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Hypervirial perturbation theory revisited

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Abstract

A wide range of topics in the area of hypervirial perturbation theory (HVPT) is discussed. It is shown that with the use of a few simple procedures HVPT is capable of high accuracy for many problems; results from many previous works in the literature are found to be improvable by the careful use of HVPT with appropriate choice of the unperturbed potential and of the origin at which the energy expansion is carried out. Two multi-well problems from the literature are analysed in detail to show the value of a combination of HVPT and finite-difference methods.

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1. Introduction

After the recent publication of a hypervirial method for some Penning-trap calculations [1] it was decided to survey the literature on numerical perturbation methods for simple potentials, with particular emphasis on hypervirial techniques, which one of the authors helped to develop some years ago [2–4]. A close study of over a hundred publications led to some surprising and in some ways disappointing results. In several works it is difficult to ascertain the exact potential or Hamiltonian being treated and sometimes a trial and error approach reveals that the numerical results are for a potential different from the declared one. It is also clear that there is a recent tendency to lay great emphasis on very impressive algebraic formalisms which in application produce numerical results of not equally impressive accuracy; one section of the literature tends to concentrate on producing lengthy algebraic expressions for the low-order terms of divergent perturbation series. As opposed to this 'MAPLE syrup with everything' approach this paper deals with a few of the points of general interest which arose from our literature survey and which will be of most value to the many readers interested in *numerical* techniques. All the calculations reported were carried out in normal double precision using appropriate modifications of well known methods of perturbation theory. To check the energy levels predicted by our perturbation calculations we used the accurate finite-difference method

developed and reported previously [5]. Section 2 gives an outline of the mathematical methods used and of the modifications made in them to carry out some of the calculations. Sections 3 and 4 deal with the perturbed harmonic oscillator, first with smooth perturbations and then with singular perturbations. Section 5 discusses radial perturbations of the hydrogen atom and section 6 treats both symmetric and asymmetric double-well potentials. Sections 7 and 8 apply hypervirial perturbation theory (HVPT) to two special problems which have arisen in perturbation-theory literature. Section 9 gives a summary of the main conclusions produced by our study. We give illustrative numerical results throughout, although from time to time we summarize with a verbal statement the gist of the many hundreds of calculations which were carried out during our literature survey and which are too numerous to report in full. In the numerical work the perturbation series were typically taken to order 50 or 60, which is consistent with the use of ordinary double-precision calculations and is, of course, much less than the order of several hundreds used in some recent works. This makes the success of the simple methods which we describe even more interesting. We stress that all the statements made about numerical or qualitative results throughout this paper can be verified by any reader who applies the simple methods described. Several technical details are readily to be found in [1–4]; it is essentially the ideas and methods which we describe, as well as any particular result, which should be of value to readers who use perturbation techniques.

2. Hypervirial perturbation theory

Since HVPT has been used in many works we give only a brief summary of it here. We start with the case of a typical Schrödinger equation which incorporates a perturbation parameter λ, with the potential taking the form of a power series (or a finite polynomial) and the term $V(J)x^J$ having an associated factor $\lambda^{I(J)}$

$$-\alpha D^2\psi + \sum \lambda^{I(J)} V(J) x^J \psi = E\psi. \tag{1}$$

For such a potential the expectation values $\langle x^N \rangle$ for the exact eigenstates can be shown to obey the diagonal hypervirial relations (for $N = 0, 1, 2, \ldots$)

$$\tfrac{1}{2}\alpha N(N-1)\langle x^{N-2}\rangle + (2N+2)E\langle x^N\rangle = \sum (2N+2+J)\lambda^{I(J)} V(J)\langle x^{N+J}\rangle. \tag{2}$$

A perturbed oscillator problem will have $I(2) = 0$, and a perturbed Coulomb problem will have $I(-1) = 0$, with the other $I(J)$ being positive integers. In the numerical calculations we set $\lambda = 1$, so that the actual numerical magnitude of each term in V is directly equal to its coefficient $V(J)$. We now introduce the perturbation expansions which are traditionally associated with Rayleigh–Schrödinger perturbation theory

$$E = \sum E(M)\lambda^M \qquad \langle x^N\rangle = \sum X(N, M)\lambda^M \tag{3}$$

and substitute them in (2), taking the coefficients of the λ^M terms to give a set of hypervirial recurrence relations which link the $X(N, M)$ coefficients. To make the calculation more general we allow for the important case in which the potential also includes a centrifugal term $\alpha L(L+1)x^{-2}$ for the angular momentum L. This term combines with the kinetic-energy term, giving the hypervirial recurrence relations

$$\tfrac{1}{2}\alpha N[(N^2-1) - 4L(L+1)]X(N-2, M) + (2N+2)\sum_0^M E(K)X(N, M-K)$$
$$= \sum (2N+2+J)V(J)X(N+J, M-I(J)). \tag{4}$$

