Optimized atomic orbitals in valence bond theory applied to benzene molecule

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Abstract The valence bond theory is applied here to an *ab initio* calculation of the ground state of the benzene π electrons. A comparison of the rate of energy convergence of p_z orbitals, nearest-neighbour optimized, and fully optimized orbitals calculations is made for benzene π electrons in the minimum basis set approximation. It is shown that making a full orbital optimization, only the covalent structures can reproduce the results of the full configuration interaction limit.

1. Introduction

The first quantum-mechanical discussion of how atoms combine to form stable molecular bonds was given by Beitler and London[1], introducing the basic concepts of the valence bond (VB) theory, in which atoms are recognized as the natural building blocks out of which molecules are constructed. Since those early days the theoretical foundations laid by the founders of the field have been considerably extended and many interesting applications of VB theory have been made[2].

VB theory in its modern form[3-6] is capable of giving a good account of both localized and non-localized bonding, using wavefunctions which are compact, accurate and easy to interpret using the language of classical chemistry, Gerratt et al[3-6] have developed the spin-coupled VB description of molecular electronic structure, in which a system of N electrons is described by N distinct non-orthogonal orbitals whose spins are coupled to the required overall resultant S according to a particular coupling scheme k. The orbitals are expanded on a basis set, much as in

molecular orbital (MO) theory, and all the variational parameters are optimized simultaneous to minirnize the energy.

Optimization of the atomic orbitals (AOs) in VB theory was introduced by Goddard[7]; in his calculations of the energies of some molecules, the orbitals and the orbital exponents were optimized.

Recently, McWeeny[8] has shown that the full configuration interaction (CI) limit may be closely approached, using only a small number of structures, by slightly modifying the nearest-neighbour orbitals in order to enhance their mutual overlap. The energies obtained with this approach for some molecules have been reported[9-10].

In this report a VB calculation is made, where each orbital is expanded in terms of the minimal set basis, and the expansion coefficients are optimized to minimize the energy. Apart from the above, comparison of the energies obtained with the pure p_z orbitals, the optimized nearest-neighbour and the fully optimized orbitals of the benzene molecule is made.

2. The classical VB theory: the benzene molecule

Benzene is the archetypical aromatic hydrocarbon, and over the years it has been used as a test of many chemical theories, both qualitative and quantitative. Thus, among the early tests of quantum mechanics on molecular systems, the one on benzene done by Pauling and Wheland[11] occupies a position of importance both intrinsically and because it provided a qualitative picture capable of extension to more complicated aromatic hydrocarbons. That work used Slater's generalization of the Heitler - London (see op. cit) H_2 wavefunction, and applied this to the A electrons only.

To describe the electronic structure of benzene, we first performed a standard molecular orbital self-consistent field (SCF) calculation using a minirnal Clementi basis set - (7s 3p/3s) Gaussian contracted to [2s 1p/1s]. In the following, we consider the 36 electrons comprising the a bonds and the 1s shells of the carbon atoms as the core electrons of a set of doubly occupied orbitals, and the one-electron Hamiltonian for the A electrons is replaced by an effective Hamiltonian.

The p_z orbitals are orthogonal to the core (see [9] and references therein). The total energy in this case is equal to the π electron energy plus the core energy[9,12]. Since the core energy is the same in all calculations done here it will only be included in the next section.

Thus, our VB calculations involves only six π electrons and six non-orthogonal p_z atomic orbitals. Consequently, there are 175 structures of singlet type[13].

