

## VI. PERTURBATION THEORY WITHOUT WAVE FUNCTION

### 29. 1D Models

We showed in section 9 how the RSPT allows one to obtain the energy and the wave function corrections via the resolution of some differential equations. Here we present a method that combines HR and PT and has proven to be extremely powerful when it is applied to simple models.

Since the wave function does not require any explicit evaluation at any moment, this procedure is called Perturbation Theory Without Wave Function (PTWWF).

Let us consider a dimensionless 1D Hamiltonian

$$H = -\frac{1}{2}D^2 + V(x) \quad (1)$$

whose bound states  $\psi_j$  meet the boundary condition

$$\lim_{|x| \rightarrow \infty} x^n \psi_j(x) = 0 \quad (2)$$

We have deduced in section 5 the way to get a recursion relationship for the matrix elements of the x-powers:

$$\begin{aligned} \frac{1}{4}N(N-1)(N-2)\langle i|x^{N-3}|j\rangle + N\Omega_{ij}\langle i|x^{N-1}|j\rangle - 2N\langle i|x^{N-1}V|j\rangle - \\ - \langle i|x^N V'|j\rangle + \frac{2}{N+1}\langle i|x^{N+1}|j\rangle = 0 \end{aligned} \quad (3)$$

$$\frac{1}{4}N(N-1)(N-2)\langle x^{N-3}\rangle + 2NE\langle x^{N-1}\rangle - 2N\langle x^{N-1}V\rangle - \langle x^N V'\rangle = 0 \quad (4)$$

The true recursion is obtained when  $V$  can be expanded in an x-power series. Supposing the potential  $V(x)$  is

$$V(x) = \frac{1}{2}x^2 + \alpha x^{2m} \quad (5)$$

and replacing (5) in (4) we obtain

$$2NEA^{N-1} + \frac{1}{4}N(N-1)(N-2)A^{N-3} - (N+1)A^{N+1} - 2(N+m)\alpha A^{N+2m-1} = 0; A^N_{E=\langle x^N \rangle} \quad (6)$$

Since  $H$  depends on the parameter  $\alpha$ , we can apply the HFT

$$\partial E / \partial \alpha = A^{2m} \quad . \quad (7)$$

Swenson and Danforth [1] showed the convenience of combining Eq. (6) with PT. Expanding all the terms in  $\alpha$ -power series

$$A^N = \sum_{s=0}^{\infty} A_s^N \alpha^s \quad ; \quad E = \sum_{s=0}^{\infty} E^s \alpha^s \quad ; \quad E_n^0 = n + \frac{1}{2} \quad (8)$$

and resorting to the equality

$$\sum_s s E^s \alpha^{s-1} = \sum_s A_s^{2m} \alpha^s \quad \therefore \quad s E^s = A_{s-1}^{2m} \quad (9)$$

we can write (6) as follows:

$$\begin{aligned} & 2N \sum_{s=0}^M E^s A_{M-s}^{N-1} + \frac{1}{4} N(N-1)(N-2) A_M^{N-3} - (N+1) A_M^{N+1} - 2(N+m) A_{M-1}^{N+2m+1} = \\ & = 2NE^0 A_M^{N-1} + 2N \sum_{s=1}^M A_{s-1}^{2m} A_{M-s}^{N-1} s^{-1} + \frac{1}{4} N(N-1)(N-2) A_M^{N-3} - \\ & - (N+1) A_M^{N+1} - 2(N+m) A_{M-1}^{N+2m+1} = 0 \quad . \end{aligned}$$

This last equation can be rearranged in such a manner to obtain a recursion formula to calculate the whole set of  $A_M^N$  elements:

$$\begin{aligned} A_M^{N+1} = & \frac{2NE^0}{N+1} A_M^{N-1} + \frac{N(N-1)(N-2)}{4(N+1)} A_M^{N-3} + \frac{2N}{N+1} \sum_{s=1}^M A_{s-1}^{2m} A_{M-s}^{N-1} s^{-1} - \\ & - 2 \frac{(N+m)}{(N+1)} A_{M-1}^{N+2m+1} \quad . \quad (10) \end{aligned}$$

Eq. (10) together with the normalization condition

$$A_M^0 = 0 \quad \text{when } M \neq 0; \quad A_M^0 = 1 \quad \text{for } M=0$$

solves completely the problem [1].