These equations involve the $E(J)$ as well as the $X(N, M)$ and so we need an extra equation which will express the $E(J)$ in terms of the $X(N, M)$. Differentiating the potential V with

respect to λ and equating $\langle dV/d\lambda \rangle$ to $dE/d\lambda$ by the Hellmann–Feynman theorem leads to the energy equation

$$(M+1)E(M+1) = \sum I(J)V(J)X(J, M+1-I(J)) \tag{5}$$

on comparing coefficients of λ^M on both sides of the equality. To apply the equations we set $X(0,0) = 1$, with $X(0, M) = 0$ for $M > 0$; this simply asserts that $\langle x^0 \rangle = 1$ for both the perturbed and unperturbed states. The $E(0)$ can also be given a precise value, since the initial problem is an oscillator one (with $I(2) = 0$) or a Coulomb one (with $I(-1) = 0$). This $E(0)$ value will depend on the quantum numbers of the unperturbed state and so specifies the particular unperturbed state which is to be treated. With the values of $E(0)$ and $X(0,0)$ known, the $X(N,0)$ can be calculated by putting the term $(2N+4)V(2)X(N+2, M)$ on the left of (4), so that $X(N+2, M)$ is found in terms of the already known $X(N, M)$ with a smaller N index and a smaller or equal M index.

The energy equation (5) then gives $E(1)$ and permits the $X(N,1)$ to be found using (4). Equation (5) then gives $E(2)$ and so on, so that many terms of the series for E and $\langle x^N \rangle$ can be found, without the need to calculate the perturbed wavefunction at each order as in the more traditional approach to the use of Rayleigh–Schrödinger perturbation theory. The sequence of partial sums of $E(M)$ or $X(N, M)$ can be stored as the calculation progresses and can be treated by the Wynn algorithm in the simple multi-purpose form presented previously [6], if, as often happens, the sequence does not converge. We note that we have not made use of any of the more recent summation methods which have been proposed (and which will be mentioned later). To treat isotropic potentials in D dimensions it is only necessary to replace the angular momentum L in the equations by $AM + (D-3)/2$, where AM is the generalized angular momentum. $AM = 0$ always refers to fully isotropic states, so, for example, the ground state in two dimensions requires $L = -1/2$. As was pointed out long ago [4], by setting $\alpha = 0$ in the equations it is possible to obtain the first-order JWKB quantities for the problem being treated; we shall mention such calculations later in this paper. This possibility arises because the classical time averages of the x^N for trapped oscillating particles obey the hypervirial equation (4) with the α term omitted, and JWKB theory in the first order gives just these time averages as its estimate of the quantum mechanical $\langle x^N \rangle$ [4]. The generalized Wynn algorithm used [6], although not mentioned in the survey [7], is a flexible triple-purpose one which can produce the usual Padé approximants, iterated Aitken results or the transformation studied in [8], by setting an integer parameter K equal to 1, 0 or -1. We note that by setting K to vary at each stage of a computation it would be possible to study iterated N-step Padé transformations. By constructing sequentially the ascending diagonals of the usual lozenge algorithm for the approximants it is possible to perform a running analysis in which the analysed results can be displayed alongside the partial sums while the calculation is in progress. A careful study of the hypervirial equations for particular problems often reveals that to obtain a given order of the energy series needs a diminishing number of terms $X(N, M)$ as M increases, so that a triangular (rather than rectangular) array of $X(N, M)$ will suffice. By packing the elements $X(N, M)$ into a long linear array by means of an indexing algorithm it is then possible to increase by about 40% the order attainable with a given storage capacity. For example, to find $E(10)$ for the perturbed potential $x^2 + \lambda x^4$, we see from (5) that $X(4, 9)$ would be needed. It follows from (4) that to find $X(4, 9)$ we need to know $X(8, 8)$, $X(12, 7)$ and so on, down to $X(40, 0)$. Further, since the $\langle x^N \rangle$ for odd N are all zero by symmetry, we only need to use the N values $0, 2, 4, \ldots$ in (4). We can thus pack the non-zero elements of the X array into about half the storage space by re-labelling them using the integer index $N/2$. The result is a tapering array with its long edge at the $M = 0$ end. Various coding formulae can be devised to put the $X(N, M)$ coefficient into the appropriate location in the close-packed tapered array. The

various auxiliary techniques described above have been tested during the calculations reported in this paper; however, it is the numerical results themselves on which we shall concentrate, together with the insight which they produce for several particular problems.

