

Self-consistent field calculations for anharmonic oscillators

I. Coupled double barrier Hamiltonian

The Hamiltonian is

$$H = -\frac{1}{8} \frac{\partial^2}{\partial x^2} - \frac{1}{8} \frac{\partial^2}{\partial y^2} + \frac{1}{2} \omega_x^2 x^2 \exp(-x^2) + \frac{1}{2} \omega_y^2 y^2 + x^2 \exp(-x^2) (V_2 y - \frac{1}{2} \eta \omega_y^2 y^2),$$

see [D. Farrelly, J. Chem. Phys. 1986, **84** (11), 6285], eq. (2.1) - (2.4). The calculations were done for parameters ω_x , ω_y , V_2 , η and for quantum numbers n_x and n_y from Tables I and III of Farrelly's paper.

We introduce an expansion parameter δ :

$$H(\delta) = -\frac{\delta^2}{8} \frac{\partial^2}{\partial x^2} - \frac{\delta^2}{8} \frac{\partial^2}{\partial y^2} + \frac{1}{2} \omega_x^2 x^2 \exp(-x^2) + \frac{1}{2} \omega_y^2 y^2 + x^2 \exp(-x^2) (V_2 y - \frac{1}{2} \eta \omega_y^2 y^2),$$

calculate the semiclassical eigenvalue series, and finally sum it for $\delta = 1$. The SCF results are presented in the following table:

Energies of Farrelly coupled barrier Hamiltonian

without rescaling, SCF only

50 coefficients were calculated

$$\omega_x, \omega_y, V_2, \eta = 14.140000 \quad 14.140000 \quad 0.000000 \quad 1.000000$$

nx, ny =	3	0		
order / coeff. / Padé sum / quadratic Padé: SCF				exact
19	-0.74058D-06	25.476950789	25.477264481	0.000000000
20	-0.49575D-06	25.476950699	25.476952545	0.000000000
21	-0.33904D-06	25.476950287	25.477901539	0.000000000
22	-0.23680D-06	25.476951156	25.477874302	0.000000000
23	-0.16887D-06	25.476950944	25.477389225	0.000000000
24	-0.12293D-06	25.476950865	25.477130941	0.000000000
25	-0.91335D-07	25.476950807	25.476997963	0.000000000
26	-0.69253D-07	25.476950696	25.476986799	0.000000000
27	-0.53581D-07	25.476948173	25.476985745	0.000000000
28	-0.42295D-07	25.476950998	25.476972168	0.000000000
29	-0.34059D-07	25.476950884	25.476952778	0.000000000
30	-0.27977D-07	25.476950810	25.477098292	0.000000000
31	-0.23438D-07	25.476950693	25.476955858	0.000000000
32	-0.20023D-07	25.476951913	25.476950701	0.000000000
33	-0.17440D-07	25.476950954	25.476950655	-0.000000283
34	-0.15486D-07	25.476950852	25.476950881	0.000000192

35	-0.14015D-07	25.476950769	25.476951367	0.000000000
36	-0.12925D-07	25.476950291	25.476950829	0.000000090
37	-0.12145D-07	25.476951024	25.476950836	-0.000000089
38	-0.11623D-07	25.476950873	25.476950835	-0.000000090
39	-0.11328D-07	25.476950790	25.476950842	-0.000000116
40	-0.11241D-07	25.476950496	25.476950839	-0.000000103
41	-0.11354D-07	25.476951054	25.476950849	0.000000071
42	-0.11671D-07	25.476950876	25.476950840	-0.000000102
43	-0.12205D-07	25.476950788	25.476950840	-0.000000093
44	-0.12983D-07	25.476950422	25.476950829	-0.000000165
45	-0.14045D-07	25.476951016	25.476950846	-0.000000101
46	-0.15446D-07	25.476950863	25.476950846	0.000000105
47	-0.17267D-07	25.476950766	25.476950845	-0.000000105
48	-0.19615D-07	25.476949163	25.476950845	0.000000105
49	-0.22639D-07	25.476950955	25.476950845	0.000000105
Farrelly, complex coordinate SCF:			25.478	0.000000100

nx, ny =		4	0	
order / coeff. / Padé	sum / quadratic	Padé: SCF		exact
19	-0.35393D-04	30.673375879	30.673251263	0.000000000
20	-0.27537D-04	30.673311198	30.673246178	0.000000000
21	-0.21802D-04	30.673284389	30.673281088	0.000000000
22	-0.17559D-04	30.673254283	30.673324711	0.000000000
23	-0.14381D-04	30.673191209	30.673306614	0.000000000
24	-0.11975D-04	30.673549216	30.673277287	0.000000000
25	-0.10136D-04	30.673329770	30.673232497	0.000000000
26	-0.87210D-05	30.673288425	30.673301283	0.000000000
27	-0.76261D-05	30.673257648	30.673255636	0.000000000
28	-0.67773D-05	30.673167828	30.673259418	0.000049532
29	-0.61211D-05	30.673442680	30.673231925	0.000000000
30	-0.56182D-05	30.673311216	30.673279097	0.000052369
31	-0.52404D-05	30.673276733	30.673278935	0.000050972
32	-0.49673D-05	30.673228027	30.673277376	-0.000049636
33	-0.47848D-05	30.680747903	30.673276924	0.000050222
34	-0.46837D-05	30.673328277	30.673285550	0.000047409
35	-0.46589D-05	30.673284848	30.673285675	0.000047373
36	-0.47089D-05	30.673240805	30.673280072	-0.000046912
37	-0.48360D-05	30.672741016	30.673281565	0.000047112
38	-0.50459D-05	30.673333349	30.673282107	0.000044819
39	-0.53489D-05	30.673285369	30.673282489	0.000045691
40	-0.57598D-05	30.673238708	30.673282173	0.000045602
41	-0.62999D-05	30.671278355	30.673282109	-0.000045622
42	-0.69982D-05	30.673324379	30.673282118	0.000045685
43	-0.78943D-05	30.673279442	30.673282110	-0.000045678
44	-0.90420D-05	30.673221873	30.673282103	0.000045680
45	-0.10514D-04	30.673547410	30.673282098	0.000045687
46	-0.12410D-04	30.673308461	30.673282673	0.000045371
47	-0.14866D-04	30.673267361	30.673282118	-0.000045696
48	-0.18072D-04	30.673163732	30.673282102	-0.000045714
49	-0.22289D-04	30.673369761	30.673282110	-0.000045723
Farrelly, complex coordinate SCF:			30.675	0.0000441

nx, ny =		5	0	
order / coeff. / Padé	sum / quadratic	Padé: SCF		exact
19	-0.95097D-03	35.203634455	35.211115082	-0.002319111
20	-0.84755D-03	35.174294113	35.211611519	0.003333043
21	-0.76669D-03	35.224189848	35.211426745	-0.003261230
22	-0.70363D-03	35.213067100	35.211080025	0.003869501
23	-0.65491D-03	35.208975701	35.210423061	0.000000000
24	-0.61803D-03	35.203224765	35.214110581	0.003855910
25	-0.59121D-03	35.160463844	35.210658202	-0.005225434
26	-0.57320D-03	35.218801340	35.210431855	0.006523251
27	-0.56319D-03	35.211590573	35.210808708	0.007075277
28	-0.56074D-03	35.206700872	35.209964251	0.006273289

29	-0.56573D-03	35.196152359	35.209742342	-0.006090543
30	-0.57834D-03	35.227248911	35.209598944	0.006367751
31	-0.59908D-03	35.213142411	35.209624719	-0.006216538
32	-0.62883D-03	35.207867527	35.209620206	0.006210117
33	-0.66886D-03	35.199554072	35.209629251	-0.006210032
34	-0.72095D-03	35.233029826	35.209633076	0.006208695
35	-0.78751D-03	35.213458113	35.209639381	-0.006215889
36	-0.87179D-03	35.207879288	35.209639621	-0.006216167
37	-0.97810D-03	35.198639862	35.209649736	-0.006227687
38	-0.11122D-02	35.227728452	35.209547244	-0.006109132
39	-0.12818D-02	35.212593897	35.209644125	0.006209979
40	-0.14972D-02	35.206895691	35.209647820	0.006209319
41	-0.17725D-02	35.192174960	35.209649752	-0.006206978
42	-0.21269D-02	35.220141235	35.209649211	0.006206570
43	-0.25865D-02	35.210968527	35.209648406	0.006206519
44	-0.31878D-02	35.204631751	35.209640106	0.006202503
45	-0.39818D-02	35.085045870	35.209634712	-0.006202925
46	-0.50399D-02	35.215084538	35.209646988	0.006207581
47	-0.64641D-02	35.208794794	35.209646831	0.006207303
48	-0.84006D-02	35.198848551	35.209646789	-0.006207974
49	-0.11061D-01	35.226811245	35.209646999	0.006207887
Farrelly, complex coordinate SCF:		35.212		0.00594