The great advantage offered by this kind of perturbative recursion equations is that they can be easily programmed for a computer and besides they admit straightforward developments to arrive at analytical expressions.

This powerful method has found, for example, an interesting application in rotational-vibrational spectroscopy because it permits the calcula-

tion of the matrix elements for the powers of internuclear displacements (measured from the equilibrium position) of diatomic molecules in a  $^1\Sigma$  state [2-4]. The numerical results arising from this methodology are more exact than other ones obtained by different techniques, as demonstrated for  $H_2$ ,  $HCl$  [2,3] and  $CO$  [4].

### 30. Central Potential Systems

The applicability of the method presented in section 29 is not restricted to 1D quantum models, but it may as well be employed to study ND systems with central fields. It is due to the well-known fact that, after the angular variables are set aside, the resulting radial Schrödinger equation is 1D.

The procedure is similar to that described previously. For example, for the 3D case we can start from Eq. (72), section 5:

$$\frac{1}{2}N(N-1)(N-2)\langle r^{N-3} \rangle + 2NE\langle r^{N-1} \rangle - 2N\langle r^{N-1} U_\ell \rangle - \langle r^N U_\ell' \rangle = 0$$

$$E = E_{n\ell}$$

$$\frac{1}{2}N(N-1)(N-2)\langle r^{N-3} \rangle + 2NE\langle r^{N-1} \rangle + 2N\langle r^{N-1} V \rangle - \langle r^N V' \rangle - \ell(\ell+1)(N-1)\langle r^{N-3} \rangle = 0 \quad (11)$$

The application of the PTWV to central potential systems was made for the first time by Killingbeck [5]. He studied the spherically symmetric states of the hydrogen atom under a perturbation  $\lambda r$ , i.e.

$$V(r) = -r^{-1} + \lambda r \quad (12)$$

The replacement of (12) in (11) (with  $\ell=0$ ) gives

$$\frac{1}{2}N(N-1)(N-2)A^{N-3} + 2NEA^{N-1} + (2N-1)A^{N-2} - (2N+1)\lambda A^N = 0 \quad (13)$$

where

$$A^N \equiv \langle r^N \rangle$$

The expansion of  $A^N$  and  $E$  in  $\lambda$ -power series plus the application of the HFT as described in section 29, gives:

$$A_M^N = \frac{1}{2(N+1)E^0} \left\{ -2(N+1) \sum_{s=1}^M s^{-1} A_{s-1}^1 A_{M-s}^M - \frac{1}{2} N(N^2-1) A_M^{N-2} + \right. \\ \left. + (2N+3) A_{M-1}^{M+1} - (2N+1) A_M^{N-1} \right\} \quad (14)$$

This last equation together with the initial conditions

$$A_0^0 = 1; E_n^0 = -(2n^2)^{-1} \quad (15)$$

permits us to solve completely the problem.

The energy corrections are calculated with the relation

$$ME^{(M)} = A_{M-1}^1 \quad (16)$$

that arises from the HFT.

Grant and Lai [6] applied this procedure to study screened Coulomb potentials

$$V(r) = -Zr^{-1} f(\lambda r); \quad f(\lambda r) = \sum_{s=0}^{\infty} V_s(\lambda r)^s \quad (17)$$

These authors derived an analytic energy formula corrected up to the sixth-order, and with computer calculations, up to the twentieth-order, showing in a conclusive manner that whenever possible, this method is better than the RSPT and the analytical PT.

It is necessary and convenient to remember that the validity of all previous expressions in this section require the fulfillment of the limit condition

$$\lim_{r \rightarrow \infty} r^n \psi = 0 \quad (18)$$

### 31. 1D Systems with Periodic Potentials

The examples given before to apply PTWWF are referred to infinite spatial systems, where the wave functions corresponding to bound states tend to zero in an exponential manner when the coordinates tend towards infinite (Eqs. (2), (18)).