3. The classical perturbed oscillator problem

The case of an x^4 perturbation of the x^2 potential has been treated in hundreds of works, while the cases of the x^6 and x^8 perturbations have more recently received greater emphasis, particularly since it has been found that the Padé approximants of even and odd order do not converge to the same limit when applied to the sequence of partial sums of the x^8 energy series [9, 10]. The formal theory of perturbation series has almost universally been applied to the λ series arising from the potential $x^2 + \lambda x^J$. In our calculations we partially side-stepped this by using a combination of renormalization and of variation of the powers of λ attached to the terms. For example, it turns out to be useful to re-write the potential as follows (for $J = 6, 8$)

$$V(2)x^2 + \lambda^2 V(J)x^J = \beta x^2 + \lambda^2 V(J)x^J - (\beta - V(Z))\lambda x^2 \tag{6}$$

so that the resulting energy series is an unorthodox series. When this series is treated by the Wynn–Padé algorithm it gives results which are better than the typical ones used as representative by the proponents of various more recent summation methods. Most of the comparative studies tend to use a particular restricted form of a renormalized series, in which $V(J)$ is prefixed by λ rather than λ^2 and β is found by a fixed algebraic prescription. By using λ^2 and varying β empirically to obtain an optimum result we are able to do much better than previous studies would suggest for the usually treated one-dimensional problem. We find that an effective way to judge optimality is to vary the renormalization parameter so as to obtain the maximum number of stable digits in the Wynn-analysed sequence of partial sums; this is analogous to the traditional approach of estimating the sum of an asymptotic series by taking the value at the smallest term in the series. This approach requires careful (often interactive) computing of the kind which is easily carried out on a microcomputer. It is perhaps the modern tendency to go for quick results via fully automatic programs which partly explains the failure of many authors to get the most out of HVPT. If we move on from the two most commonly treated cases $L = -1$ and 0 and treat the perturbed oscillator states with $L = 1, 2$, etc, the situation improves even further, since we can then move the origin from $r = 0$ to the r value corresponding to the minimum of the effective potential $V(r) + \alpha L(L + 1)r^{-2}$. We then expand V in a Taylor series about the minimum and carry out a perturbation calculation in which the quadratic term is the unperturbed oscillator term and the term $V(J)x^J$ has the index $I(J) = J - 2$ (i.e. $\lambda V(3)x^3 + \lambda^2 V(4)x^4 + \cdots$). A detailed account of this approach is given in the recent work in which it was applied to treat a Penning-trap problem [1]; we note that the approach has the interesting feature of transforming a perturbed Coulomb problem into a perturbed oscillator problem (see also section 7). The assignment $I(J) = J - 2$ for the powers of x goes back at least as far as the remarkable work of Sprandel and Kern [11], who explicitly solved the equations for the perturbed wavefunctions of various orders using a finite-difference method. We have confirmed their results quickly using the hypervirial approach, which of course does not need the perturbed wavefunctions. To illustrate the effect of the simple modifications which we describe here we quote some results for the ground state of the potential $x^2 + \lambda x^J$, using the particular cases of the work [12], which compares the Padé summation method with some more recent summation methods. In [12] the order 45 was used, at which point the summation results appear to be beginning to lose stability. Going to order 50 with our calculation we found the following results, using the self-explanatory

