Self Consistent Field and Adiabatic Approximations for Coupled Oscillations

FRANCISCO M. FERNÁNDEZ, GUSTAVO A. ARTECA,
SERGIO A. MALUENDES, HUGO O. VILLAR and EDUARDO A. CASTRO

Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas, Sección Química Teórica, Sucursal 4 — Casila de Correo 16, La Plata 1900, Argentina

Coupled oscillators are chosen as convenient models in order to show the practical utilization of the Self Consistent Field Method and the Adiabatic Approximation for instructional purposes. Results are compared with exactly values and a good agreement is found in every case.

1. INTRODUCTION

The Self Consistent Field (SCF) Method is so much important in different Physical fields that it deserves to have severa1 pedagogical examples in order to be able to show them in those introductory courses of Quantum Mechanics. There have been published some interesting articles on the theme up to now: the unidimensional He atom[1], and harmonic coupled oscillators.[2,3] The Adiabatic Approximation (AA) isanother well known method which is currently applied to study the electronic distribution in molecules and solids.[4,5] However, this method has not received an appropriate care from the pedagogical point of view because there are not simple enough models to show its application. It is well known that hamonic and anharmonic oscillator model have been widely used as illustrative ways to present the fundamental principles of the Quantum Mechanics. The purpose of this paper is to choose oscillators in order to call attention about the possible utilization as an instructional aid for analysing the SCF method and the AA. For that purpose we have chosen harmonic oscillators with anharmonic coupling terms. Such selection rests

upon the three following main reasons: a) these models appear in a natural way in molecular theory and the solution through SCF equations have been recently given[6-9], b) for certain coupling potentials, the resulting equations can be solved in an iterative way with the assistance of an ordinary manual calculator, and c) if one hss a series of examples which can be solved with great accuracy, then it is possible to examine the numerical methods which are currently used and so to know their deqrees of confidence.

The plan of the paper is as follows: in Section 2 we deduce the SCF equations we apply thcm to an anharmonic potential for which there are exact snlutions. Numerical results are compared with exact ones which were obtained previously. In Section 2 we make use of the AA to calcuiate a pair of oscillators which are coupled by an harmonic potential. Again, we compare with exact values, and the conditions of the applicability of the approximation is discussed.

2. SCF EQUATIONS

We start froin a Hamiltonian H given by

$$H = \sum_{i=1}^{N} H_i^0(x_i) + V(x_1, x_2, \ldots, x_N) \tag{1}$$

where

$$H_i^0 = T_i + V_i^0 \tag{2}$$

$$V(x_1, x_2, \ldots, x_N) = \sum_{i=1}^{N} \sum_{j>i}^{N} g_{ij} \, v_i(x_i) \, v_j(x_j) \tag{3}$$

As approximate eigenfunctions of H we choose

$$\phi(x_1, \ldots, x_N) = \prod_{i=1}^{N} \phi_i(x_i) \tag{4}$$

such that

$$\langle \phi_i | \phi_i \rangle = 1 \tag{5}$$

1054

The method consists in searching for an extremum of the energy E

$$E = \sum_{i=1}^{N} <\phi_i| H_i^0 \phi_i> + \sum_{i=1}^{N} \sum_{j>i}^{N} g_{ij} <\phi_i|v_i\phi_i> <\phi_j|v_j\phi_j>$$ (6)

through all possible variations $\delta\phi_i$ for $i = 1,\ldots,N$, and taking into account the condition (5). Consequently, we are led to introduce the Lagrange miiltipliers e_i and to consider the inconditional extremum of the functional $J(\phi)$ given by

$$J(\phi) = E(\phi) - \sum_{i=1}^{N} e_i <\phi_i | \phi_i>$$ (7)

