The Centre for Theoretical and Computational Chemistry

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

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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

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Part I

Recipe & ingredients for a vibrational calculation

Vibrational spectrum of H_2O

- How to compute very accurately the vibrational levels of H_2O 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 $V(r_1, r_2, \alpha)$ directly on grid or via analytical model function
  - ✓ Select basis functions for description of vibrational wave functions. If $V(r_1, r_2, \alpha)$ 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:

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

$$\nu_n(x) = \sigma \cos\left(\frac{n\pi(x-a)}{(b-a)}\right), n = 0,1,2,\ldots,N-1 \quad \begin{cases} \sigma = \sqrt{\frac{1}{b-a}}, n = 0 \\ \sigma = \sqrt{\frac{2}{b-a}}, n \neq 0 \end{cases}$$

See e.g. Colbert & Miller, JCP **96**, 1982 (1992)

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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)

$$\int_a^b f(x)\,dx = w\sum_{k=1}^{N} f(x_k) \qquad \begin{cases} w = \dfrac{b-a}{N+1}, \ for\ \mu_n \\[2ex] w = \dfrac{b-a}{N}, \ for\ \nu_n \end{cases}$$

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

$$\hat{T}_{bend} = -c_{bend}\left(\frac{\partial^2}{\partial x^2} + \cot(x)\frac{\partial}{\partial x}\right) \qquad c_{bend} = \frac{1}{2\Theta}$$

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Legendre basis for bending motion

- ✓ In this form, T_{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_{bend}
- ✓ The standard basis functions for T_{bend} are derived from Legendre polynomials $P_l(x)$:

$$\sigma_0 P_0(\cos(x)) = \sqrt{\frac{1}{2}}$$

$$\sigma_2 P_2(\cos(x)) = \sqrt{\frac{5}{2^5}}(3\cos(x) + 5\cos(3x))$$

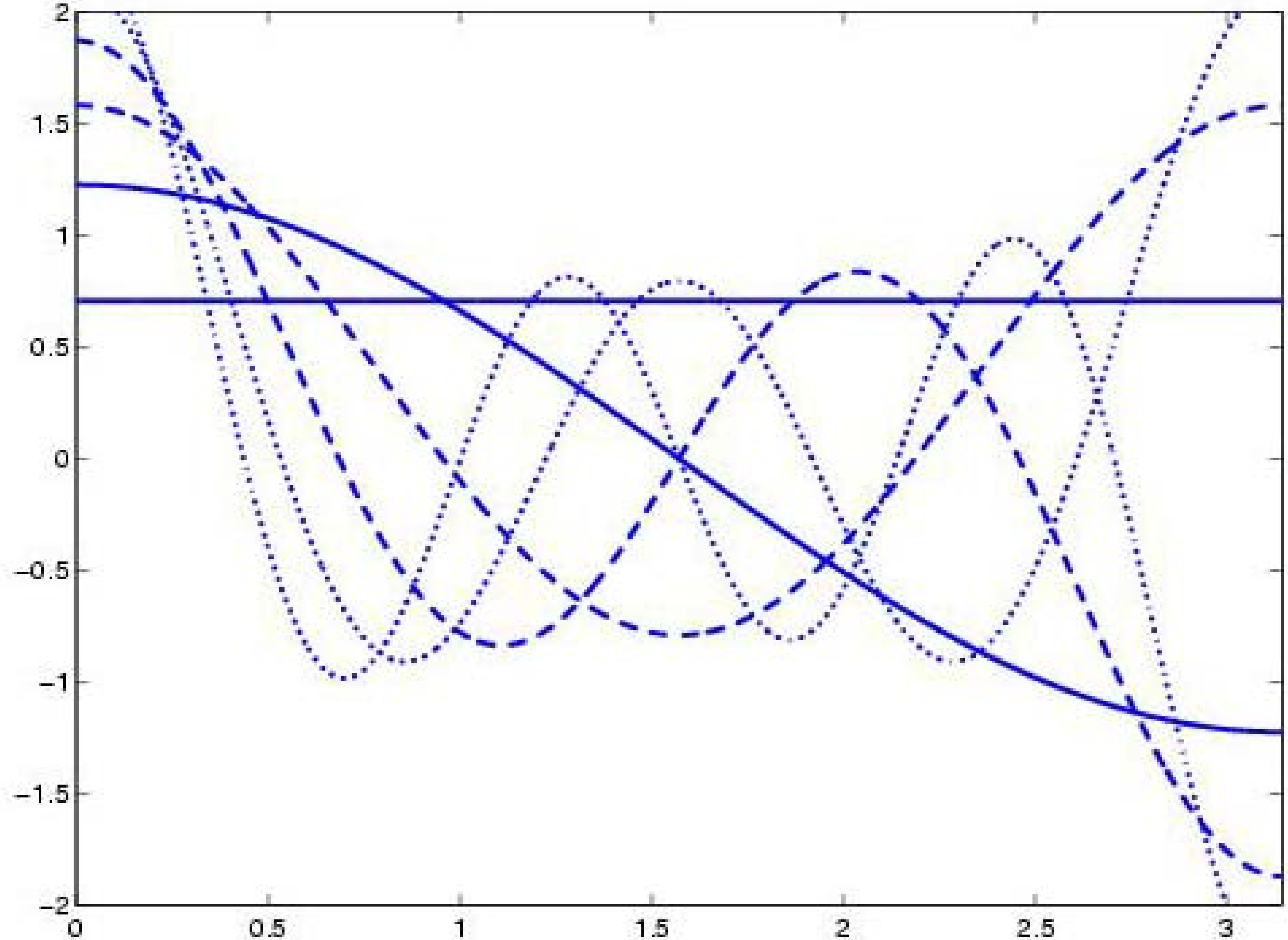
$$\sigma_1 P_1(\cos(x)) = \sqrt{\frac{3}{2}}\cos(x)$$

$$\sigma_3 P_3(\cos(x)) = \sqrt{\frac{9}{2^{13}}}(9 + 20\cos(2x) + 35\cos(4x))$$

- ✓ $P_l(\cos(x))$ are the eigenfunctions of T_{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 η_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:

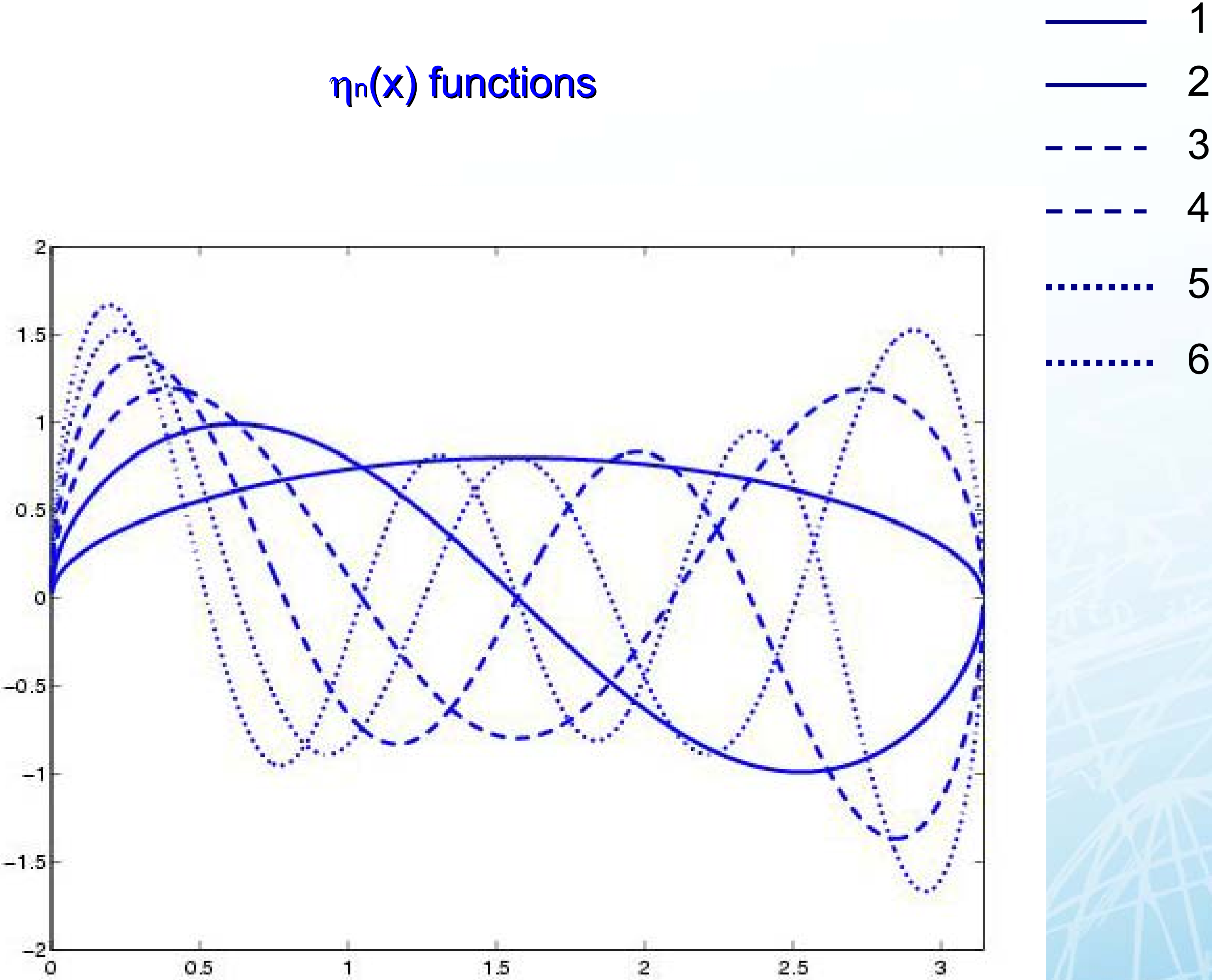
$$\eta_n(x) = \sqrt{\frac{2}{\pi}}\frac{\sin(nx)}{\sqrt{\sin(x)}}, n = 1,2,\ldots, N$$

- Properties of $\eta_n(x)$ functions :
  - ✓ they are orthonormal on [0,π] 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

$$\int_0^\pi f(x)\sin(x)\,dx = \sum_{k=1}^{N} w_k f(x_k) \qquad w_k = \sqrt{\frac{\pi}{N+1}}\sin\left(\frac{\pi k}{N+1}\right)$$