notation $E(V(2), \lambda, J)$: $E(1, 0.2, 6) = 1.173\,889\,345$, $E(1, 0.02, 8) = 1.064\,2078$. Both of these results compare well with the best results of [12]; we even obtain the very respectable results $E(0, 1, 6) = 1.144\,8025$ and $E(0, 1, 8) = 1.225\,81$. For the case $J = 4$, of course, the hypervirial method gives results of very high accuracy. As would be expected, our results for $J = 4$ are much more accurate than those published in the 1960s and 1970s; they also turn out to be more accurate, at least for some λ values, than those appearing in some more recent works (e.g. [13–15]). For example, for the case $\alpha = 1/2$ and $V = x^2/2 + \lambda x^4$, [14] gives a ground-state best estimate (using a summation method for 100 terms) of 60.099 729 606 at $\lambda = 10^6$, while our HVPT and finite-difference calculations give 66.800 062 59. For the same problem with $\lambda = 1$, [15] gives a first-excited-state energy of 2.737 91 while HVPT gives 2.737 892 263 0085. For the Hamiltonian with $\alpha = 1/2$ and $V = x^2/2 + 100x^6$ [16] gives a ground-state energy of 2.1925 while HVPT gives 2.193 3398. Our results for the case $\alpha = 1/2$ and $V = x^2/2 + \lambda x^J (J = 6, 8)$ are of about the same numerical accuracy as the quadratic Padé approximant results of [17] based on 300 or so terms of the traditional energy perturbation series, for λ values of 0.1 and 0.01 used as examples in [17]. Including the angular-momentum term and applying the hypervirial method with the origin at the minimum of the effective potential produces the results shown in table 1. No renormalization was used; we simply applied the standard Wynn algorithm to the partial sums based on using as the unperturbed oscillator the 'natural' quadratic term in the Taylor expansion about the minimum. By contrast, the use of a more traditional form of the renormalized perturbation approach with the origin at $r = 0$ and including the appropriate L value in the hypervirial equations gives markedly less accurate energy values except for the specially favourable case $J = 4$. To the best of our knowledge, almost all theoretical analyses of the perturbation series have been for the case $L = -1$ and for a factor λ attached to the perturbing term; our results suggest some more promising avenues for a more formal analysis. It might be possible to perform an extrapolation in L which would derive the results for the standard cases $L = 0$ and -1 starting from the better results obtainable for higher values of L. For the special case of $J = 4$ we undertook an investigation of the way in which the lowest order JWKB results approach the quantum mechanical results as the state number n increases; we took the case of the pure x^4 potential, since this can be treated quite easily using the renormalization approach. The folk theorem that the JWKB results tend to the quantum results for $n \to \infty$ turned out to need slight modification. The $\langle x^6 \rangle$ values from the JWKB method were found to be lower than the quantum ones, with a difference which tends to a constant value of about 0.335 99, while the higher $\langle x^N \rangle$ have an increasing error as n increases. Accordingly, we found that the correct statement of the link between the two methods is that lowest order JWKB results have a fractional error which varies as n^{-2} as $n \to \infty$. This investigation is possible because the HVPT with $\alpha = 0$ is equivalent to the use of the lowest-order JWKB theory [4] and is much speedier than traditional approaches using integrals for the favourable case of x^4 perturbations. Fernandez [18] has extended the work of [4] to deal with higher orders of JWKB theory. We show some typical results in table 2 to indicate the particular efficiency of HVPT for quartic perturbations.

4. Various single minimum potentials

The perturbed potential $V(2)x^2 + \lambda x^{-J}$ has a single minimum which can be used as the origin for the hypervirial perturbation approach. This gives what is usually called the large-coupling expansion for this singular potential problem. For $\lambda \to 0$ it has been shown that the shift of the eigenvalue from its unperturbed value varies as λ^A where $A = (J - 2)^{-1}$ for $J > 3$ [19]. The special case $J = 2$ corresponds to the use of an angular-momentum

Table 1. Some results for the x^J perturbed oscillator ($J = 6, 8, 10$) $H = -D^2 + L(L+1)r^{-2} + r^2 + r^J$. Perturbation order 60. $I(J) = 2$.

J	L	E
6	1	9.455 535 286
6	2	14.584 132 945 7
6	3	20.338 610 333 013
8	1	10.311 312 3
8	2	16.202 827 935
8	3	22.959 396 724 18
10	1	11.011 573 8
10	2	17.491 751 74
10	3	25.017 602 225 9

Table 2. Some results for the quantum and JWKB approaches to the Hamiltonian $-D^2 + x^4$. $I(4) = 1$ for these calculations. All results were obtained to 16 digits but the truncated values shown suffice to show the effects described in the text. The JWKB result for each case is below the quantum one, disregarding any common digits shared by both results.

n	$\langle x^2 \rangle$	$\langle x^6 \rangle$	$\langle x^8 \rangle$
20	7.965 923 2944	1452.864 125 26	22 008.152
	8976 491	52 813 080	21 990.134
40	12.592 993 5330	5738.940 118 32	137 370.522
	832 815	60 412 718	42.038
60	16.478 698 0356	12 858.785 367 89	402 735.699
	20 498	44 937 736	698.426
80	19.948 710 1395	22 812.399 871 6	864 909.291
	060 553	0638 814	864.169
100	23.138 809 7258	33 599.783 629 4	1565 551.401
	66 902	4476 391	499.064