nx, ny =		6	0	
order	coeff.	Padé sum	quadratic Padé	SCF exact
19	-0.16597D-01	38.842630051	38.802970438	-0.192691301
20	-0.16723D-01	38.704999462	38.802718664	0.189389328
21	-0.17073D-01	38.429655393	38.802751498	-0.189419327
22	-0.17651D-01	39.524616535	38.802956918	0.189449726
23	-0.18473D-01	38.948056471	38.802272569	0.189249478
24	-0.19564D-01	38.786505036	38.802126737	-0.189246197
25	-0.20962D-01	38.621707468	38.801924398	0.189335599
26	-0.22718D-01	33.847800971	38.801891806	0.189418676
27	-0.24900D-01	39.038611989	38.804802624	-0.186908044
28	-0.27598D-01	38.823334535	38.809316840	-0.183369983
29	-0.30928D-01	38.669178066	38.801686779	-0.188551072
30	-0.35043D-01	37.519772701	38.802817000	-0.188286105
31	-0.40146D-01	39.073702753	38.801352482	-0.187297930
32	-0.46500D-01	38.828440959	38.801965925	0.187433691
33	-0.54455D-01	38.665712224	38.802033845	0.187376920
34	-0.64480D-01	36.903331182	38.802033818	0.187392862
35	-0.77200D-01	39.029660761	38.802061446	-0.187424586
36	-0.93464D-01	38.806602498	38.802116160	-0.187607848
37	-0.11443D+00	38.616409446	38.802073694	-0.187397617
38	-0.14168D+00	41.063617011	38.802090391	0.187457720
39	-0.17741D+00	38.950175658	38.802090473	-0.187480580
40	-0.22470D+00	38.760436980	38.801986008	0.187382830
41	-0.28785D+00	38.473625332	38.801975463	-0.187278363
42	-0.37301D+00	39.268146880	38.802141636	-0.187506906
43	-0.48896D+00	38.868676261	38.801704766	0.186980192
44	-0.64839D+00	38.681638956	38.802094841	0.187486002
45	-0.86982D+00	37.453949819	38.802104664	-0.187511622
46	-0.11805D+01	38.989799588	38.802146680	0.187433958
47	-0.16208D+01	38.785517311	38.802154737	0.187429876
48	-0.22512D+01	38.495607980	38.802134992	-0.187431656
49	-0.31634D+01	39.336788662	38.802130231	-0.187429317
Farrelly, complex coordinate SCF:		38.805		0.185

nx, ny =		7	0	
order	coeff.	Padé sum	quadratic Padé	SCF exact
19	-0.20726D+00	47.427292640	41.478843731	-1.151816894
20	-0.23343D+00	42.326454453	41.471233731	1.162037474
21	-0.26604D+00	41.433539691	41.471034999	-1.161583864
22	-0.30665D+00	40.271612998	41.470781406	1.161428494

23	-0.35733D+00	26.134502476	41.470698776	1.161492364
24	-0.42079D+00	42.817852215	41.470699262	-1.161577686
25	-0.50061D+00	41.637388772	41.470986511	1.161290448
26	-0.60155D+00	40.560991526	41.471395415	-1.161355629
27	-0.72996D+00	34.520448268	41.471136996	-1.165082299
28	-0.89435D+00	42.972498031	41.471030704	-1.167020157
29	-0.11062D+01	41.652453809	41.471665654	1.157976514
30	-0.13813D+01	40.514933030	41.471437894	-1.160989937
31	-0.17409D+01	30.468805261	41.469250917	1.164989269
32	-0.22148D+01	42.711156744	41.472949434	1.160283055
33	-0.28439D+01	41.500093497	41.472794589	1.161209384
34	-0.36860D+01	40.153854075	41.472899973	-1.161348727
35	-0.48223D+01	54.434898597	41.472972235	1.161309026
36	-0.63682D+01	42.261699641	41.472825301	-1.161527641
37	-0.84891D+01	41.200660527	41.472769029	1.161635071
38	-0.11424D+02	39.017563134	41.754558344	-0.876487259
39	-0.15521D+02	44.236049943	41.472881745	1.161726078
40	-0.21290D+02	41.782908772	41.472878865	-1.161774586
41	-0.29486D+02	40.691939488	41.472871041	-1.161741257
42	-0.41238D+02	20.411298058	41.472875568	1.161745038
43	-0.58240D+02	42.576834659	41.472871706	-1.161751782
44	-0.83067D+02	41.269190727	41.472923068	1.161594774
45	-0.11966D+03	39.433392958	41.472913142	-1.161626400
46	-0.17410D+03	44.038023540	41.472991998	1.161836732
47	-0.25586D+03	41.775097513	41.473006402	1.161904943
48	-0.37983D+03	40.496344756	41.473035180	-1.161689006
49	-0.56960D+03	81.631884003	41.473042056	-1.161668611
Farrelly, complex coordinate SCF:			41.474	1.160

nx, ny =	8	0		
order / coeff. / Padé	sum / quadratic	Padé: SCF		exact
19	-0.19822D+01	43.176321670	43.820601616	-3.149483115
20	-0.24713D+01	38.837622549	43.886619733	3.160033542
21	-0.31147D+01	65.900519964	43.886099725	-3.161079358
22	-0.39663D+01	46.131948411	43.886375712	3.162080715
23	-0.51011D+01	43.542191476	43.886046977	-3.162032057
24	-0.66234D+01	39.608279378	43.885984531	3.162041966
25	-0.86793D+01	72.263663826	43.886105913	3.162092196
26	-0.11476D+02	46.135529535	43.885639843	-3.161729003
27	-0.15305D+02	43.409883973	43.881149130	-3.142604630
28	-0.20588D+02	38.886950043	43.885762055	-3.163408518
29	-0.27927D+02	58.064951494	43.886746840	3.166574308
30	-0.38195D+02	45.521657654	43.885853556	3.163484469
31	-0.52667D+02	42.828304476	43.885523786	3.161864222
32	-0.73213D+02	35.520428093	43.885714927	-3.165910361
33	-0.10260D+03	50.347335308	43.885222405	-3.163728674
34	-0.14493D+03	44.583073806	43.884941959	-3.163380433
35	-0.20637D+03	41.647420169	43.884700087	3.164150219
36	-0.29622D+03	-25.502744481	43.884662848	-3.163474626
37	-0.42863D+03	46.950634337	43.884533939	3.163062677
38	-0.62524D+03	43.397546551	43.884540409	-3.162764490
39	-0.91945D+03	38.837652434	43.884195765	3.163076052
40	-0.13632D+04	51.925051236	43.884209545	3.163090122
41	-0.20377D+04	44.952600674	43.884240319	-3.163102770
42	-0.30712D+04	41.631328733	43.884222401	3.163089525
43	-0.46677D+04	-2.195590341	43.884193465	3.163175868
44	-0.71541D+04	46.476301120	43.887116640	3.163464773
45	-0.11058D+05	43.211930331	43.884998639	-3.163237442
46	-0.17240D+05	36.394324430	43.884149368	3.163213864
47	-0.27109D+05	49.584276407	43.884177229	-3.163216899
48	-0.43000D+05	44.177245463	43.884193043	-3.163352190
49	-0.68807D+05	40.471745167	43.884219335	-3.163452612
Farrelly, complex coordinate SCF:			43.885	3.162

$\omega_x, \omega_y, V_2, \eta = 14.140000 \quad 14.140000 \quad 20.000000 \quad 2.000000$

$nx, ny =$	3	0			
order / coeff. / Padé	sum / quadratic	Padé: SCF		exact	
19	-0.11313D-05	25.204433176	25.204434901	0.000000000	
20	-0.76424D-06	25.204433004	25.204433276	0.000000000	
21	-0.52705D-06	25.204431802	25.204433368	0.000000000	
22	-0.37095D-06	25.204433701	25.209448643	0.000000000	
23	-0.26638D-06	25.204433425	25.206395854	0.000000000	
24	-0.19515D-06	25.204433304	25.236115505	0.000000000	
25	-0.14583D-06	25.204433204	25.204593582	0.000000000	
26	-0.11115D-06	25.204432987	25.204573613	0.000000000	
27	-0.86396D-07	25.204437223	25.204466498	0.000000000	
28	-0.68485D-07	25.204433497	25.204438676	0.000000000	
29	-0.55357D-07	25.204433332	25.204438539	0.000000000	
30	-0.45623D-07	25.204433207	25.204437785	0.000000000	
31	-0.38336D-07	25.204432974	25.204437877	0.000000000	
32	-0.32839D-07	25.204434193	25.204439438	0.000000000	
33	-0.28672D-07	25.204433434	25.204435592	0.000000000	
34	-0.25515D-07	25.204433279	25.204445893	0.000000000	
35	-0.23136D-07	25.204433129	25.204434094	0.000000000	
36	-0.21374D-07	25.204431353	25.204433764	0.000000000	
37	-0.20115D-07	25.204433525	25.204433085	-0.000000470	
38	-0.19279D-07	25.204433313	25.204433270	0.000000175	
39	-0.18814D-07	25.204433169	25.204433268	0.000000171	
40	-0.18692D-07	25.204432380	25.204433274	0.000000173	
41	-0.18901D-07	25.204433558	25.204433277	-0.000000173	
42	-0.19447D-07	25.204433317	25.204433277	-0.000000175	
43	-0.20357D-07	25.204433165	25.204433279	-0.000000179	
44	-0.21673D-07	25.204432038	25.204433283	0.000000188	
45	-0.23464D-07	25.204433512	25.204433353	0.000000000	
46	-0.25825D-07	25.204433295	25.204433284	-0.000000176	
47	-0.28889D-07	25.204433120	25.204433284	0.000000176	
48	-0.32840D-07	25.204437248	25.204433284	-0.000000176	
49	-0.37927D-07	25.204433431	25.204433284	0.000000176	
Farrelly, complex coordinate SCF:		25.205		0.0000001815	