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 H_2O

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

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

- **V**ariational **B**asis **R**epresention (VBR) for H

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

✓ For a true VBR, all matrix elements must be evaluated exactly

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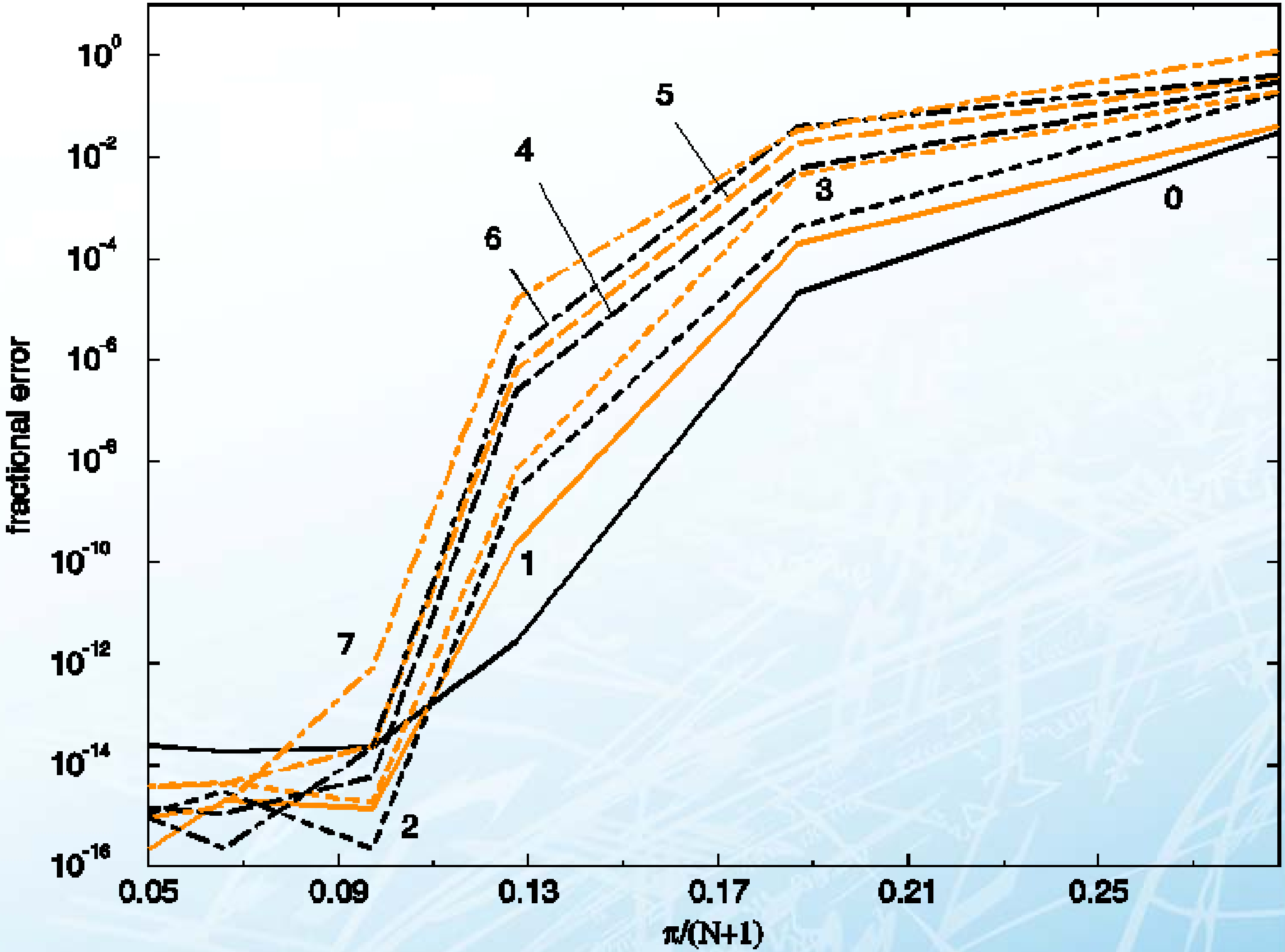
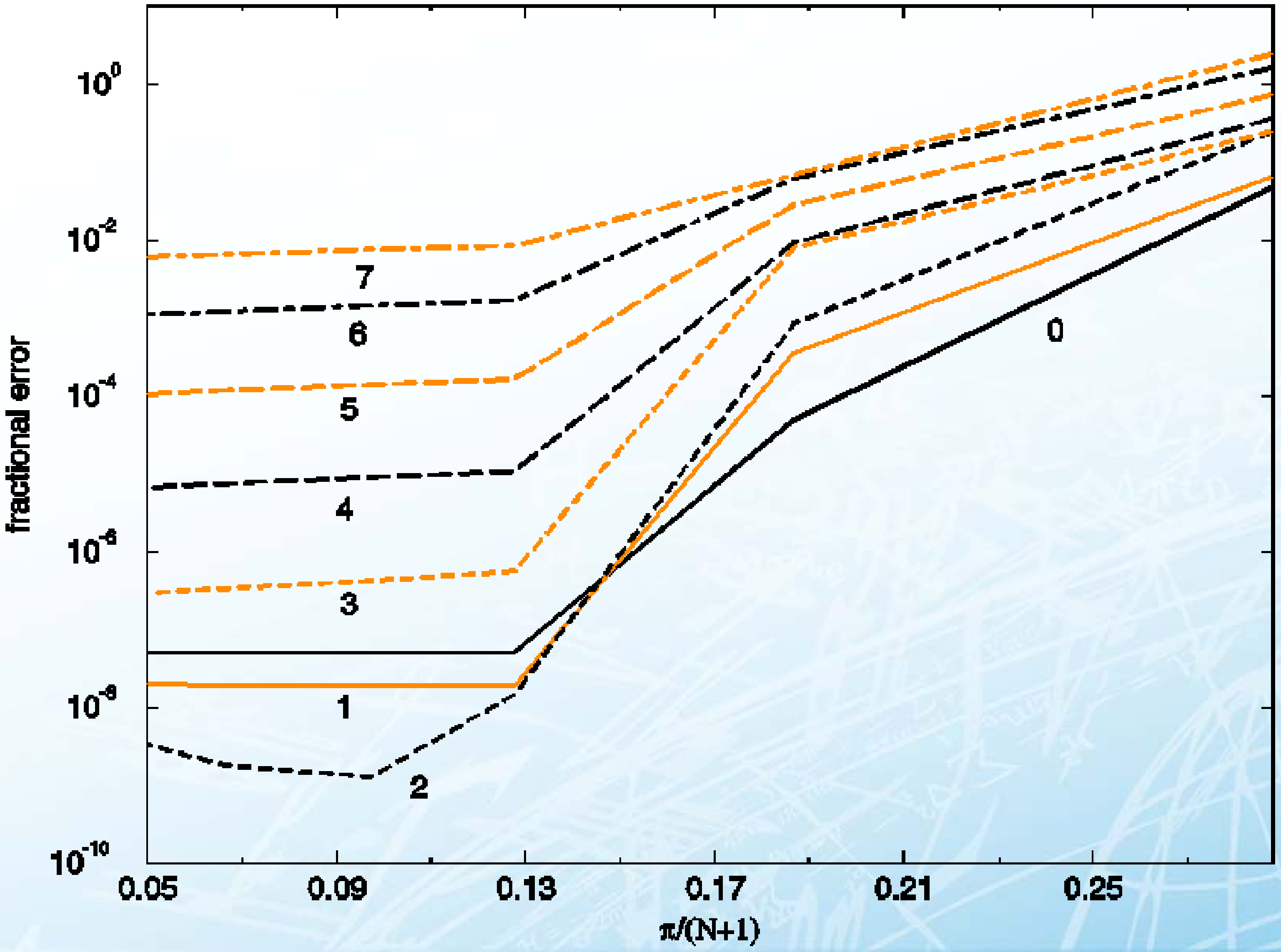
Legendre VBR for H_2O bending



$\eta_n(x)$ VBR for H_2O bending



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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:

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

✓ We construct representation of H in this mixed basis → symmetric matrix ***A***

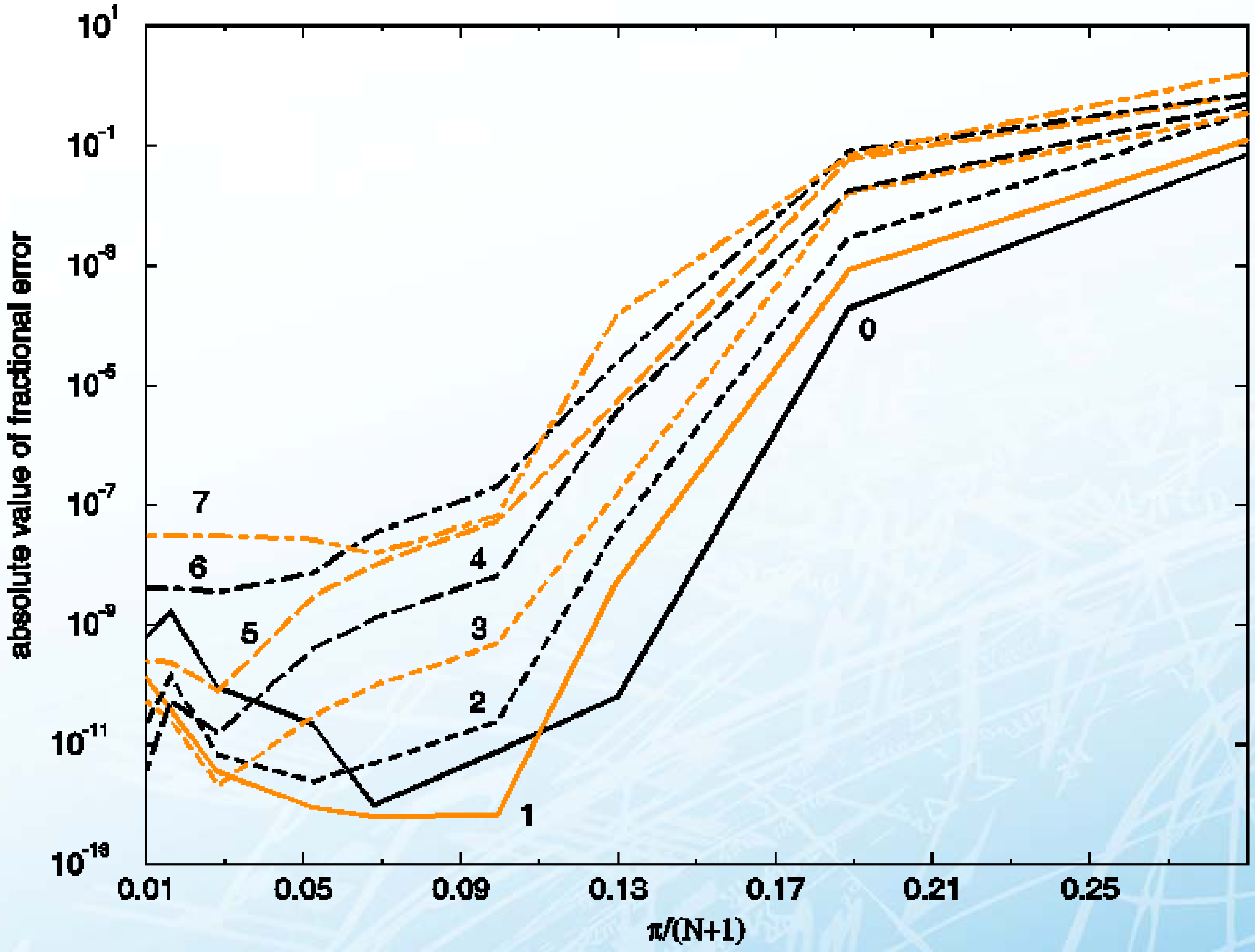
✓ Loewdin (symmetric) orthogonalization of mixed basis:

- Diagonalization of overlap matrix yields eigenvector matrix ***U*** and the matrix ***X***=diag($1/\sqrt{\varepsilon_1}$, $1/\sqrt{\varepsilon_2}$, … , $1/\sqrt{\varepsilon_N}$)
- Orthogonalization of mixed basis according to:

$$\left(U\,X\,U^T\right)A\left(U\,X\,U^T\right) = H$$

✓ ***H*** is the desired representation of H in orthonormal mixed basis

Mixed basis (+ P_0,P_1) VBR H_2O 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
- **D**iscrete **V**ariable **R**epresentation (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:

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

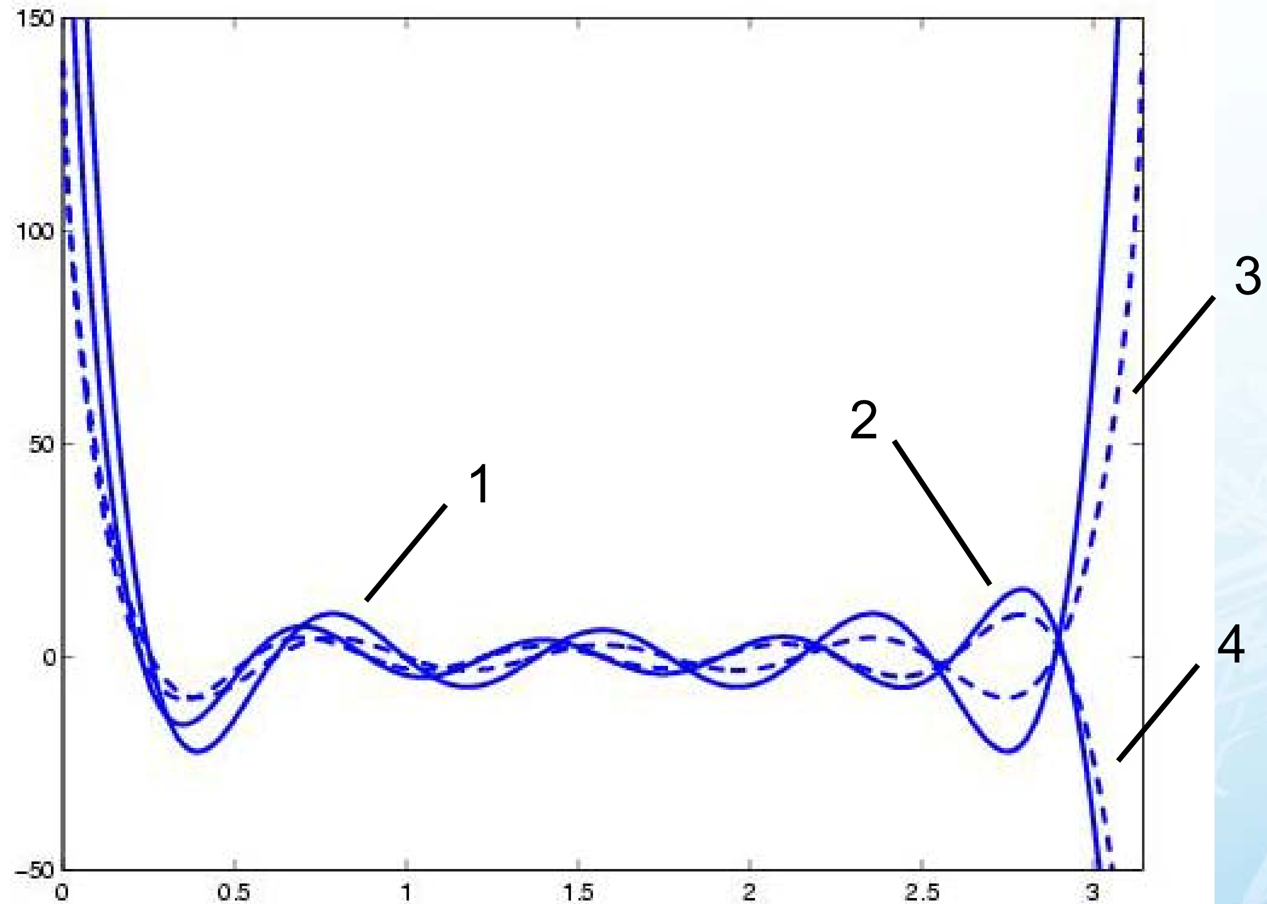
then we can define a **F**inite **B**asis **R**epresentation (FBR):

$$\int_a^b \varphi_m(x)\left[\hat{O}\,\varphi_n(x)\right] w(x)\,dx \approx \sum_{k=1}^{N} \varphi_m(x_k)\left[\hat{O}\,\varphi_n(x_k)\right] w_k$$

