

Renormalized perturbation theory by the moment method for degenerate states

Marcelo D. Radicioni and Carlos G. Diaz

Departamento de Química, Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Mar del Plata, Funes 3350, 7600 Mar del Plata, Argentina

Francisco M. Fernández

CEQUINOR, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calle 47 y 115, Casilla de Correo 962, 1900 La Plata, Argentina

(Received 9 September 1996; revised manuscript received 14 May 1997)

We apply renormalized perturbation theory by the moment method to an anharmonic oscillator in two dimensions with a perturbation that couples unperturbed degenerate states. The method leads to simple recurrence relations for the perturbation corrections to the energy and moments of the eigenfunction. We generalize the approach and systematize its application to excited states. [S1050-2947(97)10310-9]

PACS number(s): 03.65.Ge

I. INTRODUCTION

Perturbation theory without a wave function is one of the simplest and most efficient ways to calculate of perturbation corrections of large order to the energies of quantum-mechanical problems. Swenson and Danforth [1] developed the first such method, which was based on the application of the hypervirial and Hellmann-Feynman theorems. Later Killingbeck [2] rederived the main equations in a clearer way and the method became popular because of its simplicity and because it yields perturbation corrections to a representative energy eigenvalue in terms of the quantum numbers (for reviews see some of the references below [3,4]). At present this approach is only applicable to completely separable problems.

Ader [5] developed a perturbation theory for nondegenerate states based on recurrence relations for the moments of the wave function, and applied it to central-field problems in the framework of the $1/D$ expansion, D being the number of spatial dimensions. Blankeubecler *et al.* [6] generalized the recurrence relations in order to treat anharmonic oscillators in one and two dimensions nonperturbatively.

Fernández and Castro [7] proposed a perturbative version of this approximation that proved useful to treat the hydrogen atom in magnetic and electric fields [4,7,8–11], and pointed out its application to coupled anharmonic oscillators [9].

Rediscovering this method, Killingbeck *et al.* [12] and Killingbeck and Jones [13] applied it to one- and two-dimensional anharmonic oscillators, respectively. Witwit [14–17] recently used this approach extensively, in combination with the renormalization method proposed by Killingbeck [18,19], to calculate accurate eigenvalues of anharmonic oscillators and other quantum-mechanical models. Those applications of perturbation theory by the moment method rely, in some way or another, on symmetry to avoid the explicit treatment of degeneracy. For instance, Witwit [15] stated that a successful application of the moment method requires a certain relationship between coefficients in the potential-energy function of a particular anharmonic oscillator in two dimensions. Such symmetry conditions re-

strict considerably the applicability of the method.

Fernández [20] and Fernández and Morales [21] showed how to apply perturbation theory by the moment method to degenerate states, and calculated the splitting of several energies of the hydrogen atom in electric and magnetic fields. Later, Fernández and Ogilvie [22] applied this approach to anharmonic oscillators to illustrate the treatment of degenerate states coupled by the perturbation, thus overcoming the difficulties pointed out by Witwit [15]. They obtained analytic expressions for the corrections to the energy of the lowest states of the two-dimensional anharmonic oscillator

$$H = H_0 + \lambda H',$$

$$H_0 = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + x^2 + y^2, \quad H' = ax^4 + by^4 + 2cx^2y^2. \quad (1)$$

The energy eigenvalues $E_N^{(0)} = 2(N+1)$, $N=0,1,\dots$ of the unperturbed Hamiltonian H_0 are $(N+1)$ -fold degenerate. When $a=b$ the operator H is invariant under the exchange $x \leftrightarrow y$, and because of this high symmetry the perturbation does not couple the unperturbed states, which can therefore be treated as if they were nondegenerate. Previous simpler treatments of this model were restricted to this particular case [13,15–17]. On the other hand, if we allow $a \neq b$ the perturbation breaks the degeneracy at first order of perturbation theory, giving rise to a richer and more interesting application of the moment method.