The variation δJ is equal to

$$\delta J = \sum_{i}^{N} <\delta\phi_i|H_i^0\phi_i> + \sum_{i=1}^{N} \sum_{j>i}^{N} g_{ij}\{<\delta\phi_i|v_i\phi_i><\phi_j|v_j\phi_j> +$$

$$+ <\phi_i|v_i\phi_i><\delta\phi_j|v_j\phi_j>\} - \sum_{i=1}^{N} e_i <\delta\phi_i|\phi_i> + c.c. = 0$$ (8)

where $c.c$ denotes the complex conjugate of all terms in the r.h.s. of Eq. (8). The previous equation can be arranged in the following way

$$\delta J = \sum_{i=1}^{N} <\delta\phi_i| (H_i^0 + \sum_{j\neq i}^{N} g_{ij} <\phi_j|v_j\phi_j> v_i - e_i \phi_i > + c.c = 0$$

with $g_{ij} = g_{ji}$. We now define the SCF operators F_i as

$$F_i = H_i^0 + \sum_{j\neq i} g_{ij} <\phi_j|v_j\phi_j> v_i$$ (9)

since the variations $\delta\phi_i$ are arbitrary. Then, Eq.(8) will be satisfy for those ϕ_{n_i} which are eigenfunctions of F_i, i.e.

$$F_i \phi_{n_i} = e_{n_i} \phi_{n_i}$$ (10)

Eqs. (10) are easily solved for the case where

$$H_i^0 = -0.5\, D_i^2 + 0.5\, w_i^2\, x_i^2 \; ; \quad D_i \equiv \partial/\partial x_i \tag{11}$$

$$V = \sum_{i=1}^{N} \sum_{j>i}^{N} \{ g_{ij}^{(1)}\, x_i^2\, x_j \;\; + g_{ij}^{(2)}\, x_i\, x_j^2 + g_{ij}^{(3)}\, x_i^2\, x_j^2 \} \tag{12}$$

because now the SCF operators are identical with the corresponding to shifted harmonic oscillators

$$F_i = -0.5\, D_i^2 \;\; + 0.5\, (w_i^2 + 2\, A_i^{(1)} + 2\, A_i^{(3)})x_i + A_i^{(2)}\, x_i \tag{13}$$

where

$$A_i^{(1)} = \sum_{j\neq i} g_{ij}^{(1)} <\phi_j|x_j\phi_j> \; ; \; A_i^{(2)} = \sum_{j\neq i} g_{ij}^{(2)} <\phi_j|x_j^2\phi_j>$$

$$A_i^{(3)} = \sum_{j\neq i} g_{ij}^{(3)} <\phi_j|x_j^2\phi_j> \tag{14}$$

Energies e_{n_i} are equal to

$$e_{n_i} = (n_i+0.5)\, (w_i^2 + 2(A_i^{(2)} + A_i^{(3)}))^{1/2} - (A_i^{(2)})^2 / \; (w_i^2 + 2(A_i^{(1)} +$$

$$+ A_i^{(3)})) \tag{15}$$

The total energy of the system is calculated from Eq.(6), which can be written as

$$E = \sum_{i=1}^{N} e_{n_i} - <\phi|V\,\phi> \tag{16}$$

In order to exemplify the procedure in a precise and self-explanatory manner, we present a coupled of bidimensional examples:

Exarnple I. This case has previously been considered with the help of the SCF method[g]

$$H = -0.5\, D_1^2 - 0.5\, D_2^2 + 0.5\, w_1^2\, x_1^2 \;\; + 0.5\, w_2^2\, x_2^2 + a\, x_1^2\, x_2^2 \tag{17}$$

$$\phi = \phi_{n_1}(x_1)\ \phi_{n_2}(x_2)$$

$$F_1 = -\,0.5\,D_1^2 + 0.5\,(w_1^2 + 2\,a\,A_1)\,x_1^2 \ ; \ A_1 = \langle\phi_{n_2}|x_2^2\ \phi_{n_2}\rangle \tag{18}$$

$$F_2 = -\,0.5\,D_2^2 + 0.5\,(w_2^2 + 2\,a\,A_2)\,x_2^2 \ ; \ A_2 = \langle\phi_{n_1}\ x_1^2\ \phi_{n_1}\rangle \tag{19}$$