Here we will show how it is possible to extend such a methodology for periodic systems. In particular, we will pay special attention to two belonging to the field of Theoretical Chemistry:

- a) Rotation of atomic groups in polyatomic molecules and crystals;
- b) Electrons in metals.

a) Periodic boundary conditions appear in a natural manner in several fields of the Theoretical Chemistry and the following examples are representative.

Considering the diatomic molecules in a crystal as hindered rotators Pauling [7] showed theoretically that if the intermolecular forces and inertia moments are large enough, such molecules behave as an oscillator while in the case these quantities are small, the molecules resemble a free rotator. Later on, Stern [8] continued Pauling's analysis in a deeper way with the purpose to obtain a better information about the statistical weights for the first quantum states. Some molecules have two or more polar groups incapable to rotate freely owing to the electric fields produced by such groups.

Lennard-Jones [9] studied the dipolar moments of this kind of molecules with the aim to determine the interaction among these polar groups.

Periodic potentials also appear when studying the internal rotation of a group of atoms in a molecule [10]. For example, Koehler and Dennison [11] discussed the OH hindered rotation problem in the methanol molecule with the help of the hindered rotor model for the periodic potential  $V(x) = \frac{1}{2}H(1 - \cos 3x)$ .

Kilb et al. [12] proposed a similar potential function to study the energy levels associated to the internal torsion in molecules such as  $\text{CH}_3\text{CHO}$ ,  $\text{CD}_3\text{CHO}$ ,  $\text{CH}_2\text{DCHO}$ ,  $\text{CH}_3\text{SiH}_2\text{D}$ ,  $\text{CH}_3\text{OH}$ , etc.

Other excellent contributions have been published on this field [13-20] which show clearly the attention paid by theoretical chemists to the phenomena of internal rotation in molecules.

Some of these works have been mentioned previously, i.e. [15-17] in section 19. References [19,20] present a detailed account on this theme.

The basic problem may be stated as

$$H\psi = E\psi \quad ; \quad H = -\frac{1}{2}D^2 + V(x) \quad (19)$$

where  $V(x)$  is a periodic potential describing the rotation

$$V(x+p) = V(x) \quad . \quad (20)$$

Among all the  $H$ -eigenfunctions the only acceptable ones are those that have the same periodicity as the potential function, i.e.

$$\psi_i(x+p) = \psi_i(x) \quad . \quad (21)$$

In order to be valid the HT presented in this first part, it is necessary that the  $H_0$  satisfy the equation

$$\langle \psi_i | H\omega\psi_j \rangle = \langle H\psi_i | \omega\psi_j \rangle \quad . \quad (22)$$

Taking into account that

$$\int_0^P \psi_i^* T\omega\psi_j dx = \int_0^P (T\psi_i)^* \omega\psi_j dx + \frac{1}{2} \{ |\psi_i^* \omega\psi_j|_0^P - |\psi_i^* (\omega\psi_j)'|_0^P \} \quad (23)$$

then we see that (22) implies

$$|\psi_i^* \omega\psi_j|_0^P - |\psi_i^* (\omega\psi_j)'|_0^P = 0 \quad . \quad (24)$$

The simplest way to meet this requisite is to choose the  $H_0$   $\omega$  such that  $\omega\psi_j$  has a period  $p$ .

But we made precisely this choice in section 5, obtaining the equations

$$ik_s \left\{ \frac{\Omega}{nm} - \frac{k_s^2}{4} - \frac{\omega}{k_s^2} \right\} \langle n | f_s | m \rangle - 2ik_s \langle n | f_s V | m \rangle - \langle n | f_s V' | m \rangle = 0 \quad (25)$$

$$f_s(x) = \exp(ik_s x) \quad ; \quad k_s = 2\pi sp^{-1} \quad . \quad (26)$$

Since the potential is periodic, it can be expanded as a Fourier power series:

$$V(x) = \sum_{s=-\infty}^{+\infty} C_s p^{-\frac{1}{2}} \exp(2\pi i s x p^{-1}) = \sum_{s=-\infty}^{+\infty} V_s f_s(x) \quad (27)$$

where  $V_s = \rho^{-\frac{1}{2}} C_s = \rho^{-1} \int_0^p V(x) f_s(x) dx$ .