$nx, ny =$	3	1			
order / coeff. / Padé	sum / quadratic	Padé: SCF		exact	
19	-0.39787D-05	31.274656402	31.275535812	0.000000000	
20	-0.27847D-05	31.274654355	31.274738732	0.000000000	
21	-0.19853D-05	31.274663078	31.276268616	0.000000000	
22	-0.14415D-05	31.274658460	31.276745747	0.000000000	
23	-0.10657D-05	31.274657708	31.277856658	0.000000000	
24	-0.80210D-06	31.274657159	31.274658366	0.000000000	
25	-0.61461D-06	31.274656492	31.274658358	0.000000000	
26	-0.47944D-06	31.274652924	31.275778207	0.000000000	
27	-0.38074D-06	31.274659627	31.275128283	0.000000000	
28	-0.30783D-06	31.274657889	31.274658316	0.000000000	
29	-0.25337D-06	31.274657267	31.274658432	0.000000000	
30	-0.21233D-06	31.274656458	31.274657653	0.000000000	
31	-0.18116D-06	31.274651351	31.274656893	0.000000000	
32	-0.15737D-06	31.274658805	31.274660551	0.000000000	
33	-0.13918D-06	31.274657661	31.274658114	0.000000000	
34	-0.12532D-06	31.274656951	31.274657384	-0.000000686	
35	-0.11488D-06	31.274655507	31.274657570	0.000000696	
36	-0.10720D-06	31.274660324	31.274657357	-0.000000820	
37	-0.10181D-06	31.274657903	31.274657289	0.000000872	
38	-0.98417D-07	31.274657125	31.274657355	0.000000940	
39	-0.96809D-07	31.274655973	31.274657332	0.000000935	
40	-0.96890D-07	31.274661587	31.274657331	-0.000000935	
41	-0.98647D-07	31.274657962	31.274657331	-0.000000933	
42	-0.10216D-06	31.274657132	31.274657331	-0.000000933	

43	-0.10758D-06	31.274655880	31.274657328	-0.000000933
44	-0.11519D-06	31.274660563	31.274657294	0.000000930
45	-0.12538D-06	31.274657837	31.274657308	-0.000000927
46	-0.13870D-06	31.274657000	31.274657350	-0.000000924
47	-0.15591D-06	31.274655143	31.274657350	0.000000924
48	-0.17804D-06	31.274659138	31.274657332	-0.000000920
49	-0.20652D-06	31.274657596	31.274657340	-0.000000922
Farrelly, complex coordinate SCF:			31.276	0.00000094

nx, ny =		4	0	
order	coeff.	Padé sum	quadratic Padé	SCF exact
19	-0.53355D-04	30.291520816	30.291294970	0.000000000
20	-0.41954D-04	30.291435118	30.291300156	0.000000000
21	-0.33548D-04	30.291392462	30.291257884	0.000657996
22	-0.27269D-04	30.291337634	30.298073286	0.000000000
23	-0.22527D-04	30.291187471	30.302039019	0.000000000
24	-0.18908D-04	30.291657296	30.291306220	0.000000000
25	-0.16124D-04	30.291459916	30.291243474	0.000000000
26	-0.13967D-04	30.291398161	30.291482437	0.000000000
27	-0.12290D-04	30.291342821	30.291497655	0.000000000
28	-0.10985D-04	30.291101748	30.291658229	0.000000000
29	-0.99737D-05	30.291576155	30.291293944	0.000000000
30	-0.91982D-05	30.291432901	30.291401045	-0.000121713
31	-0.86169D-05	30.291377573	30.291395196	-0.000080889
32	-0.82002D-05	30.291277195	30.291395485	0.000081192
33	-0.79272D-05	30.291941598	30.291396007	0.000081202
34	-0.77847D-05	30.291456011	30.291395819	-0.000080845
35	-0.77660D-05	30.291391134	30.291405236	-0.000075885
36	-0.78700D-05	30.291305631	30.291392416	-0.000079896
37	-0.81015D-05	30.292821398	30.291396837	0.000078137
38	-0.84714D-05	30.291461960	30.291393398	0.000072824
39	-0.89974D-05	30.291391701	30.291396853	0.000076614
40	-0.97056D-05	30.291300077	30.291396969	-0.000076623
41	-0.10633D-04	30.292036217	30.291396956	-0.000076639
42	-0.11828D-04	30.291449854	30.291396954	-0.000076678
43	-0.13360D-04	30.291381242	30.291396914	0.000076744
44	-0.15321D-04	30.291258078	30.291396973	0.000076687
45	-0.17835D-04	30.291631340	30.291396945	0.000076738
46	-0.21072D-04	30.291427364	30.291396911	-0.000076838
47	-0.25267D-04	30.291359074	30.291396997	0.000076719
48	-0.30742D-04	30.291054976	30.291396995	-0.000076728
49	-0.37946D-04	30.291502535	30.291397016	0.000076740
Farrelly, complex coordinate SCF:			30.292	0.000077

nx, ny =		4	1	
order	coeff.	Padé sum	quadratic Padé	SCF exact
19	-0.16152D-03	36.012836488	36.015093604	0.000000000
20	-0.13172D-03	36.012598300	36.013622526	0.001076256
21	-0.10906D-03	36.012396543	36.013439919	-0.000718246
22	-0.91648D-04	36.011917096	36.013177775	0.000464646
23	-0.78142D-04	36.017216687	36.013176983	-0.000401141
24	-0.67590D-04	36.012975872	36.015295602	0.000000000
25	-0.59301D-04	36.012661644	36.012540305	0.001175108
26	-0.52771D-04	36.012407862	36.014094173	0.000000000
27	-0.47629D-04	36.011916303	36.014287069	0.000000000
28	-0.43600D-04	36.014203352	36.013920248	0.000000000
29	-0.40482D-04	36.012867750	36.014962667	0.000000000
30	-0.38126D-04	36.012558800	36.012765679	-0.000398484
31	-0.36425D-04	36.012253434	36.012777081	0.000212793
32	-0.35304D-04	36.007955635	36.012577272	0.000368635
33	-0.34715D-04	36.013052764	36.012580753	0.000362496
34	-0.34637D-04	36.012628947	36.012579675	-0.000357959
35	-0.35067D-04	36.012339852	36.012575219	0.000358882
36	-0.36026D-04	36.010692400	36.012575409	-0.000358610

37	-0.37561D-04	36.013127569	36.012575841	0.000356209
38	-0.39743D-04	36.012639740	36.012576308	-0.000354268
39	-0.42677D-04	36.012335158	36.012574104	0.000355972
40	-0.46510D-04	36.010087618	36.012574424	-0.000355302
41	-0.51439D-04	36.013040214	36.012574351	0.000355041
42	-0.57734D-04	36.012598745	36.012574204	0.000355078
43	-0.65758D-04	36.012250060	36.012574342	0.000354971
44	-0.75998D-04	36.022335831	36.012574359	-0.000354946
45	-0.89117D-04	36.012879581	36.012574409	-0.000354955
46	-0.10602D-03	36.012513548	36.012574436	-0.000354957
47	-0.12795D-03	36.012011206	36.012574896	0.000355050
48	-0.15664D-03	36.013605714	36.012573656	0.000354820
49	-0.19448D-03	36.012719213	36.012574577	-0.000354932
Farrelly, complex coordinate SCF:			36.013	0.000354

nx, ny =		5	0	
order	coeff. / Padé	sum / quadratic	Padé: SCF	exact
19	-0.14162D-02	34.665797125	34.680359548	-0.006829970
20	-0.12770D-02	33.432415065	34.680728323	-0.007123967
21	-0.11680D-02	34.695525881	34.679510354	0.006681400
22	-0.10832D-02	34.683136311	34.682702906	-0.007089447
23	-0.10181D-02	34.676616201	34.683026521	-0.007163489
24	-0.96971D-03	34.664313041	34.683320457	-0.006912131
25	-0.93572D-03	34.872540912	34.679641398	-0.008853174
26	-0.91462D-03	34.690019354	34.678994952	0.008996683
27	-0.90552D-03	34.680837957	34.679769949	0.008958114
28	-0.90799D-03	34.672127126	34.683641571	-0.006980960
29	-0.92212D-03	34.638410535	34.679785313	-0.009806562
30	-0.94846D-03	34.697210696	34.679497609	-0.010044403
31	-0.98805D-03	34.683022206	34.679606715	-0.010275156
32	-0.10425D-02	34.674370544	34.679576590	0.010259876
33	-0.11142D-02	34.652166570	34.679575116	0.010260398
34	-0.12063D-02	34.700638276	34.679573960	-0.010262865
35	-0.13230D-02	34.683401076	34.679577167	0.010260847
36	-0.14700D-02	34.674318002	34.679579241	0.010252172
37	-0.16548D-02	34.648187369	34.679579696	0.010258313
38	-0.18875D-02	34.697108604	34.679583252	-0.010269296
39	-0.21813D-02	34.682141403	34.679605367	-0.010495577
40	-0.25544D-02	34.672289391	34.679586727	-0.010256084
41	-0.30310D-02	34.606295942	34.679589998	0.010263032
42	-0.36445D-02	34.690908916	34.679592490	0.010261391
43	-0.44405D-02	34.679651078	34.679592142	0.010262635
44	-0.54823D-02	34.667073909	34.679592027	-0.010266353
45	-0.68583D-02	34.745026191	34.679591896	-0.010267481
46	-0.86933D-02	34.685376596	34.679593079	-0.010265615
47	-0.11164D-01	34.675927102	34.679592478	0.010266997
48	-0.14526D-01	34.647940466	34.679592744	0.010267483
49	-0.19147D-01	34.696157403	34.679592853	-0.010267523
Farrelly, complex coordinate SCF:			34.680	0.01025

nx, ny =		5	1	
order	coeff. / Padé	sum / quadratic	Padé: SCF	exact
19	-0.37901D-02	39.536380703	39.949444165	-0.035850826
20	-0.35420D-02	40.012969047	39.950632287	0.035752415
21	-0.33536D-02	39.970048907	39.951019565	-0.036006996
22	-0.32154D-02	39.943775253	39.947694194	0.026819288
23	-0.31210D-02	39.908915953	39.951491729	0.037424734
24	-0.30659D-02	43.301310391	39.951605601	-0.037232969
25	-0.30476D-02	40.000653954	39.951602178	0.034614289
26	-0.30649D-02	39.959857208	39.951238288	0.034934357
27	-0.31182D-02	39.932871088	39.953086637	-0.039363629
28	-0.32091D-02	39.837666424	39.953616817	0.039774036
29	-0.33410D-02	40.042362269	39.956379411	0.039788825
30	-0.35185D-02	39.968914176	39.942908864	-0.035591202