term and thus allows the method to be applied to many radial potential problems which have been treated in the literature. For the case $\alpha = 1/2$ and $V = L(L+1)/(2r^2)\ -2^{0.8}r^{-0.8}$, with $L = 3$, [20] and [21] give the ground-state energies $-0.201\,91$ and $-0.201\,913\,6566$, respectively, while our HVPT and finite-difference methods give $-0.201\,913\,669\,032$. For the case $\alpha = 1$ and $V = x^2 + 10x^{-2.5}$, [22] gives a best ground-state energy (an upper bound) of 7.735 136 while HVPT based on the minimum of V gives 7.735 111 1035. For $\alpha = 1$ and $V = x^2 + 4x^{-4}$, [23] gives the best extrapolated ground-state energy of 5.559 083 while HVPT centred on the minimum of V gives 5.559 082 869. For the case $\alpha = 1/2$ and $V = r^2/2 + 500r^3$, [24] gives the ground-state energy 33.316 76 while HVPT based on the minimum of V gives 33.316 761 240 9378. For the Kratzer–Fues potential $25r^{-2} - 10r^{-1}$, with $\alpha = 1/2$ [25] our HVPT calculations centred on the potential minimum give the correct analytical ground-state energy $-0.868\,225\,031\,212$ to 12 decimal places. In [26] an r^{-2} term was added to the perturbing term λx^{-4}; our HVPT calculations at the minimum gave most of the results of table 1 of [26] to several more digits and revealed that the later digits of the energies quoted in [26] are incorrect. For example, the ground-state energy for $V = r^2 + 10r^{-4} + 2r^{-2}$ is given as 7.240 710 184 39 in [26], while HVPT at the minimum and the finite-difference calculation agree on the value 7.223 520 3931. Several of the original results in the literature were obtained using $1/N$ perturbation theory, which appears to involve a much more complicated and less accurate formalism than that of the 'direct' attack on the problem which we have employed here. As an illustration of the method we show in table 3 some

Table 3. The lowest two HVPT energies for $H = -D^2 + x^N + \lambda x^{-J}$, using 50 terms of the energy series plus a Wynn analysis. Note that the order of the levels as a function of J changes as λ increases.

λ	N	J	E_1	E_2
0.1	2	4	3.575 552	7.766 30
1	2	4	4.494 177 98	8.845 673 1
10	2	4	6.606 622 512 02	11.137 508 255
0.1	2	6	3.915 665	8.274 636
1	2	6	4.659 939 97	9.206 193 5
10	2	6	6.003 209 028 90	10.773 338 296
0.1	4	4	4.891 303	13.779 75
1	4	4	6.838 648 94	16.903 248 1
10	4	4	12.176 953 910 64	24.219 553 274 02
0.1	4	6	5.682 93	15.492 7
1	4	6	7.511 347 32	18.587 429
10	4	6	11.418 705 671 2	24.367 080 418 1

results for the singular perturbation problem with various J values and for the unperturbed potentials x^2 and x^4. As a further example, we note that HVPT gives the lowest two levels $-97.539\,755\,610$ and $-27.438\,632\,899$ for the Lennard-Jones potential $625(r^{-12} - r^{-6})$ with $\alpha = 1$.

5. The perturbed hydrogen-atom problem

The perturbed hydrogen Hamiltonian $-\frac{1}{2}D^2 - Zr^{-1} + \lambda V(1)r + \lambda V(2)r^2$ has been treated by many authors. For the case in which $V(1) = 0$ and $V(2) = \gamma^2/12$ it gives a good estimate of the 1s energy of the hydrogen atom perturbed by the term $\frac{1}{8}\gamma^2(x^2 + y^2)$, the quadratic Zeeman effect [27]. The so-called spherical Stark effect problem, with $V(1)$ small and $V(2) = 0$ has been treated in several works. To apply the hypervirial method to the problem involves careful sequencing of the equations. The coefficients $X(-1, M)$ have to be worked out first at each order M, to permit the $X(N, M)$ with $N > 0$ to be computed. To apply a renormalizing approach we introduce a reference nuclear charge Z_0 and split $-Zr^{-1}$ into $-Z_0r^{-1} + \lambda(Z_0 - Z)r^{-1}$. Varying Z_0 then produces an energy series in which Z_0 controls the rate of decrease of the early terms in the series as well as the number of digits accuracy which is observed when the Wynn algorithm is applied to the partial sums. Results for the case of the spherical Stark effect have been found using a range of perturbation techniques [28–30]; we were able to obtain much more accurate results for almost every reported energy level given in these works. For example, for the case $\alpha = 1/2$ and the potential $V = -r^{-1} + 4r$, [28] and [29] give the ground-state energy values 2.795 598 and 2.796 0028, respectively. The HVPT calculation with $Z_0 = 4$ gave the energy 2.795 751 283. For the 'Airy Hamiltonian' $-\frac{1}{2}\nabla^2 + r$ of [30] we found the 1s, 2p and 3d levels to have the respective energies 1.855 757 09, 2.667 829 48 and 3.371 784 49; these values are more accurate than both the reported perturbation results and the cited 'exact' comparison energies in [30]. Results for the Zeeman problem were given in [27]. We note that the choice $I(1) = I(2) = 1$ proved to be satisfactory in our numerical calculations and turns out to be an important feature of the HVPT approach to the special case treated in section 7, where we give some more numerical results.

