match no. 15 pp. 133-143 1984

THE HYPERVIRIAL PERTURBATIVE METHOD (HPM)

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SUMMARY - The well-known perturbation method that combines the perturbation theory with the Hellmann-Feynman and hypervirial theorems is shown to apply to any one-dimensional Hamiltonian, provided its potential function has a well-defined general form. This quite general formulation of the method is proved to be suitable to handle a large number of problems of actual chemical and physical interest.

INTRODUCTION

Some years ago, Swenson and Danforth /1/ developed a powerful and elegant method to obtain the eigenvalue perturbation corrections for some simple (though non-trivial) one-dimensional quantum-mechanical systems. The procedure, which combines the perturbation theory (PT) with the Hellmann-Feynman and hypervirial theorems, was first applied to the anharmonic oscillator model /1/.

The Swenson and Danforth's method, which from now on will be called hypervirial perturbative method (HPM) was found to be suitable to handle a wide variety of one-particle quantum-mechanical models /1-35/. Despite of their apparent simplicity, some of these models are of great interest in Chemistry and Physics. For example, the hydrogen atom with a radial perturbation

$$H = -D^2/2 - 1/r + \ell(\ell+1)/(2r^2) + \lambda r \ , \quad D \equiv d/dr \ , \qquad (1)$$

that is useful in quarkonium physics /36/ (and references therein)

was first studied by Killingbeck /2/. Arteca et al /12/ and Requena et al /11/ applied the HPM to the harmonic oscillator perturbed with a polynomial function

$$H = (x^2-D^2)/2+V(x) \ , \ D\equiv d/dx \ , \ V(x) = \lambda \sum_{s=0}^{n} v_s x^s \quad \text{or}$$

$$V(x) = \sum_{s=0}^{\infty} v_s \lambda^s x^s \ , \tag{2}$$

which is a well-known approximation to the nuclear motion of a diatomic molecule /37/. Another appropriate approach to this problem is the perturbed Morse oscillator /38/

$$H = -D^2/2 + v_2(1-e^{-x})^2 + \sum_{s=4}^{n} v_s(1-e^{-x})^s \ , \tag{3}$$

to which the HPM was applied by Fernández and Castro /17,18/. Recently, the HPM was proved to be fruitful for dealing with some periodic quantum-mechanical models like a polar rigid rotator in a uniform electric field /20/

$$H = -(1/\sin\theta)(d/d\theta)\sin\theta(d/d\theta) + m^2/\sin^2\theta - \lambda\cos\theta \ , \tag{4}$$

that poses a first approximation to the Stark effect in a polar diatomic molecule /39,40/. The Stark shifts for a polar symmetric-top molecule (including polarization effects) /21/ and the rotational energies of the hydrogen molecule-ion H_2^+ in a uniform magnetic field /22/ can also be obtained through the HPM.

Although a very large number of papers on the HPM have appeared in the last years /1-35/, none of them shows what exactly are the conditions that the potential function has to obey so that the method can be applied. This very important question will be partly

answered in this article. Firstly, we will develop a simple and compact form of the hypervirial theorem in the remaining of this section.

Since any Sturm-Liouville eigenvalue equation can be changed into the Schrödinger form /41/, we only need to consider one-dimensional Hamiltonian operators of the form

$$H = -D^2/2 + U(x) \ , \ D \equiv d/dx \ . \tag{5}$$

Let Ψ be an eigenfunction of H with eigenvalue E ($H\Psi = E\Psi$), then the hypervirial theorem states that

$$<\left[H,W\right]> = 0 \ , \ \left[H,W\right] = HW - WH \ , \tag{6}$$

where W is any linear operator and $<A>$ holds for the expectation value $<\Psi|A\Psi>$. When $W\Psi$ does not belong to the domain of H, the form of the hypervirial theorem has to be changed /32-35/.