The substitution of (27) in (25) gives an equation that relates the  $f_s$  matrix elements among themselves:

$$k_s \left\{ \Omega_{nm} - \frac{k_s^2}{4} - \frac{\omega_{nm}^2}{k_s^2} \right\} \langle n | f_s | m \rangle - \sum_{t=-\infty}^{\infty} V_t (2k_s + k_t) \langle n | f_{s+t} | m \rangle = 0 \quad (28)$$

When  $n=m$  Eq. (28) simplifies to

$$k_s \left( 2E - \frac{k_s^2}{4} \right) A^s - \sum_{t=-\infty}^{+\infty} V_t (2k_s - k_t) A^{s+t} = 0; \quad A^s \equiv \langle f_s \rangle \quad (29)$$

The expansion of the real function  $\rho(x) = |\psi|^2$  in Fourier series

$$\rho(x) = \sum_{s=-\infty}^{\infty} \rho_s f_s; \quad \rho_s = \rho^{-1} \int_0^p \rho(x) f_s(x) dx = \rho^{-1} A^s \quad (30)$$

shows clearly that

$$A^s = A^{-s} \quad (31)$$

Then, all the calculations can be reduced to the case  $s \geq 0$ .

The expansion of the periodic potential (usually unknown) in Fourier series is the procedure usually employed to solve Eq. (19) [7,9,11-20]. In many cases one retains just one term of the complete expansion.

For simplicity sake here we use a periodic potential such that  $V_s = 0$  when  $s > 1$  and  $p = \pi$ :

$$V(x) = V_0 (1 + 2V_1 V_0^{-1} \cos 2x) \quad (32)$$

This kind of potential is widely used [7,9,18-20] and leads us to the Mathieu equation [21]. Usually this equation is written in one of the following equivalent forms:

$$-\frac{1}{2}\psi'' + \psi \alpha \cos 2x = \epsilon \psi \quad (33a)$$

$$\psi'' + (a - 2\alpha \cos 2x)\psi = 0 \quad (33b)$$

$$\psi'' + (b - S \cos^2 x)\psi = 0 \quad (33c)$$

where

$$\epsilon = E - V_0; \alpha = 2V_1 V_0^{-1}; a = 2\epsilon; S = 4\alpha; b = 2\epsilon + S/2. \quad (34)$$

As stated at the beginning of this section, our interest is to apply the PTWWF for periodic problems. Eq. (33a) is the more appropriate for our needs, so we get the relationships:

$$\left\{ \Omega_{nm} - s^2 - \frac{\omega_{nm}^2}{4s} \right\} \langle n | f_s | m \rangle = \frac{2s+1}{s} \alpha \langle n | f_{s+1} | m \rangle + \frac{2s-1}{s} \alpha \langle n | f_{s-1} | m \rangle \quad (35)$$

$$(2E - s^2) A^s = \alpha \frac{2s+1}{s} A^{s+1} + \frac{2s-1}{s} \alpha A^{s-1}. \quad (36)$$

The expansion of  $E$  and  $A^s$  in  $\alpha$ -power series and the posterior equalization of the polynomial coefficients in (36) yields:

$$2 \sum_{t=0}^M E^t A_{M-t}^s - s^2 A_M^s = \frac{2s+1}{2s} A_{M-1}^{s+1} + \frac{2s-1}{2s} A_{M-1}^{s-1}. \quad (37)$$

The application of the HFT permits that Eq. (37) may be written in terms of the elements  $A_M^s$ :

$$\partial E / \partial \alpha = \langle \cos 2x \rangle = \frac{1}{2} (A^1 + A^{-1}) = A^1 \quad (38)$$

$$t E^t = A_{t-1}^1. \quad (39)$$

Finally, the substitution of (39) in (37) gives

$$(2E^0 - s^2) A_M^s = \frac{2s+1}{2s} A_{M-1}^{s+1} + \frac{2s-1}{2s} A_{M-1}^{s-1} - 2 \sum_{t=1}^M \frac{A_{t-1}^1 A_{M-t}^s}{t}. \quad (40)$$