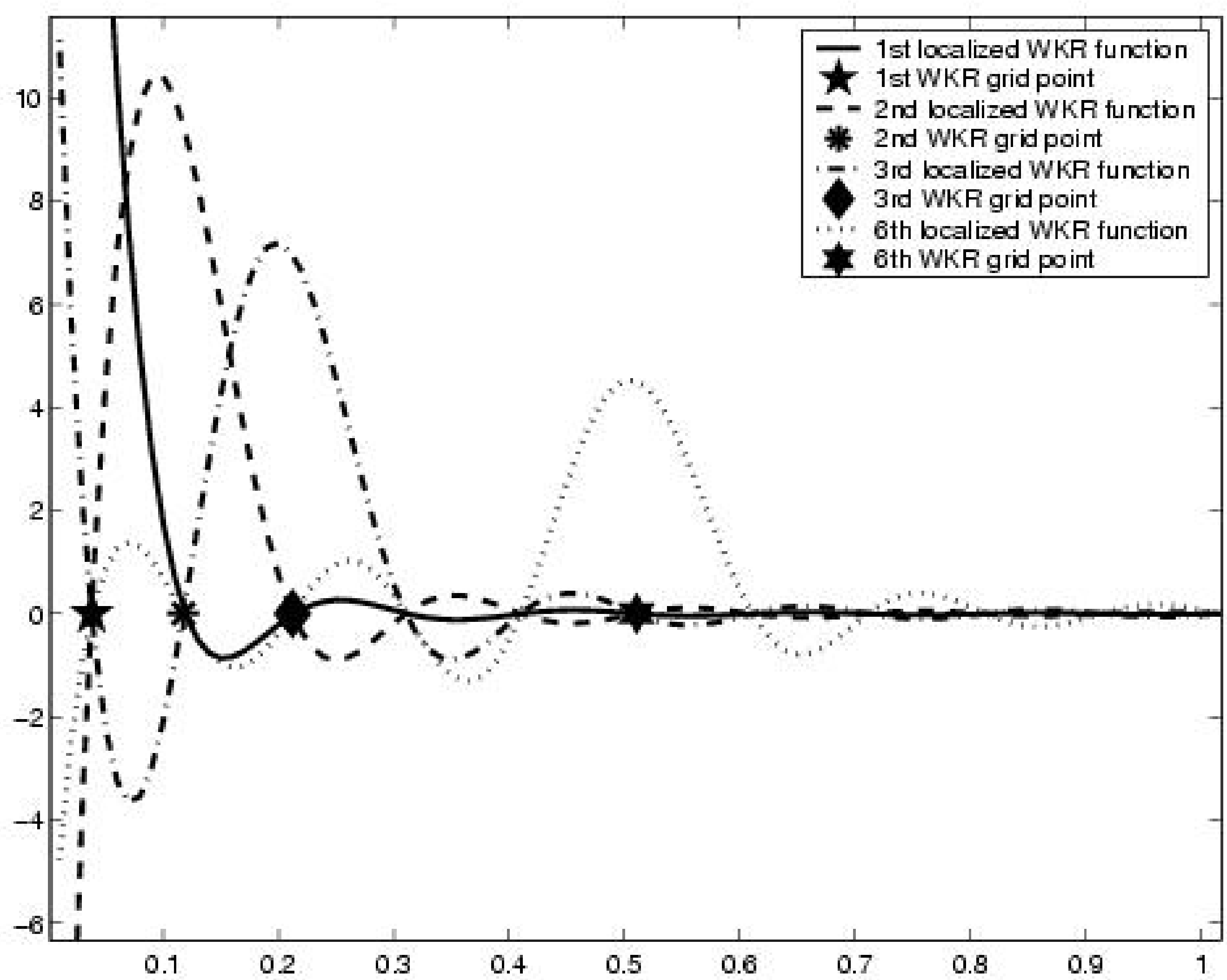
VBR, FBR, DVR, NDVR

- FBR matrix is an approximation to the VBR matrix
- FBR and DVR are equivalent: $^{FBR}O = \Lambda \; {}^{DVR}O \; \Lambda^t$
- In analogy we can define: $^{VBR}O = \Lambda \; {}^{NDVR}O \; \Lambda^t$
- 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: $^{DVR}H = {}^{NDVR}T + {}^{DVR}V$
  - ✓ 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 $P_M(\cos(x))$) $\rightarrow$ explicit derivation of orthogonal mixed basis
  - ✓ Establishment of quadrature rule for mixed basis $\rightarrow$ derivation of $\boldsymbol{\Lambda}$ 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)

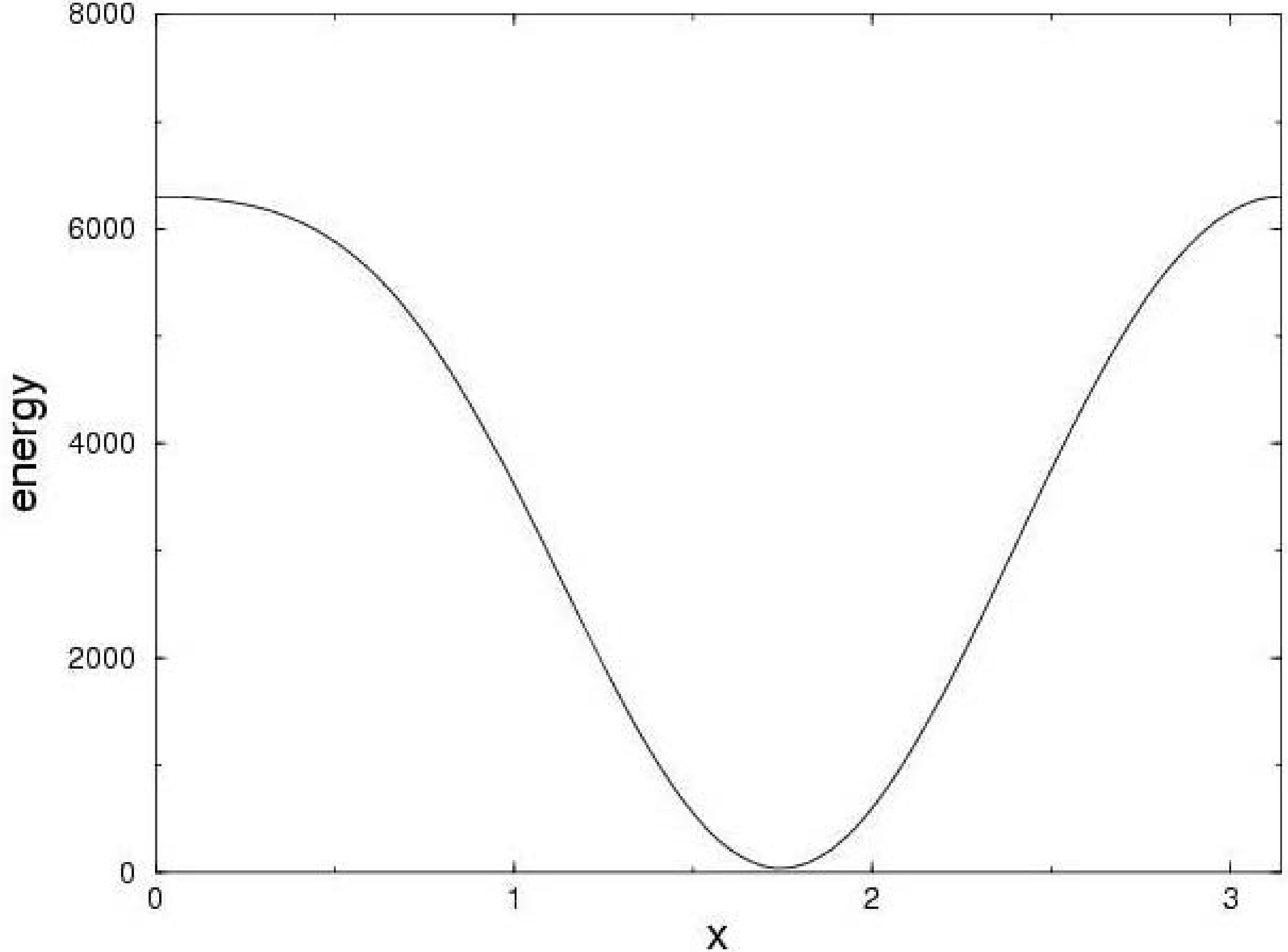


$Q_m(x)$ NDVR localized at x_k, k=1,2,3,6 from $\eta_n(x)$ (n=1-30) , $P_l(\cos(x))$ (l=1-2)

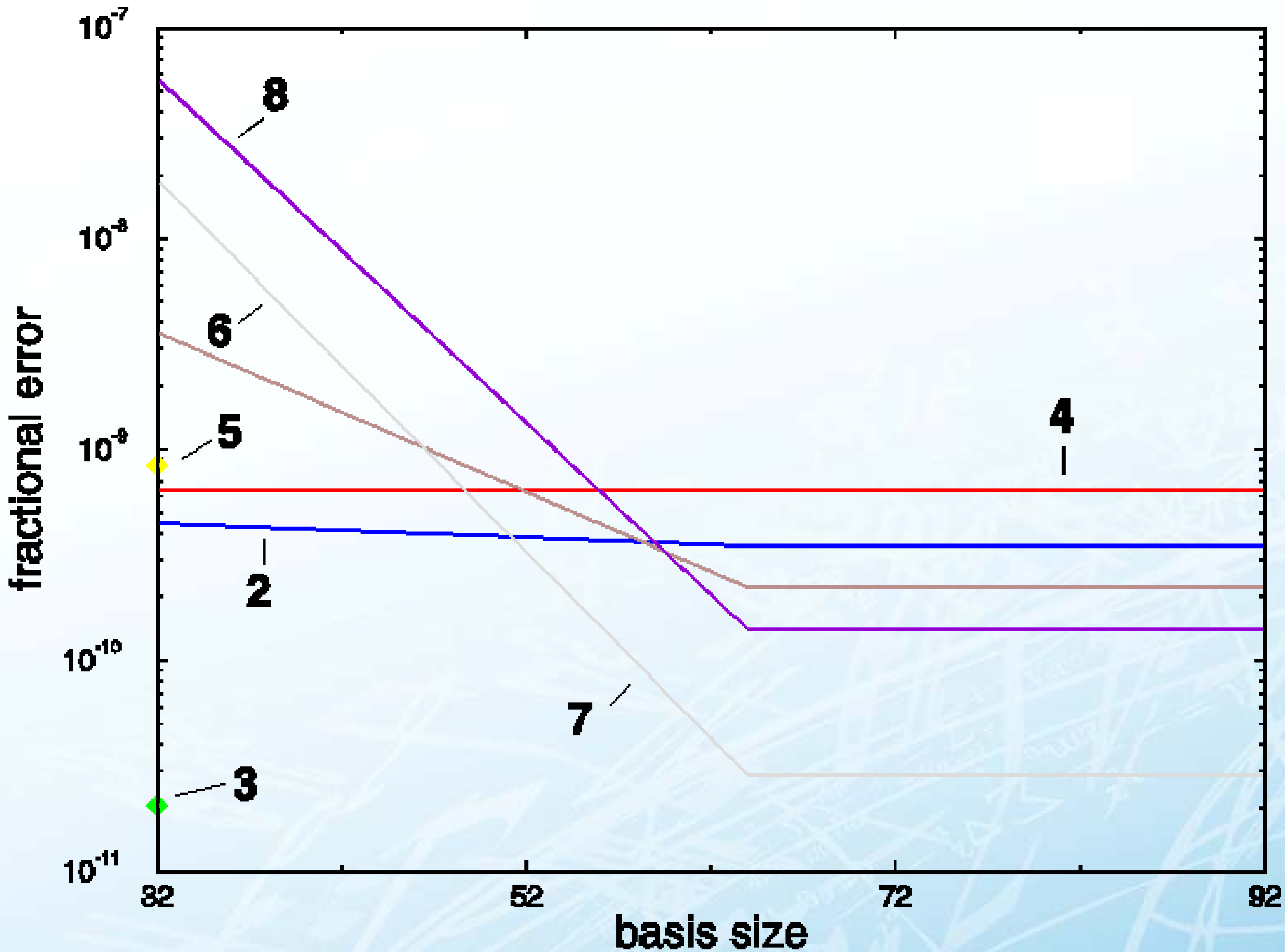


$$V_1 = 300 + 3000\cos(x) + 8000(\cos(x))^2 - 3000(\cos(x))^3 - 2000(\cos(x))^4$$