The functions $\phi_{n_i}(i{=}1,2)$ are eigenfunctions of a Hamiltonian operator corresponding to harmonic oscillators with effective frequencies $W_i = (w_i^2 + 2\,a\,A_1)^{1/2}$, so that the eigenvalues are

$$e_{n_i} = (n_i + 0.5)W_i \ ; \ i = 1,2 \tag{20}$$

The resolution is completed by applying the virial theorem

$$\langle|F_i,x_i D_i|\rangle = 2\langle T_i\rangle - W_i^2\ \langle x_i^2\rangle = 2\,e_{n_i} - 2\,W_i^2\ \langle x_i^2\rangle = 0 \tag{21}$$

from which one obtains two equations for A_i $(i{=}1,2)$. There with the equations (22-23) can be solved numerically in an iterative way with a manual calculator

$$A_2 = (n_1 + 0.5)(w_1^2 + 2\,a\,A_1)^{-1/2} \tag{22}$$

$$A_1 = (n_2 + 0.5)(w_2^2 + 2\,a\,A_2)^{-1/2} \tag{23}$$

After obtaining A_i, one calculates e_{n_i} from Eq. (20) and lastly the total energy E_{n_1,n_2} is given by

$$E_{n_1,n_2} = e_{n_1} + e_{n_2} - a\,A_1\,A_2 \tag{24}$$

In Table I results are shown, together with exact values given by Percival and Pomphrey[10] and energies for free oscillators (e_{n_1,n_2}^{H0}). The comparison is made taking into account the dissociation energy E_D

$$E_D = -\,w_1^2 w_2^2\,/\,4\,a = 58817.9\ cm^{-1} \tag{25}$$

and the following values for the constants

1057

Tabie I - Comparison of exact, free, and SCF method eigenvalues for two coupled oscillators with interaction potencial a $x_1^2 x_2^2$.

		$w_1^2 = 1 \quad - \quad w_2^2 = 0.5 \quad - \quad a = -0.003$		
n_1	n_2	$e_{n_1 n_2}^{HO}$	$E_{n_1 n_2}^{SCF}$	$e_{n_1 n_2}$ (Ref.10)
0	0	1204.90	1203.40	1203.29
0	1	2203.07	2198.56	2198.35
1	0	2616.53	2612.01	2611.77
0	2	3201.25	3193.71	3193.39
1	1	3614.70	3601.12	3600.78
2	0	4028.16	4020.61	4020.23

$$w_1^2 = 1 \; ; \; w_2^2 = 0.5 \; ; \; a = -0.003 \qquad (26)$$

We can see that a is small enough so that the SCF solutions are very alike to the exact functions.

Example II. Our second example is the Barbanis' Hamiltonian, and it has been widely studied. The Hamiltonian operator is

$$H = -0.5 \ (D_1^2 + D_2^2) + 0.5 \ w_1^2 \ x_1^2 + 0.5 \ w_2^2 \ x_2^2 + a \ x_1 \ x_2^2 \qquad (27)$$

The calculation scheme is similar to the corresponding one is Example I and results are

$$F_1 = -0.5 \ D_1^2 + 0.5 \ w_1^2 \ x_1^2 + a \ A_1 \ x_1 \ ; \ A_1 = <\phi_{n_2}|x_2^2|\phi_{n_2}> \qquad (28)$$

$$F_2 = -0.5 \ D_2^2 + 0.5 \ (w_2^2 + 2 \ a \ A_2)x_2^2 \ ; \ A_2 = <\phi_{n_1}|x_1 \ \phi_{n_1}> \qquad (29)$$

Over again, F_2 is an Hamiltonian operator associated to an harmonic oscillator, while F, corresponds to a shifted oscillator. The eigenvalues are