31	-0.37486D-02	39.940737569	39.954097428	-0.036206264
32	-0.40404D-02	39.875654486	39.953294111	0.037045090
33	-0.44061D-02	40.072045581	39.953294484	0.037061916
34	-0.48617D-02	39.971281496	39.953300267	-0.037067346
35	-0.54285D-02	39.941272201	39.953307756	0.037063042
36	-0.61343D-02	39.870857895	39.953282801	0.037046657
37	-0.70160D-02	40.050984331	39.953294406	0.037049412
38	-0.81224D-02	39.967184630	39.953318818	-0.037047907
39	-0.95192D-02	39.935766766	39.953365304	-0.037053175
40	-0.11294D-01	39.815692633	39.953302375	-0.037030292
41	-0.13568D-01	40.013161118	39.953318623	0.037029003
42	-0.16503D-01	39.958444703	39.953320632	0.037025266
43	-0.20326D-01	39.922510389	39.953320749	0.037025457
44	-0.25351D-01	42.288777332	39.953322150	-0.037025963
45	-0.32017D-01	39.985105735	39.953324573	-0.037027133
46	-0.40948D-01	39.945989105	39.953322703	-0.037024759
47	-0.53033D-01	39.888140072	39.953323861	0.037024830
48	-0.69553D-01	40.040828642	39.953329053	0.037024389
49	-0.92368D-01	39.964749121	39.953316890	0.037024907
Farrelly, complex coordinate SCF:			39.954	0.0370

These data are located in a file: chemalpha1.chem.smu.edu:/users/chem/alexei/fortran/farrelly/x2y2_sep.out

Results of Farrelly are reproduced within 1 last digit in a real part and within last 1 or 2 digits in an imaginary part. Note that our real part is always less than Farrelly' result, and our imaginary part in the first half of the table is larger than Farrelly's results from Table I.

A table of SCF coefficients is enclosed.

To avoid Fermi resonances for excited states for $\omega_x = \omega_y$, we used special rescaling:

$$H(\delta) = -\frac{\delta^2}{8} \frac{\partial^2}{\partial x^2} - \frac{\delta^2}{8} \frac{\partial^2}{\partial y^2} + \frac{1}{2} \omega_x^2 x^2 \exp(-x^2) + \frac{1}{4} \omega_y^2 y^2 + \frac{1}{4} \delta \omega_y^2 y^2 + x^2 \exp(-x^2) (V_2 y - \frac{1}{2} \eta \omega_y^2 y^2),$$

For such potential, the frequencies of classical zero-order vibrations relate as $\sqrt{2}:1$. We calculate both SCF and exact series and compare their rates of convergence:

Energies of Farrelly coupled barrier Hamiltonian

with rescaling, SCF vs exact

30 coefficients were calculated

		$\omega_x, \omega_y, V_2, \eta = 14.140000 \quad 14.140000 \quad 0.000000 \quad 1.000000$			
$n_x, n_y =$		3		0	
order	coeff. /	Padé sum /	quadratic	Padé: SCF	exact
20	-0.383D-04	25.47695	25.47695	0.00000	-0.500D+01 25.46927 32.31279 0.00000
21	0.268D-04	25.47695	25.47695	0.00000	0.222D+02 25.46927 29.95457 0.00000
22	-0.197D-04	25.47695	25.48152	0.00000	-0.295D+02 25.46927 27.13352 0.00000
23	0.139D-04	25.47695	25.47695	0.00000	0.868D+02 25.46928 26.92797 0.00000
24	-0.103D-04	25.47695	25.47695	0.00000	-0.146D+03 25.46927 26.84354 0.00000
25	0.733D-05	25.47695	25.47695	0.00000	0.358D+03 25.46926 26.71159 0.00000
26	-0.547D-05	25.47695	25.47695	0.00000	-0.675D+03 25.46932 26.90185 0.00000
27	0.390D-05	25.47695	25.47695	0.00000	0.153D+04 25.46923 26.67054 0.00000
28	-0.294D-05	25.47695	25.47695	0.00000	-0.304D+04 25.46922 26.50373 0.00000

29	0.209D-05	25.47695	25.47695	0.00000	0.661D+04	25.46921	27.23127	0.00000
nx, ny =		4	0					
order / coeff. /	Padé sum /	quadratic	Padé: SCF		exact			
20	-0.331D-04	30.67323	30.67311	0.00000	-0.109D+06	30.66357	30.66358	0.00000
21	-0.175D-04	30.67324	30.67804	0.00000	0.120D+07	30.66348	30.66321	0.00000
22	-0.199D-04	30.67323	30.68163	0.00000	-0.132D+08	30.66365	30.66070	0.00000
23	-0.125D-04	30.67298	30.69702	0.00000	0.146D+09	30.66343	30.75053	0.00000
24	-0.130D-04	30.67338	30.67568	0.00000	-0.161D+10	30.66350	30.85143	0.00000
25	-0.926D-05	30.67334	30.68646	0.00000	0.177D+11	30.66331	30.66308	0.00000
26	-0.914D-05	30.67363	30.67315	0.00000	-0.195D+12	30.66536	30.66306	0.00000
27	-0.721D-05	30.67328	30.67309	0.00000	0.215D+13	30.66295	30.66312	0.00000
28	-0.695D-05	30.67326	30.67308	0.00000	-0.236D+14	30.66275	30.66310	0.00000
29	-0.592D-05	30.67322	30.67327	0.00000	0.260D+15	30.66259	31.01565	0.00000
nx, ny =		5	0					
order / coeff. /	Padé sum /	quadratic	Padé: SCF		exact			
20	-0.844D-03	35.21917	35.22491	0.00000	-0.676D+06	35.21696	36.52522	0.00000
21	-0.763D-03	35.21234	35.22040	0.00000	0.760D+07	35.21030	35.20087	0.00000
22	-0.701D-03	35.20765	35.21372	0.00000	-0.853D+08	35.21069	35.20508	0.00000
23	-0.653D-03	35.20588	35.21374	0.00000	0.958D+09	35.21025	36.54701	0.00000
24	-0.617D-03	35.20940	35.22414	0.00000	-0.108D+11	35.21775	35.20754	0.00000
25	-0.591D-03	35.13614	35.22038	0.00000	0.121D+12	35.20706	36.84322	0.00000
26	-0.573D-03	35.22517	35.21317	0.00146	-0.136D+13	35.20291	35.20108	0.00000
27	-0.564D-03	35.21407	35.21013	0.00194	0.153D+14	35.20260	35.21156	0.00000
28	-0.562D-03	35.20699	35.20951	-0.00435	-0.171D+15	35.20300	35.20439	0.00000
29	-0.567D-03	35.20634	35.20993	0.00532	0.192D+16	35.20312	35.33003	0.00000
nx, ny =		6	0					
order / coeff. /	Padé sum /	quadratic	Padé: SCF		exact			
20	-0.168D-01	39.14088	38.79975	0.19323	-0.250D+07	38.80303	38.76314	0.27383
21	-0.171D-01	39.15227	38.80011	0.19338	0.286D+08	38.82258	38.79694	0.27416
22	-0.177D-01	39.14119	38.80203	0.19734	-0.328D+09	38.86097	38.74589	0.27835
23	-0.186D-01	38.81369	38.78743	0.16968	0.375D+10	38.81811	38.79254	0.26161
24	-0.197D-01	38.68562	38.80210	0.18895	-0.430D+11	38.83156	38.71025	0.00000
25	-0.211D-01	38.44643	38.80389	-0.18949	0.492D+12	38.81353	38.62450	0.00000
26	-0.229D-01	39.00674	38.80277	-0.18995	-0.563D+13	38.70359	38.76042	0.25425
27	-0.251D-01	39.02756	38.80361	0.18916	0.645D+14	38.75320	38.63701	-0.23427
28	-0.279D-01	39.00832	38.80375	0.18880	-0.738D+15	38.72677	38.64166	0.27003
29	-0.313D-01	38.74757	38.80272	-0.18816	0.845D+16	38.64420	38.68478	0.26534
nx, ny =		7	0					
order / coeff. /	Padé sum /	quadratic	Padé: SCF		exact			
20	-0.236D+00	40.83563	41.48015	1.16547	-0.714D+07	40.04945	41.58698	1.26601
21	-0.269D+00	38.54709	41.47425	1.15910	0.834D+08	39.97804	41.63633	0.88456
22	-0.310D+00	43.71396	41.46973	-1.16085	-0.973D+09	38.55993	41.62381	1.42698
23	-0.361D+00	42.45218	41.47021	-1.15982	0.114D+11	39.89970	41.70160	-1.61132
24	-0.426D+00	36.93945	41.47056	1.16151	-0.132D+12	41.47575	41.62938	1.27944
25	-0.507D+00	40.82199	41.47050	-1.16140	0.155D+13	39.12416	41.63729	1.40400
26	-0.610D+00	40.09711	41.47046	1.16140	-0.180D+14	34.60053	41.75322	-1.52834
27	-0.741D+00	47.62693	41.47036	1.16146	0.210D+15	57.91255	41.58823	1.21888
28	-0.909D+00	42.22671	41.47175	1.16085	-0.245D+16	39.39529	41.49972	2.65301
29	-0.113D+01	41.50128	41.47086	-1.16154	0.286D+17	43.21189	41.07399	0.00000
nx, ny =		8	0					
order / coeff. /	Padé sum /	quadratic	Padé: SCF		exact			
20	-0.250D+01	43.18871	43.87776	-3.15639	-0.174D+08	34.03859	44.33084	3.11986
21	-0.316D+01	43.60484	43.94149	-3.16452	0.207D+09	55.30424	42.05257	0.38526
22	-0.403D+01	43.26589	43.88563	-3.16149	-0.246D+10	51.58757	41.57662	-0.95317
23	-0.518D+01	30.40973	43.88556	3.16299	0.293D+11	54.99504	43.12466	2.79077
24	-0.674D+01	50.72979	43.88596	3.16187	-0.348D+12	48.21464	43.96607	2.91923
25	-0.884D+01	45.32864	43.88598	3.16207	0.413D+13	47.45622	44.46916	2.92989
26	-0.117D+02	41.81588	43.88603	-3.16214	-0.491D+14	48.48379	43.78279	3.01265
27	-0.156D+02	38.97381	43.88619	3.16201	0.583D+15	44.72277	43.93203	2.96571
28	-0.210D+02	44.02296	43.88700	-3.16184	-0.693D+16	39.64395	43.86331	-2.84532
29	-0.285D+02	46.90036	43.88582	3.16193	0.823D+17	44.17594	43.83327	2.93233
omx, omy, V2, eta =				14.140000	14.140000	20.000000	2.000000	
nx, ny =		3	0					
order / coeff. /	Padé sum /	quadratic	Padé: SCF		exact			
20	-0.488D-06	25.20443	25.20443	0.00000	0.946D+14	25.16275	29.13057	0.00000
21	-0.580D-06	25.20443	25.20443	0.00000	-0.916D+15	25.16119	25.43778	0.00000
22	-0.273D-06	25.20443	25.20443	0.00000	0.887D+16	25.15951	25.76194	0.00000
23	-0.274D-06	25.20443	25.20443	0.00000	-0.859D+17	25.16080	27.11485	0.00000
24	-0.159D-06	25.20443	25.20443	0.00000	0.832D+18	25.16142	27.03011	0.00000
25	-0.143D-06	25.20443	25.20443	0.00000	-0.805D+19	25.16181	27.37878	0.00000
26	-0.964D-07	25.20443	25.20443	0.00000	0.780D+20	25.16139	25.53382	0.00000
27	-0.829D-07	25.20443	25.20443	0.00000	-0.755D+21	25.15477	26.78679	0.00000
28	-0.620D-07	25.20443	25.20443	0.00000	0.731D+22	25.16098	27.06997	0.00000
29	-0.527D-07	25.20443	25.20443	0.00000	-0.708D+23	25.15958	26.70076	0.00000