It is very easy to show that any differentiable function $f=f(x)$ obeys:(primes denote differentiation with respect to x)

$$\left[H,fD\right] = \frac{1}{4}f''' + \frac{1}{2}\left[H,f'\right] + f'(H-U) - fU' \ , \tag{7}$$

and that the hypervirial theorem (6), with W=fD, leads to

$$\frac{1}{4}<f'''> + 2E<f'> - 2<f'U> - <fU'> = 0 \ . \tag{8}$$

This equation is the starting-point of most HPM calculations performed earlier /1-22/ (bounded systems are excluded) and also of the more general formulation that will be discussed later on in the next section.

In closing this section, we want to point out that our goal is to develop a sufficient condition for the potential function U(x) so that the HPM can be applied. There are many other methods for

obtaining large-order perturbation corrections /42-46/, but when the HPM can be applied it seems to be preferable to all other existing procedures /1-35/. This fact will be briefly discussed at the end of this paper.

RESULTS AND DISCUSSION

In order to apply PT, the potential function $U(x)$ is splitted into two parts $U(x)=V_0(x)+V(x)$ in such a way that the eigenvalues and eigenfunctions of the (zeroth-order) Hamiltonian $H_0=-D^2/2+V_0(x)$ are known

$$H_0\Psi^{(0)} = E^{(0)}\Psi^{(0)} \quad . \tag{9}$$

The remaining term $V(x)$ in the potential function is considered to be a perturbation that changes $E^{(0)}$ and $\Psi^{(0)}$ into E and Ψ, respectively. PT assumes that E and Ψ can be expanded in λ-power series

$$E = \sum_{p=0}^{\infty} E^{(p)}\lambda^p \quad , \quad \Psi = \sum_{p=0}^{\infty} \Psi^{(p)}\lambda^p \quad , \tag{10}$$

where λ is a perturbation parameter properly chosen.

We will show that the HPM can be used to obtain every perturbation correction $E^{(p)}$ if the potential function $U(x)$ can be written as a linear combination of functions belonging to a set $G=\{f_s(x),\ s=0,1,\ldots\}$ which obey:

$$f_N'(x) = \sum_{i=0}^{N} a_{Ni} f_i(x) \quad , \quad a_{0i} = 0 \quad , \tag{11a}$$

$$f_N(x) f_M(x) = \sum_{i=0}^{N+M} b_{NMi} f_i(x) \quad , \quad b_{NMi} = b_{MNi} \quad . \tag{11b}$$

We will refer to these functions as G-functions.

The zeroth-order potential function is supposed to be a finite sum

$$V_0(x) = \sum_{i=0}^{k} v_i f_i(x) , \tag{12}$$

but that corresponding to the perturbation can be finite or infinite. For the sake of simplicity, let us consider both cases separately.

Case A

If V(x) is a finite sum, the whole potential function U(x) can be written as

$$U(x) = \sum_{s=0}^{K} u_s f_s(x) , \quad K > k . \tag{13}$$

This form of the potential function and the properties (11) of the G-functions clearly suggest that the hypervirial theorem (8) with $f \equiv f_N$ should provide us an equation relating E and the expectation values of G-functions. The calculation is straightforward and the result is:

$$\frac{1}{4} \sum_{i=0}^{N} \sum_{j=0}^{i} \sum_{m=0}^{j} a_{Ni} a_{ij} a_{jm} F^{(m)} + 2E \sum_{i=0}^{N} a_{Ni} F^{(i)}$$

$$-2 \sum_{i=0}^{N} \sum_{s=0}^{K} \sum_{j=0}^{s+i} a_{Ni} u_s b_{isj} F^{(j)} - \sum_{s=0}^{K} \sum_{i=0}^{s} \sum_{j=0}^{N+i} u_s a_{si} b_{Nij} F^{(j)} = 0, \tag{14}$$

where $F^{(s)} = \langle f_s \rangle$.

