

Zero point energy of the Pullen–Edmonds Hamiltonian

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Abstract Here we wish to apply the newly developed Generalized Moments Expansion (GMX) to the well-known potential

$$U(x, y) = \frac{1}{2} (x^2 + y^2) + \alpha x^2 y^2,$$

which is used to model such molecular systems as formamide (HCONH₂) and carbon suboxide (C₃O₂). Our motivation is to investigate the numerical accuracy as well as the viability of the GMX for evaluating ground-state energies of quantum Hamiltonian systems. The zero-point energy of this potential is calculated and results are compared to those of a related Canonical Sequence Method approach (CSM).

Keywords t -Expansion · Connected moments

1 Introduction

Over twenty years ago a systematic and non-perturbative scheme was developed by Horn and Weinstein [1] to evaluate ground-state expectation values for any

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Hamiltonian system. Their method was based on the use of the operator $\exp[-t\hat{H}]$, where \hat{H} is the Hamiltonian. This operator was then used to contract any trial state $|\phi_0\rangle$ onto the true ground-state of \hat{H} , $|\psi_0\rangle$ with the proviso of nonzero overlap, $\langle\phi_0|\psi_0\rangle \neq 0$. All operator expectation values are expressible in the contracted state as a power series in the parameter t . Then, by utilizing Padé approximants [2] the $t \rightarrow \infty$ behavior may be reconstructed. A very useful theorem regarding the ground-state energy e_0 was also given in [1] wherein an expression for e_0 may be written which converges to the true ground-state energy E_0 in the $t \rightarrow \infty$ limit and is expressible in terms of connected moments of the Hamiltonian. More recently Cioslowski [3] expounded upon the Horn–Weinstein theorem to obtain a simple and systematic expansion (in terms of the moments of the Hamiltonian) for the ground-state energy. A major advantage of this “Connected Moments Expansion” (CMX) of Cioslowski over other variational and perturbational approximation schemes, is that it is size extensive, usually convergent and perhaps most importantly, trivial to program.

Cioslowski was then poised to apply his new scheme, (CMX) to calculate the zero-point energy of an arbitrary system of coupled anharmonic oscillators [4–6], a model system of great interest to quantum chemists. An early version of this system is the modified Hénon–Heiles Hamiltonian [7]

$$H = \frac{1}{2} (p_x^2 + p_y^2 + x^2 + y^2) + \alpha \left(x^2 y \pm \frac{1}{3} y^3 \right) \quad (1)$$

which has been the focus of a number of numerical studies [8–10]. Here we have defined $p_x = \dot{x}$, $p_y = \dot{y}$ and units are normalized so that $m = 1$. In particular two harmonic oscillators coupled by a quartic term was studied by Pullen and Edmonds [11]. Specifically the potential $U(x, y)$ has the form

$$U(x, y) = \frac{1}{2} (x^2 + y^2) + \alpha x^2 y^2. \quad (2)$$

This potential describes a number of molecular systems, such as formamide (HCONH₂) and carbon suboxide (C₃O₂) [12], a bent chain which has all five atoms bound to each other with double bonds: O=C=C=C=O. It is this potential which we shall study here while making comparisons with the CMX calculation of Cioslowski. The standard method of calculating the ground-state energy for this potential is to construct a set of basis functions from harmonic oscillator wavefunctions. One then proceeds to diagonalize the associated Hamiltonian matrix. Although this procedure is straightforward, a number of disadvantages exist which are worth mentioning. Among them is a systematic way to decide, prior to actually doing the calculation, the size of the basis necessary to achieve the prescribed accuracy of the ground state energy. Also problematic is the fact that the actual size of the basis increases very rapidly as one includes a greater number of vibrational modes. Furthermore, these matrix elements are quite tedious to calculate and in general non-trivial to program. Finally size extensivity issues arise, especially when dealing with weakly interacting systems in the computation of zero-point energies.

2 Theory

Our purpose here is to use the potential given by Eq. 2 as a testing ground for a newly developed scheme, the Generalized Moments Expansion, GMX [13] to calculate the zero-point energy. We will also compare our results to a related moments scheme, the Canonical Sequence Method (CSM) [14], which along with the GMX is just one of many related moments schemes derivable from the t -expansion of Horn and Weinstein [1]. A great deal of literature has been devoted to the t -expansion and its derivatives with special note to the work of Knowles [15] and also that of Stubbins [16] who examined a number of alternate extrapolation schemes for the t -expansion such as an extended connected moments expansion as well as Laplace and inversion methods. A very detailed and useful discussion of the analytic properties of these expansions was given by Witte and Shankar [17]. The GMX expression for the ground-state energy may be written as [13]