nx, ny =		3		1					
order	/ coeff.	/ Padé sum	/ quadratic	Padé: SCF		exact			
20	-0.285D-05	31.27466	31.27466	0.00000		0.155D+16	31.15198	33.21368	0.00000
21	-0.109D-05	31.27466	31.27466	0.00000		-0.164D+17	31.15490	33.67064	0.00000
22	-0.133D-05	31.27466	31.27466	0.00000		0.173D+18	31.10093	34.84014	0.00000
23	-0.702D-06	31.27466	31.28270	0.00000		-0.182D+19	31.14457	33.01452	0.00000
24	-0.698D-06	31.27466	31.27466	0.00000		0.192D+20	31.15302	32.62413	0.00000
25	-0.454D-06	31.27466	31.27466	0.00000		-0.202D+21	31.14504	32.97392	0.00000
26	-0.407D-06	31.27465	31.27466	0.00000		0.213D+22	31.14217	33.30809	0.00000
27	-0.303D-06	31.27466	31.27466	0.00000		-0.225D+23	31.14603	33.05131	0.00000
28	-0.261D-06	31.27466	31.27463	0.00000		0.237D+24	31.13926	33.17289	0.00000
29	-0.212D-06	31.27466	31.27466	0.00000		-0.249D+25	31.13325	33.17121	0.00000

nx, ny =		4		0					
order	/ coeff.	/ Padé sum	/ quadratic	Padé: SCF		exact			
20	-0.390D-04	30.29138	30.30077	0.00000		0.880D+14	30.18763	30.20558	0.00000
21	-0.313D-04	30.29071	30.32238	0.00000		-0.817D+15	30.18379	30.96462	0.00000
22	-0.255D-04	30.29175	30.29723	0.00000		0.758D+16	30.18734	30.26004	-0.00729
23	-0.212D-04	30.29146	30.33218	0.00000		-0.703D+17	30.19097	30.24782	0.00000
24	-0.179D-04	30.29143	30.29130	0.00000		0.652D+18	30.18686	30.22654	0.02472
25	-0.153D-04	30.29150	30.29151	0.00057		-0.604D+19	30.09643	30.30570	0.00000
26	-0.133D-04	30.29137	30.29126	0.00064		0.560D+20	30.18237	30.24291	0.00000
27	-0.118D-04	30.29132	30.29173	0.00022		-0.519D+21	30.15941	30.22564	0.00000
28	-0.106D-04	30.29024	30.29223	0.00000		0.481D+22	30.19496	30.22766	0.00000
29	-0.967D-05	30.29159	30.29221	0.00000		-0.446D+23	30.25181	30.23302	0.00000

nx, ny =		4		1					
order	/ coeff.	/ Padé sum	/ quadratic	Padé: SCF		exact			
20	-0.113D-03	36.01128	36.03652	0.00000		0.157D+16	35.81821	35.79842	0.00000
21	-0.944D-04	36.01656	36.03610	0.00000		-0.159D+17	35.86545	35.82874	0.00000
22	-0.800D-04	36.01272	36.02859	0.00000		0.162D+18	35.79530	35.80683	0.00000
23	-0.689D-04	36.01281	36.01428	0.00000		-0.164D+19	35.87972	36.04424	0.00000
24	-0.603D-04	36.01275	36.01969	0.00000		0.166D+20	35.91687	35.81638	0.00000
25	-0.534D-04	36.01246	36.01435	-0.00084		-0.169D+21	35.86554	36.13777	0.00000
26	-0.481D-04	36.01212	36.01651	0.00000		0.171D+22	35.87932	35.82076	0.00000
27	-0.439D-04	36.01119	36.01584	0.00000		-0.173D+23	35.86661	35.79793	0.00000
28	-0.407D-04	36.01269	36.01289	-0.00079		0.176D+24	35.82064	35.66786	0.00000
29	-0.383D-04	36.01293	36.01296	-0.00056		-0.178D+25	35.79289	35.76299	0.00000

nx, ny =		5		0					
order	/ coeff.	/ Padé sum	/ quadratic	Padé: SCF		exact			
20	-0.124D-02	34.67961	34.69021	0.00000		0.653D+14	34.60266	34.48517	0.18233
21	-0.114D-02	34.66160	34.92493	0.00000		-0.579D+15	34.62008	34.56356	0.00000
22	-0.106D-02	34.65391	34.68041	0.00000		0.513D+16	34.59319	34.71235	-0.16222
23	-0.100D-02	34.66365	34.67789	-0.00674		-0.454D+17	34.62339	35.36117	0.00000
24	-0.959D-03	34.70363	34.67970	0.00732		0.402D+18	34.61233	35.96035	0.00000
25	-0.929D-03	34.68615	34.67884	-0.00817		-0.355D+19	34.65346	34.87003	0.00000
26	-0.913D-03	34.67870	34.67879	0.00825		0.314D+20	34.60654	34.60582	-0.59458
27	-0.908D-03	34.67098	34.67890	0.00866		-0.277D+21	34.54204	35.68300	0.00000
28	-0.915D-03	34.48299	34.67904	0.00982		0.244D+22	34.67483	34.58863	0.00000
29	-0.933D-03	34.70206	34.67981	-0.00945		-0.215D+23	34.61712	34.59146	0.00000

nx, ny =		5		1					
order	/ coeff.	/ Padé sum	/ quadratic	Padé: SCF		exact			
20	-0.344D-02	39.90610	39.94649	0.04082		0.128D+16	40.06999	39.53660	0.00000
21	-0.328D-02	39.88281	39.94578	-0.03486		-0.125D+17	39.98187	39.88399	0.82155
22	-0.318D-02	39.91827	39.95049	-0.03785		0.121D+18	40.06686	40.03932	0.00000
23	-0.312D-02	40.01375	39.94946	0.03767		-0.118D+19	40.17225	39.92117	0.00000
24	-0.309D-02	39.97664	39.95017	-0.03690		0.115D+20	39.99863	39.93566	0.00000
25	-0.310D-02	39.95042	39.95121	0.03385		-0.112D+21	34.19345	40.03001	0.00000
26	-0.315D-02	39.90322	39.95661	-0.04513		0.109D+22	39.95116	40.20886	0.00000
27	-0.324D-02	39.83922	39.95155	-0.03805		-0.106D+23	39.91554	41.86214	0.00000
28	-0.338D-02	39.93575	39.95207	0.03860		0.102D+24	39.95822	40.20737	0.00000
29	-0.355D-02	39.98533	39.95343	0.03829		-0.992D+24	40.06370	40.54725	0.00000

These data are located in a file: chemalpha1.chem.smu.edu/users/chem/alexei/fortran/farrelly/x2y2.out

SCF coefficients appear to be much smaller than exact ones, and convergence of SCF results is much faster probably because of absence of square-root curve-crossing singularities.

