Theoretical Study of Weakly-Bound Triatomic Systems with Discrete Variable Representation method

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Formulation of the problem

We denote the reduced Jacobi coordinates in $\mathbb{R}^3$ by two three-dimensional vectors $\boldsymbol{x}_\alpha, \boldsymbol{y}_\alpha$ for the particle α. These vectors can be combined into a six-dimensional vector $\boldsymbol{X} = \{\boldsymbol{x}_\alpha, \boldsymbol{y}_\alpha\}$. The Hamiltonian H of a system with a separated motion of the center of mass is determined by the expression:

$$H = H_0 + V(\boldsymbol{X}), \quad H_0 = -\Delta_{\boldsymbol{X}} = -\Delta_{\boldsymbol{x}_\alpha} - \Delta_{\boldsymbol{y}_\alpha}. \tag{1}$$

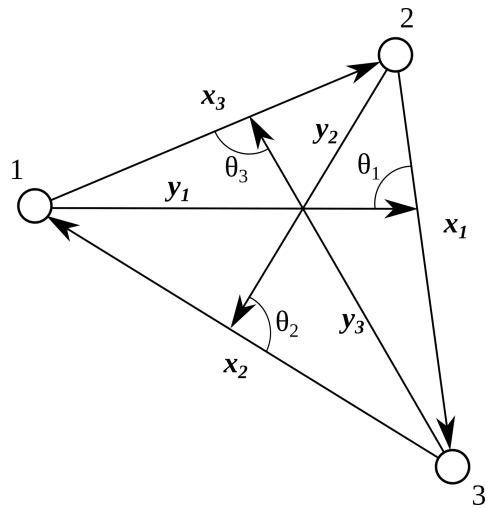

Figure 1: Jacobi coordinates for three particles.

Hamiltonian of the total angular momentum of three particles

The wave-function of a system $\Psi(\boldsymbol{X})$:

$$\Psi_M^{J\tau}(\boldsymbol{X}) = \sum_{M'=0}^{J} (D_{MM'}^{J\tau})^*(\phi_\alpha, \vartheta_\alpha, \varphi_\alpha)\Psi_{M'}^{J\tau}(x_\alpha, y_\alpha, \theta_\alpha) \tag{2}$$

Substitution in Shrödinger equation:

$$\sum_{M'=0}^{J} (H_{MM'}^{J\tau} - E\delta_{MM'})\Psi_{M'}^{J\tau}(x_\alpha, y_\alpha, \theta_\alpha) = 0, \quad M = 0, \ldots, J. \tag{3}$$

The diagonal components of the matrix $H^{J\tau}_{MM'}$ are given by the formulas $H^{J\tau}_{MM} = (1 + (1/2)(\tau(-1)^J - 1)\delta_{M0})\hat{H}^{J\tau}_{MM'}$,

$$\begin{aligned}\hat{H}^{J\tau}_{MM} = \quad & - \quad \frac{1}{x_\alpha}\frac{\partial^2}{\partial x_\alpha^2}x_\alpha - \frac{1}{y_\alpha}\frac{\partial^2}{\partial y_\alpha^2}y_\alpha + \frac{J(J+1) - 2M^2}{y_\alpha^2)} + V(x_\alpha, y_\alpha, \theta_\alpha) \\ & - \quad \left(\frac{1}{x_\alpha^2} + \frac{1}{y_\alpha^2}\right)\left(\frac{\partial^2}{\partial\theta_\alpha^2} + \cot\theta_\alpha\frac{\partial}{\partial\theta_\alpha} - \frac{M^2}{\sin^2\theta_\alpha}\right) \end{aligned} \tag{4}$$