1058

$$e_{n_1} = (n_1 + 0.5)w_1 - a^2 A_1^2 / (2 w_1^2) \tag{30}$$

$$e_{n_2} = (n_2 + 0.5)(w_2^2 + 2 a A) ^{1/2} \tag{31}$$

From the virial relationship

$$<\phi_{n_1} | |F_1, D_1| | \phi_{n_1}> = 0 \tag{32}$$

it follows the first equation which relates A_1 with A_2, i.e.

$$A = - a A_1 / w_1^2 \tag{33}$$

while the second equation is obtained from the virial theorem for F_2

$$A_1 = (n_2 + 0.5)(w_2^2 + 2 a A_2)^{-1/2} \tag{34}$$

The total energy is $E_{n_1, n_2} = e_{n_1} + e_{n_2} - a A_1 A_2$

In Table II our results are given, together with the exact eigenvalues[11-15], and the corresponding values to a pair of harmonic oscillators (HO). Two main facts can be observed from numerical values; a) SCF values are between harmonic oscillators and exact ones, in accordance with theoretical predictions; b) errors for SCF results increase with n_1. Then, 4_{n_1} does not represent well the behavior of the exact function. Let us suppose that $\delta\phi$ is a possible variation for which ϕ is stable, i.e.

$$\mathbf{SE} = <\delta\phi|H\phi> + <\phi|H \delta \phi> = 0 \tag{35}$$

and, furthermore, that H depends on a parameter a. Then,

$$\partial E/\partial a = <\partial\phi/\partial a|H\phi> + <\phi|H\partial\phi/\partial a> + <\partial H/\partial a> \tag{36}$$

We can see that if $\partial\phi/\partial a$ represents one compatible variation which satisfies Eq. (35) then ϕ will satisfy the Hellmann-Feynman theorem. In our actual case it is so because

$$\partial\phi/\partial a = \sum_i \partial\phi_{n_i}/\partial a \prod_{j \neq i} \phi_{n_j} \tag{37}$$

Table II - Comparison of exact, free, and SCF eigenvalues for the Barbanis' Hamiltonian.

n_1	n_2	$e^{HO}_{n_1 n_2}$	$E^{AA}_{n_1 n_2}$	$e_{n_1 n_2}$ (Ref.6)
$w_1^2 = 1.6$	$-$	$w_2^2 = 0.9$	$-$	$\alpha = -0.008$
0	0	1.1068	1.1062	1.1058
0	1	2.0555	2.0504	2.0491
1	0	2.3717	2.3712	2.3679
0	2	3.0042	2.9901	2.9896
1	1	2.3204	3.3154	3.3056
2	0	3.6366	3.6360	3.6301

is one of the compatible variations with the SCF functions. For the Barbanis' Hamiltonian we have

$$\partial E_{n_1,n_2}/\partial a = \partial e_{n_1}/\partial a - A_1 A_2 - a \, \partial A_1/\partial a \, A_2 - a \, A_1 \, \partial A_2/\partial a + \partial e_{n_2}/\partial a \tag{38}$$

$$\partial e_{n_1}/\partial a = A_1 A_2 + a \, A_2 \, \partial A_1/\partial a \tag{39}$$

$$\partial e_{n_2}/\partial a = A_1 A_2 + a \, A_1 \, \partial A_2/\partial a \tag{40}$$

Replacing Eq. (39) and Eq. (40) in Eq. (38) we get the desired result

$$\partial E_{n_1,n_2}/\partial a = A_1 A_2 = \langle \partial H/\partial a \rangle \tag{41}$$

3. ADIABATIC APPROXIMATION

In order to offer a clear presentation of the AA in such a way that details can be transparently apprehended, we have chosen a kind of interaction potential which has the property of being disengaged through an appropriate change of variables. Then, equations are

solved in an exact form and it allows us to offer an illustrative comparison. The Hamiltonian operator is

$$H = - D_1^2/2m_1 - D_2^2/2m_2 + k_1 \, r_1^2/2 + k_2 \, r_2^2/2 + g \, r_1 \, r_2 \qquad (1)$$

where $D_i \equiv \partial/\partial r_i$.