$$E_0^{\text{GMX}(m,n)} = I_1 - \sum_{i=1}^k \frac{S_{i,m+1} S_{i,n+1}}{\prod_{j=1}^i S_{j,m+n+1}} \quad (3)$$

where

$$S_{i+1,k} = S_{i,k} S_{i,k+(m+n)} - S_{i,k+m} S_{i,k+n} \quad (4)$$

with $S_{1,k} = I_k$. Here the connected moments I_k of the Hamiltonian \hat{H} are defined recursively by

$$I_k = \langle \hat{H}^k \rangle - \sum_{i=0}^{k-2} \begin{bmatrix} k-1 \\ i \end{bmatrix} I_{i+1} \langle \hat{H}^{k-i-1} \rangle \quad (5)$$

where $\langle \hat{H}^k \rangle$ represents ground-state expectation values. Explicitly to fourth-order ($k = 3$) we may write

$$E_0^{\text{GMX}(m,n)} = I_1 - \frac{S_{1,m+1} S_{1,n+1}}{S_{1,m+n+1}} - \frac{S_{2,m+1} S_{2,n+1}}{S_{1,m+n+1} S_{2,m+n+1}} - \frac{S_{3,m+1} S_{3,n+1}}{S_{1,m+n+1} S_{2,m+n+1} S_{3,m+n+1}} \quad (6)$$

where

$$S_{1,m+n+1} = I_{m+n+1}$$

$$S_{2,m+n+1} = I_{m+n+1} I_{2(m+n)+1} - I_{2m+n+1} I_{m+2n+1}$$

$$\begin{aligned}
 S_{3,m+n+1} &= (I_{m+n+1}I_{2(m+n)+1} - I_{2m+n+1}I_{m+2n+1}) \\
 &\quad \times (I_{2(m+n)+1}I_{3(m+n)+1} - I_{3m+2n+1}I_{2m+3n+1}) \\
 &\quad - (I_{2m+n+1}I_{3m+2n+1} - I_{3m+n+1}I_{2(m+n)+1}) \\
 &\quad \times (I_{m+2n+1}I_{2m+3n+1} - I_{2(m+n)+1}I_{m+3n+1}) \\
 S_{3,m+1} &= (I_{m+1}I_{2m+n+1} - I_{2m+1}I_{m+n+1})(I_{2m+n+1}I_{3m+2n+1} \\
 &\quad - I_{3m+n+1}I_{2(m+n)+1}) - (I_{2m+1}I_{3m+n+1} - I_{3m+1}I_{2m+n+1}) \\
 &\quad \times (I_{m+n+1}I_{2(m+n)+1} - I_{2m+n+1}I_{m+2n+1}) \\
 S_{3,n+1} &= (I_{n+1}I_{m+2n+1} - I_{2n+1}I_{m+n+1})(I_{m+2n+1}I_{2m+3n+1} \\
 &\quad - I_{m+3n+1}I_{2(m+n)+1}) - (I_{m+n+1}I_{2(m+n)+1} - I_{2m+n+1}I_{m+2n+1}) \\
 &\quad \times (I_{2n+1}I_{m+3n+1} - I_{3n+1}I_{m+2n+1}). \tag{7}
 \end{aligned}$$

It is useful to note that the CMX of Cioslowski [3] who applied an exponentially decreasing series rather than a Padé expansion to study the $t \rightarrow \infty$ limit, corresponds to GMX(1, 1) while a more recently derived Alternate Moments Expansion [18] is just GMX(1, 2) = GMX(2, 1). Hence the GMX truly is a “generalized moments expansion”. Also the AMX is computationally more tedious and hence requires more work than the CMX. That this is true may be seen by looking at the second-order expressions wherein the CMX expression requires the evaluation (to leading order) of $I_3 \sim \langle H^3 \rangle$ while the AMX has $I_4 \sim \langle H^4 \rangle$.

It is worthwhile at this point to make mention of the fact that all moments schemes are plagued by singularities [18–22]. Numerically this occurs when, for particular values of the parameter of interest, the denominators in Eq. 3 vanish. Mancini et al. [18] have given an analytic proof of the cancellation of singularities in successive orders of the truncation. However for a finite number of terms in the expansion, these numerically troublesome points can and do obscure the asymptotic behavior of the series. For the second order poles which arise in the second order CMX, Ullah [21, 22] applied a method he had developed for use in the many-nucleon problem in which a probability density function is introduced. At the present, the method of Ullah has not been generalized beyond second-order, although it is feasible that such a scheme could be developed for the GMX to all orders. In fact, as has been pointed out [13], one possible advantage of the GMX(m, n) is that all regions of parameter space may be studied without worrying about singularities. If, for a particular choice of (m, n) and parameter value, a pole does arise, one may simply choose a different set (m, n) as well as a different order, to avoid the trouble point.