Off-diagonal components can be represented as $H^{J\tau}_{MM'} = (1 + (1/2)(\tau(-1)^J - 1)(\delta_{M0} + \delta_{M'0}))\hat{H}^{J\tau}_{MM'}$,

$$\begin{aligned}\hat{H}^{J\tau}_{MM'} = \hat{H}^{J\tau}_{MM'}\delta_{MM\pm1} \quad = \quad & \pm\frac{\lambda_\pm(J,M)}{y_\alpha^2}\sqrt{1 + \delta_{M0}\delta_{M'1} + \delta_{M1}\delta_{M'0}} \times \\ & \left(\frac{\partial}{\partial\theta_\alpha} + (1 \mp M)\cot\theta_\alpha\right), \end{aligned} \tag{5}$$

and $\lambda_\pm(J,M) = \sqrt{J(J+1) - M(M \pm 1)}$

Gaussian quadrature formula

An integral over $[-1,\ 1]$ can be approximated with the Gaussian quadrature rule based on the polynomials $P(z)$:

$$\int_{-1}^{1} f(z)\,dz \approx \sum_{i=1}^{n} \frac{w_i}{\rho(z_i)} f(z_i), \tag{6}$$

where $\rho(z)$ is a weight function, $z_1, \ldots, z_n$ are the zeros of the polynomial P_n, w_i are the weights.

DVR-functions and potential energy operator

The DVR-functions are defined as:

$$\varphi_i(z) = \frac{P_n(z)}{P_n'(z_i)(z - z_i)}, \qquad \varphi_i(z_k) = \delta_{ik}. \tag{7}$$

The property of the DVR-functions allows us to simplify the potential energy operator

$$V_{ij} = \sum_k \frac{w_k}{\rho(z_k)} V(x, y, z_k) \frac{\varphi_i(z_k)}{\sqrt{w_i}} \frac{\varphi_j(z_k)}{\sqrt{w_j}} = \frac{V(x, y, z_i)}{\rho(z_i)} \delta_{ij}. \tag{8}$$

DVR-functions and kinetic energy operator

To obtain the matrix of the kinetic energy operator, it is necessary to get the first derivatives $\varphi_i'(z)$ at the points $z_1, \ldots, z_n$.

$$\varphi_i'(z_k) = \frac{P_n'(z_k)}{P_n'(z_i)(z_k - z_i)} \text{ (for } k \neq i), \qquad \varphi_i'(z_i) = -\frac{P_n''(z_i)}{2P_n'(z_i)}. \tag{9}$$

The angular parts of kinetic-energy operator in terms of $z = \cos\theta$.

$$\frac{d^2}{d\theta^2} + \cot\theta \frac{d}{d\theta} - \frac{M^2}{\sin^2\theta} = (1 - z^2)\frac{d^2}{dz^2} - 2z\frac{d}{dz} - \frac{M^2}{1 - z^2}, \tag{10}$$

$$\frac{d}{d\theta} + (1 \pm M)\cot\theta = -\sqrt{1 - z^2}\frac{d}{dz} + (1 \pm M)\frac{z}{\sqrt{1 - z^2}}. \tag{11}$$

DVR-functions and kinetic energy operator

Matrix elements of the diagonal and off-diagonal parts:

$$T_{ij}^{diag} = \sum_k \frac{w_k}{\rho(z_k)} \frac{\varphi_i'(z_k)}{\sqrt{w_i}} \frac{\varphi_j'(z_k)}{\sqrt{w_j}} (1 - z_k^2) - \frac{1}{\rho(z_i)} \frac{M^2}{1 - z_i^2} \delta_{ij}. \tag{12}$$

$$T_{ij}^{off} = \frac{\sqrt{w_i}}{\rho(z_k)} \frac{\varphi_j'(z_i)}{\sqrt{w_j}} (1 - z_i^2) - \frac{1}{\rho(z_i)} (1 \pm M) \frac{z_i}{1 - z_i^2} \delta_{ij}. \tag{13}$$

Legendre polynomials

For the Legendre polynomials weight function $\rho(z) = 1$. Weights in Gauss quadrature rule

$$w_i = \frac{2(1 - z_i^2)}{(n+1)^2 [P_{n+1}(z_i)]^2}. \tag{14}$$

The first derivative of the dvr-function

$$\psi_i'(z_k) = \frac{\varphi_i'(z_k)}{\sqrt{w_i}} = \text{sign}(P_n'(z_i)) P_n'(z_k) \frac{\sqrt{1 - z_i^2}}{\sqrt{2}} \quad \text{for } k \neq i, \tag{15}$$

$$\psi_i'(z_i) = \frac{\varphi_i'(z_i)}{\sqrt{w_i}} = \frac{z_i |P_n'(z_i)|}{\sqrt{2(1 - z_i^2)}}. \tag{16}$$