6. The double-well averaging effect

Careful examination of the symmetric double-well perturbation problems treated in the literature reveals several of them to be such that the wells are either so deep that no even–odd splitting is present at a double-precision level of accuracy or so shallow that (although they are used to set out advanced techniques) they can in fact be handled by the simple renormalized perturbation theory based on the origin $x = 0$. For the first case (deep wells) it suffices to take the origin at the right (or left) hand minimum and apply HVPT based on the Taylor expansion of the potential about that origin. This quickly gives energy levels of double precision. For example, taking the potential $-x^2 + V(4)x^4$ with $V(4)$ equal to 0.02 and 1, respectively, gives the hypervirial ground-state energies $-11.106\,472\,413\,902\,15$ (origin at minimum) and $0.657\,653\,0051$ (origin at $x = 0$). For the potential $-25x^2 + 0.5x^4$, with a deep potential well, treated in [31], the states 38 and 39 were found to be degenerate by a Rayleigh–Ritz calculation, with a common energy of $-130.556\,400\,499$. The HVPT method with origin at the right-hand minimum quickly gives the energy to be $130.556\,400\,498\,4943$. Many numerical trials have shown that the HVPT results contain internal evidence of the presence or absence of even–odd splitting for such symmetric double-well problems. Quick convergence to all digits shows that the splitting is in effect zero at the precision used. Slower convergence to a limited number of digits indicates the presence of a splitting, with the computed HVPT energy being the accurate arithmetic mean of the even and odd energies. This averaging effect is shown in table 4 and has been checked to hold for various published double-well calculations. For the case of the potential $-x^2 + 0.03x^4$ [32] we found (using HVPT) the converged energies $-6.9507(297\,194)$ ($n = 0$) and $-4.32(6981)$ ($n = 3$), while the very accurate finite-difference method of [5] shows that even and odd levels have the bracketed digits (318 893), (275 495) for $n = 0$ and (7284), (6678) for $n = 3$. These numerical results illustrate the averaging effect. Our calculations also showed a similar effect for the potential 200 $(3x^4 - 6x^2 - 1)$, $\alpha = 1$, treated in [33]. In fact, the splitting is so small for the two lowest pairs of levels that it should not be observable at the level of precision used in [33]; HVPT is able to show that the numerical results of [33] are in error, while our finite-difference method [5] confirms this and also the very accurate results of [34]. For example, [33] gives the two lowest levels as $-751.522\,3121$ and $-751.522\,3116$, while HVPT at the right-hand minimum gives the energy $-751.522\,312\,3838(413)$. The finite-difference calculation shows that the two lowest levels actually have the last three digits (462) and (363). When a small odd-parity term is added to a symmetric V the result is a dramatic localization of the low-energy levels into either the left or the right well. It is possible to calculate the probability $P(x > 0)$ by finite-difference calculations [35] and so to establish the degree of localization of these states. However, once again HVPT at the appropriate left or right minimum gives its own internal clue by producing a large or small number of converged digits in the Wynn-analysed energy series. This effect is also shown in table 4; once again, the HVPT levels are all confirmed by a finite-difference calculation in the full space.

7. A special perturbed Coulomb problem

The interesting properties of the Hamiltonian

$$-\tfrac{1}{2}D^2 - r^{-1} + 2\lambda r + 2\lambda^2 r^2 \tag{7}$$

have been pointed out previously [36]. The form of the potential is such that bound states exist for both positive and negative λ. Applying Rayleigh–Schrödinger theory gives an energy perturbation series which takes the simple form $E = -\frac{1}{2} + 3\lambda$. This gives the exact energy for

Table 4. Some energy levels for the double-well Hamiltonian $-D^2 - x^2 + 0.01x^4 + \lambda x$, using HVPT at the right (R) or left (L) minimum of V. For the symmetric case $\lambda = 0$ the accurate even- and odd-state energies from finite-difference calculation straddle the HVPT value, with the varying digits being shown in parentheses. The averaging phenomenon is clearly visible. The loss of digits in HVPT for the two highest levels indicates that the levels are not perfectly localized. Finite difference methods [35] give $P = 0.999\,999\,9746$ for these states.