I. Model Davis - Heller (or Eastes - Marcus) potential

The Hamiltonian is

$$H = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} \omega_x^2 x^2 + \frac{1}{2} \omega_y^2 y^2 - \lambda xy^2 - \lambda \eta x^3,$$

see [W. Eastes and R. A. Marcus, J. Chem. Phys. 1974, **61**, 4301 or M. J. Davis and E. J. Heller, J. Chem. Phys. 1981, **75**, 246]. The calculations were done for parameters ω_x , ω_y , λ , η from Tables I and III of Andrei's paper. We calculate both SCF and exact series (without scaling) and compare their rates of convergence:

Energies of Davis - Heller potential

SCF vs exact

30 coefficients were calculated

$\omega_x, \omega_y, \lambda, \eta = 1.000000 \quad 1.100000 \quad 0.110000 \quad 0.000000$

nx, ny =		0		0	
order	coeff.	Padé sum	SCF	exact	
0	0.10500D+01	1.050000000	1.050000000	0.10500D+01	1.050000000
1	-0.12500D-02	1.048751486	1.048751486	-0.20313D-02	1.047972672
2	-0.56818D-05	1.048744292	1.048744292	-0.22166D-04	1.047946339
3	-0.51653D-07	1.048744266	1.048744266	-0.55697D-06	1.047946013
4	-0.61631D-09	1.048744266	1.048744266	-0.20638D-07	1.047946005
5	-0.85377D-11	1.048744266	1.048744266	-0.98409D-09	1.047946005
6	-0.13007D-12	1.048744266	1.048744266	-0.56699D-10	1.047946005
7	-0.21168D-14	1.048744266	1.048744266	-0.38098D-11	1.047946005
8	-0.36167D-16	1.048744266	1.048744266	-0.29188D-12	1.047946005
9	-0.64145D-18	1.048744266	1.048744266	-0.25099D-13	1.047946005
10	-0.11718D-19	1.048744266	1.048744266	-0.23939D-14	1.047946005
11	-0.21928D-21	1.048744266	1.048744266	-0.25090D-15	1.047946005
12	-0.41857D-23	1.048744266	1.048744266	-0.28675D-16	1.047946005
13	-0.81251D-25	1.048744266	1.048744266	-0.35506D-17	1.047946005
14	-0.15999D-26	1.048744266	1.048744266	-0.47365D-18	1.047946005
15	-0.31896D-28	1.048744266	1.048744266	-0.67738D-19	1.047946005
16	-0.64277D-30	1.048744266	1.048744266	-0.10341D-19	1.047946005
17	-0.13077D-31	1.048744266	1.048744266	-0.16785D-20	1.047946005
18	-0.26829D-33	1.048744266	1.048744266	-0.28872D-21	1.047946005
19	-0.55458D-35	1.048744266	1.048744266	-0.52462D-22	1.047946005
20	-0.11542D-36	1.048744266	1.048744266	-0.10042D-22	1.047946005
21	-0.24167D-38	1.048744266	1.048744266	-0.20199D-23	1.047946005
22	-0.50883D-40	1.048744266	1.048744266	-0.42592D-24	1.047946005
23	-0.10768D-41	1.048744266	1.048744266	-0.93958D-25	1.047946005
24	-0.22892D-43	1.048744266	1.048744266	-0.21642D-25	1.047946005
25	-0.48876D-45	1.048744266	1.048744266	-0.51958D-26	1.047946005
26	-0.10476D-46	1.048744266	1.048744266	-0.12980D-26	1.047946005
27	-0.22537D-48	1.048744266	1.048744266	-0.33693D-27	1.047946005
28	-0.48646D-50	1.048744266	1.048744266	-0.90741D-28	1.047946005
29	-0.10533D-51	1.048744266	1.048744266	-0.25323D-28	1.047946005

nx, ny =		4		0	
order	coeff.	Padé sum	SCF	exact	
0	0.50500D+01	5.050000000	5.050000000	0.50500D+01	5.050000000
1	-0.12500D-02	5.048750309	5.048750309	-0.13490D-01	5.036546354
2	-0.56818D-05	5.048744292	5.048744292	-0.30964D-02	5.032491519
3	-0.51653D-07	5.048744266	5.048744266	-0.85160D-03	5.032239494
4	-0.61631D-09	5.048744266	5.048744266	-0.25670D-03	5.032187826
5	-0.85377D-11	5.048744266	5.048744266	-0.77192D-04	5.032195333
6	-0.13007D-12	5.048744266	5.048744266	-0.22735D-04	5.032196437
7	-0.21168D-14	5.048744266	5.048744266	-0.64127D-05	5.032197622
8	-0.36167D-16	5.048744266	5.048744266	-0.16791D-05	5.032197313
9	-0.64145D-18	5.048744266	5.048744266	-0.38430D-06	5.032197269

10	-0.11718D-19	5.048744266	-0.64231D-07	5.032197266
11	-0.21928D-21	5.048744266	0.39254D-09	5.032197266
12	-0.41857D-23	5.048744266	0.69916D-08	5.032197266
13	-0.81251D-25	5.048744266	0.42620D-08	5.032197266
14	-0.15999D-26	5.048744266	0.18731D-08	5.032197266
15	-0.31896D-28	5.048744266	0.69083D-09	5.032197266
16	-0.64277D-30	5.048744266	0.21984D-09	5.032197266
17	-0.13077D-31	5.048744266	0.58600D-10	5.032197266
18	-0.26829D-33	5.048744266	0.11251D-10	5.032197266
19	-0.55458D-35	5.048744266	0.13871D-12	5.032197266
20	-0.11542D-36	5.048744266	-0.12982D-11	5.032197266
21	-0.24167D-38	5.048744266	-0.86705D-12	5.032197266
22	-0.50883D-40	5.048744266	-0.40682D-12	5.032197266
23	-0.10768D-41	5.048744266	-0.15867D-12	5.032197266
24	-0.22892D-43	5.048744266	-0.53204D-13	5.032197266
25	-0.48876D-45	5.048744266	-0.14996D-13	5.032197266
26	-0.10476D-46	5.048744266	-0.31333D-14	5.032197266
27	-0.22537D-48	5.048744266	-0.15267D-15	5.032197266
28	-0.48646D-50	5.048744266	0.30371D-15	5.032197266
29	-0.10533D-51	5.048744266	0.22272D-15	5.032197266

nx, ny =		0	4		
order	coeff.	Padé sum:	SCF	exact	
0	0.54500D+01	5.450000000		0.54500D+01	5.450000000
1	-0.10125D+00	5.350596712		-0.10047D+00	5.351349830
2	-0.41420D-02	5.344431280		-0.14827D-02	5.348026328
3	-0.33889D-03	5.344241395		0.60328D-03	5.348565813
4	-0.36393D-04	5.344228003		0.20855D-03	5.348944109
5	-0.45373D-05	5.344227441		0.41811D-04	5.348909300
6	-0.62210D-06	5.344227402		0.35685D-05	5.348903719
7	-0.91120D-07	5.344227400		-0.12860D-05	5.348903366
8	-0.14012D-07	5.344227400		-0.75598D-06	5.348903428
9	-0.22366D-08	5.344227400		-0.20999D-06	5.348903485
10	-0.36773D-09	5.344227400		-0.26577D-07	5.348903477
11	-0.61931D-10	5.344227400		0.66091D-08	5.348903476
12	-0.10640D-10	5.344227400		0.53128D-08	5.348903476
13	-0.18588D-11	5.344227400		0.17831D-08	5.348903476
14	-0.32941D-12	5.344227400		0.31164D-09	5.348903476
15	-0.59104D-13	5.344227400		-0.28067D-10	5.348903476
16	-0.10720D-13	5.344227400		-0.43623D-10	5.348903476
17	-0.19628D-14	5.344227400		-0.17703D-10	5.348903476
18	-0.36242D-15	5.344227400		-0.39891D-11	5.348903476
19	-0.67424D-16	5.344227400		-0.10264D-12	5.348903476
20	-0.12629D-16	5.344227400		0.35785D-12	5.348903476
21	-0.23799D-17	5.344227400		0.18165D-12	5.348903476
22	-0.45097D-18	5.344227400		0.50112D-13	5.348903476
23	-0.85891D-19	5.344227400		0.51901D-14	5.348903476
24	-0.16434D-19	5.344227400		-0.27498D-14	5.348903476
25	-0.31579D-20	5.344227400		-0.18790D-14	5.348903476
26	-0.60919D-21	5.344227400		-0.62073D-15	5.348903476
27	-0.11795D-21	5.344227400		-0.10195D-15	5.348903476
28	-0.22913D-22	5.344227400		0.16652D-16	5.348903476
29	-0.44651D-23	5.344227400		0.19066D-16	5.348903476

nx, ny =		4	4		
order	coeff.	Padé sum:	SCF	exact	
0	0.94500D+01	9.450000000		0.94500D+01	9.450000000
1	-0.10125D+00	9.349823322		-0.20359D+00	9.250700031
2	-0.41420D-02	9.344431280		-0.24278D-01	9.218841168
3	-0.33889D-03	9.344240553		-0.79806D-02	9.210586701
4	-0.36393D-04	9.344228003		-0.15866D-02	9.212054754
5	-0.45373D-05	9.344227440		0.11692D-02	9.207457091
6	-0.62210D-06	9.344227402		0.17732D-02	9.217795343
7	-0.91120D-07	9.344227400		0.11755D-02	9.215968894
8	-0.14012D-07	9.344227400		0.29453D-03	9.216062864
9	-0.22366D-08	9.344227400		-0.29589D-03	9.216055722
10	-0.36773D-09	9.344227400		-0.44573D-03	9.216061460
11	-0.61931D-10	9.344227400		-0.29369D-03	9.215921624
12	-0.10640D-10	9.344227400		-0.61387D-04	9.216134188
13	-0.18588D-11	9.344227400		0.95158D-04	9.216134623
14	-0.32941D-12	9.344227400		0.13209D-03	9.216134153
15	-0.59104D-13	9.344227400		0.86732D-04	9.216189292
16	-0.10720D-13	9.344227400		0.20529D-04	9.216147289
17	-0.19628D-14	9.344227400		-0.23499D-04	9.216143322
18	-0.36242D-15	9.344227400		-0.33975D-04	9.216143283
19	-0.67424D-16	9.344227400		-0.22026D-04	9.216143327
20	-0.12629D-16	9.344227400		-0.48686D-05	9.216142717
21	-0.23799D-17	9.344227400		0.60047D-05	9.216142715
22	-0.45097D-18	9.344227400		0.80597D-05	9.216142717
23	-0.85891D-19	9.344227400		0.47029D-05	9.216142887
24	-0.16434D-19	9.344227400		0.55378D-06	9.216142845