In order to use the recursion formula (40) it is necessary to know the zero order solutions ( $\alpha=0$ ). In this actual case, they are the free rotor eigenfunctions and eigenvalues

$$\psi_n^0 = \pi^{-\frac{1}{2}} \exp(2inx); \quad E_n^0 = 2n^2. \quad (41)$$

Every zero-order level is doubly degenerate. On the other hand, it is known that there are not two different eigenfunctions of the Mathieu equation corresponding to the same eigenvalue [21]. These properties assure us that when using PT the degeneracy must be broken. However, considering the equality

$$\langle n | \cos 2x | n \rangle = \int_0^\pi \cos^2 x dx = 0 \quad (42)$$



we conclude that the degeneration is split when the corrections of orders higher than 1 are calculated. This property was not taken into account by some authors [22], but later on it was recognized [23,24]. The PT as presented in Appendix IV is useful to treat this problem and it shows easily that when calculating the second-order correction only the first excited state degeneration is broken [23,24].

Eq.(23) of Appendix IV allows us to deduce that a non-zero second-order correction requires that the following matrix elements

$$\langle n | \cos 2x | m \rangle \langle m | \cos 2x | -n \rangle ; m \neq n$$

must be non-vanishing, and it is possible only when

$$m - n = \pm 1 \quad \text{and} \quad -n - m = \pm 1 \quad . \quad (43)$$

The only states satisfying (43) are  $n=0$  and  $n=1$ , but since  $n=0$  is non-degenerate, the unique level capable to split in the second-order correction is, as stated before, the first excited state.

Consequently, it is supposed that the remaining levels are split for higher-order correction. This possibility poses a problem to employ PTWWF not found before. However, the solution is straightforward: since the even potential  $\cos 2x$  demands even or odd solutions, we just have to combine the functions  $\psi_n^o$  in such a manner that the resulting linear combinations possess a definite parity:

$$\psi_{ne}^o = 2^{-\frac{1}{2}} (\psi_n^o - \psi_{-n}^o) \quad (44)$$

$$\psi_{no}^o = 2^{-\frac{1}{2}} (\psi_n^o + \psi_{-n}^o) \quad . \quad (45)$$

Having solved this difficulty for the zero-order solution we can proceed with the procedure:

$$\underline{M = 0}$$

$$(4n^2 - s^2)A_0^s = 0 \quad (46)$$

$$A_0^s = 0 \text{ for } s \neq 2n.$$

$$\begin{aligned} A_0^{2n} &= 2^{-1} \int_0^\pi \exp(4inx) \{ 2\pi^{-1} \pm \psi_n^{o2} \pm \psi_{-n}^{o2} \} dx = \\ &= (2\pi)^{-1} \int_0^\pi (2 \exp(4inx) \pm \exp(8inx) \pm 1) dx \end{aligned}$$

Then  $A_0^\circ(n) = 1 \forall n$ ;  $A_0^{2n}(n) = 2^{-1}$  for  $n$  even;  $A_0^{2n}(n) = -2^{-1}$  for  $n$  odd. (47)

M = 1

$$(4n^2 - s^2)A_1^s = \frac{2s+1}{2s} A_0^{s+1} + \frac{2s-1}{2s} A_0^{s-1} \quad . \quad (48)$$

Here we have several possibilities, so that it is convenient to write between parenthesis the state involved (for example  $A_H^S(n)$ ).

a)  $n \neq 1$

$a_1$ )  $s = 2n-1$

$$A_1^{2n-1}(n) = \frac{1}{2(2n-1)} A_0^{2n} = \pm \frac{1}{4(2n-1)} \quad (49)$$

$a_2$ )  $s = 1$

$$A_1^1 = \frac{1}{2(4n^2-1)} A_0^\circ = \frac{1}{2(4n^2-1)} \quad (50)$$

$$E_n^2 = \frac{1}{4(4n^2-1)} \quad . \quad (51)$$

b)  $n = 1$

$$A_1^1 = \frac{1}{3} \left( \frac{3}{2} A_0^2 + \frac{1}{2} A_0^\circ \right) ; \quad A_1^1 = 5/12 \text{ (1 even)} \\ A_1^1 = -1/12 \text{ (1 odd)} \quad . \quad (52)$$

These results show in a nice and simple way that the symmetric fitting of the zero-order functions avoids the degeneracy problems and the levels split occurs naturally

$$E_1^2 = 5/24 \text{ (1e)} ; \quad E_1^2 = -1/24 \text{ (1o)} \quad . \quad (53)$$