The perturbation parameter λ can be easily introduced by redefining the coefficients u_i as follows:

$$u_s = v_s \text{ if } s \leq k \quad \text{and} \quad u_s = \lambda v_s \text{ if } s > k . \tag{15}$$

Since all the coefficients v_s and the perturbation parameter λ are supposed to be independent each other, then the Hellmann-Feynman theorem states that

$$\partial E/\partial v_s = F^{(s)} \quad s \leq k \ , \quad \partial E/\partial \lambda = \sum_{s>k}^{K} v_s F^{(s)} \ . \tag{16}$$

The HPM consists in expanding the expectation values $F^{(s)}$ (instead of the eigenfunctions as in the usual PT) in powers of λ

$$F^{(s)} = \sum_{p=0}^{\infty} F_p^{(s)} \lambda^p \ , \quad F_0^{(s)} = \langle \psi^{(0)} | f_s \psi^{(0)} \rangle \ . \tag{17}$$

The power series expansions for E and $F^{(s)}$ (Eqs. (10) and (17)) and the Hellmann-Feynman theorem (16) lead to

$$\partial E^{(p)}/\partial v_s = F_p^{(s)} \ , \quad s \leq k \ , \tag{18a}$$

$$pE^{(p)} = \sum_{s>k}^{K} v_s F_{p-1}^{(s)} \ . \tag{18b}$$

In the same way, if the perturbation series for E and $F^{(s)}$ are introduced into (14) and the coefficient of λ^p is set null, we will obtain

$$\frac{1}{4} \sum_{i=0}^{N} \sum_{j=0}^{i} \sum_{m=0}^{j} a_{Ni} a_{ij} a_{jm} F_p^{(m)} + 2 \sum_{q=0}^{p} \sum_{i=0}^{N} a_{Ni} E^{(q)} F_{p-q}^{(i)}$$

$$-2 \sum_{i=0}^{N} \sum_{s=0}^{k} \sum_{j=0}^{s+i} a_{Ni} b_{isj} v_s F_p^{(j)} - \sum_{s=0}^{k} \sum_{i=0}^{s} \sum_{j=0}^{N+i} v_s a_{si} b_{Nij} F_p^{(j)}$$

$$-2\sum_{i=0}^{N}\sum_{s>k}^{K}\sum_{j=0}^{s+i} a_{Ni}b_{isj}v_s F_{p-1}^{(j)} - \sum_{s>k}^{K}\sum_{i=0}^{s}\sum_{j=0}^{N+i} v_s a_{si}b_{Nij}F_{p-1}^{(j)} = 0 \ . \tag{19}$$

This recursion relationship and Eqs. (18) enable us to compute every perturbation correction $E^{(p)}$ in terms of $E^{(0)}$ as can be proved by a simple inductive reasoning. The starting point of the calculation is the normalization condition for Ψ: $F_p^{(0)}=\delta_{0p}$.

Case B

When the perturbation potential V(x) is an infinite linear combination of G-functions, the whole potential can be written as

$$U(x) = \sum_{s=0}^{\infty} u_s f_s(x) \ . \tag{20}$$

Although multiple PT (i.e. considering every u_s with s>k as a perturbation parameter) can be directly applied to this problem (for a particular case see Ref. /11/), we will use here the usual one-parameter PT /12/. In order to do this, the coefficients u_s are redefined in the following way:

$$u_s = v_s \text{ if } s \leq k \text{ and } u_s = \lambda^{s-k} v_s \text{ if } s > k \ . \tag{21}$$

Since the application of the HPM to this case is straightforward following a reasoning similar to that in case A, we will only give the results. Any perturbation correction $E^{(p)}$ can be obtained in terms of $E^{(0)}$ by way of the recursion relationship

$$\frac{1}{4}\sum_{i=0}^{N}\sum_{j=0}^{i}\sum_{m=0}^{j} a_{Ni}a_{ij}a_{jm}F_p^{(m)} + 2\sum_{q=0}^{p}\sum_{i=0}^{N} a_{Ni}F^{(q)}F_{p-q}^{(i)}$$

$$-2\sum_{i=0}^{N}\sum_{s=0}^{k}\sum_{j=0}^{s+i} a_{Ni}b_{isj}v_s F_p^{(j)} - \sum_{s=0}^{k}\sum_{i=0}^{s}\sum_{j=0}^{N+i} v_s a_{si}b_{Nij}F_p^{(j)}$$