25	-0.31579D-20	9.344227400		-0.16615D-05	9.216142839
26	-0.60919D-21	9.344227400		-0.16832D-05	9.216142836
27	-0.11795D-21	9.344227400		-0.64741D-06	9.216142806
28	-0.22913D-22	9.344227400		0.25582D-06	9.216142834
29	-0.44651D-23	9.344227400		0.51067D-06	9.216142835

These data are located in a file: titan.smu.edu:/home/users/ alexei/fortran/hell/x2y2.out

50 coefficients of the SCF series are located in a file: chemalpha1.chem.smu.edu:/users/chem/alexei/fortran/hell/coef_sep.out

30 coefficients of the exact series are located in a file: titan.smu.edu:/home/users/ alexei/fortran/hell/coef_exa.out

Energies of Eastes - Marcus potential

SCF vs exact

30 coefficients were calculated

$$\omega_x, \omega_y, \lambda, \eta = 0.541984225 \quad 1.458015775 \quad 0.111600000 \quad 0.084140000$$

nx, ny =		0	0		
order	/ coeff. /	Padé	sum: SCF		exact
0	0.10000D+01	1.000000000			0.10000D+01 1.000000000
1	-0.72840D-02	0.992768657			-0.80655D-02 0.991999014
2	-0.23051D-03	0.992477939			-0.28778D-03 0.991636048
3	-0.13884D-04	0.992470738			-0.19920D-04 0.991625364
4	-0.11202D-05	0.992470362			-0.18752D-05 0.991624690
5	-0.10825D-06	0.992470347			-0.21408D-06 0.991624657
6	-0.11912D-07	0.992470346			-0.28111D-07 0.991624655
7	-0.14531D-08	0.992470346			-0.41255D-08 0.991624654
8	-0.19345D-09	0.992470346			-0.66513D-09 0.991624654
9	-0.27844D-10	0.992470346			-0.11652D-09 0.991624654
10	-0.43076D-11	0.992470346			-0.22020D-10 0.991624654
11	-0.71348D-12	0.992470346			-0.44664D-11 0.991624654
12	-0.12619D-12	0.992470346			-0.96881D-12 0.991624654
13	-0.23785D-13	0.992470346			-0.22410D-12 0.991624654
14	-0.47690D-14	0.992470346			-0.55157D-13 0.991624654
15	-0.10154D-14	0.992470346			-0.14415D-13 0.991624654
16	-0.22917D-15	0.992470346			-0.39927D-14 0.991624654
17	-0.54720D-16	0.992470346			-0.11699D-14 0.991624654
18	-0.13795D-16	0.992470346			-0.36196D-15 0.991624654
19	-0.36643D-17	0.992470346			-0.11803D-15 0.991624654
20	-0.10234D-17	0.992470346			-0.40492D-16 0.991624654
21	-0.29994D-18	0.992470346			-0.14586D-16 0.991624654
22	-0.92058D-19	0.992470346			-0.55076D-17 0.991624654
23	-0.29535D-19	0.992470346			-0.21760D-17 0.991624654
24	-0.98880D-20	0.992470346			-0.89800D-18 0.991624654
25	-0.34486D-20	0.992470346			-0.38648D-18 0.991624654
26	-0.12510D-20	0.992470346			-0.17319D-18 0.991624654
27	-0.47138D-21	0.992470346			-0.80698D-19 0.991624654
28	-0.18423D-21	0.992470346			-0.39039D-19 0.991624654
29	-0.74588D-22	0.992470346			-0.19583D-19 0.991624654

nx, ny =		2	0		
order	/ coeff. /	Padé	sum: SCF		exact
0	0.20840D+01	2.083968450			0.20840D+01 2.083968450
1	-0.43819D-01	2.041051754			-0.48440D-01 2.036628569
2	-0.33001D-02	2.036580512			-0.39639D-02 2.031211069
3	-0.44630D-03	2.036336606			-0.58169D-03 2.030887597
4	-0.77593D-04	2.036307776			-0.10985D-03 2.030845125
5	-0.15609D-04	2.036305528			-0.24060D-04 2.030841386
6	-0.34631D-05	2.036305245			-0.58310D-05 2.030840845
7	-0.82561D-06	2.036305218			-0.15244D-05 2.030840785
8	-0.20819D-06	2.036305215			-0.42333D-06 2.030840775
9	-0.54966D-07	2.036305214			-0.12365D-06 2.030840774
10	-0.15089D-07	2.036305214			-0.37734D-07 2.030840773
11	-0.42863D-08	2.036305214			-0.11974D-07 2.030840773
12	-0.12555D-08	2.036305214			-0.39376D-08 2.030840773
13	-0.37831D-09	2.036305214			-0.13387D-08 2.030840773
14	-0.11705D-09	2.036305214			-0.46976D-09 2.030840773
15	-0.37146D-10	2.036305214			-0.16992D-09 2.030840773
16	-0.12081D-10	2.036305214			-0.63313D-10 2.030840773
17	-0.40251D-11	2.036305214			-0.24288D-10 2.030840773
18	-0.13736D-11	2.036305214			-0.95910D-11 2.030840773
19	-0.48012D-12	2.036305214			-0.38984D-11 2.030840773
20	-0.17194D-12	2.036305214			-0.16312D-11 2.030840773
21	-0.63103D-13	2.036305214			-0.70275D-12 2.030840773
22	-0.23745D-13	2.036305214			-0.31180D-12 2.030840773
23	-0.91645D-14	2.036305214			-0.14251D-12 2.030840773
24	-0.36297D-14	2.036305214			-0.67113D-13 2.030840773
25	-0.14758D-14	2.036305214			-0.32570D-13 2.030840773
26	-0.61618D-15	2.036305214			-0.16291D-13 2.030840773
27	-0.26427D-15	2.036305214			-0.83975D-14 2.030840773
28	-0.11644D-15	2.036305214			-0.44609D-14 2.030840773
29	-0.52709D-16	2.036305214			-0.24415D-14 2.030840773

nx, ny =		2	2		
order	/ coeff. /	Padé	sum: SCF		exact
0	0.50000D+01	5.000000000			0.50000D+01 5.000000000
1	-0.17137D+00	4.834307977			-0.19412D+00 4.813134864

2	-0.24047D-01	4.800657287	-0.30407D-01	4.769825682
3	-0.61233D-02	4.796475328	-0.86144D-02	4.763636882
4	-0.20024D-02	4.795387214	-0.31273D-02	4.761761498
5	-0.75395D-03	4.795196398	-0.13057D-02	4.761375390
6	-0.31102D-03	4.795144579	-0.59728D-03	4.761248733
7	-0.13683D-03	4.795134204	-0.29161D-03	4.761217835
8	-0.63161D-04	4.795131335	-0.14960D-03	4.761206393
9	-0.30263D-04	4.795130714	-0.79831D-04	4.761203480
10	-0.14942D-04	4.795130538	-0.44011D-04	4.761201791
11	-0.75614D-05	4.795130498	-0.24947D-04	4.761201667
12	-0.39067D-05	4.795130486	-0.14489D-04	4.761201903
13	-0.20546D-05	4.795130483	-0.86005D-05	4.761201239
14	-0.10973D-05	4.795130482	-0.52089D-05	4.761201136
15	-0.59402D-06	4.795130482	-0.32149D-05	4.761201040
16	-0.32546D-06	4.795130482	-0.20207D-05	4.761200976
17	-0.18026D-06	4.795130482	-0.12930D-05	4.761200933
18	-0.10082D-06	4.795130482	-0.84235D-06	4.761200905
19	-0.56899D-07	4.795130482	-0.55891D-06	4.761200890
20	-0.32379D-07	4.795130482	-0.37792D-06	4.761200880
21	-0.18568D-07	4.795130482	-0.26063D-06	4.761200875
22	-0.10725D-07	4.795130482	-0.18346D-06	4.761200869
23	-0.62375D-08	4.795130482	-0.13192D-06	4.761200866
24	-0.36513D-08	4.795130482	-0.96941D-07	4.761200756
25	-0.21508D-08	4.795130482	-0.72821D-07	4.761200848
26	-0.12746D-08	4.795130482	-0.55904D-07	4.761200835
27	-0.75981D-09	4.795130482	-0.43827D-07	4.761200917
28	-0.45556D-09	4.795130482	-0.35048D-07	4.761200887
29	-0.27471D-09	4.795130482	-0.28546D-07	4.761200877

nx, ny =	4	0		
order / coeff. / Padé	sum / quadratic	Padé: SCF		exact
0	0.31679D+01	3.167936900	0.31679D+01	3.167936900
1	-0.11101D+00	3.060685512	-0.11947D+00	3.052808199
2	-0.13247D-01	3.041885631	-0.15200D-01	3.031050518
3	-0.28028D-02	3.040165761	-0.34292D-02	3.028892786
4	-0.75541D-03	3.039818775	-0.98574D-03	3.028417114
5	-0.23374D-03	3.039773741	-0.32548D-03	3.028349185
6	-0.79197D-04	3.039764301	-0.11780D-03	3.028333322
7	-0.28642D-04	3.039762857	-0.45561D-04	3.028330571
8	-0.10886D-04	3.039762540	-0.18549D-04	3.028329878
9	-0.43045D-05	3.039762485	-0.78703D-05	3.028329737
10	-0.17584D-05	3.039762472	-0.34571D-05	3.028329698
11	-0.73842D-06	3.039762470	-0.15645D-05	3.028329688
12	-0.31759D-06	3.039762469	-0.72691D-06	3.028329686
13	-0.13950D-06	3.039762469	-0.34584D-06	3.028329685
14	-0.62454D-07	3.039762469	-0.16815D-06	3.028329684
15	-0.28448D-07	3.039762469	-0.83427D-07	3.028329684
16	-0.13168D-07	3.039762469	-0.42186D-07	3.028329684
17	-0.61873D-08	3.039762469	-0.21723D-07	3.028329684
18	-0.29490D-08	3.039762469	-0.11384D-07	3.028329684
19	-0.14250D-08	3.039762469	-0.60683D-08	3.028329684
20	-0.69770D-09	3.039762469	-0.32894D-08	3.028329684
21	-0.34607D-09	3.039762469	-0.18129D-08	3.028329684
22	-0.17386D-09	3.039762469	-0.10158D-08	3.028329684
23	-0.88461D-10	3.039762469	-0.57868D-09	3.028329684
24	-0.45584D-10	3.039762469	-0.33523D-09	3.028329684
25	-0.23792D-10	3.039762469	-0.19751D-09	3.028329684
26	-0.12580D-10	3.039762469	-0.11839D-09	3.028329684
27	-0.67401D-11	3.039762469	-0.72217D-10	3.028329684
28	-0.36600D-11	3.039762469	-0.44848D-10	3.028329684
29	-0.20151D-11	3.039762469	-0.28364D-10	3.028329684