M = 2

$$(4n^2 - s^2)A_2^s = \frac{2s+1}{s} A_1^{s+1} + \frac{2s-1}{s} A_1^{s-1} - A_1^1 A_0^s \quad (54)$$

a)  $n \neq 1$

a<sub>1</sub>) s=1

$$A_2^1(n) = 0 \quad ; \quad E_n^3 = 0 \quad . \quad (55)$$

When s=2n, the coefficient of  $A_2^{2n}(n)$  is zero and it avoids its calculation.

a<sub>2</sub>) s=2

$$A_2^2(n) = \frac{3}{32(n^2-1)(4n^2-1)} \quad (56)$$

b) n=1

The coefficient of  $A_2^2$  makes null, so it is not possible to calculate such element.

$$A_2^1 = 0 \quad ; \quad E_1^1 = 0 \quad (57)$$

M = 3

$$(4n^2-s^2)A_3^s = \frac{2s+1}{s} A_2^{s+1} + \frac{2s-1}{s} A_2^{s-1} - A_1^1 A_1^s \quad (58)$$

a) n=1

The calculation of  $A_3^1(1)$  implies the evaluation of  $E_1^4$ , and in turn this requires to know  $A_2^2$ . But this term cannot be determined, so that it brings about the interruption of the procedure for the first excited state.

b) n≠1

b<sub>1</sub>) s=1

$$A_3^1(n) = \frac{20n^2+7}{64(n^2-1)(4n^2-1)^3} \quad (59)$$

$$E_n = \frac{20n^2+7}{256(n^2-1)(4n^2-1)^3} \quad (60)$$

b<sub>2</sub>) s=2n-1

The element  $A_3^{2n-1}(n)$  cannot be calculated because we do not know  $A_2^{2n}(n)$ .

$b_3) s=3$

$$A_3^3(n) = \frac{5}{64(4n^2-9)(4n^2-1)} ; n \neq 2 \quad (61)$$

$$A_3^3(2) = -\left(\frac{1}{2520} - \frac{1}{9408}\right) . \quad (62)$$

It can be seen that as we go on towards the calculation of higher perturbation orders, the number of terms that we are incapable to determine increases and it stops the procedure.

The only level that offers no trouble at all is the ground level, so that we pass to study it in a separate fashion.

#### Ground State

$$-s^2 A_M^s = \frac{2s+1}{s} A_{M-1}^{s+1} + \frac{2s-1}{s} A_{M-1}^{s-1} - 2 \sum_{t=1}^M t^{-1} A_{t-1}^1 A_{M-t} . \quad (63)$$

From Eq. (63) we conclude that no one coefficient of the elements  $A_M^s$  is zero (except, obviously, for  $s=0$ ; but this fact does not hinder the procedure because we know all the  $A_M^0$  values).

The results are:

$$\underline{M = 1}$$

$$A_1^1 = 1/2 ; E_0^2 = -1/4 \quad (64)$$

$$\underline{M = 2}$$

$$A_2^2 = 3/32 ; E_0^3 = 0 \quad (65)$$

$$\underline{M = 3}$$

$$A_3^1 = 7/64 ; E_0^4 = 7/256 ; A_3^3 = -5/576 \quad (66)$$

$$\underline{M = 4}$$

$$E_0^5 = 0 ; A_4^2 = -272/9216 ; A_4^4 = -35/393216 \quad (67)$$

$$\underline{M = 5}$$

$$A_5^1 = -696/18432 ; E_0^6 = -696/110592 . \quad (68)$$

The combination of these results enables us to obtain the energy expressions for the different levels:

$$E_0 \cong -\frac{1}{4} \alpha^2 + \frac{7}{256} \alpha^4 - \frac{696}{110592} \alpha^6 \quad (69)$$

$$E_1 \cong 2 + \frac{5}{24} \alpha^2 \quad (\text{even}) \quad (70)$$

$$E_2 \cong 2 - \frac{1}{24} \alpha^2 \quad (\text{odd})$$

$$E_n \cong 2n^2 + \frac{\alpha^2}{4(4n^2-1)} + \frac{(20n^2+7)\alpha^4}{256(n^2-1)(4n^2-1)^3} ; n \neq 1 . \quad (71)$$