If the six p_z atomic orbitals (AOs) are denoted by a_1, a_2, a_3, a_4, a_5, a_6, reading counterclockwise around the ring, the Rumer diagrams of the 5 covalent structures (Kekulé plus Dewar) are

$$(2.1)$$
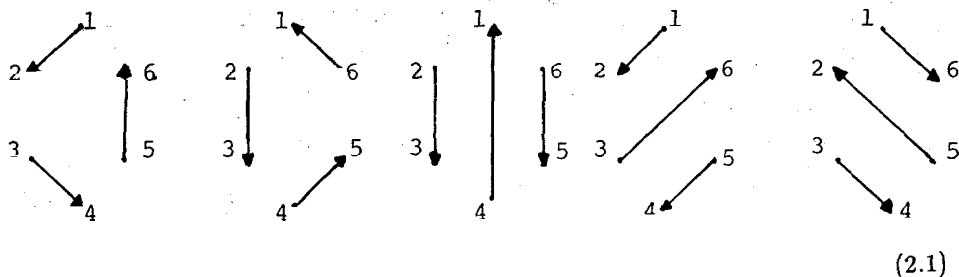
and the correspondent VB structures are

I - Kekulé structures   II - Dewar structures (2.2)
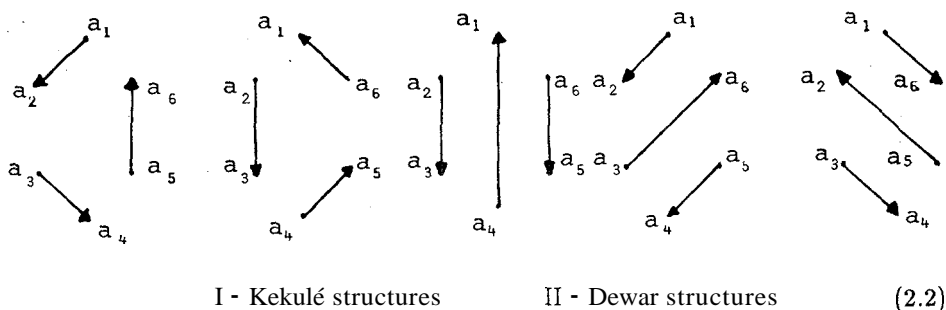
The wavefunction of the ground state of $^1A_{ig}$ symmetry constructed from the all linearly independent structures has the form (not normalized)

$$\Psi = A\left[b_1\, b_2\, b_3\, b_4\, b_5\, b_6 \left(\sum_{i=1}^{n} \Theta_i\right)\right] \tag{2.3}$$

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where A is the antisymmetrizer, n is the number of structures considered in the calculation (for example, it is equal to 2 or 5 if we consider only Kekulé or Kekulé plus Dewar structures, respectively) and the b_k's (k = $1, 2, ..., 6$) are arbitrary, equivalent and non-orthogonal AOs. The Θ_i's are the spin functions associated to the Rumer diagrams (2.1). For example, the spin function Θ_1 corresponding to the first Rumer diagram of (2.1) is equal to

$$\Theta_1 = \frac{1}{\sqrt{8}}([\alpha(s_1)\beta(s_2) - \alpha(s_2)\beta(s_1)]$$
$$[\alpha(s_3)\beta(s_4) - \alpha(s_4)\beta(s_3)]$$
$$[\alpha(s_5)\beta(s_6) - \alpha(s_6)\beta(s_5)]]$$

As the AOs of the eq.(2.3) are arbitrary, we can use the p_z orbitals

$$a_1; a_2; a_3; a_4; a_5; a_6 \tag{2.4}$$

or, of we want to improve the effectiveness of the covalent structures in describing the bonding, we can increase the mutual overlap of neighbouring orbitals. Orbitals of this kind were first used by Coulson and Fisher[14], and later by Mueller and Eyring[15]. Because of the non-orthogonality problem the use of these orbitals was restricted.