He_3

The most accurate energy value we obtained

$$E = 0.08246 \text{ cm}^{-1} = 0.11792 \text{ K}$$

Table 1: Binding energies E_1 of He_3, runtime t and calculation error δE_1 for n functions in DVR decomposition.

n	10	20	30	40
Legendre decomposition				
E_1, см$^{-1}$	$-3.13 \cdot 10^{-3}$	$-7.05 \cdot 10^{-2}$	$-7.99 \cdot 10^{-2}$	$-8.18 \cdot 10^{-2}$
δE_1	$9.26 \cdot 10^{-1}$	$1.42 \cdot 10^{-1}$	$2.80 \cdot 10^{-2}$	$5.34 \cdot 10^{-3}$
t, с	12.3	84.4	277.9	662.9
DVR decomposition				
E_1, см$^{-1}$	$-1.29 \cdot 10^{-2}$	$-9.72 \cdot 10^{-2}$	$-8.35 \cdot 10^{-2}$	$-8.26 \cdot 10^{-2}$
δE_1	$5.69 \cdot 10^{-1}$	$1.81 \cdot 10^{-1}$	$1.59 \cdot 10^{-2}$	$4.21 \cdot 10^{-3}$
t, с	2.4	9.5	21.6	40.0
Acceleration factor				
	5.1	8.9	12.9	16.6

He_3

The DVR method was also developed for constructing functions with Jacobi polynomials $P_n^{(\alpha,\beta)}(z)$. The advantage of this method is the choice of parameters α and β that helps to compensate potential singularity with weight function $\rho(z)$.

Table 2: Binding energies He_3 and relative error for different parameters α and β of Jacobi polynomials $P_n^{(\alpha,\beta)}$ in DVR decomposition.

$\alpha = \beta$	-0.75	-0.50	-0.25	0.0	0.25	0.50	0.75
E, $\text{cm}^{-1} \cdot 10^{-2}$	-8.648	-8.372	-7.164	-9.716	-8.850	-8.627	-8.544
δE	0.049	0.015	0.131	0.178	0.073	0.046	0.035

$Na\text{-}He_2$

Table 3: Binding energies E_1 of $Na\text{-}He_2$, runtime t and calculation error δE_1 for n functions in DVR decomposition.

n	5	10	15
Legendre decomposition			
E_1, см$^{-1}$	$-9.298 \cdot 10^{-2}$	$-1.038 \cdot 10^{-1}$	$-1.034 \cdot 10^{-2}$
δE_1	$1.007 \cdot 10^{-1}$	$2.743 \cdot 10^{-3}$	–
t, с	112	802	2641
DVR decomposition			
E_1, см$^{-1}$	$-1.211 \cdot 10^{-1}$	$-1.074 \cdot 10^{-1}$	$-1.027 \cdot 10^{-1}$
δE_1	$1.718 \cdot 10^{-1}$	$3.849 \cdot 10^{-2}$	$6.535 \cdot 10^{-3}$
t, с	35	130	285
Acceleration factor			
	3.2	6.2	9.3