$$c_{bend} = 10.0$$



Legendre VBR for V_1



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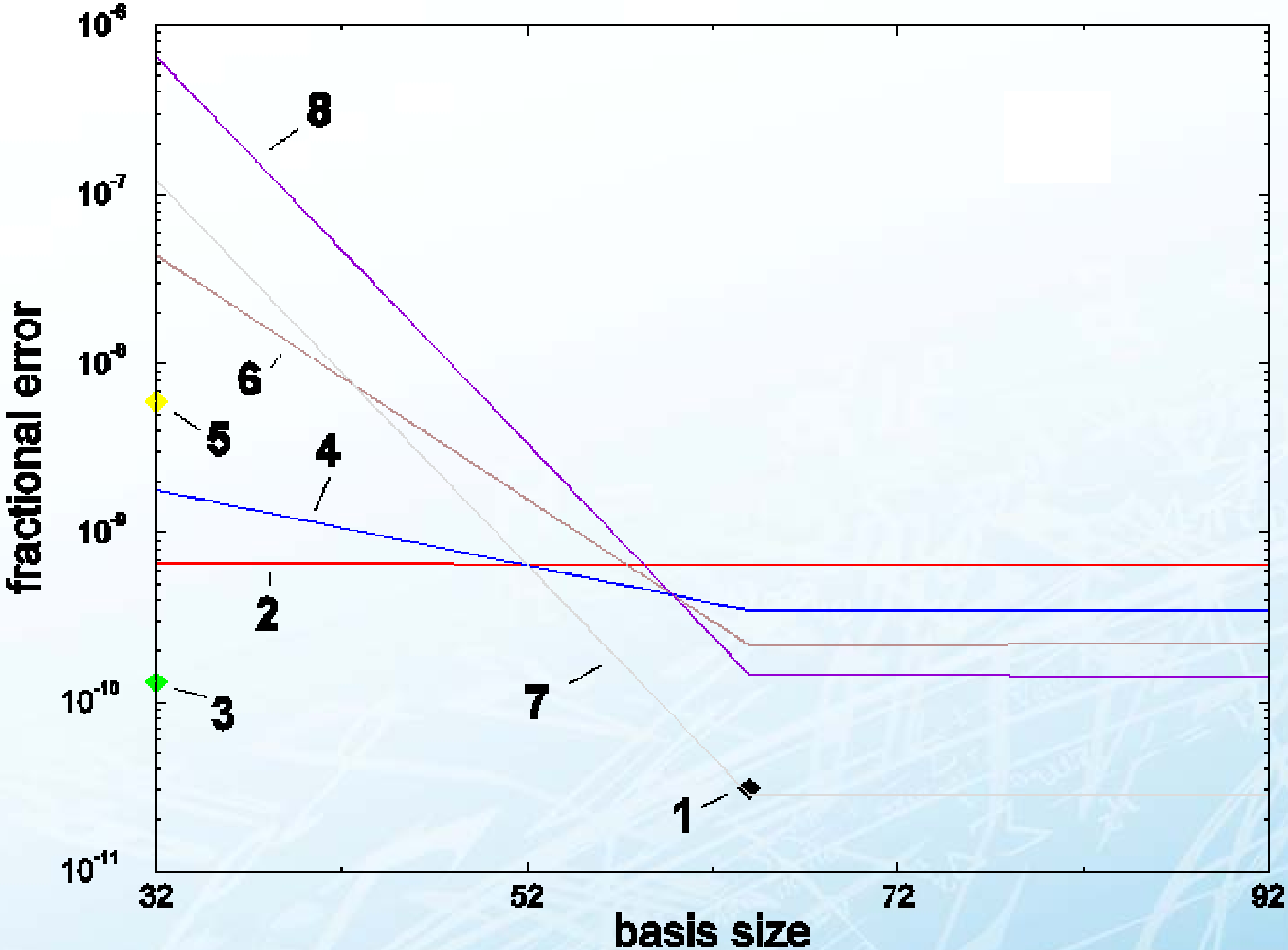
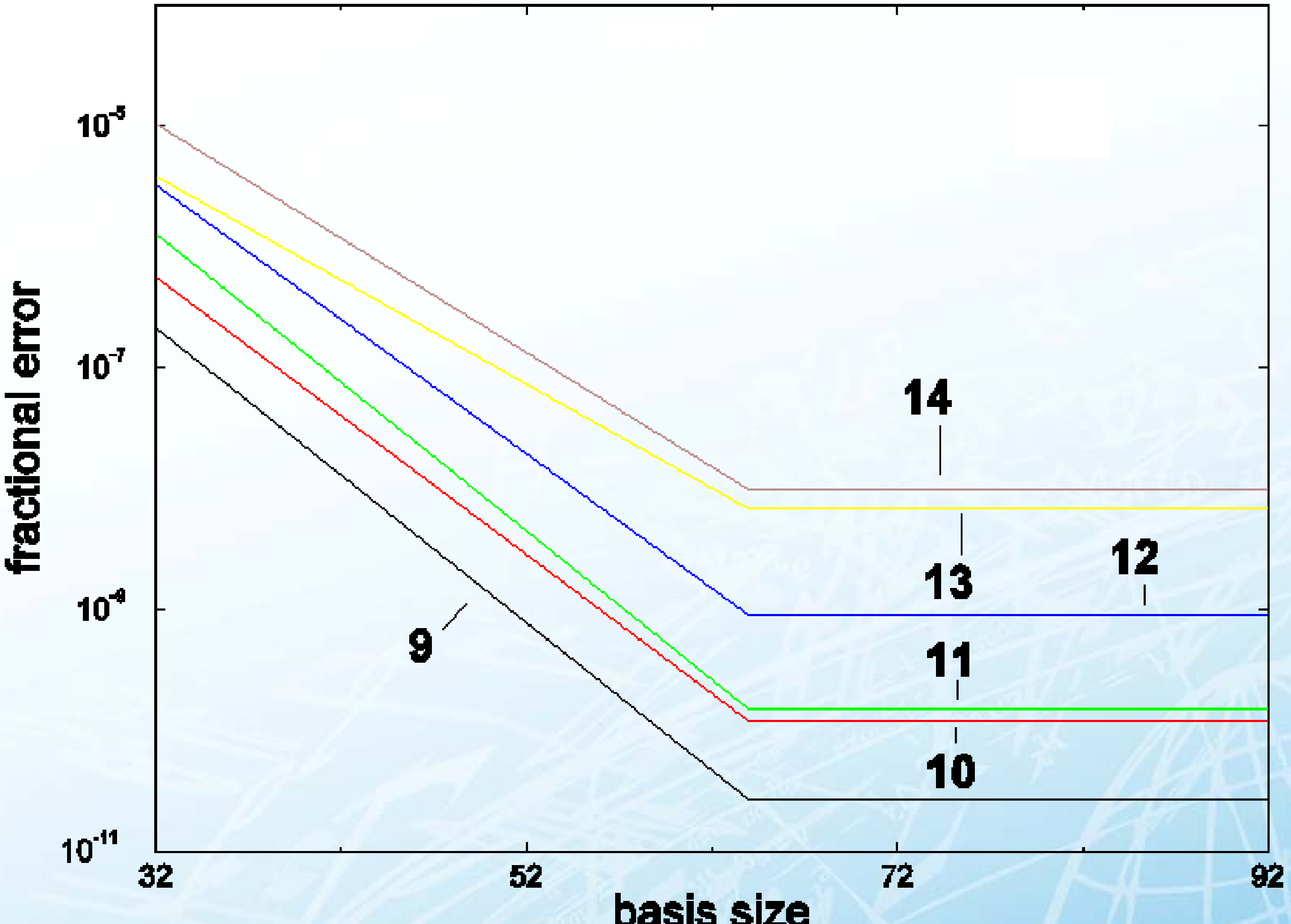
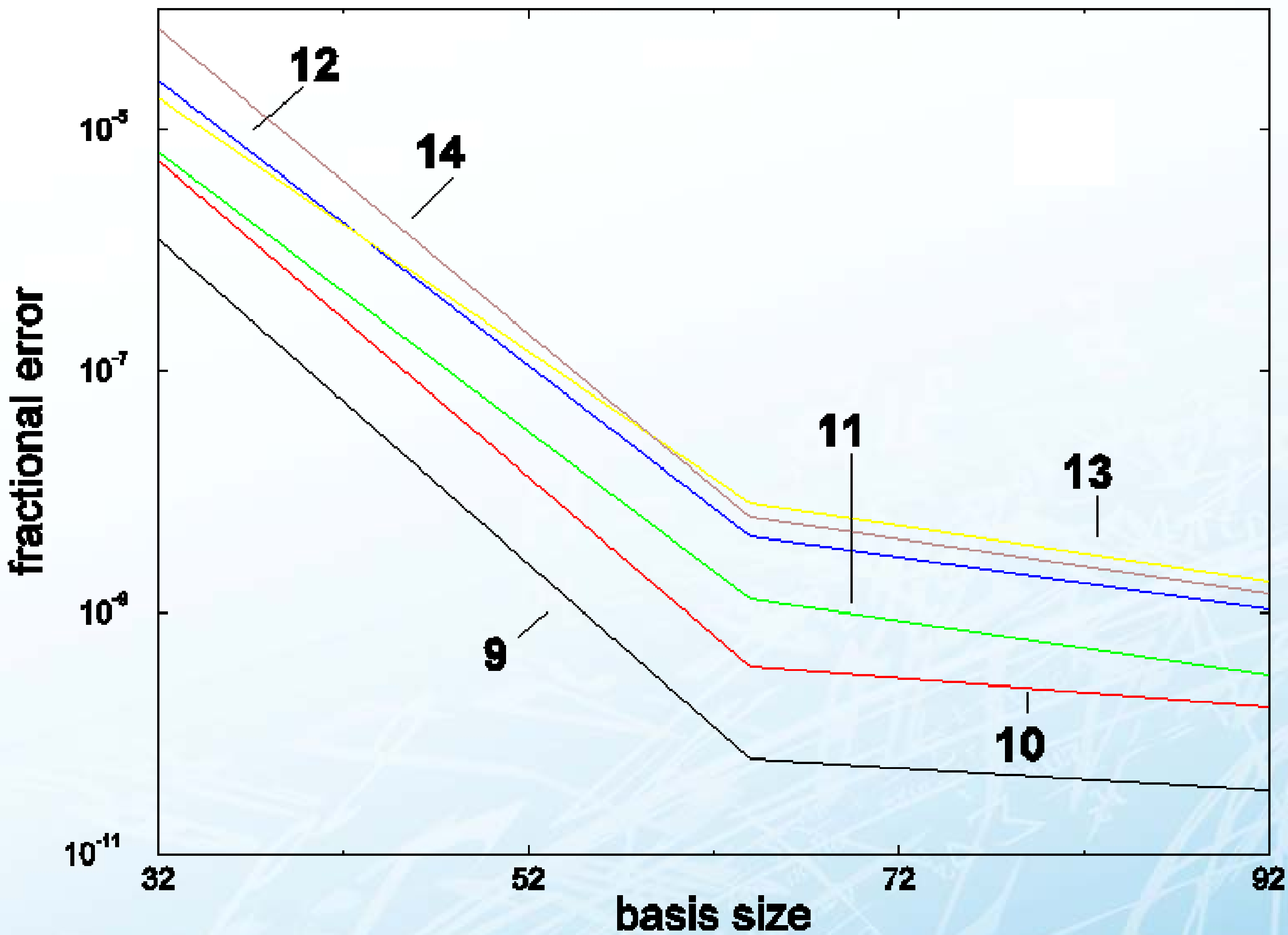
$Q_m(x)$ VBR for V_1 from $\eta_n(x)$ (n=1-N-2) , $P_l(\cos(x))$ (l=1-2)



