Comparison of different separability approximations (complete and partial) with exact results obtained by perturbation theory for three-mode system

The hamiltonian of our model system is

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

where $\omega_x = 0.7$, $\omega_y = 1.3$, $\omega_z = 1.0$, $\lambda = \mu = -0.10$, and $\eta = \varsigma = 0.10$ [K. M. Christoffel, J. M. Bowman, Chem. Phys. Lett. **85**, 220, 1982]. This problem is solved perturbatively by introducing a small parameter δ:

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

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 $n\ n\ n$	Method	$\lvert E\ \ \rvert$	Result	Relative error, %	Earlier results
000	x - y - z	$-1.513\cdot10^{-37}$	1.4950326406	0.086	1.4951^{SCF}
	xy - z	$-8.008\cdot10^{-26}$	1.4943544117	0.040	
	yz - x	$-2.906\cdot10^{-32}$	1.4944331140	0.046	
	xyz	$\mathbf{-2.307\cdot10^{-25}}$	**1.4937521357**		$\mathbf{1.494^{EQ}}$
100	x - y - z	$-2.954\cdot10^{-34}$	2.1883657294	0.15	2.1884^{SCF}
	xy - z	$-2.255\cdot10^{-23}$	2.1857650339	0.028	
	yz - x	$-1.371\cdot10^{-31}$	2.1877614725	0.12	
	xyz	$\mathbf{-5.576\cdot10^{-23}}$	**2.1851484018**		$\mathbf{2.185^{EQ}}$
001	x - y - z	$-4.315\cdot10^{-35}$	2.4882497042	0.10	2.4883^{SCF}
	xy - z	$-1.244\cdot10^{-24}$	2.4875188435	0.074	
	yz - x	$-2.263\cdot10^{-29}$	2.4864147734	0.030	
	xyz	$\mathbf{-1.861\cdot10^{-23}}$	**2.4856745881**		$\mathbf{2.486^{EQ}}$
010	x - y - z	$-1.060\cdot10^{-30}$	2.7780366885	0.25	2.7782^{SCF}
	xy - z	$-3.172\cdot10^{-22}$	2.7759331355	0.17	

	yz - x	$-5.426\cdot10^{-28}$	2.7739809691	0.10	
	xyz	$\mathbf{-7.834\cdot10^{-22}}$	**2.7711863549**		**2.771** **EQ**
200	x - y - z	$-2.923\cdot10^{-31}$	2.8783852089	0.18	2.8786 SCF
	xy - z	$-2.917\cdot10^{-21}$	2.8737413934	0.022	
	yz - x	$-1.292\cdot10^{-30}$	2.8777760386	0.16	
	xyz	$\mathbf{-6.418\cdot10^{-21}}$	**2.8731087679**		**2.873** **EQ**
101	x - y - z	$-5.993\cdot10^{-32}$	3.1815029223	0.15	3.1815 SCF
	xy - z	$-3.557\cdot10^{-22}$	3.1786111559	0.060	
	yz - x	$-108.6\cdot10^{-28}$	3.1796530303	0.092	
	xyz	$\mathbf{-3.756\cdot10^{-21}}$	**3.1767160381**		**3.177** **EQ**
011	x - y - z	$-2.657\cdot10^{-29}$	3.7696405783	0.39	
	xy - z	$6.263\cdot10^{-21}$	3.7675504499	0.33	
	yz - x	$-4.362\cdot10^{-25}$	3.7571924860	0.057	
	xyz	$\mathbf{-5.631\cdot10^{-20}}$	**3.7550630846**		
020	x - y - z	$-4.420\cdot10^{-25}$	4.0474588740	0.26	
	xy - z	$-1.095\cdot10^{-18}$	4.0443553973	0.19	
	yz - x	$-1.940\cdot10^{-24}$	4.0399814168	0.11	
	xyz	$\mathbf{-1.876\cdot10^{-18}}$	**4.0368054973**		

Coefficients of the perturbation series are calculated up to the 60th order for complete separability, up to the 40th order for partial separability, and up to the 30th order for the exact problem. All coefficients E_1, E_2, E_3, ... appear to be negative. The 30th 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 (more rigorously, we give only digits that are common for at least 3 approximants among the last 10 approximants).

The last column of the table contains earlier SCF results of Christoffel and Bowman and exact quantum results [D. W. Noid et al., J. Chem. Phys. **73**, 391, 1980]. SCF results almost agree with our complete-separability results; sometimes there is a disagreement in the last digit. Exact quantum results of Noid completely agree with our xyz-results.

For $\delta = 1$, imaginary parts of quadratic approximants vanish, because the width is extremely small. For larger perturbation parameters, they may be non-zero. Results for $\delta = 4$, $\delta = 9$, and $\delta = 25$ are given below. They correspond to anharmonicity that is proportionally larger two, three, or five times.