It is our purpose to round off the application of perturbation theory without a wave function to anharmonic oscillators by means of an approach that gives a renormalized series for the most general and difficult cases of degenerate states.

II. PERTURBATION THEORY BY THE MOMENT METHOD

Because the perturbation series in powers of λ for the anharmonic oscillator (1) is divergent [23], we look for a convergent renormalized series [18,19], writing

$$H = -\frac{\partial^2}{\partial x^2} - \frac{\partial^2}{\partial y^2} + \mu^2(x^2 + y^2) + \lambda[H' - \beta(x^2 + y^2)], \quad (2)$$

where

$$\mu^2 = 1 + \lambda\beta. \quad (3)$$

In the application of perturbation theory we consider μ to be independent of λ and invoke Eq. (3) just at the end of the calculation [18,19]. Here we choose $\lambda = 1$.

In order to apply perturbation theory by the moment method we first derive a recurrence relation for the moments of an eigenfunction Ψ of the Hamiltonian operator H . Such a recurrence relation is a convenient substitute for the Schrödinger equation and follows from

$$\langle Hf|\psi\rangle - E\langle f|\Psi\rangle = 0, \quad (4)$$

where E is the eigenvalue and the function f is chosen so that the moment $\langle f|\psi\rangle$ exists. In the case of the renormalized Hamiltonian operator (2) we substitute

$$f_{m,n} = x^m y^n \exp\left[-\frac{\mu}{2}(x^2 + y^2)\right], \quad m, n = 0, 1, \dots \quad (5)$$

for f in Eq. (4) thus obtaining a recurrence relation for the moments $F_{m,n} = \langle f_{m,n}|\Psi\rangle$. Substitution of the series

$$E = \sum_{i=0}^{\infty} E^{(i)}\lambda^i, \quad F_{m,n} = \sum_{i=0}^{\infty} F_{m,n}^{(i)}\lambda^i \quad (6)$$

into the recurrence relation for the moments gives us an expression from which we obtain all the coefficients $E^{(i)}$ and $F_{m,n}^{(i)}$, [22]. In the present case the perturbation is a particular case of

$$H' = \sum_{r,s} c_{r,s} x^r y^s \quad (7)$$

that leads to

$$\begin{aligned} 2(m+n-N)\mu F_{m,n}^{(p)} &= m(m-1)F_{m-2,n}^{(p)} + n(n-1)F_{m,n-2}^{(p)} \\ &+ \sum_{j=1}^p E^{(p)} F_{m,n}^{(p-j)} - \sum_{r,s} c_{r,s} F_{m+r,n+s}^{(p-1)} \\ &+ \beta[F_{m+2,n}^{(p-1)} + F_{m,n+2}^{(p-1)}]. \end{aligned} \quad (8)$$

The aim of renormalization is to determine a value of β that renders the sequence of partial sums

$$S_Q(\beta) = \sum_{i=0}^Q E^{(i)}(\beta)\lambda^i \quad (9)$$

convergent as $Q \rightarrow \infty$ [18,19].

III. NUMERICAL RESULTS

We have systematically extended the procedure developed by Fernández and Ogilvie [22] and written a computer code for the application of perturbation theory by the mo-