Let us assume that k_1, k_2 and g are numerically of comparative orders. Defining the new set of variables x_i from the relarionships

$$x_i = m_i^{1/2} \, r_i \qquad (2)$$

the Hamiltonian (1) is re-written in the following way

$$H = - (d_1^2 + d_2^2)/2 + (w_1^2 \, x_1^2 + w_2^2 \, x_2^2)/2 + a \, x_1 \, x_2 \qquad (3)$$

where

$$d_i \equiv \partial/\partial x_i \; ; \; w_i = (k_i/m_i)^{1/2} \; ; \; a = g \, (m_1 m_2)^{-1/2} \qquad (4)$$

If $m_1 \ll m_2$, then

$$w_2^2/w_1^2 = (m_1 \, k_2)/(m_2 \, k_1) \ll 1 \quad \text{and} \quad a/w_1^2 = g \, m_1^{1/2} \, / (k_1 \, m_2^{1/2}) \ll 1 \qquad (5)$$

The variable x_1, being associated to the lighter mass, will describe the faster movement (greater vibration frequency) and, consequently, x_2 correspond to the slower movement. Under such conditions we can make use of the AA, starting from an approximate wavefunction defined by

$$\phi(x_1, x_2) = X_{n_1, n_2}(x_2) \, \phi_{n_1}(x_1; x_2) \qquad (6)$$

where $\phi_{n_1}(x_1; x_2)$ is eigenfunction of the Hamiltonian operator H_1

$$H = - d^2/2 + w_1^2 \, x_1^2/2 + a \, x, \; x_2 = - d_1^2 + w_1^2 (x_1 + ax_2/w_1^2)^2 -$$

$$- (a \, x_2)^2 \, /(2w_1^2) \qquad (7)$$

and the eigenvalues are given by the formula

$$e_n(x_2) = (n_1 + 0.5)w_1 - (ax_2)^2/(2\ w_1^2) \tag{8}$$

$X_{n_1\ n_2}(x_2)$ has to be eigenfunction of E_n

$$H_{n_1} = -0.5\ d_2^2 + 0.5(w_2^2 - a^2/w_1^2)x_2^2/(n_1 + 0.5)w_1 \tag{9}$$

The Hamiltonian (9) corresponds to an harmonic oscillator provided that the condition

$$a < w_1\ w_2 = (k_1\ k_2/(m_1\ m_2))^{1/2}$$

is fulfilled. This condition is equivalent to

$$g < (k_1 k_2)^{1/2}$$

Under such supposition, the eigenvalues of H_{n_1} are

$$e_{n_1\ n_2} = (n_2 + 0.5)(w_2^2 - a^2/w_1^2)^{1/2} + (n_1 + 0.5)\ w_1 \tag{10}$$

For the purpose of getting the exact solutions, it is necessary to perform a change of variables which transforms the potentiaf energy in a sum of square terms; i.e. the matrix

$$\begin{pmatrix} w_1^2 & a \\ a & w_2^2 \end{pmatrix} \tag{11}$$

must be diagonalized.