For our purposes an appropriate combination of the original p, AOs will be

$$\bar{a}_1 = a_1 + \lambda(a_2 \text{ t } a_6) + \mu(a_3 + a_5) + \nu a_4$$
$$\bar{a}_2 = a_2 + \lambda(a_1 + a_3) + \mu(a_4 + a_6) + \nu a_5$$
$$\bar{a}_3 = a_3 + \lambda(a_2 + a_4) + \mu(a_1 + a_5) + \nu a_6 \tag{2.5}$$
$$44 = a_4 + \lambda(a_3 + a_5) + \mu(a_2 + a_6) + \nu a_1$$
$$\bar{a}_5 = a_5 + \lambda(a_4 + a_6) + \mu(a_1 + a_3) + \nu a_2$$
$$\bar{a}_6 = a_6 + \lambda(a_1 + a_5) + \mu(a_2 + a_4) + \nu a_3$$

that is, each orbitas is expanded in terrns of the complete set basis, and A, μ and v are numerical parameters, which will be chosen to increase the overlaps. To enhance the mutual overlap only for the nearest-neighbour orbitals[8-10], we need to make μ and v equal to zero in eq. (2.5). In this case the rnodified orbitals reduce to

$$\bar{a}'_1 = a_1 + \lambda(a_2 + a_6)$$
$$\bar{a}'_2 = a_2 + \lambda(a_1 + a_3)$$
$$\bar{a}'_3 = a_3 + \lambda(a_2 + a_4) \qquad (2.6)$$
$$\bar{a}'_4 = a_4 + \lambda(a_3 + a_5)$$
$$\bar{a}'_5 = a_5 + \lambda(a_4 + a_6)$$
$$\bar{a}'_6 = a_6 + \lambda(a_1 + a_5)$$

The three pararneters of eq.(2.5) or the unique parameters of eq. (2.6) rnay be varied in order to minimize the energy. It is clear that using eq. (2.6) the compu-tational labour for the full orbital optimization can be reduced. However, in the next section it is shown that the energy obtained for the benzene rnolecule with the full optimization is always better than with the nearest-neighbour optimization.

3. **Results** and Conclusions

Table I shows the total energies (core plus π electron energies) of the ground state of the benzene molecule, for some partial calculations and the full-CI calcu-lations, obtained with the approaches described in the last section.

For comparison purposes, the SCF energy is also given in the table. All energies are in units of E_h (Hartrees) and we use in our calculations a minimal Clernenti basis set - (7s 3p/3s) Gaussian contracted to [2s 1p/1s]. The core energy obtained by us is -223.43406 E_h. In the second column of the table we give the corresponding nurnber of structures used in each case.

We can see from table I that the energy obtained with the p_z AOs of eq. (2.4), using the 5 covalent structures, is inferior to the single determinant MO

function. This difference is considerable, about 0.0857 E_h. This situation can only be corrected by adding a large number of polar structures, e.g. the 12 ortho-polar structures (see table I) of the type below

$$+ .a_1$$

$$a_2 \downarrow \qquad\qquad - .a_6$$

$$z_3 \downarrow \qquad\qquad \blacktriangledown a_5$$

$$a_4 \nearrow$$
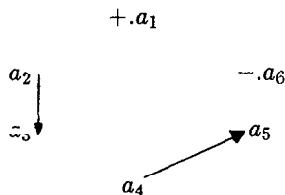
The situation is dramatically changed when the AOs involved are replaced by overlap-enhanced orbitals. The results of the parameter optimization of eqs. (2.5) and (2.6) are also shown in the table. It is at once clear that convergence towards the full-CI limit is now rapid.

If we use only the Kekulé structures, but modified AOs of the type described in eq. (2.6), the energy obtained in this case is better than the SCF and the energy obtained by eq. (2.4), using the covalent plus 12 ortho-polar structures. Furthermore, the difference between the energy obtained with this approach and the full-CI limit now is lower, 0.0133 E_h. On the other hand, if we use the fully optimized orbitals described by eq. (2.5) and only the Kekulé structures we have a better result than using the eq. (2.6), with all covalent structures.

Finally, the energy that we obtain using eq. (2.5) and all covalent structures is very closely equal to the result that we obtain if we use the full-CI calculation; the difference is only 0.0078 E_h. When using the spin-coupled theory instead one gets[6] a difference of the same order, 0.0070 E_h.