	$\lambda = 0$		
Initial digits	Even	HVPT(R, L)	Odd
−23.595 951 394 702	(29)	(29)	(29)
−20.829 806 394 000	(69)	(69)	(69)
−18.129 911 166 28	(60)	(60)	(60)
−15.501 421 612 8	(088)	(105)	(121)
−12.950 690 513	(3270)	(4964)	(6660)
−10.485 794 9	(51 879)	(64 449)	(77 019)
−8.117 45	(292 513)	(361 657)	(430 801)
	$\lambda = 0.001$		
HVPT(R)		HVPT(L)	
−23.588 957 072 802		−23.602 945 976 466	
−20.822 972 039 181		−20.836 641 030 933	
−18.123 248 475 760		−18.136 574 166 004	
−15.494 944 807 678		−15.507 898 760 913	
−12.944 417 357 451		−12.956 964 055 997	
−10.479 748 457 000		−10.491 841 916 766	
−8.111 665 064 9		−8.123 242 696 4	

$\lambda > 0$, but for $\lambda < 0$ it is incorrect; a non-analytic term gives an increasing contribution as $|\lambda|$ increases. HVPT makes it possible to study the properties of (7) for $\lambda < 0$ by combining the two types of perturbation theory used in this paper. To give a precise example we present the details for the case $\lambda = -0.03$. The first essential step is to find the profile of the potential, i.e. find the positions of the maxima and minima of V and the values of V and of its second derivative at those extrema. This then allows a preliminary judgement of whether any potential wells present in V are likely to be deep enough to have any trapped levels. For $\lambda = -0.03$ the V in (7) has the following profile (using truncated values):

$$r = 4.84 \qquad V = -0.455 \qquad \text{maximum}$$
$$r = 15.51 \qquad V = -0.562 \qquad V'' = 0.0031 \qquad \text{minimum.}$$

These numbers suggest that the outer well in the potential V, although it is shallow, should be able to contain at least one level, while the V value at the maximum appears to be sufficiently low to 'strip off' all the usual hydrogenic levels except the ground state one at $-1/2$. To carry out a detailed numerical perturbation calculation we use harmonic oscillator HVPT, together with the Taylor expansion of V, at the position of the minimum and also a Coulomb HVPT centred on $r = 0$. However, for this $r = 0$ calculation we know that a traditional approach will give the wrong result $-\frac{1}{2} + 3\lambda$. Accordingly, we try the approach of 'changing the powers'; we replace λ^2 attached to r by λ, in order to produce a different series (just as in the oscillator problems of section 3 we made a change in the opposite direction). Thus to treat the specific case $\lambda = -0.03$ we rewrite the perturbation as $-0.06\lambda r + 0.0018\lambda r^2$, with λ taken as 1 in the numerical calculation. We can also use the renormalization approach of section 5 by writing the Coulomb term as $-Z_0 r^{-1} + (Z_0 - 1)\lambda r^{-1}$. When we do this the energy series (when used with the Wynn algorithm) gives a ground-state energy of $-0.589\,996\,7663$, showing the presence of the small non-analytic term which changes the energy from the standard perturbation value

of -0.59 exactly. The calculation thus has used perturbation theory to evaluate a non-analytic perturbation term! Applying oscillator HVPT in the outer well leads to a lowest-energy level of -0.5348 and a second level of -0.482; the small number of converged digits implies that the levels are perhaps not strongly localized. However, a checking finite-difference calculation in the full region $r = 0$–100 shows that there is indeed a level at $-0.534\,76$ and that it has a $\langle r \rangle$ value of 15.31; the minimum of V is at 15.51. Thus the 'weak' perturbation with $\lambda = -0.03$ has produced three levels (at -0.590, -0.535 and -0.482) close to the unperturbed energy -0.5. The level nearest to it in energy is thus not the inner one which arises naturally from it but the outer one which is concentrated in the distant potential well. For smaller values of $|\lambda|$ HVPT at the outer minimum gives much sharper results and indicates that the lowest outer level tends to $-1/2 - |\lambda|$ as $|\lambda|$ tends to zero. At $\lambda = -0.01$ HVPT gives many levels in the outer well, the lowest five of them being to 12 or more decimal places.

8. Some multiple-well problems

We may note in passing that the HVPT applied at the minimum of the Nth well of the potential $V = \cos(|x|^{\frac{1}{2}})$ gives many energy levels in that well with double-precision accuracy, since the barrier between the wells is so thick that each well contains a large number of almost perfectly localized levels. Nevertheless, the finite-difference method of [5], when carefully applied [37], is sufficiently robust to find these levels in a full space calculation and to correctly assign them to their appropriate wells. Rather than using that case as an example we have chosen another one which has been discussed in the recent literature of perturbation theory. In [38] calculations were performed for several polynomial radial potentials which have more than one minimum. As an illustrative example we take the particular case of the Hamiltonian

$$-\tfrac{1}{2}D^2 + 2r^{-2} - r^{-1} - 4.743\,42r + 10.158\,11r^2 - 2r^3 + 0.1r^4. \tag{8}$$

The profile of the potential function is as follows:

$r = 0.759$	$V = 3.565$	$V'' = 43.412$	minimum
$r = 4.673$	$V = 43.131$		maximum
$r = 10.075$	$V = -31.763$	$V'' = 21.232$	minimum.