If s_1, s_2 are the new variables, then the Hamiltonian (3) will adopt the form

$$H = -(der_1^2 + der_2^2)/2 + (p_1\ s_1^2 + p_2\ s_2^2)/2 \tag{12}$$

where

$$der_i \equiv \partial/\partial s_i \; ; \; i \; = 1,2$$

and p_1, p_2 are the eigerivalues of the matrix (11) and they are given by

$$p_1 \; = 0.5 \; (w_1^2 + w_2^2) \; + \; ((w_1^2 - w_2^2)^2/4 + a^2)^{1/2} \qquad (13)$$

$$p_2 \; = 0.5 \; (w_1^2 + w_2^2) \; - \; ((w_1^2 - w_2^2)^2/4 + a^2)^{1/2} \qquad (14)$$

If the Hamiltonian (12) stands for two harmonic oscillators, then p_1 and p_2 have to positive, and we are carried again to the previously assumed condition

$$a < w_1 \; w_2$$

This point deserves special attention because it makes plain that the conditions which constants have to satisfy to obtain bonding states are the same for approximate and exact functions. The exact energy of the systeni is

$$E_{n_1 n_2} \; = (n_1 + 0.5) \; p_1^{1/2} + (n_2 + 0.5) \; p_2^{1/2} \qquad (15)$$

Now we wish to show that when the condition $m_1 \ll m_2$ is satisfied, then exact eigenenergies (15) approach to approxirnate energies (10). Starting from a power series expansion of the square root, we have

$$((w_1^2 - w_2^2)^2/4 + a^2)^{1/2} = 0.5(w_1^2 - w_2^2)(1 + 4a^2/(w_1^2 - w_2^2)^2)^{1/2} \simeq$$

$$\simeq 0.5 \; (w_1^2 - w_2^2)(1 + 2a^2/(w_1^2 - w_2^2)^2) = 0.5(w_1^2 - w_2^2) +$$

$$+ \; a^2/(w_1^2 - w_2^2)$$

Then

$$p_1 \simeq w_1^2 + a^2(w_1^2 - w_2^2)^{-1} \simeq w_1^2 + a^2/w_1^2 - w_1^2(1 + a^2/w_1^4) \qquad (16)$$

$$p_2 \simeq w_2^2 - a^2/(w_1^2 - w_2^2)^{-1} \simeq w_2^2 - a^2/w_1^2 \qquad (17)$$

Taking into account that

$$1 \gg a^2/w_1^4$$

and replacing Eqs. (16-17) in Eq. (15), we get Eq. (10). Due to

$$p_1 > w_1^2 \quad \text{and} \quad p_2 > w_2^2 - a^2/w_1^2$$

we can be sure that

$$E_{n_1 \ n_2} > e_{n_1 \ n_2} \tag{18}$$

It is in agreement with the general results presented by Epstein[16] for the ground state. In Figure I exact eigenvalues E , are compared with those obtained from the $AA(e_{0 \ 0})$ for the following constants
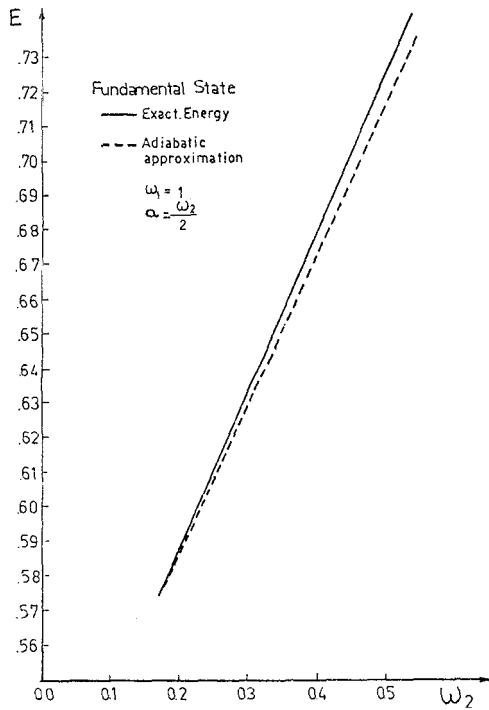
$$w_1 = 1 \ ; \ a = w_2/2 \ ; \quad 0.1 < w_2 < 0.6$$

Fig. I - Comparison of exact and adiabatic approximation energies for the ground state of two coupled oscillators with interaction potential $ar_1 r_2$.

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