Comparing of DVR and classical algorithms

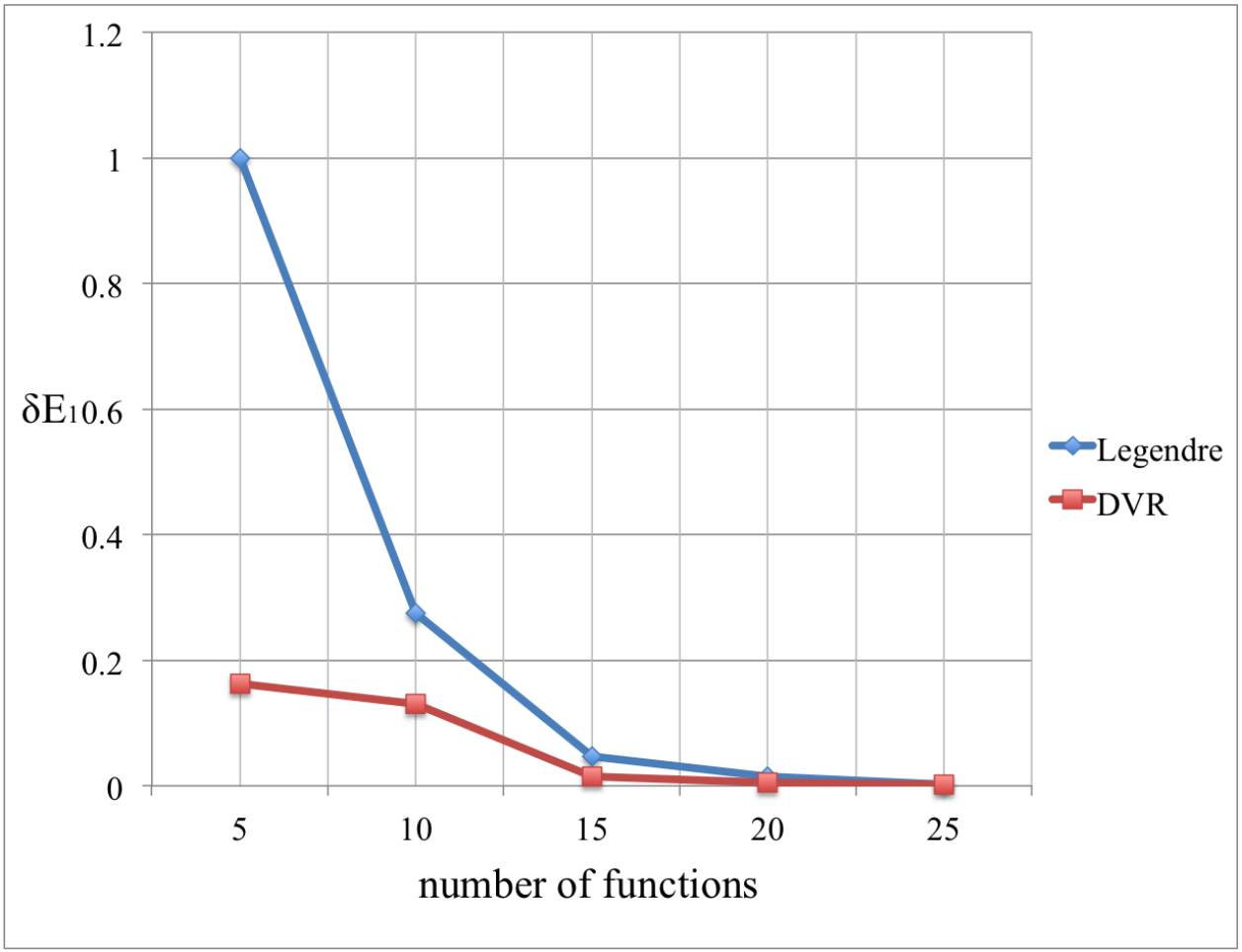

Figure 2: Convergence of algorithm for the Legendre and DVR decomposition for the ^{7}Li–He_2 system are shown.