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)



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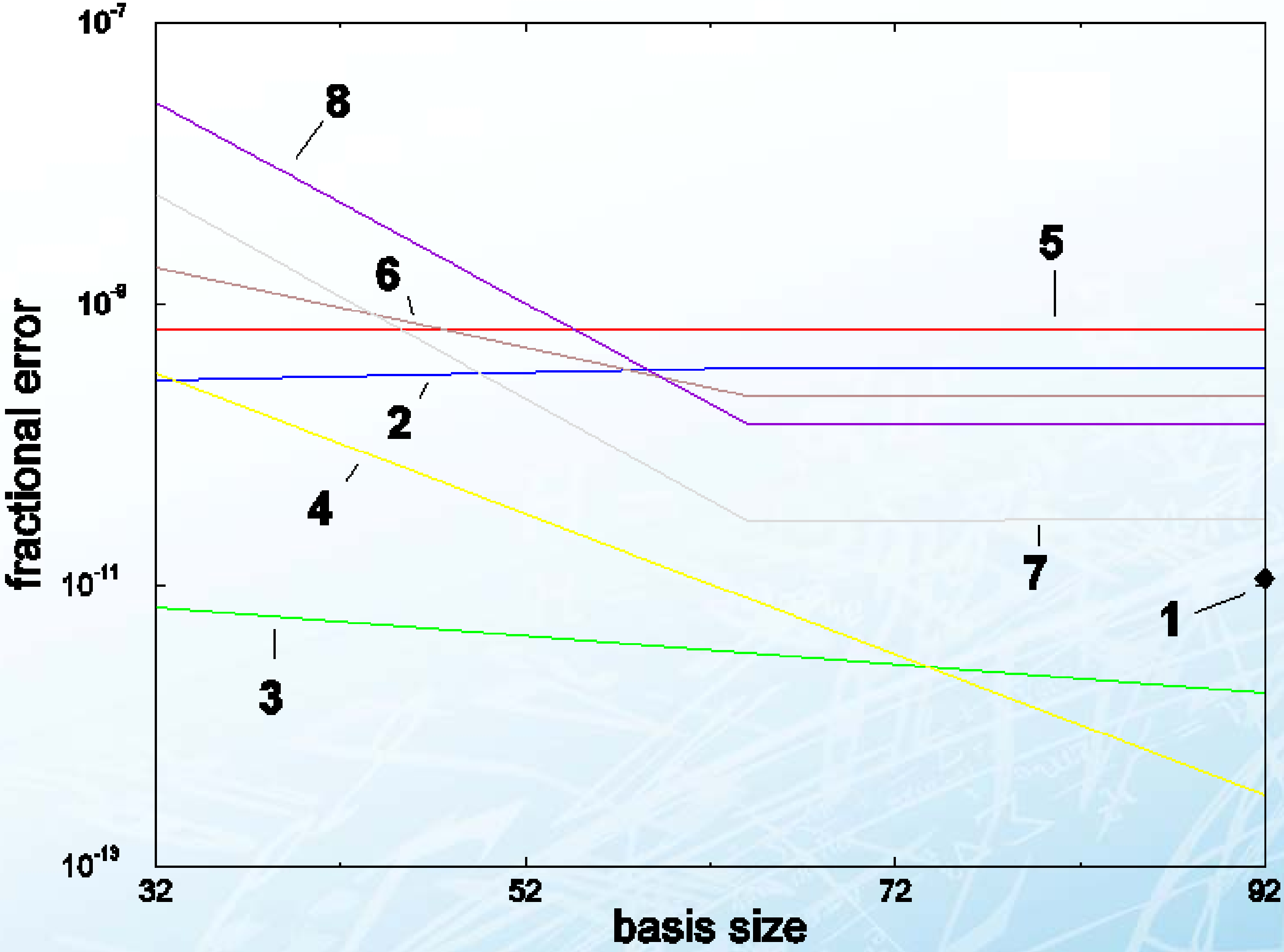
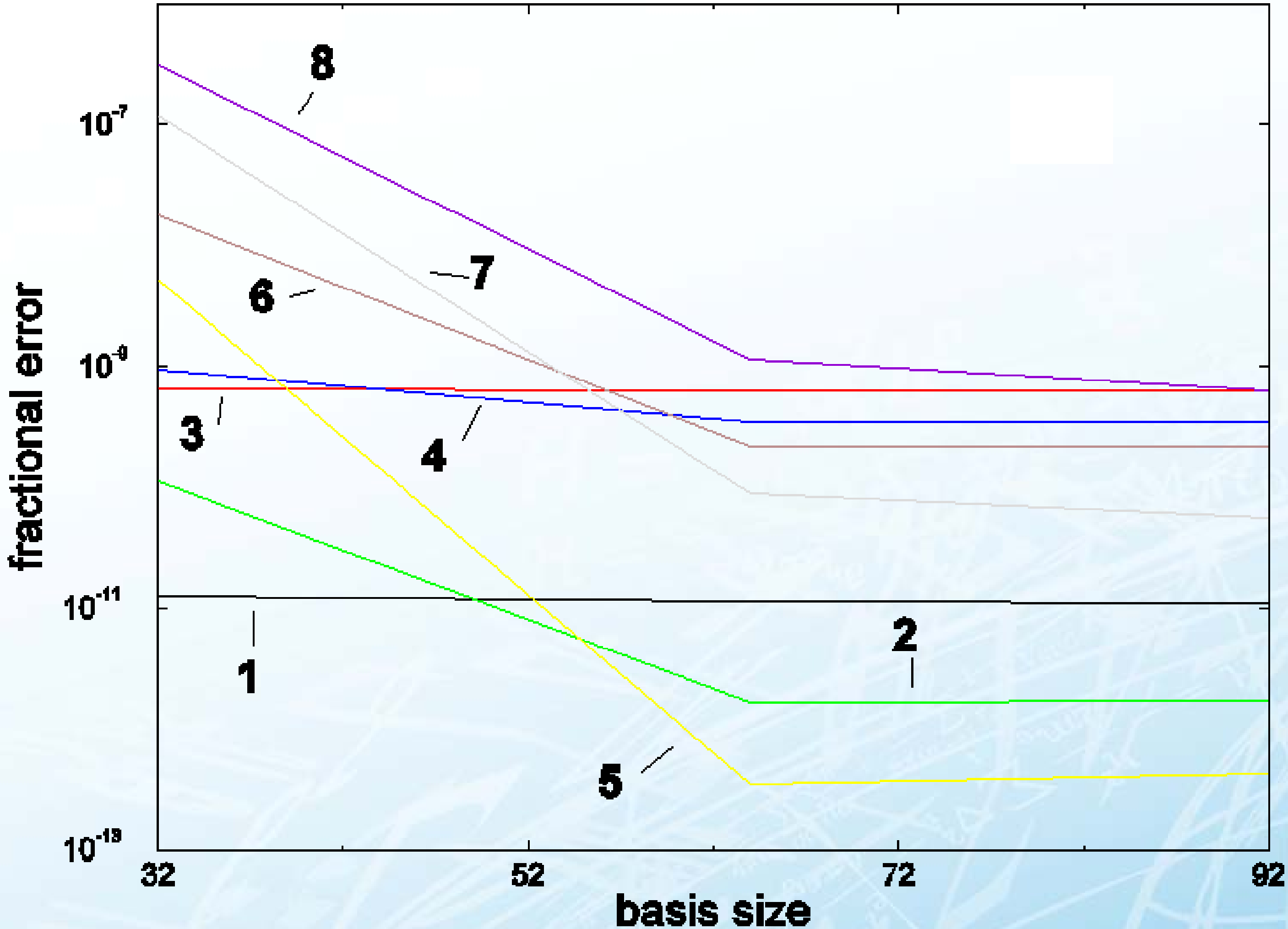
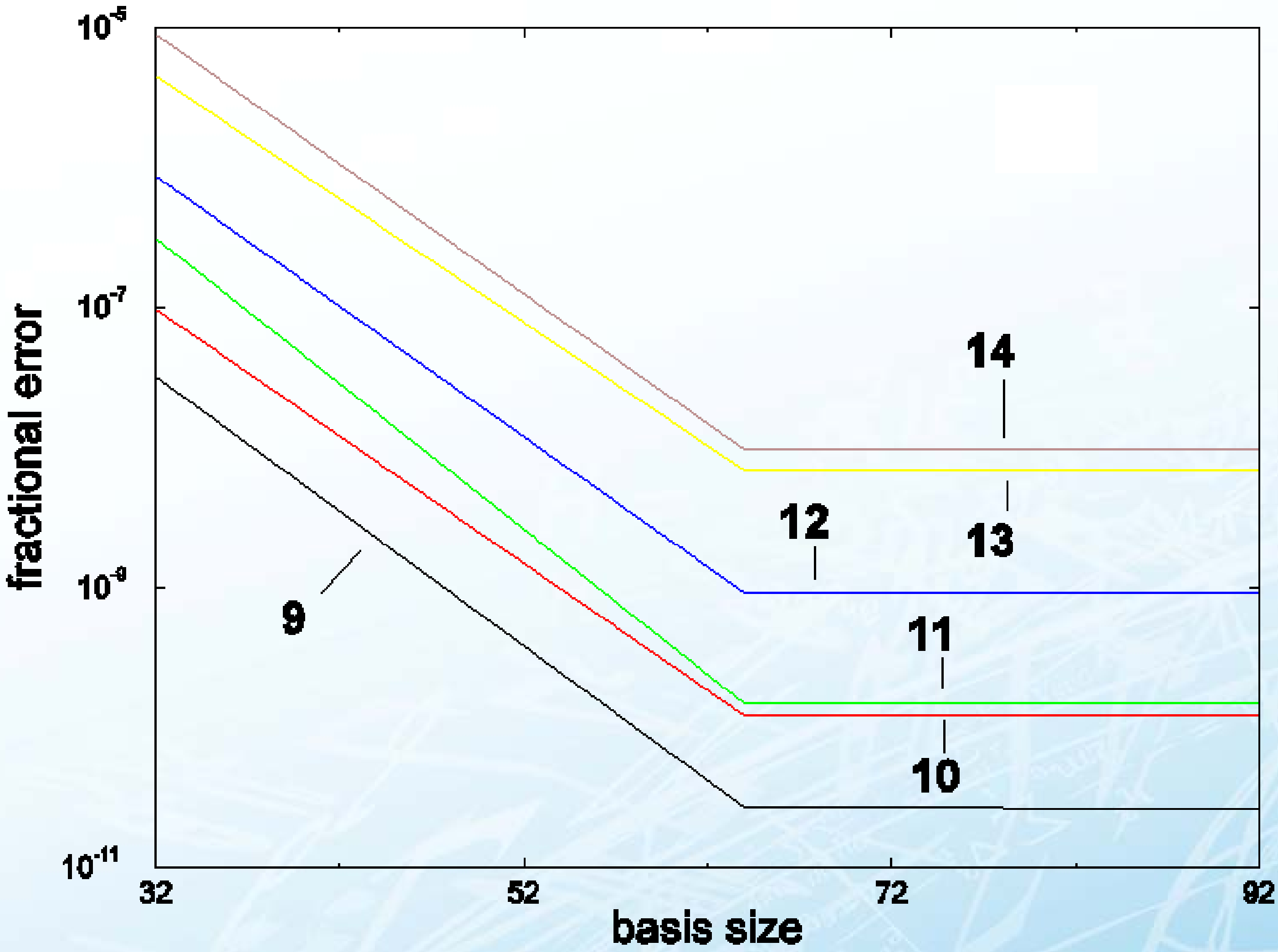
Legendre DVR for V_1



$Q_m(x)$ DVR for V_1 from $\eta_n(x)$ (n=1-N-2) , $P_l(\cos(x))$ (l=1-2)



