:

NDVR basis functions are approximately localized at grid points $x_k$.

The term “DVR calculation” is not exact:

DVR results are not variational!

How to perform “DVR calculation” for mixed basis functions $Q_n(x)$?

Definition of grid points through zeroes of $Q_{N+M+1}(x)$ (from $\eta_{N+1}(x)$ and $P_M(\cos(x))$)

→ explicit derivation of orthogonal mixed basis

Establishment of quadrature rule for mixed basis → derivation of $\Lambda$ matrix
$Q_m(x)$ VBR for $m=1,2,3,4$ from $\eta_n(x) \ (n=1-8)$, $P_l(\cos(x)) \ (l=1-4)$
\( Q_m(x) \) NDVR localized at \( x_k, \ k=1,2,3,6 \) from \( \eta_n(x) (n=1-30), \ P_l(\cos(x)) (l=1-2) \)
\[ V_1 = 300 + 3000 \cos(x) + 8000 (\cos(x))^2 - 3000 (\cos(x))^3 - 2000 (\cos(x))^4 \]

\[ c_{bend} = 10.0 \]
Legendre VBR for $V_1$
$Q_m(x)$ VBR for $V_1$ from $\eta_n(x)$ ($n=1-N-2$), $P_l(\cos(x))$ ($l=1-2$)
Legendre VBR for $V_1$
$Q_m(x)$ VBR for $V_1$ from $\eta_n(x)$ ($n=1$-$N$-$2$), $P_l(\cos(x))$ ($l=1$-$2$)
Legendre DVR for $V_1$
$Q_m(x)$ DVR for $V_1$ from $\eta_n(x)$ $(n=1-N-2)$, $P_l(\cos(x))$ $(l=1-2)$
Legendre DVR for $V_1$
$Q_m(x)$ DVR for $V_1$ from $\eta_n(x) \ (n=1-N-2)$, $P_l(\cos(x)) \ (l=1-2)$
\[ V_2 = 420 - 4000 \cos^2(x) + 10000 \cos^4(x) \]

\[ c_{\text{bend}} = 10.0 \]
Legendre VBR for $V_2$
$Q_m(x)$ VBR for $V_2$ from $\eta_n(x)$ ($n=1-N-2$), $P_l(\cos(x))$ ($l=1-2$)
Legendre VBR for $V_2$
$Q_m(x)$ VBR for $V_2$ from $\eta_n(x)$ ($n=1-N-2$), $P_l(\cos(x))$ ($l=1-2$)
Legendre DVR for $V_2$
$Q_m(x)$ DVR for $V_2$ from $\eta_n(x)$ ($n=1-N-2$), $P_l(cos(x))$ ($l=1-2$)
Legendre DVR for $V_2$
$Q_m(x)$ DVR for $V_2$ from $\eta_n(x) \ (n=1-N-2) , \ P_l(cos(x)) \ (l=1-2)$
Part IV

Conclusions
- Legendre functions form for many applications a good basis set for bending degrees of freedom.

- However, they offer a limited flexibility in particular for the description of states with larger density close to the center of the interval.

- The combination of $\eta_n(x)$ and $P_l(\cos(x))$ functions appears to be an interesting alternative to the pure Legendre basis.

- For mixed basis VBR calculations:
  - all matrix elements can be evaluated analytically.
  - computationally efficient because of Loewdin orthogonalization.
  - more homogeneous accuracy distribution for different eigenstates.

- For mixed basis DVR calculations:
  - explicit orthogonalization complicated → but needs to be performed only once since kinetic energy operator is always the same.
  - quadrature rule for mixed basis set has been derived.
  - accuracy similar to Legendre DVR can be reached, but further improvement necessary.
Acknowledgments

- **Cooperation:**
  - U Kassel: Dietmar Kolb

- **Financial Support:**
  - CTCC at the University of Tromsø

- **And to you:**
  - **TUSEN TAKK!**