Cooper et. al,[6] concluded that the π electrons of benzene are essentially localized when described by deformed atomic orbitals (optimized orbitals). This description of the π electrons of the benzene molecule is in accordance with our results, because the modified orbitals used here are slightly delocalized, by admixture of the other orbitals, in order to enhance their mutual overlap.

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Table I - Total ground state snergy of the benzene molecule (with different ap-proaches)

Approach (theory)	Number of structures	Total energy (Hartrees)
eq. (2.4) Kekulé	2	-229.99247
eq. (2.4) Kekulé and **Dewar**	5	-229.99810
Single-configuration SCF	1	-230.08378
eq. (2.4) Kekulé, Dewar and orthopolar	17	-230.10768
eq. (2.6) Kekulé	2	-230.15269
eq. (2.6) Kekulé and Dewar	5	-230.15341
eq. (2.5) Kekulé	2	-230.15600
eq. (2.5) Kekulé and Dewar	5	-230.15810
Full-CI	175	-230.16595

The reason that classical VB theory associated to p, AOs (see eq. (2.4)) requires a vast number of physically untenable ionic structures is that those AOs are not allowed to distort on molecule formation. With the optimized orbitals (eqs. (2.5) and (2.6)) this problem. does not arise (becaiise the orbitals are deformed now). Such conclusions are equally applicable to molecules of different type. In summary, we conclude:

When we use the optimized orbitals (eq. (2.4) or (2.5)) the convergence of the energy to the full-CI limit is more rapid than when using the p, AOs. The full optimization of the orbitals is not always essential[8−10], but if this approach is

used, only the covalent structures can reproduce the results of the 175-structures on the benzene π electrons.

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Resumo

Aplica-se a teoria de ligação de valência para calcular a energia do estado fundamental dos elétrons π da molécula de benze.io. Usa-se uma base mínima para comparar a taxa de convergência da energia utilicando três aproximações a saber: orbitais atômicos puros, parcialmente otimizados e completamente otimizados. Verifica-se que quando se faz uma otimização completa dos orbitais atômicos, somente as estruturas covalentes são capazes de reproduzir os resultados de um cálculo completo de interação de configurações.

Existence of infinite exact eigensolutions for the $x^2 + \lambda x^2/(1 + gx^2)$ interaction

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Abstract   We show that a recent conjecture about the possible existence of an infinite number of exact eigensolution pairs for the $x^2 + \lambda x^2/(1 + gx^2)$ interaction having λ and g connected by $\lambda = -(6g^2 + 4g)$ is true. A constructive method for explicitly obtaining these solutions is given. In addition, we present a REDUCE implementation of the constructive method which allows solution pairs to be easily generated on personal computers.

1. Introduction

In a recent paper[1], we showed that the perturbed harmonic oscillator

$$x^2 + \lambda x^2/(1 + gx^2)$$

admits five pairs of exact analytical eigensolutions having the parameters λ and g connected by the relation $\lambda = -6g^2 - 4g$. It was also conjectured that an infinite number of such solution pairs should exist. Our conjecture was proved by Vanden Berghe and Meyer[2] and Lakhtakia[3]. The purpose of this brief paper is to provide a simple constructive proof of the same conjecture. Our proof was obtained by us simultaneously and independently of the aforementioned authors. We believe our result to be of interest because it provides a trivial mean of generating, in principle, all solution pairs. The generation of an arbitrary number of solution pairs can be easily implemented on personal computers able to perform algebra and an example of one such implementation, written in REDUCE, is given here.

The potential $x^2 + \lambda x^2/(1 + gx^2)$ is of interest in laser physics (as the reduction of the Fokker-Planck equation of a single-mode laser under suitable conditions), in

elementary particle physics (as a one-dimensional Schrödinger equation associated with a zero-dimensional field theory) and in nuclear physics (as being able to reproduce sequences of energy levels in the shell model). (For specific references see, for example, reference 1 and references therein.)