Although the method does not include the explicit calculation of the eigenstates, Eq. (30) permits us to express the probability density  $\rho(x) = |\psi(x)|^2$  expanded in a Fourier power series

$$\rho(x) = \pi^{-1} + 2\pi^{-1} \sum_{s=1}^{\infty} A_s^s \cos 2sx = \pi^{-1} + 2\pi^{-1} \sum_{t=0}^{\infty} \left( \sum_{s=1}^{\infty} A_t^s \cos 2sx \right) \alpha^t . \quad (72)$$

Eq. (72) yields the following results for the different states:

$$\begin{aligned} \rho_0(x) \cong \pi^{-1} - \alpha \pi^{-1} \cos 2x + \frac{3}{16\pi} \alpha^2 \cos 4x + \alpha^3 \pi^{-1} \left\{ \frac{7}{32} \cos 2x - \right. \\ \left. - \frac{5}{288} \cos 6x \right\} - \alpha^4 \pi^{-1} \left\{ \frac{272}{4608} \cos 4x + \frac{35}{196608} \cos 8x \right\} \end{aligned} \quad (73)$$

$$\rho_1(x) \cong \pi^{-1} + \pi^{-1} \cos 4x + 2\alpha \pi^{-1} \left\{ \frac{5}{12} \cos 2x - 12^{-1} \cos 6x \right\} \quad (\text{even}) \quad (74)$$

$$\rho_1(x) \cong \pi^{-1} - \pi^{-1} \cos 4x + 2\alpha \pi^{-1} \left\{ -\frac{1}{12} \cos 2x - 12^{-1} \cos 6x \right\} \quad (\text{odd})$$

$$\begin{aligned} \rho_n(x) \cong \pi^{-1} + 2\pi^{-1} A_0^{2n}(n) \cos 4nx + 2\alpha \pi^{-1} \left\{ A_1^1(n) \cos 2x + A_1^{2n-1} \cos (4n-2)x + \right. \\ \left. A_1^{2n+1} \cos (4n+2)x \right\} . \end{aligned} \quad (75)$$

In order to know the degree of accuracy of the expressions (69)-(71),

we compare in Table I our present results with the exact values given in Ref. [25] for the quantity

$$b_n = 2E_n + S/2 \quad . \quad (76)$$

In 1) and 2) we compare  $b_0$  and  $b_3$ . The data reveal that the accuracy of the perturbation results increases when  $\alpha$  decreases and  $n$  increases. This fact is entirely sound because under such conditions the solutions resemble to those of the free rotator model ( $\alpha \rightarrow 0$ ).

Since formula (63) is easily programmed for a computer calculation, the  $b_0$  computation ( $\alpha=1, S=4$ ) for 10, 20, 30, 40 and 50 perturbative terms is reported here (see 3) in Table I). The computer program for an HP 1000 minicomputer is given (Program VII, Appendix XI) and the results are exact up to the seventh decimal place.

The method may be applied for any periodic potential if an enough number of terms in the Fourier series are considered. This procedure could be useful to calculate torsional energies in polyatomic molecules, and in a general case, for any hindered rotator. Notwithstanding this, one has to take into account that only the ground state energy can be determined up to any desired degree of accuracy.

When the  $\alpha$ -value is large enough, the rotation turns to be a vibration [21] hence it is also possible to use the method, but as presented in section 29, so that it is only necessary to expand  $\cos 2x$  in a power series [18].

b) As mentioned earlier, PTWWF is applicable to the electron within a crystal lattice model, when the potential is periodic.

In order to perform the proper comparison with well-known solutions, we introduce here in a brief way one of the Slater's results [26].