Legendre DVR for V_1



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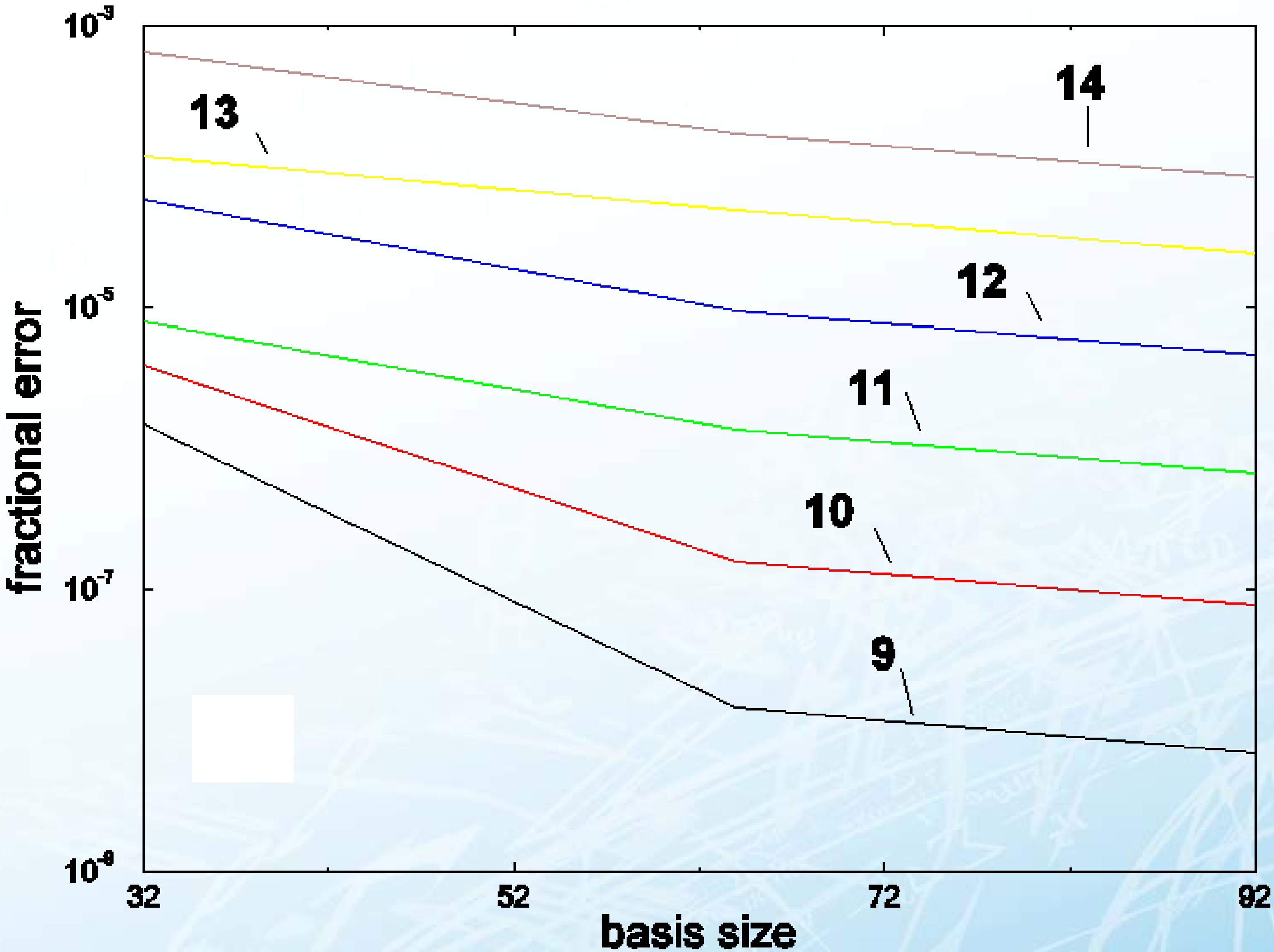
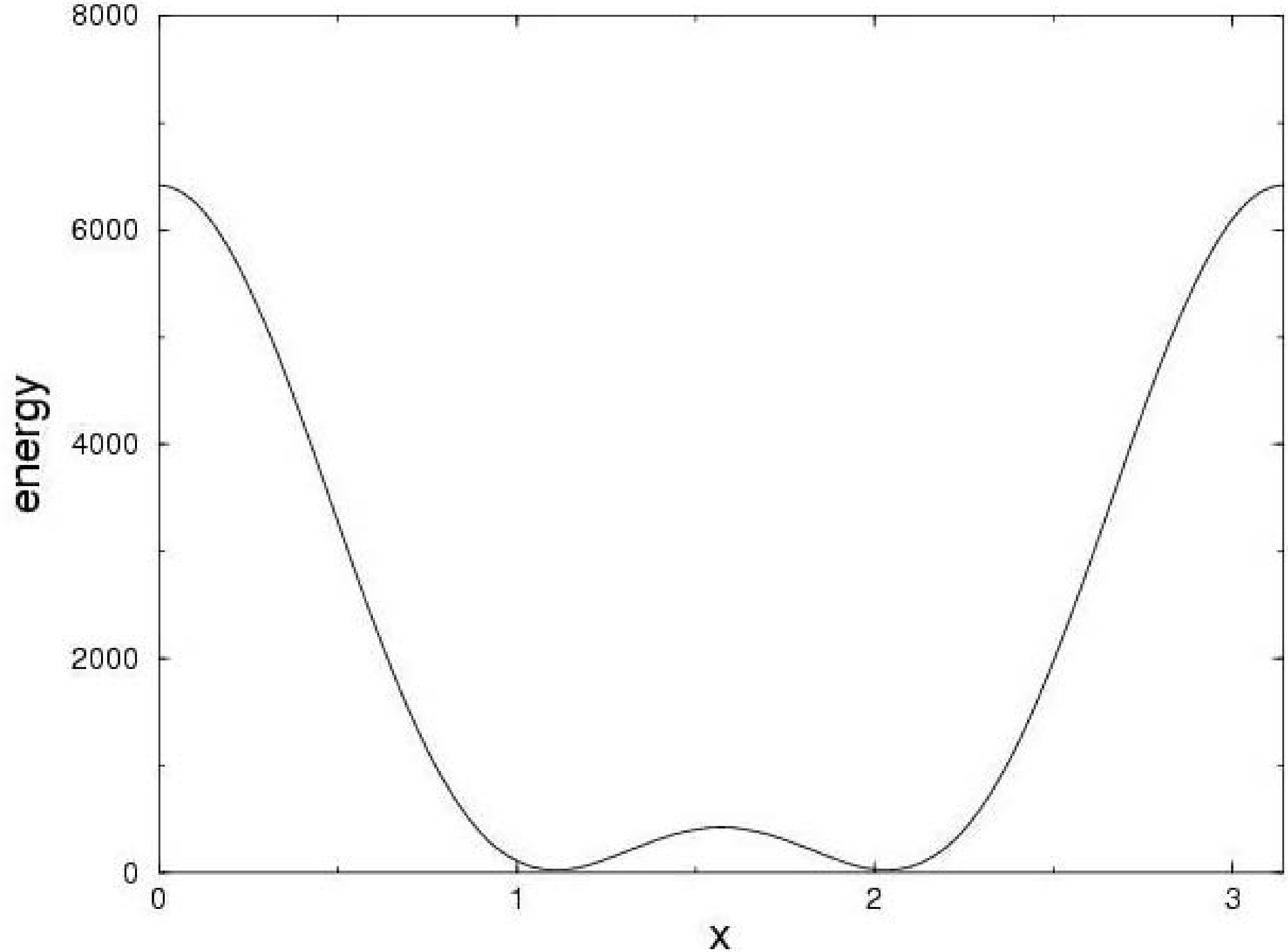
$Q_m(x)$ DVR for V_1 from $\eta_n(x)$ (n=1-N-2) , $P_l(\cos(x))$ (l=1-2)