An interesting aspect of the $x^2 + \lambda x^2/(1 + gx^2)$ interaction with negative λ (as is the case here since $\lambda = -6g^2 - 4g$, $g > 0$) is that the potential behaves asymptotically like a harmonic oscillator but contains a double minimurn. Double minimum potentials have been used in the quantum theory of molecules as simple dynamical models to describe the motion of a particle subject to two centers of force. Double minimum potentials are also of great interest in the investigation of diffusive processes in general (quantum tunneling), models for bistable dynamics[4] and in the quantum theory of instantons[5]. The most used examples of double minimum potentials involve functions containing discontinuous derivatives. The potential considered in this paper, as well as its derivatives, is continuous and has a pair of analytical eigensolutions. For a discussion of these matters we refer to the recent review paper of Razavy and Pimpale[6].

The problem we want to address consists of obtaining pairs of simultaneous eigensolutions of the Schrödinger equation

$$\psi'' + [\varepsilon - x^2 - \lambda x^2/(1 + gx^2)]\psi = 0, \quad g > 0, \tag{1}$$

for x in the interval $(-\infty, \infty)$, having the generic form

$$\psi_o(x) = \exp\left(-\tfrac{1}{2}x^2\right)(1 + gx^2)x, \tag{2}$$

$$\psi_e(x) = \exp\left(-\tfrac{1}{2}x^2\right)(1 + gx^2)\varphi_N(x), \tag{3}$$

with

$$\varphi_N(x) = \sum_{i=0}^{N} c_i x^{2i}, \tag{4}$$

where the subindices o and e refer to the symmetry of the eigensolutions. The first five twin solutions have been obtained in reference 1. We now show how to generate twin solutions for arbitrary N.

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Substituting ψ_o from equation *(2)* in the Schrödinger equation *(1)* one obtains equations yielding

$$\varepsilon_o = 3 - 6g, \tag{5}$$

$$\lambda = -6g^2 - 4g. \tag{6}$$

From the substitution of ψ_e in equation *(1)* one readily obtains

$$\sum_{i=0}^{N} 2i(2i-1)c_i x^{2i} + \sum_{i=0}^{N} \left(\varepsilon_e + 4gi^2 + 6gi + 2g - 4i - 1\right) c_i x^{2i+2} \tag{7}$$
$$+ \sum_{i=0}^{N} \left(g\varepsilon_e - \lambda - 4gi - 5g\right) c_i x^{2i+4} = 0.$$

From the coefficients of x^{2i} it follows that

$$2i(2i-1)c_i + [2i(2i-1)g - 4i + 3 + \varepsilon_e]c_{i-1}$$
$$+ [3g + g\varepsilon_e - \lambda - 4gi]c_{i-2} = 0, \tag{8}$$

valid for $i = 1, 2, \ldots, N + 2$. When $i = N + 2$ equation *(8)* gives

$$4Ng + 5g - g\varepsilon_e + \lambda = 0. \tag{9}$$

Since according to equation *(6)* we have $\lambda = -6g^2 - 4g$, it follows that

$$\varepsilon_e = 4N - 6g + 1. \tag{10}$$

It is interesting to observe that the energy difference between the two states depends only on N:

$$\Delta\varepsilon = \varepsilon_e - \varepsilon_o = 4N - 2. \tag{11}$$

Equations *(6)* and *(10)* may now be used to simplify relation (8), giving the relation

$$c_i = \frac{-1}{2i(2i-1)}\{[2i(2i-1)g - 6g + 4(N - i + 1)]c_{i-1} + 4g(N - i + 2)c_{i-2}\}, \tag{12}$$

valid for $i = 1, 2, \ldots, N + 2$. For $i = 1$ equation *(12)* gives

$$c_1 = (2g - 2N)c_0. \tag{13}$$

Now, equations (12) and (13) can be used to generate all coefficients c, appearing in (4) as functions of c_0. For convenience we may set c_0 **r** 1, since the exact normalization is not important here.