These data are located in a file: titan.smu.edu/home/users/ alexei/fortran/hell/x2y2-2.out

50 coefficients of the SCF series are located in a file: chemalpa1.chem.smu.edu/users/chem/alexei/fortran/hell/coefsep2.out

30 coefficients of the exact series are located in a file: titan.smu.edu/home/users/ alexei/fortran/hell/coefexa2.out

I. A. Eastes - Marcus (or Barbanis) potential without $\lambda\eta x^3$ term

The Hamiltonian is

$$H = -\frac{1}{2} \frac{\partial^2}{\partial x^2} - \frac{1}{2} \frac{\partial^2}{\partial y^2} + \frac{1}{2} \omega_x^2 x^2 + \frac{1}{2} \omega_y^2 y^2 - \lambda xy^2.$$

For this particular system, SCF energy may be calculated exactly, without invoking of perturbation theory:

$$E_{\text{sep}} = \left(n_x + \frac{1}{2}\right) \omega_x + \left(n_y + \frac{1}{2}\right) \tilde{\omega}_y + \frac{1}{2} \left(n_y + \frac{1}{2}\right)^2 \frac{\lambda^2}{\omega_x^2 \tilde{\omega}_y^2},$$

where $\tilde{\omega}_y$ is determined from the equation

$$\tilde{\omega}_y^2 = \omega_y^2 - (2n_y + 1) \frac{\lambda^2}{\omega_x^2 \tilde{\omega}_y^2},$$

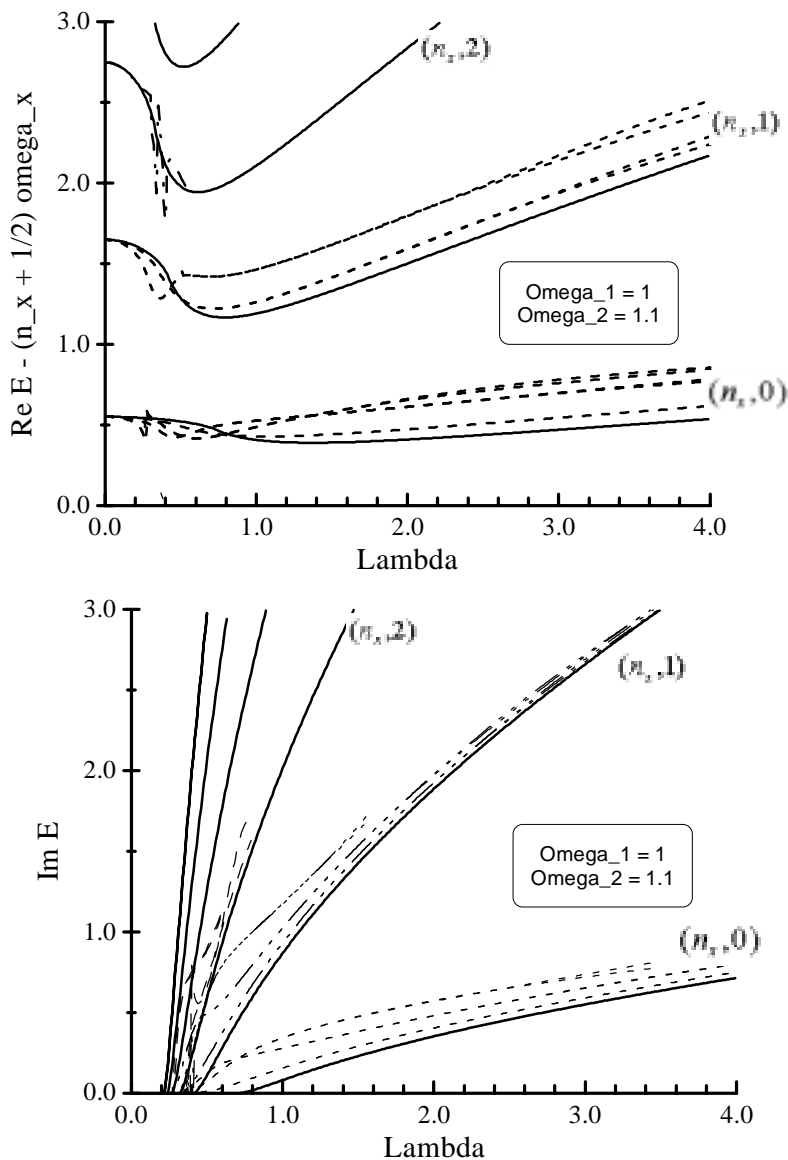
The SCF energy is real for

$$(2n_y + 1) \frac{\lambda^2}{\omega_x^2 \omega_y^3} \leq \frac{2}{9} \sqrt{3},$$

This inequality determines a radius of convergence of the series which is non-zero in contrast to exact series.

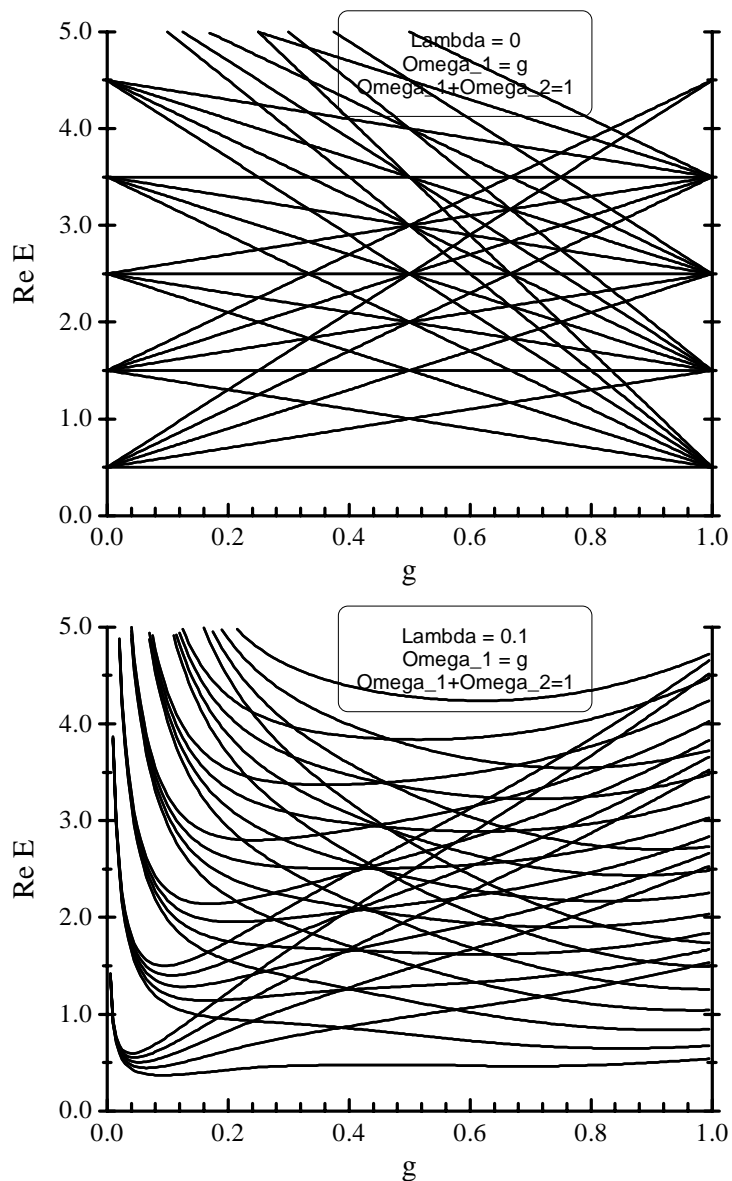
Note that only the first term, $\left(n_x + \frac{1}{2}\right) \omega_x$, depends on n_x in the expression for SCF energy. The rest of the expression is independent on n_x . So, the imaginary part of the energy is also independent on n_x .

An accuracy of separability approximation for real and imaginary parts of the energy is illustrated on the following figures:



Real and imaginary parts of the energy for two-dimensional anharmonic oscillator with λxy^2 anharmonicity. Solid lines - SCF results that can be calculated exactly. We subtract $(n_x + \frac{1}{2})\omega_x$ from the real part of the energy to make SCF energy independent on n_x . The exact energy (nonsolid lines) appears to be weakly dependent on n_x . Jerks on curves for excited states are associated with curve crossings.

Dependence of the SCF energy on frequencies ω_x and ω_y with a fixed parameter of anharmonicity λ is illustrated on the following figures (real part only):



Real part of the SCF energy levels for two-dimensional anharmonic oscillator with λxy^2 anharmonicity. Here, $\lambda = \text{const}$, and frequencies are linearly dependent on a parameter g which varies from 0 to 1: $\omega_x = g$, $\omega_y = 1 - g$. The upper figure corresponds to a purely harmonic oscillator ($\lambda = 0$), and the lower figure corresponds to $\lambda = 0.1$. Note that SCF levels do not exhibit avoided-crossings.