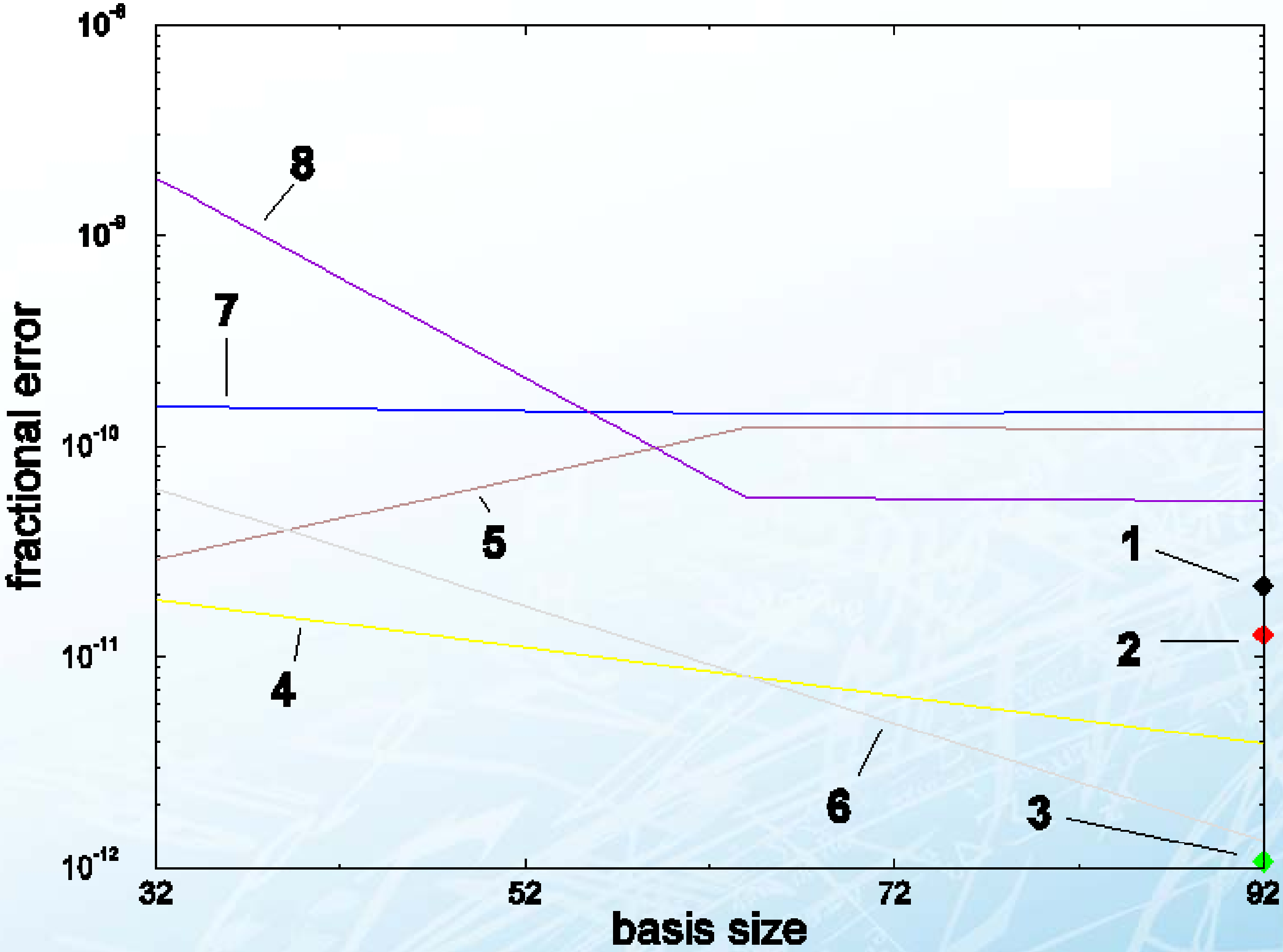


$$V_2 = 420 - 4000\,(\cos(x))^2 + 10000\,(\cos(x))^4$$

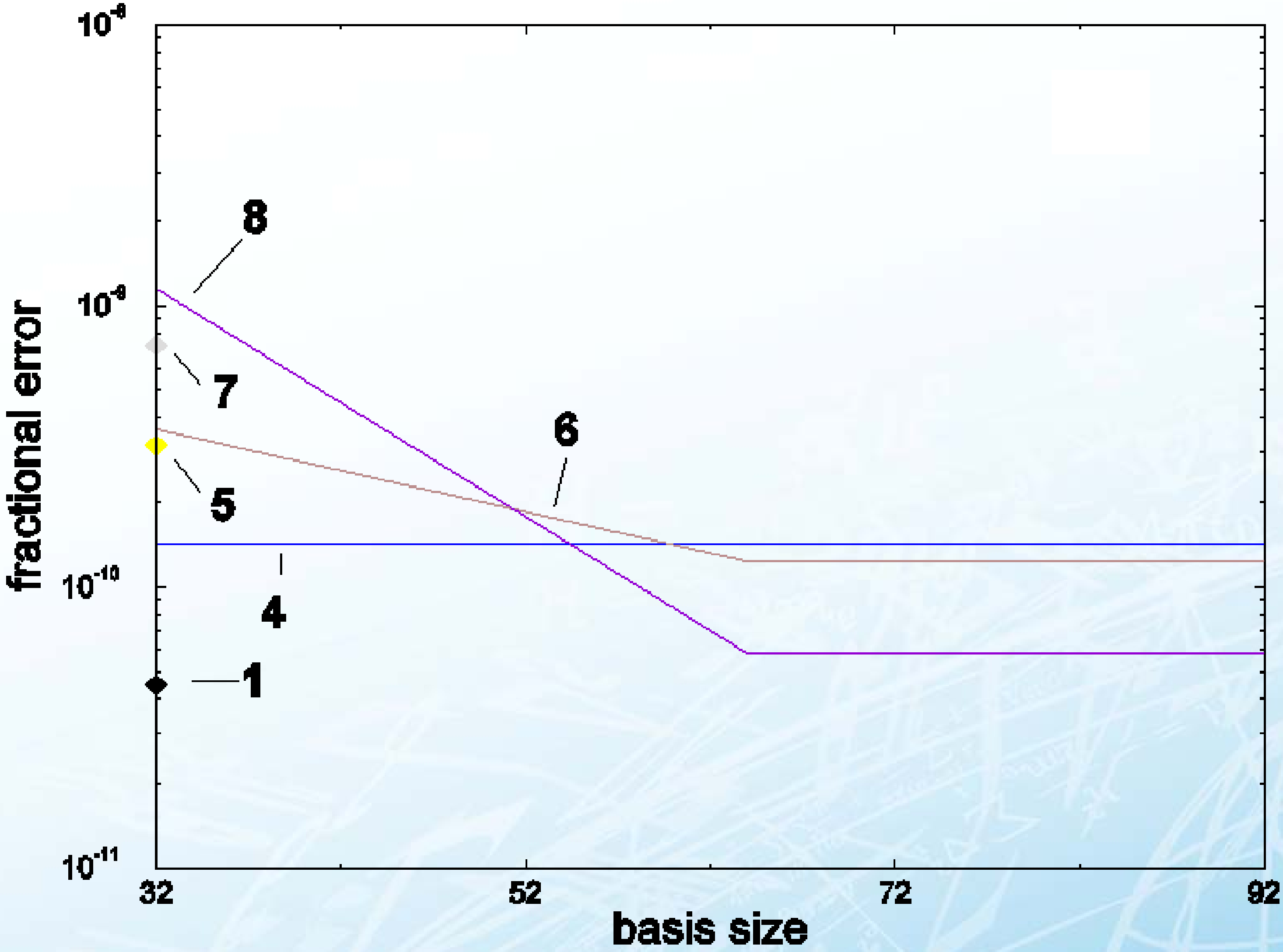
$$c_{bend} = 10.0$$



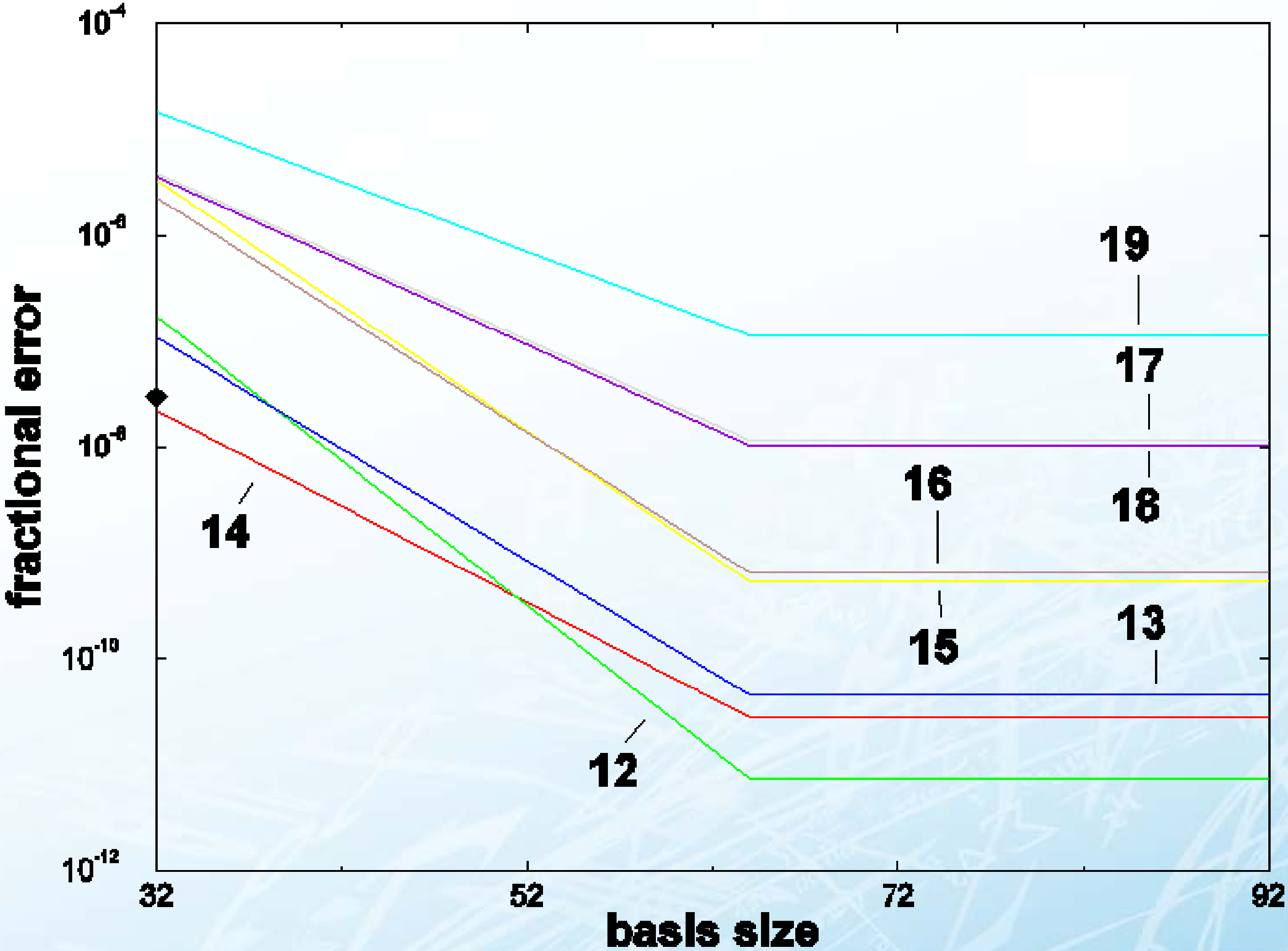
Legendre VBR for V_2



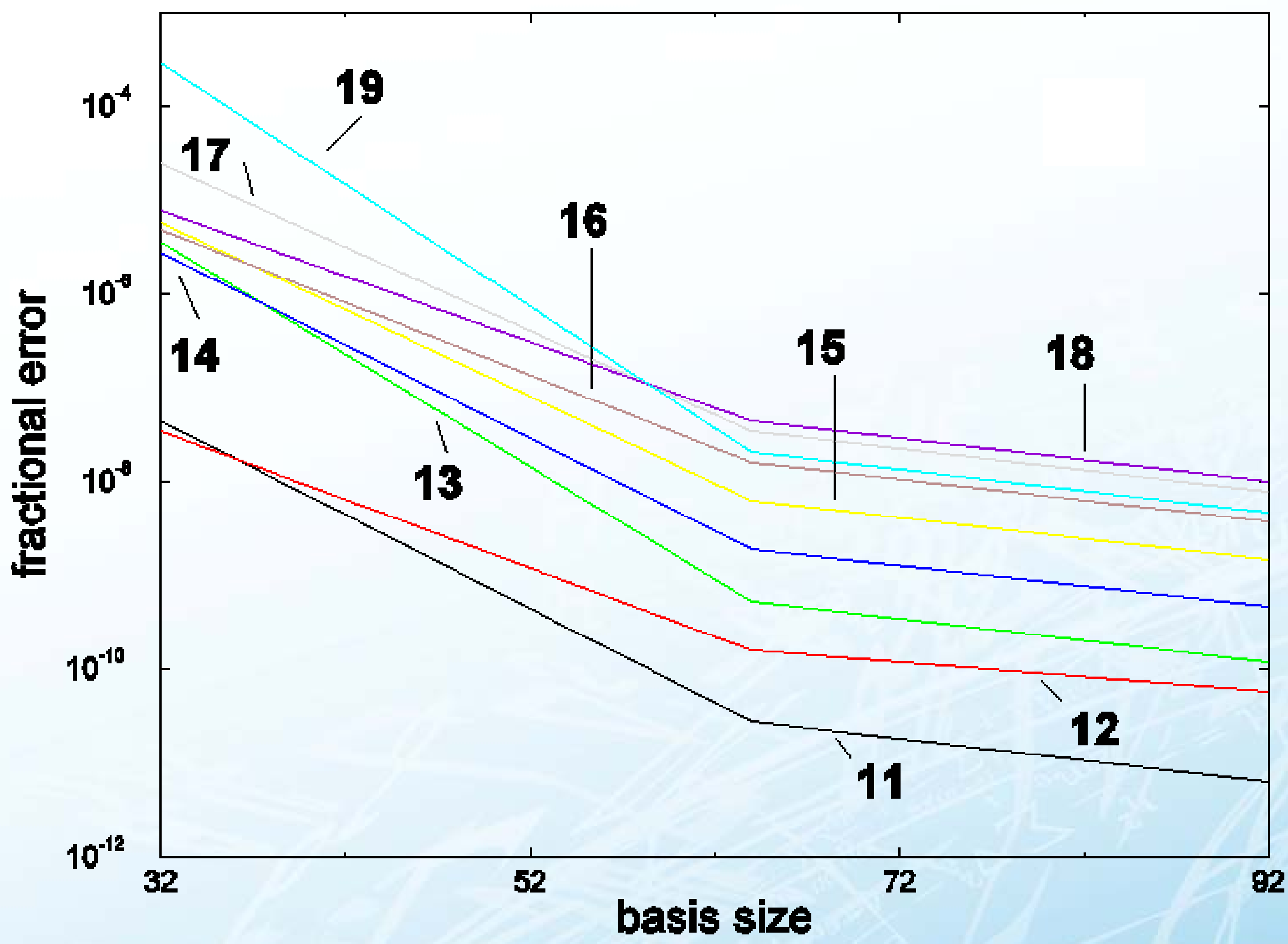
$Q_m(x)$ VBR for V_2 from $\eta_n(x)$ (n=1-N-2) , $P_l(\cos(x))$ (l=1-2)



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)