The condition that all c, should vanish for $i > N$ ailows us to obtain (from equation (12) with $i = N + 1$) a relation between c_N and c_{N-1} :

$$c_N = \frac{-2}{(N+2)(2N-1)} c_{N-1}. \tag{14}$$

The polynomial equation defining the possible g values[1] may now be easily obtained by forcing c_N and c_{N-1} obtained from the recurrence relation (12) to obey the constraint relation (14).

. The above results were used to write the following REDUCE program:

```
OFF ECHO $
OPERATOR C $
N      := 5 $
C(0)   := 1 $
C(1)   := 2*(G-N) $
CTE    := -2/((N+2)*(2*N-1)) $
LAST   := CTE*C(N-1) $
FOR I := 2:N DO
C(I)   := - ( (2*I*(2*I-1)*G - 6*G + 4*(N-I+1))*C(I-1)
             +4*G*(N-I+2)*C(I-2) )/(2*I*(2*I-1)) $
FOR I := 1:N-1 DO WRITE "C(",I,")= ",C(I) $
WRITE "C(",N,")= ",CTE," * C(",N-1,")" $
WRITE " G POLYNOMIAL : " $
WRITE NUM(C(N)-LAST)," = O " $
END $
```

This program was implemented on a personal computer and, by changing the value of N on the third program line, used to generate all five solutions presented earlier[1]. The program was further used to generate new twin solutions. Table I presents a summary of the first 15 solutions, together with the corresponding values of ε_o, ε, and $V_{\min}$, the value of the minimum of the potential. Defining

$R^2 = 2g(3g + 2) = -\lambda$ it is easy to see that the minima are located at $x_{min}^2 = (R-1)/g$ and that

$$V_{min} = -\frac{1}{g}(R-1)^2. \tag{15}$$

Table I - Values of g for which twin solutions exist. $\Delta g \equiv g_N - g_{N-1}.\lambda, V_{min}, \varepsilon_o$ and ε_e are defined in equations (6), (15), (5) and (10) respectively. Note that for $N = 1$ and 2 the energy of the even state lies above the relative maximum $V = 0$ at $x = 0$.

N	g	Δg	λ	V_{min}	ε_o	ε_e
1	0.66667	—	−5.3	−2.6	−1.0	1.0
2	1.45743	0.79076	−18.6	−7.5	−5.7	0.3
3	2.23486	0.77743	−38.9	−12.3	−10.4	−0.4
4	3.00979	0.77494	−66.4	−17.0	−15.1	−1.1
5	3.78383	0.77403	−101.0	−21.7	−19.7	−1.7
6	4.55743	0.77361	−142.9	−26.3	−24.3	−2.3
7	5.33080	0.77337	−191.8	−31.0	−29.0	−3.0
8	6.10403	0.77322	−248.0	−35.6	−33.6	−3.6
9	6.87716	0.77313	−311.3	−40.3	−38.3	−4.3
10	7.65022	0.77306	−381.8	−44.9	−42.9	−4.9
11	8.42323	0.77302	−459.4	−49.6	−47.5	−5.5
12	9.19622	0.77298	−544.2	−54.2	−52.2	−6.2
13	9.96917	0.77295	−636.2	−58.9	−56.8	−6.8
14	10.74210	0.77293	−735.3	−63.5	−61.5	−7.5
15	11.51502	0.77292	−841.6	−68.1	−66.1	−8.1