In [38] the authors used a fairly complicated approach via $1/N$ theory in hypervirial form, whereas we proceed simply and directly by carrying out HVPT at the potential minima. This means that we use the true potential rather than the modified potential of $1/N$ theory; however, we can still interpret meaningfully the criticisms which the authors of [38] make of the work of [39]. The gist of the criticism is that in the case of potential (8) and of several others the authors of [39] chose the 'wrong' minimum on which to base their calculations and so obtained energy levels which are 'seriously in error'. By using HVPT (with our checking finite-difference method to confirm all the results) we can establish that the results of [39] are in fact acceptable when they are properly placed in context. HVPT calculations carried out at the outer minimum give a sequence of oscillator levels. The $n = 0$ level has $E = -28.523\,425\,470\,899$ while the $n = 8$ level has $E = 18.973\,361\,2620$. These values are confirmed by a finite-difference calculation, which also produces $\langle r \rangle$ values close to 10. HVPT calculations at the inner minimum clearly show some local levels, although the convergence is not as good as for the outer minimum. The inner $n = 0$ level is 8.516 023 and the $n = 2$ and 3 values are 17.094 78 and 24.9273. The finite-difference checking calculation confirms these energies to the decimal places quoted (although it gives many more digits) and gives $\langle r \rangle$ values close to 0.8. The E value given by [38] is $-28.522\,68$ and that given by [39] is 8.514 29. Allowing for the much lower accuracy of the calculations of the two works, it is clear that the result

of [39] criticized by [38] is in fact a respectable energy level, which, in the context of a full space calculation, is actually an excited state, while the level given by [38], being in the deeper well, is an estimate of the ground-state energy. The effects which we have demonstrated here for one particular case persist for the other polynomial potentials given in [39] for which the results of [38] and [39] differ. We note that our accurate energies do not agree fully with the quoted 'exact supersymmetric energies' quoted for the various cases which are treated in [39].

9. Summary

In this paper we have presented a selection of the topics and numerical results which resulted from a study of a large portion of the published literature on perturbation theory. The main points which we hope to have demonstrated are that the careful use of renormalization and 'changing the powers' (together with a style of calculation in which the renormalization parameters are left freely and empirically variable to maximize the number of stable digits arising in the Wynn analysis) make it possible to obtain numerical results which are much better than those which many previous workers have achieved and that HVPT, when combined with potential profiling, can be a useful diagnostic tool in searching for localized levels in potentials which contain multiple minima, while for simple single-well potentials it provides a way to obtain lowest-order JWKB results without the use of integrals. Renormalization methods are usually of most value when the perturbing potential has only one or at most two terms in it, since we only use a single renormalizing parameter. We surmise that a more complicated approach involving a 'distributed' renormalization, with each term having a small subtracted x^2 term, might help to improve the results for the HVPT approach at the minimum of V, where the perturbing V is a power series. Work is currently in progress on this approach.

Although in this paper we have dealt only with the model potentials which typically appear in theoretical studies, we note that asymmetric well systems appear in the potentials associated with the HD molecule and the inter-base potentials in DNA [40,41]. We hope that several of the ideas and numerical results presented here will stimulate further investigations by workers in the area of perturbation techniques and will also encourage those who use other techniques to make use of HVPT as a checking calculation when appropriate. As one obvious point we note that, since we have retained the standard Wynn algorithm throughout and have concentrated on the generation of the series as the thing to be modified, it might be that the new series arising from some of the calculations would yield even better results in the hands of experts in the more recent summation techniques. It is clear that the linkage of perturbation theory with hypervirial relations which Swenson and Danforth [42] set out long ago has led to many powerful techniques and still has the potential for further development. As a result of their large-scale trawl through hundreds of published works the authors would like to make a final plea to workers who publish tables of numerical results; please take care to show at the head of each table the full Hamiltonian used, including the kinetic term!

As an extra example, taken from a paper on matrix mechanics which appeared during the final revision of this paper, we note the case of the potential $V = 50\sinh^2(x)$ with $\alpha = 1/2$. In [43] the energy of the level $n = 5$ is given as 61.820, while HVPT centred on $x = 0$ quickly gives 61.820 235 107 690 for this energy.

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