Another scheme for calculating ground-state energies is the Canonical Sequence Method (CSM) [14] which is also derivable from the t -expansion [16]. Although the CSM method has its roots in the t -expansion, and thus is related to the GMX, the method of extraction of the series from the ratio

$$E(t) = \frac{\langle \phi_0 | \hat{H} \exp(-t\hat{H}) | \phi_0 \rangle}{\langle \phi_0 | \exp(-t\hat{H}) | \phi_0 \rangle},$$

follows closely the inversion method of Stubbins [16]. The CSM expression for the ground-state energy density may be written as

$$E_0^{\text{CSM}} = \frac{1}{N} \left[I_1 + (L - 2) \frac{d_E^{(L-2)} t(I_1)}{d_E^{(L-1)} t(I_1)} \right] \quad (8)$$

with the $(L - m)$ derivative defined by

$$d_E^{(L-m)} t(I_1) = (-1)^{L-m} \frac{[L - (m + 1)]! \alpha}{(I_1 - E_0)^{L-m}} \quad (9)$$

where α is an expansion parameter. Since $d_E^{(n)} t(I_1)$ scales as N^{-n} , we have that E_0^{CSM} is also size extensive, as is the GMX.

3 Results

In Tables 1–4 we have summarized our results for the GMX up to fifth order. In terms of scaling, the $(k + 1)$ th order of the GMX has its highest moment $\langle H^{k(m+n)+1} \rangle$. Thus for example the fifth order calculation of GMX(1, 3) involves the evaluation of $\langle H^{17} \rangle$.

In each of the Tables we have taken the “exact” results to be those of Cioslowski [4], where it is stated that for the coupling parameter α in the range between 0.1 and 0.5 one has to use a basis of about 400 functions to obtain an estimate of the ground-state energy to within an accuracy of 10^{-5} . We should also state at this point that the GMX

Table 1 Ground-state energy calculated using 2nd-order GMX

α	Exact [4]	GMX(1,1)	GMX(1,2)	GMX(1,3)
0.1	1.02340	1.02362	1.02379	1.02392
0.2	1.04434	1.04529	1.04605	1.04669
0.3	1.06350	1.06577	1.06759	1.06917
0.4	1.08128	1.08545	1.08880	1.09161
0.5	1.09797	1.10459	1.10984	1.11407

Table 2 Ground-state energy calculated using 3rd-order GMX

α	Exact [4]	GMX(1,1)	GMX(1,2)	GMX(1,3)
0.1	1.02340	1.02344	1.02360	1.02375
0.2	1.04434	1.04467	1.04539	1.04603
0.3	1.06350	1.06444	1.06615	1.06778
0.4	1.08128	1.08316	1.08632	1.08937
0.5	1.09797	1.10110	1.10615	1.11093

Table 3 Ground-state energy calculated using 4th-order GMX

α	Exact [4]	GMX(1,1)	GMX(1,2)	GMX(1,3)
0.1	1.02340	1.02341	1.02352	1.02371
0.2	1.04434	1.04448	1.04521	1.04590
0.3	1.06350	1.06403	0.06582	1.06750
0.4	1.08128	1.08251	1.08577	1.08891
0.5	1.09797	1.10015	1.10533	1.11028

Table 4 Ground-state energy calculated using 5th-order GMX

α	Exact [4]	GMX(1,1)	GMX(1,2)	GMX(1,3)
0.1	1.02340	1.02340	1.02351	1.02370
0.2	1.04434	1.04444	1.04518	1.04589
0.3	1.06350	1.06393	1.06576	1.06748
0.4	1.08128	1.08233	1.08569	1.08887
0.5	1.09797	1.09990	1.10522	1.11022

expansion that we are using here is a generalization to CMX-HW, which is one of the three variants of CMX series expansions in use [15, 17, 23]. We see that, overall, the GMX approximations for the zero point energy of this model are surprisingly good as well as consistent. In fact the higher-order terms of the GMX (that is, for (m, n) large) are not as good as the lower-order terms. We may understand this as follows. For larger values of (m, n) , the GMX expression necessarily involves the evaluation of greater powers of the Hamiltonian. Physically this means that only very high-order excitations (far from the ground-state) are being sampled while the lower order terms are completely excluded. Clearly then a truer picture of the ground-state would arise from a clever combination of all orders of the GMX so that all or most of the low order excitations (which may be important) would also contribute. As has been pointed out elsewhere [24], at the present time there does not exist any method to determine a “priori”, which values of (m, n) , nor which order truncation, will yield the lowest estimate for the ground-state energy. That is, for whatever the highest moment that has been calculated, I_{\max} , it is not clear if one should look at many terms in the expansion for (m, n) relatively small or to keep only a few terms in the series for (m, n) large.