Figure 1 shows the potential $x^2 + \lambda x^2/(1 + gx^2)$ together with two asymptotic potentials (shown as dashed lines): x^2 and $x^2 - 6g - 4$. Superimposed to these potentials we show the solutions ψ_o and ψ_e. The vertical positions of ψ_o and ψ_e correspond to the exact locations of their corresponding eigenenergies. To improve the readability of the figure, the normalization of the eigenfunctions was conveniently chosen so that their total amplitude corresponds to 25% of the full
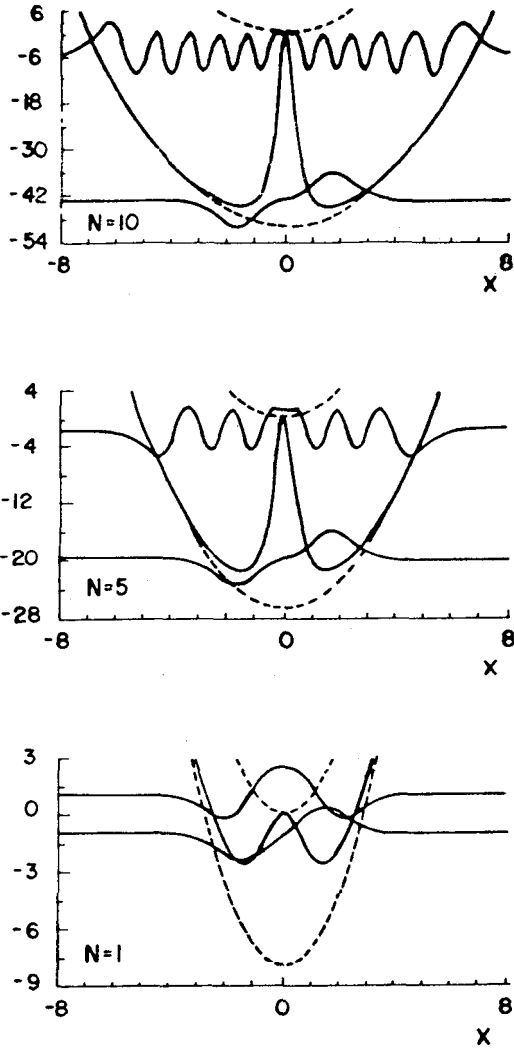
Fig. 1 - Eigenfunctions ψ_o and ψ_e together with the potential $x^2 + \lambda x^2/(1 + gx^2)$ (solid curve) and two asymptotic potentials (shown as dashed lines): x^2 and $x^2 - 6g - 4$. The height of the functions corresponds to the exact position of the energy eigenvalues.

scale. All ψ_e were obtained by evaluating numerically on a personal computer the coefficients c, in eq.(12). As a caveat to the reader we remark that the recurrence relation (12) is very sensitive to the value of g. Preliminary runs using the 6-digit values of g given in Table I, failed to generate the correct eigenfunctions. In particular, the g value used in Figure 1 to generate ψ_e for N = 10 was 7.650218591050418350. Sensitivity on parameters is a well-known property of recurrence relations. At this stage we do not see any need for a more stable (possibly backwards) recurrence relation.

In summary, the potential $x^2 + Xx^2/(1 + gx^2)$ with X and g connected by $\lambda = -6g^2 - 4g$, g > 0 contairis an infinite number of closed form eigensolution pairs. The pairs consist of an odd and an even solution having an energy difference depending only on the degree of excitation of the even funrtion (see eq.(11) above). We prescnted a computer program written in REDUCE allowing the easy generation of these eigensolutions on personal computers. The potential investigated is a quite rare example of a continuous double-minimum potential containing a pair of exact analytical eigensolutions.

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Resumo

Mostramos que uma conjectura recente sobre a possível existência de um número infinito de pares de soluções próprias exatas para a interação $x^2 + \lambda x^2/(1 + gx^2)$ com λ e g relacionados por $\lambda = -(6g^2 + 4g)$ é verdadeira. Damos ainda um método construtivo para obter explicitamente estas soluções. Além disso, apresentamos também uma implementação em REDUCE deste método construtivo que permite gerar algebricamente pares de soluções em microcomputadores do tipo PC.