Comparing of DVR and classical algorithms

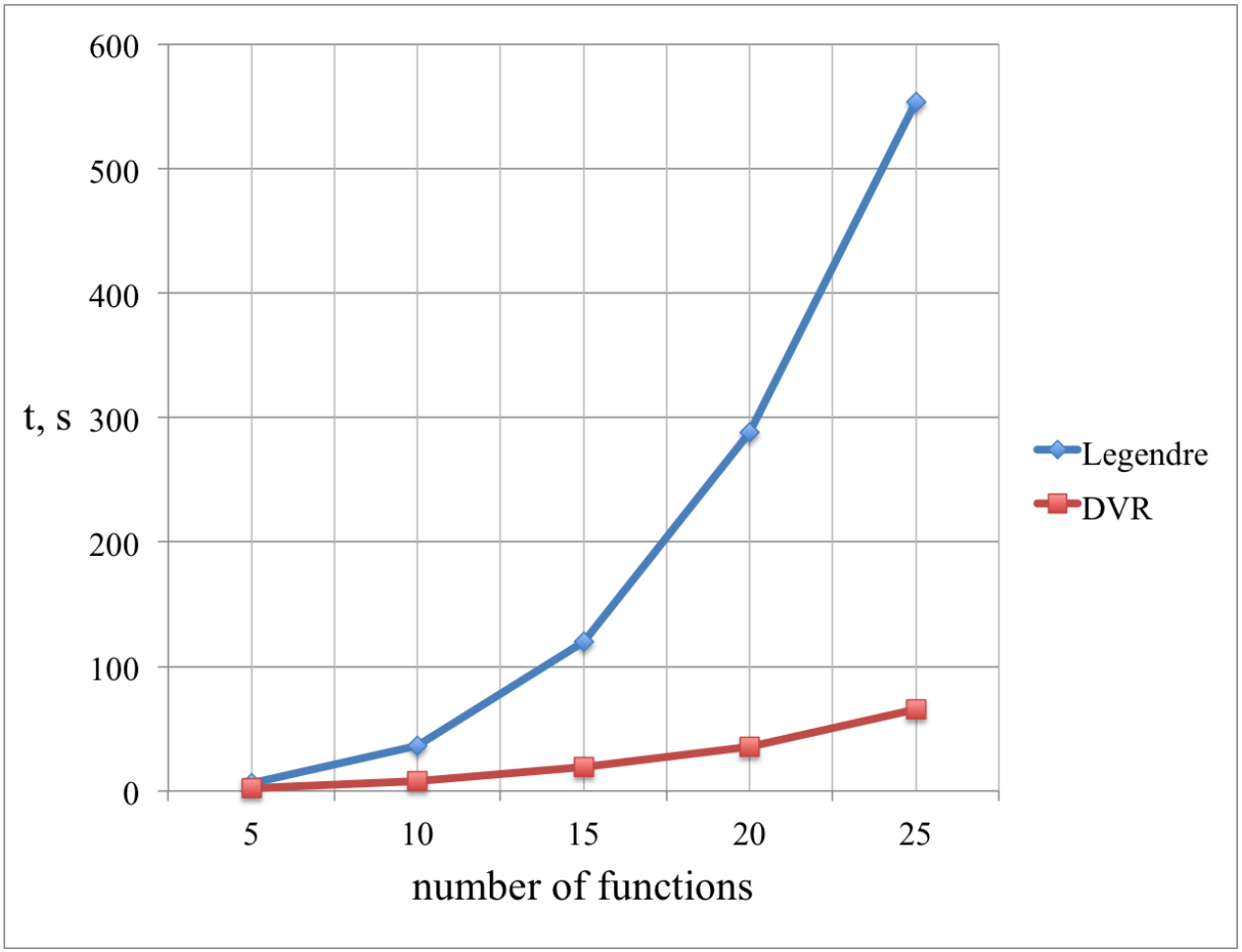

Figure 3: Computation time for the Legendre and DVR decomposition for the ^{7}Li–He_2 system are shown.

Table 4: Binding energies of the Li–He_2 system (cm^{-1}) for different interparticle potentials: TTY, LM2M2, Cvetko.

	He-He potential	Li-He potential	^{6}Li–He_2	^{7}Li–He_2
Yuan J., Lin C. D	TTY	KTTY	-2.18·10^{-2}	-3.18·10^{-2}
This work	TTY	KTTY	-3.71·10^{-2}	-5.41·10^{-2}
Baccarelli I. et al.	LM2M2	Cvetko	-3.61·10^{-2}	-5.10·10^{-2}
This work	LM2M2	Cvetko	-2.62·10^{-2}	-4.07·10^{-2}
Kolganova E.A.	LM2M2	KTTY	-2.46·10^{-2}	-3.54·10^{-2}
This work	LM2M2	KTTY	-3.71·10^{-2}	-5.41·10^{-2}