In Table 5 we have presented our results using the Canonical Sequence Method. We see that once again, for this calculational cousin of the GMX, results are indeed excellent. In this brief work we have applied a newly developed calculational scheme, the GMX, to a tractable and realistic test Hamiltonian system. We have found that for the Pullen–Edmonds potential a variety of moments methods derivable from the t -expansion, are rapidly converging and yield excellent results for the ground-state energy.

Table 5 Ground-state energy calculated using the Canonical Sequence method, orders 2–13, as a function of the parameter α

α	Exact [4]	$E_0^{\text{CSM}(2)}$	$E_0^{\text{CSM}(3)}$	$E_0^{\text{CSM}(4)}$	$E_0^{\text{CSM}(5)}$	$E_0^{\text{CSM}(6)}$	$E_0^{\text{CSM}(7)}$	$E_0^{\text{CSM}(8)}$	$E_0^{\text{CSM}(9)}$	$E_0^{\text{CSM}(10)}$	$E_0^{\text{CSM}(11)}$	$E_0^{\text{CSM}(12)}$	$E_0^{\text{CSM}(13)}$
0.1	1.02340	1.02500	1.02362	1.02352	1.02348	1.02345	1.02344	1.02342	1.02342	1.02341	1.02341	1.02341	1.02340
0.2	1.04434	1.05000	1.04529	1.04480	1.04466	1.04456	1.04450	1.04446	1.04443	1.04440	1.04438	1.04437	1.04436
0.3	1.06350	1.07500	1.06577	1.06447	1.06423	1.06401	1.06389	1.06379	1.06373	1.06367	1.06363	1.06359	1.06357
0.4	1.08128	1.10000	1.08545	1.08290	1.08260	1.08219	1.08202	1.08182	1.08173	1.08160	1.08156	1.08146	1.08146
0.5	1.09797	1.12500	1.10459	1.10032	1.10001	1.09931	1.09915	1.09877	1.09872	1.09842	1.09849	1.09814	1.09843

In the second column we list the exact value Ref. [4]

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References

1. D. Horn, M. Weinstein, Phys. Rev. **D30**, 1256 (1984)
2. G.A. Baker Jr., *Padé Approximants* (Academic Press, NY, 1975)
3. J. Cioslowski, Phys. Rev. Lett. **58**, 83 (1987)
4. J. Cioslowski, Chem. Phys. Lett. **136**, 515 (1987)
5. W.J. Hehre, L. Radom, P. von R. Schleyer, J.A. Pople, *Ab Initio Molecular Orbit Theory* (Wiley, NY, 1986)
6. M.R. Ibrahim, Z.A. Fataftah, Chem. Phys. Lett. **125**, 149 (1986)
7. M. Henon, C. Heiles, Astron. J. **69**, 73 (1964)
8. N. Pomphrey, J. Phys. **B7**, 1909 (1974)
9. D.W. Noid, M.L. Koszykowski, M. Tabor, R.A. Marus, J. Chem. Phys. **72**, 6169 (1980)
10. R.A. Pullen, A.R. Edmonds, J. Phys. **A14**, L319 (1981)
11. R.A. Pullen, A.R. Edmonds, J. Phys. **A14**, L477 (1981)
12. C.W. Peters, W.H. Weber, P.D. Maker, J. Mol. Spectroscopy **66**, 133 (1977)
13. V. Fessatidis, J.D. Mancini, R.K. Murawski, S.P. Bowen, Phys. Lett. **A349**, 320 (2006)
14. L. Šamaj, P. Kalinay, P. Markoš, I. Travěnek, J. Phys. **A30**, 1471 (1997)
15. P.J. Knowles, Chem. Phys. Lett. **134**, 512 (1987)
16. C. Stubbins, Phys. Rev. **D38**, 1942 (1988)
17. N.S. Witte, R. Shankar, Nucl. Phys. **B556**, 445 (1999)
18. J.D. Mancini, Y. Zhou, P.F. Meier, Int. J. Quantum Chem. **50**, 101 (1994)
19. J.D. Mancini, Y. Zhou, P.F. Meier, W.J. Massano, J.D. Prie, Phys. Lett. **A185**, 435 (1994)
20. V. Fessatidis, J.D. Mancini, R.K. Murawski, S.P. Bowen, W.J. Massano, Phys. Lett. **A303**, 72 (2002)
21. N. Ullah, Ind. J. Phys. **B67**, 245 (1993)
22. N. Ullah, Phys. Rev. **A51**, 1808 (1995)
23. J. Cioslowski, Int. J. Quantum Chem.: Quant. Chem. Symp. **21**, 563 (1987)
24. J.D. Mancini, R.K. Murawski, V. Fessatidis, S.P. Bowen, Phys. Rev. **B72**, 214405 (2005)