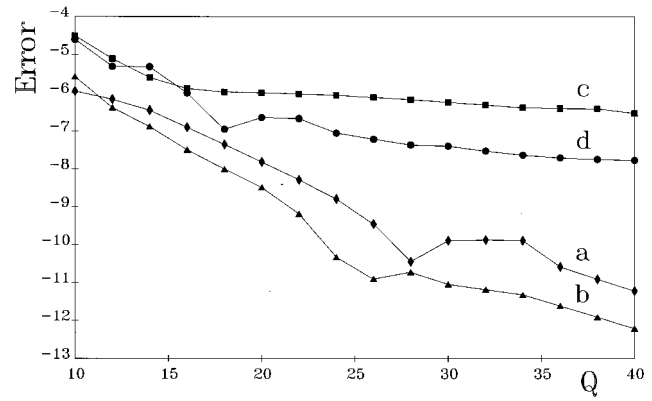


FIG. 1. Convergence of the renormalized series towards the exact variational results E_{var} given by the Rayleigh-Ritz method. The figure shows error, which is equal to $\log_{10}[(S_Q - E_{\text{var}})/E_{\text{var}}]$, vs Q for the following four cases: (a) $a = 1.0$, $b = 2.0$, $c = 1.0$, $v = 0$, (b) $a = 1.0$, $b = 2.0$, $c = 1.0$, $v = 39$, (c) $a = 1.0$, $b = 5.0$, $c = 1.0$, $v = 0$, (d) $a = 1.0$, $b = 5.0$, $c = 1.0$, $v = 39$, where v is the quantum number of the anharmonic oscillator.

ment method. Given the potential parameters a , b , and c , and the renormalization parameter β for a quantum number N , the program computes the coefficients of the perturbation series. We contrasted the eigenvalues thus obtained with those coming from diagonalization of the Hamiltonian matrix in a sufficiently large basis of eigenfunctions of H_0 (Rayleigh-Ritz method) for the required accuracy. In all the cases considered here the agreement between variational and renormalized perturbation results was remarkable.

An efficient calculation of the energy eigenvalues by means of perturbation theory requires a routine for the estimation of the optimum value of β . In the present paper we have investigated several prescriptions for it. A successful approach is based on the principle of *minimum sensitivity*: since E is independent of β one consequently requires that

$$\frac{\partial S_Q}{\partial \beta} = 0. \quad (10)$$

From straightforward differentiation of the equations of the theory given above one easily obtains the derivative of each term of the partial sum (10). We obtained the roots of Eq. (10) by means of bracketing plus secant methods [24].

Alternatively, we may choose the value of β that minimizes the sum of the squares of the last two or three perturbation corrections in a given partial sum. This approach does not require the calculation of derivatives and, when combined with an efficient one-dimensional minimization routine [24], it turns out to be faster than the previous procedure, giving similar results. Here we chose the latter strategy.

The rate of convergence of the renormalized series is remarkable as shown in Fig. 1 for four different cases, and for $Q \leq 40$ (we have joined the points by lines to guide the eye). It is clear that the partial sums with $Q = 40$ are sufficiently accurate for most purposes.

In Table I we show results for some of the lowest states of the oscillator (1) with parameters $a = 1$, $b = 2$, and $c = 1$. More precisely, Table I displays the actual quantum number for the anharmonic oscillator v , the quantum number N for

TABLE I. Lowest-energy eigenvalues of the anharmonic oscillator with potential parameters $a=1.0$, $b=2.0$, and $c=1.0$. v denotes the actual quantum number and the error is given by $\log_{10} |(S_{40} - E_{\text{var}})/E_{\text{var}}|$, where E_{var} is the corresponding eigenvalue computed by the Rayleigh-Ritz variational method.

v	N	S_{40}	Error	β
0	0	3.143 959 310 272	-10.89	12.4056
10	4	20.189 989 356 111	-12.02	14.5267
20	5	30.655 399 874 247	-11.49	16.4276
30	6	37.604 833 946 509	-11.08	17.0545
39	8	44.702 589 229 227	-12.49	17.1684

the separable, unperturbed problem, the energy eigenvalue computed with the perturbation series through order 40, the error in the computed perturbative result with respect to the variational eigenvalue, and the optimum value of β determined by minimization. We conclude that the method yields eigenvalues that are accurate enough for most practical purposes. The accuracy of the results for a given set of potential parameters appears to be almost independent of the quantum number, so that one expects similar results for higher states. On the other hand, the accuracy of the method decreases as the anharmonicity of the potential increases, as expected for a perturbative approach (see below).

In Table II we show the eigenvalues of the anharmonic oscillator with potential parameters $a=1$, $b=5$, and $c=1$, which lead to a more asymmetric potential (for the present model, the asymmetry is proportional to $|b-a|$). Comparison of both tables reveals the decrease in accuracy already mentioned before.