Comparing of DVR method for the ass. Legendre and Jacobi polynomials

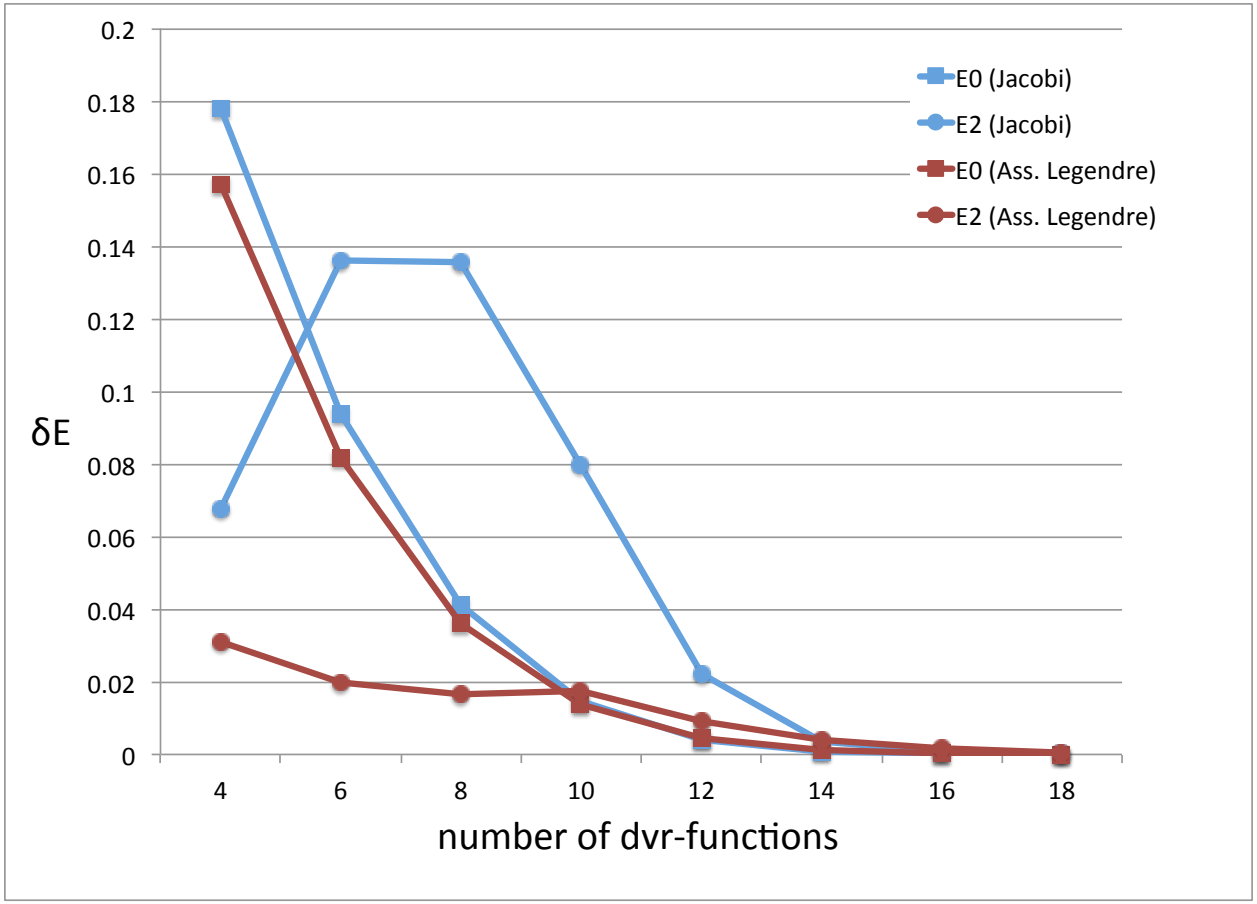

Figure 4: Convergence of DVR method for the ass. Legendre and Jacobi ($\alpha = \beta = -0.5$) polynomials for the Ne_3.

Conclusion

1. The method for calculating quantum mechanical systems of several particles was developed, combining FEM and DVR.
2. A study of the possibility of using various types of quadrature formulas for constructing DVR-functions has been carried out.
3. The DVR-method is implemented in the program for solving three-particle quantum problems ACESPA.
4. The energy levels of weakly bound systems consisting of several atoms were calculated.
5. The method was generalized to complex functions for studying resonance states and scattering processes. The resonance states of helium molecule were obtained.

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Thank you for your attention!