

Comparison of different separability approximations (complete and partial) for the case of large coupling between x and y coordinates

The hamiltonian of our model system is

$$H = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} + \frac{\omega_x^2}{2} x^2 + \frac{\omega_y^2}{2} y^2 + \frac{\omega_z^2}{2} z^2 + \lambda \eta x^3 + \mu \zeta y^3 + \lambda x y^2 + \mu y z^2.$$

where $\omega_x = 0.7$, $\omega_y = 1.3$, $\omega_z = 1.0$, $\lambda = -0.5$, $\mu = -0.1$, $\eta = 0.02$ and $\zeta = 0.1$ (frequencies are the same as for the model of [K. M. Christoffel, J. M. Bowman, Chem. Phys. Lett. **85**, 220, 1982]). This problem is solved perturbatively by introducing a small parameter δ :

$$H_\delta = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} - \frac{1}{2} \frac{\partial^2}{\partial z^2} + \frac{\omega_x^2}{2} x^2 + \frac{\omega_y^2}{2} y^2 + \frac{\omega_z^2}{2} z^2 + \delta^{1/2} (\lambda \eta x^3 + \mu \zeta y^3 + \lambda x y^2 + \mu y z^2)$$

and expanding the energy in powers of δ :

$$E(\delta) = \sum_{k=0}^{\infty} E_k \delta^k$$

The initial hamiltonian corresponds to $\delta = 1$.

We used five methods: complete separability ($x-y-z$), partial separability ($xy-z$, $zx-y$, and $yz-x$), and exact perturbation theory (all modes xyz are coupled). The results are listed in a following table. Since $zx-y$ approximation is identical to $x-y-z$ approximation for our potential (generally, it holds for any potential of the form $V_1(x,y) + V_2(y,z)$), $zx-y$ approximations are not listed.

State <i>n n n</i>	Method	$ E $	Result	Relative error, %	Earlier results
000	x - y - z	$-6.735 \cdot 10^{-8}$	1.4423561578	2.41	
	xy - z	$-1.517 \cdot 10^4$	1.40919	0.059	
	yz - x	$-7.586 \cdot 10^{-8}$	1.4415740273	2.36	
	xyz	$-1.552 \cdot 10^4$	1.40836		
100	x - y - z	$-7.894 \cdot 10^{-7}$	2.1164600320	3.4	
	xy - z	$-1.793 \cdot 10^6$	2.0476	0.01	
	yz - x	$-8.730 \cdot 10^{-7}$	2.1156066807	3.3	
	xyz	$-1.833 \cdot 10^6$	2.0473		
010	x - y - z	$-1.684 \cdot 10^{-2}$	2.2914172	-0.8	
	xy - z	$-2.795 \cdot 10^7$	2.31		
	yz - x	$-1.751 \cdot 10^2$	2.288401	-0.9	
	xyz	$-2.849 \cdot 10^7$	2.31		
001	x - y - z	$-6.254 \cdot 10^{-7}$	2.4320850780	1.5	
	xy - z	-2.720^4	2.39929	0.10	
	yz - x	$-8.146 \cdot 10^{-7}$	2.4296153561	1.4	
	xyz	$-2.913 \cdot 10^4$	2.3969		
200	x - y - z	$-6.708 \cdot 10^{-6}$	2.7850002116	0.5	
	xy - z	$-1.078 \cdot 10^8$	2.773		
	yz - x	$-7.321 \cdot 10^{-6}$	2.7840424632	0.5	
	xyz	$-1.101 \cdot 10^8$	2.77		

Footnote. Imaginary parts are not listed.

Coefficients of the perturbation series are calculated up to the 20th order for complete separability, up to the 20th order for partial separability, and up to the 20th order for the exact problem. The 20th order coefficients are given in the third column of the table to compare different methods regarding feasibility of summation of the series. Smaller coefficients, easier summation of the series.

To sum this constant-sign series, we use quadratic Padé approximants. We give only stable digits.

Below, we consider the same couplings between different coordinates as for the model of [K. M. Christoffel, J. M. Bowman, Chem. Phys. Lett. **85**, 220, 1982], but increased cubic anharmonic terms: $\lambda = \mu = -0.1$, and $\eta = \zeta = 0.5$.

State <i>n n n</i>	Method	$ E $	Result	Relative error, %
000	x - y - z	$-4.347 \cdot 10^{-2}$	1.464614	0.11
	xy - z	$-4.926 \cdot 10^{-2}$	1.46359	0.043
	yz - x	$-4.349 \cdot 10^{-2}$	1.46399	0.07
	xyz	$-4.931 \cdot 10^{-2}$	1.46296	

Footnote. Imaginary parts are not listed.