State $n_x n_y n_z$	Method		Result, $\delta = 4$	Relat. error, %	Result, $\delta = 9$	Relat. error, %	Result, $\delta = 25$	Relat. error, %
000	x - y - z	Re	1.4791284326	0.41	1.4479702519	1.6	1.311347	-0.35
		Im	0		0.0000000265	-100	0.093547	-33
	xy - z	Re	1.4757887007	0.18	1.43438642	0.61	1.326583	0.80
		Im	0.0000000608	-60	0.00224666	-40	0.121350	-12
	yz - x	Re	1.4764849642	0.23	1.44040945	1.0	1.30059	-1.2
		Im	0		0.00001473	-100	0.11554	-17
	xyz	**Re**	**1.473064833**		**1.4257081**		**1.31601**	
		Im	**0.000000151**		**0.0037213**		**0.13863**	
100	x - y - z	Re	2.1498138191	0.84	2.063168	3.1	1.865552	-2.2
		Im	0		0.0000456	-100	0.303879	-15
	xy - z	Re	2.135238325	0.15	2.00692	0.28	1.9179	0.52
		Im	0.000010087	-51	0.05213	-16	0.3548	-0.3
	yz - x	Re	2.1470544972	0.71	2.05319	2.6	1.85883	-2.6
		Im	0		0.00024	-100	0.32046	11
	xyz	**Re**	**2.1319654**		**2.0014**		**1.908**	
		Im	**0.0000204**		**0.0622**		**0.356**	
001	x - y - z	Re	2.4492803512	0.57	2.3611403	2.4	2.1719904	-1.7
		Im	0		0		0.303012	-18
	xy - z	Re	2.44460015	0.38	2.332949	1.1	2.2193	0.43
		Im	0.00000093	-89	0.022874	-45	0.3255	-12
	yz - x	Re	2.4404887892	0.21	2.32135	0.64	2.16897	-1.9
		Im	0.0000000002	-100	0.00807	-81	0.35977	-3.0
	xyz	**Re**	**2.4353476**		**2.306492**		**2.20990**	
		Im	**0.00000809**		**0.041867**		**0.37092**	
010	x - y - z	Re	2.7012659751	1.3	2.478851	0.8	2.38036743	2.6
		Im	0		0.060465	-40	0.604409	-15
	xy - z	Re	2.686743	0.74	2.507	2.	2.344	1.0
		Im	0.0001608	-45	0.067	-34	0.638	-10
	yz - x	Re	2.682360391	0.57	2.4304	-1.2	2.3293	0.4
		Im	0.000000004	-100	0.0925	-8.4	0.6745	-5
	xyz	**Re**	**2.66711**		**2.46**		**2.32**	
		Im	**0.00029**		**0.101**		**0.71**	
200	x - y - z	Re	2.8039249624	1.3	2.59203	1.4	2.4420884	-3.
		Im	0		0.03367	-82	0.605154	-8
	xy - z	Re	2.77274	0.17	2.559	0.2	2.542	1.
		Im	0.00058	-40	0.188	1	0.654	-1
	yz - x	Re	2.8010210986	1.2	2.58250	1.1	2.436092	-3.
		Im	0		0.04038	-78	0.61894	-6
	xyz	**Re**	**2.76804**		**2.555**		**2.52**	
		Im	**0.00097**		**0.187**		**0.66**	
101	x - y - z	Re	3.1180673808	1.2	2.93778	-0.2	2.7991551	-3.8
		Im	0		0.02567	-88	0.499171	7
	xy - z	Re	3.0938294	0.44	2.9199	-0.8	2.981	2.4
		Im	0.0001556	-80	0.1801	-19	0.443	-5
	yz - x	Re	3.108805372	0.92	2.90786	-1.2	2.79813	-3.9
		Im	0.000000001		0.05257	-76	0.54630	17

	xyz	**Re**	**3.080415**		**2.944**		**2.911**	
		Im	**0.000790**		**0.222**		**0.468**	
011	x - y - z	Re	3.6595081383	2.6	3.368487378	3.1	3.334375260	<0.2
		Im	0		0.154622	-32	0.803240	-24
	xy - z	Re	3.6322	1.9	3.434	5.1	3.17	-5.
		Im	0.0039	-60	0.094	-59	0.85	-19
	yz - x	Re	3.593560	0.80	3.25208	-0.46	3.2834	-1.4
		Im	0.0000035	-100	0.29053	27	1.0363	-1
	xyz	**Re**	**3.5651**		**3.267**		**3.33**	
		Im	**0.0092**		**0.228**		**1.05**	
020	x - y - z	Re	3.838340778	1.4	3.4486468218	4.	3.572830514	5.
		Im	0		0.408036	-13	1.30875	-13
	xy - z	Re	3.84	1.4	3.412	3.	3.561	5.
		Im	0		0.433	-8	1.37	-9
	yz - x	Re	3.80618	0.5	3.3740	2.	3.462	<2.
		Im	0.00001		0.4582	-3	1.421	-5
	xyz	**Re**	**3.787**		**3.32**		**3.4**	
		Im	**0.01**		**0.47**		**1.5**	

Detailed tables of coefficients and quadratic approximants for various methods are attached below.