TABLE II. The same as in Table I for $a=1.0$, $b=5.0$, and $c=1.0$.

v	N	S_{40}	Error	β
0	0	3.525 046 025 155	-6.61	20.9818
10	4	21.493 038 209 415	-7.88	25.1122
20	6	32.057 608 308 247	-9.43	25.8197
30	8	43.450 550 577 336	-8.62	27.9505
39	9	49.915 488 242 353	-7.81	27.0820

The present results show that perturbation theory by the moment method is a powerful and straightforward approach for the calculation of accurate energies of nonseparable quantum-mechanical systems with polynomial perturbations. The main advantage of the moment method is the simplicity of its recurrence relations and the absence of explicit integrals for the matrix elements. This feature becomes most desirable in the case of a nonpolynomial potential-energy function if one expands it in a Taylor series around its minimum before the application of perturbation theory. Present results suggest that perturbation theory by the moment method may be practical to treat highly excited states and more complicated perturbations, as those taking place in more realistic models for the study of vibrations in polyatomic molecules [25].

ACKNOWLEDGMENT

One of the authors (M.R.) thanks Comisión de Investigaciones Científicas (CIC) de la Provincia de Buenos Aires for financial support.

- [1] R. J. Swenson and S. H. Danforth, *J. Chem. Phys.* **57**, 1734 (1972).
- [2] J. Killingbeck, *Phys. Lett.* **65A**, 87 (1978).
- [3] F. M. Fernández and E. A. Castro, *Hypervirial Theorems*, Lecture Notes in Chemistry Vol. 43 (Springer, Berlin, 1987).
- [4] G. A. Artega, F. M. Fernández, and E. A. Castro, *Large Order Perturbation Theory and Summation Methods in Quantum Mechanics*, Lecture Notes in Chemistry Vol. 53 (Springer, Berlin, 1990).
- [5] J. P. Ader, *Phys. Lett.* **97A**, 178 (1983).
- [6] R. Blankenbecler, T. DeGrand, and R. L. Sugar, *Phys. Rev. D* **21**, 1055 (1980).
- [7] F. M. Fernández and E. A. Castro, *Int. J. Quantum Chem.* **26**, 497 (1984).
- [8] G. A. Artega, F. M. Fernández, A. M. Mesón, and E. A. Castro, *Physica A* **128**, 253 (1984).
- [9] F. M. Fernández and E. A. Castro, *Int. J. Quantum Chem.* **28**, 603 (1985).
- [10] F. M. Fernández, J. F. Ogilvie, and R. H. Tipping, *J. Phys. A* **20**, 3777 (1987).
- [11] E. J. Austin, *Int. J. Quantum Chem.* **18**, 449 (1984).
- [12] J. Killingbeck, M. N. Jones, and M. J. Thompson, *J. Phys. A* **18**, 793 (1985).
- [13] J. Killingbeck and M. N. Jones, *J. Phys. A* **19**, 705 (1986).
- [14] M. R. M. Witwit, *J. Phys. A* **24**, 3053 (1991).
- [15] M. R. M. Witwit, *J. Phys. A* **24**, 4535 (1991).
- [16] M. R. M. Witwit, *J. Math. Phys.* **33**, 4196 (1992).
- [17] M. R. M. Witwit, *J. Math. Phys.* **36**, 187 (1995).
- [18] J. Killingbeck, *J. Phys. A* **14**, 1005 (1981).
- [19] J. Killingbeck, *J. Phys. B* **14**, L461 (1981).
- [20] F. M. Fernández, *J. Phys. A* **25**, 492 (1992).
- [21] F. M. Fernández and J. A. Morales, *Phys. Lett. A* **165**, 314 (1992).
- [22] F. M. Fernández and J. F. Ogilvie, *Phys. Lett. A* **178**, 11 (1993).
- [23] B. Simon, *Ann. Phys. (N.Y.)* **58**, 76 (1970).
- [24] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986).
- [25] V. Spirko, J. Cízek, and L. Skála, *J. Chem. Phys.* **102**, 8916 (1995).