$$-2\sum_{i=0}^{N}\sum_{s>k}^{p+k}\sum_{j=0}^{s+i} a_{Ni}b_{isj}v_s F_{p+k-s}^{(j)} - \sum_{s>k}^{p+k}\sum_{i=0}^{s}\sum_{j=0}^{N+i} v_s a_{si}b_{Nij}F_{p+k-s}^{(j)} = 0 \qquad (22)$$

used together with the following equations provided by the Hellmann-Feynman theorem

$$\partial E^{(p)}/\partial v_s = F_p^{(s)} \quad , \quad s \leq k \quad , \qquad (23a)$$

$$pE^{(p)} = \sum_{q=0}^{p-1} (p-q)v_{p+k-q}F_q^{(p+k-q)} \quad . \qquad (23b)$$

Again, the starting point for the calculation is the normalization condition $F_p^{(0)}=\delta_{0p}$.

The general HPM developed above (cases A and B) can be directly applied to the quantum-mechanical models in Eqs. (1)-(4) for r^s /2/, x^s /11,12/, $(1-e^{-x})^s$ /17,18/ and $\sin^s\theta\cos^t\theta$ /20-22/ (s,t=0,1,2,...) are all G-functions.

In the usual Rayleigh-Schrödinger PT, the perturbation corrections $\psi^{(p)}$ and $E^{(p)}$ are obtained as solutions of a set of differential equations or as a result of well-known sums containing the zeroth-order eigenvalues and the matrix elements of the perturbation in the basis set of zeroth-order eigenfunctions /47/. On the contrary, the HPM recursion relationships (18)-(19) or (22)-(23) are easily solved yielding, in each step, a perturbation correction $E^{(p)}$ in terms of $E^{(0)}$ *for all states at the same time.* Besides, the HPM equations are programmed much more easily than those in the usual PT, enabling us, in this way, to compute high-order perturbation corrections quickly.

There are several other methods /42-46/ which are also much more efficient than the usual PT. It is not pur purpose to discuss all of

them in relation to the HPM because, as stated before, our goal is only to generalize the HPM and to develop a sufficient condition for it to be applied. However, it might be interesting to compare the HPM recursion relationships with that proposed by Bender and Wu /45/ in their pioneering work on large-order PT since both were applied to the anharmonic oscillator /1,5,45/. The Bender and Wu's method is preferable when the perturbation corrections to both the eigenvalues and eigenfunctions are required because the HPM only yields $E^{(p)}$ and perturbation corrections to the expectation values of G-functions. On the other hand, the HPM recursion relationships remain the same for all states whereas the complexity of Bender and Wu's one increases with the quantum number. In fact it was only applied to the ground-state eigenvalue /45/. Thus, the HPM seems to be more suitable when only eigenvalue perturbation corrections are needed.

In addition to this, we do not see how the method developed by Bender and Wu /45/ can be applied to bounded systems, even to the simplest ones which recently were successfully treated through a modified HPM /23-35/. The quantum-mechanical models for bounded systems pose a very interesting problem which is very difficult to be handled by way of PT for they give rise to an infinite number of non null matrix elements $\langle i|V|j\rangle$ (V holds for the perturbation) between a given zeroth-order state (say $|i\rangle$) and the remaining ones (say $|j\rangle$, $j=0,1,2,\ldots$). So, to obtain any $E^{(p)}$ ($p>1$) by means of the usual PT it is necessary to calculate at least one infinite sum. But, on the contrary, the HPM gives us the result of these sums directly; that is to say, it yields each $E^{(p)}$ in terms of $E^{(0)}$ for all states at the same time /23-35/.

We deem that when the HPM can be applied, it is preferable to all other existing methods developed to calculate energy perturbation corrections. This belief is strongly supported by the great number of papers in which the HPM was used /1-35/. We are inclined to generalize this procedure and to find a quite general and well-defined class of problems to which it can be applied for it is such a widespread method.

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