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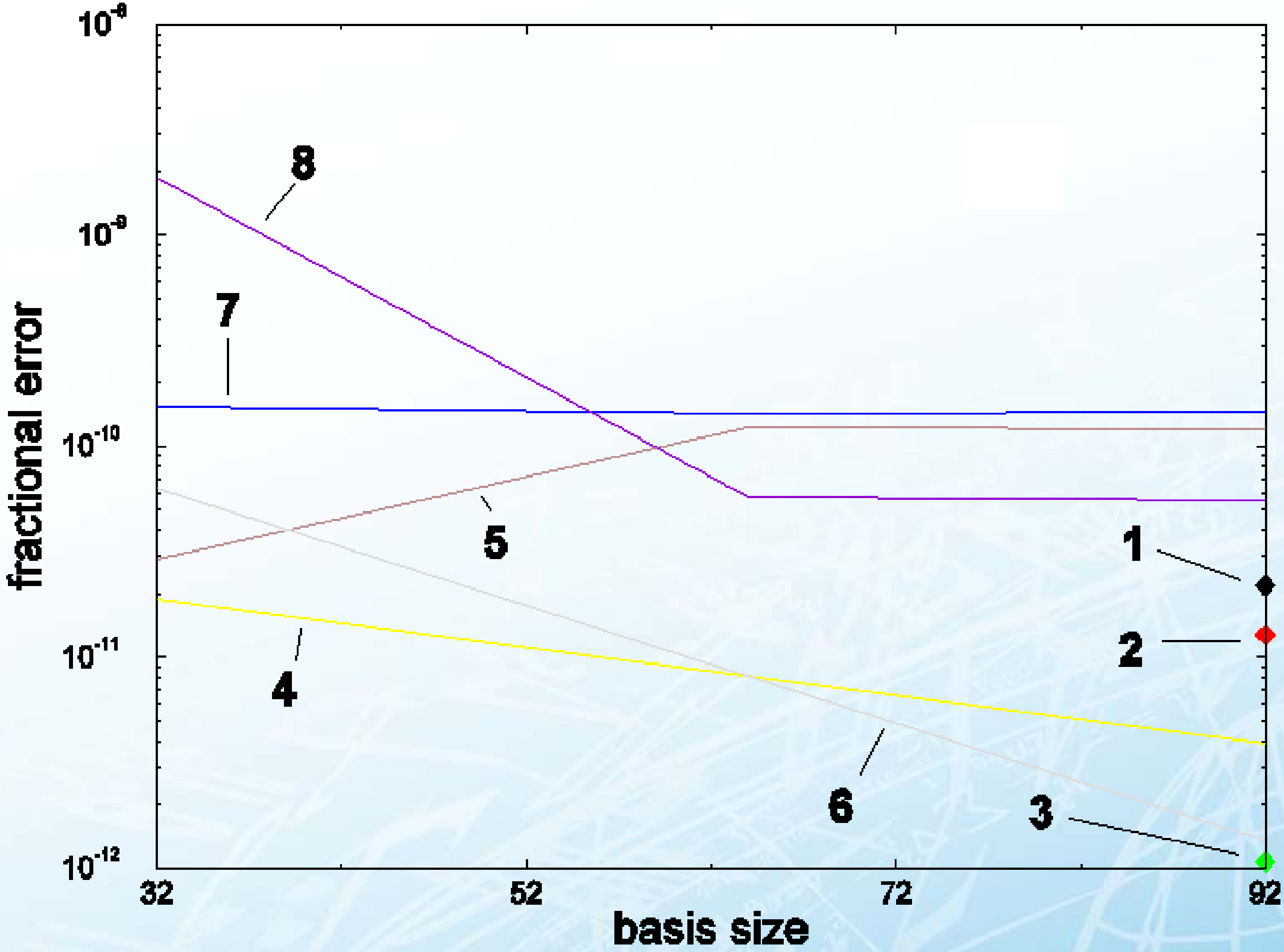
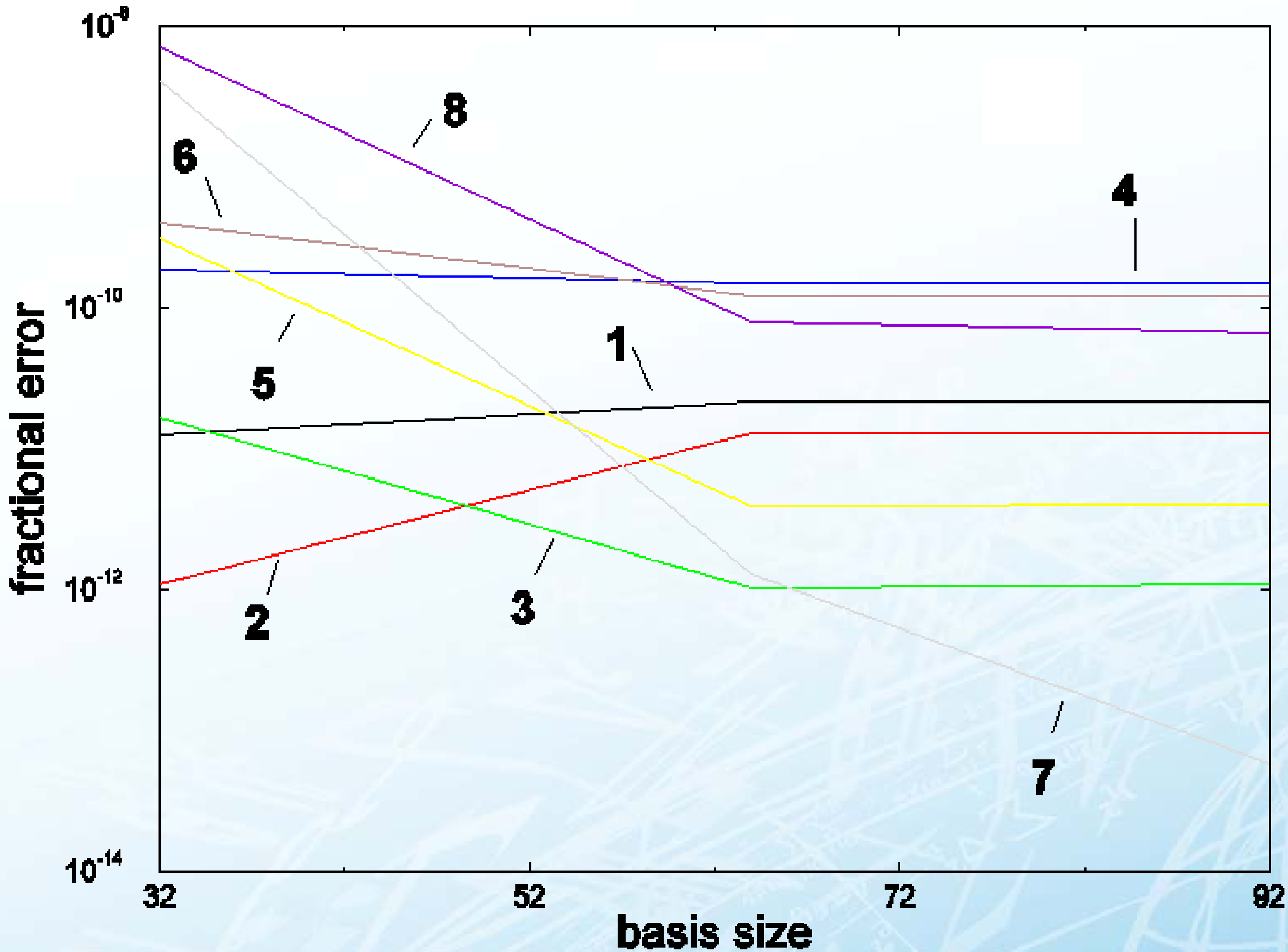
Legendre DVR for V_2



$Q_m(x)$ DVR for V_2 from $\eta_n(x)$ (n=1-N-2) , $P_l(\cos(x))$ (l=1-2)



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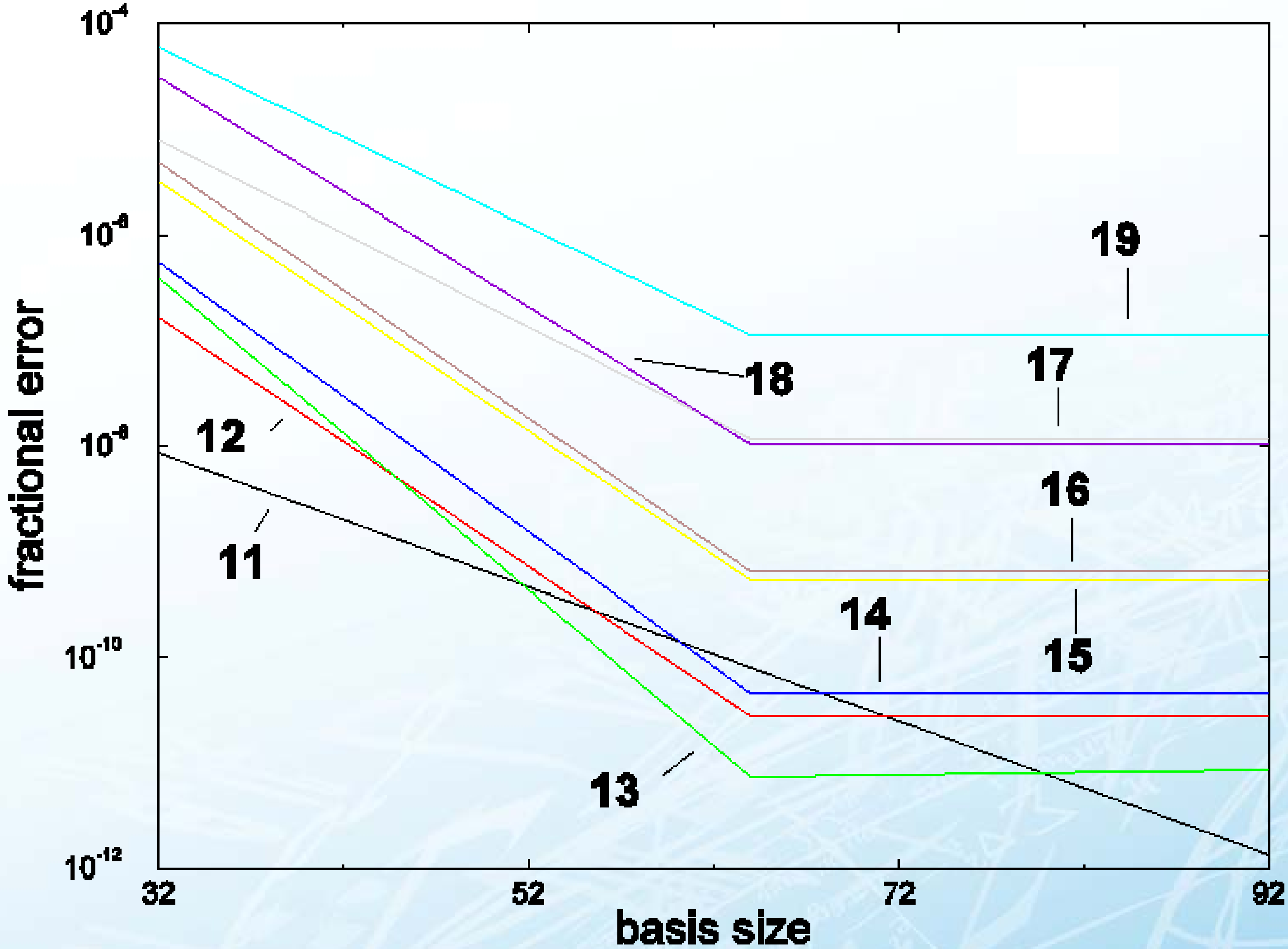
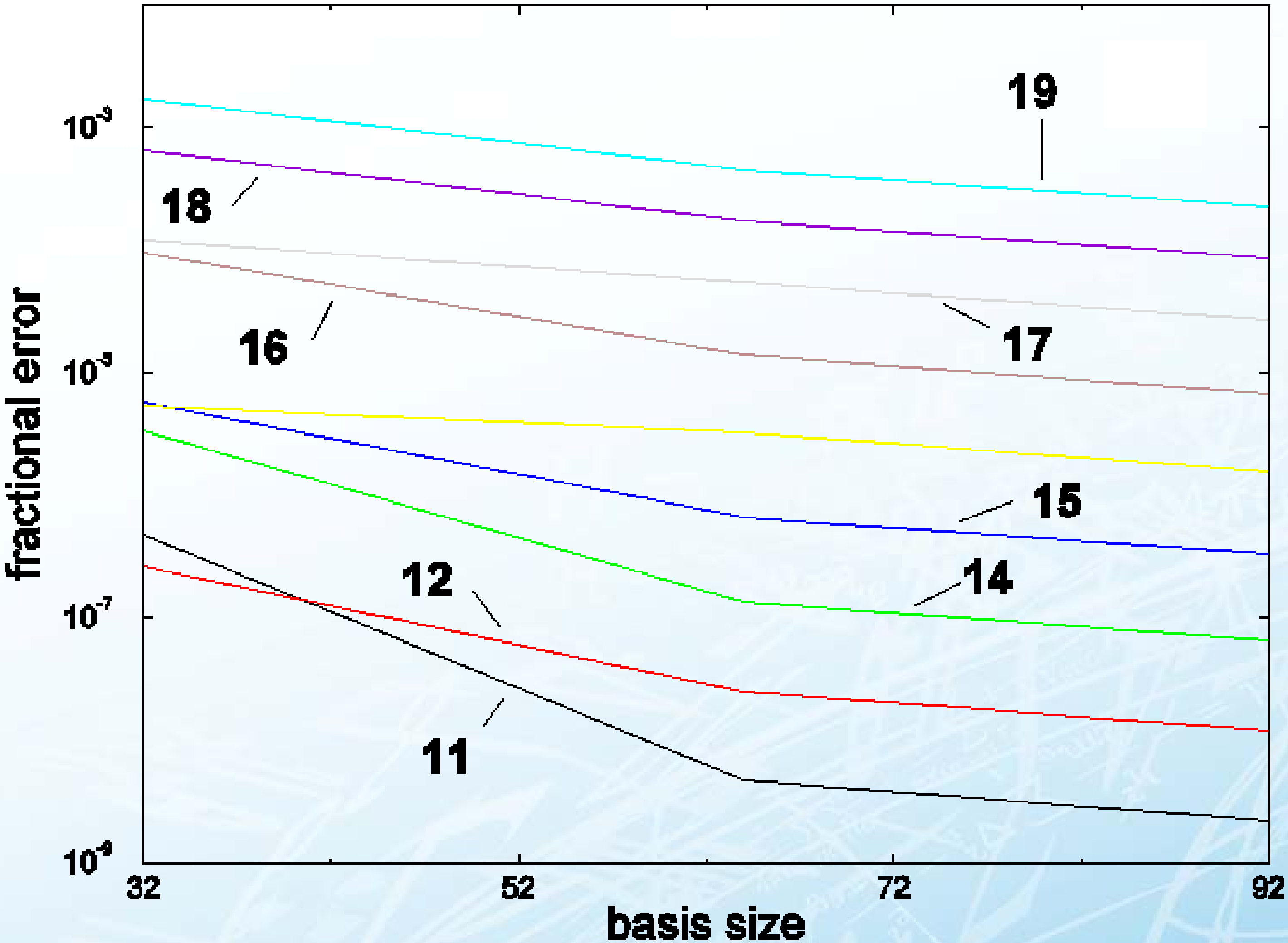
Legendre DVR for V_2



$Q_m(x)$ 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 $\rightarrow$ 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

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