Let us consider a cubic lattice with period  $L$ , and let  $\{e_1, e_2, e_3\}$  be an orthogonal basis for  $R^3$ , whose vectors are along the edge of a cube in the reticule. Then (see Appendix VIII)

$$\vec{a}_i = Le_i \quad ; \quad b_i = L^{-1}e_i \quad ; \quad i=1,2,3 \quad . \quad (77)$$

The expansion of the potential as a Fourier series

$$V(\vec{r}) = \sum_{\ell} \sum_{m} \sum_{n} V_{\ell mn} \exp\{2\pi i L^{-1}(\ell x + m y + n z)\} \quad (78)$$

for the first terms

$$V(\vec{r}) = V_0 - 2V_1 \{\cos 2\pi L^{-1}x + \cos 2\pi L^{-1}y + \cos 2\pi L^{-1}z\} \quad (79)$$

where  $V_0 \equiv V_{000}$ ;  $-V_1 = V_{\pm 100} = V_{0\pm 10} = V_{00\pm 1}$ , enables us to decouple the Schrödinger equation in three 1D equations

$$-\frac{\hbar^2}{2m} \psi''(\sigma) + V(\sigma)\psi(\sigma) = E\psi(\sigma); \quad \sigma = x, y, z \quad . \quad (80)$$

We choose arbitrarily  $V_0 = 6V_1$  (see Ref. [26]), so that each 1D potential transforms into

$$V(x) = 2V_1(1 - \cos 2\pi L^{-1}x) \quad . \quad (81)$$

The introduction of the new variable  $\omega = \pi x L^{-1}$  and the definition of

$$\alpha = 2mV_1L^2\hbar^{-2}\pi^{-2}; \quad \epsilon = mL^2\hbar^{-2}\pi^{-2}(E - 2V_1) \quad (82)$$

reduce the problem to solve the Mathieu equation [21]. We had discussed before this equation, but now we are obliged to consider all the solutions [21,27,29]

$$-\frac{1}{2}\psi'' + \alpha\psi \cos 2\omega = \epsilon\psi \quad . \quad (83)$$

Slater [26] used the following definitions

$$e = (2mV_1^{-1})^{\frac{1}{2}}L\epsilon\hbar^{-1}; \quad S = 32mL^2V_1\hbar^{-2}; \quad a = eS^{\frac{1}{2}} - S/2 \quad (84)$$

instead of (82). Then, the Schrödinger equation is

$$-\frac{1}{2}\psi'' + \frac{S}{4}\psi \cos 2\omega = \frac{a}{2}\psi \quad (85)$$

$$-\frac{1}{2}\psi'' + \frac{S}{4}\psi(1 - \cos 2\omega) = \frac{eS^{\frac{1}{2}}}{2}\psi \quad . \quad (86)$$

The equality

$$\langle \psi_k | T\omega\psi_{k'} \rangle = \langle T\psi_k | \omega\psi_{k'} \rangle + \frac{1}{2} \{ |\psi_k^{\dagger} \omega \psi_{k'}|_0^{\pi} - |\psi_k^{\dagger} (\omega\psi_{k'})'|_0^{\pi} \} \quad (87)$$

tells us that the HO

$$\omega = \exp(i(k'-k)x)f_s(x); f_s(x) = \exp(2isx) \quad (88)$$

$$\omega = \exp(i(k'-k)x)f_s(x)D$$

allow the fulfillment of the HR [29]

$$\langle \psi_k | [H, \omega] \psi_{k'} \rangle = \omega_{kk'} \langle \psi_k | \omega \psi_{k'} \rangle \quad (89)$$

Obviously, the diagonal case permits us to use the previous H0 so that Eq. (86) is valid, but the zero order functions are different

$$E_k^0 = \frac{1}{2}k^2; \psi_k^0 = \pi^{-\frac{1}{2}} \exp(ikx) \quad (90)$$

The substitution  $E_k^0$  in (40) gives the following perturbation corrections

$$A_1^1(k) = \frac{1}{2(k^2-1)} \quad (91)$$

$$A_2^2(k) = \frac{3}{8(k^2-4)(k^2-1)} \quad (92)$$

$$A_3^1(k) = \frac{5k^2+7}{16(k^2-4)(k^2-1)^3} \quad (93)$$

$$A_3^3(k) = \frac{5}{16(k^2-4)(k^2-9)(k^2-1)} \quad (94)$$

Then, with the help of these quantities we can calculate the energy corrected up to the fourth order:

$$E_k(\alpha) = \frac{1}{2}k^2 + \frac{\alpha^2}{4(k^2-1)} + \frac{(5k^2+7)\alpha^4}{64(k^2-4)(k^2-1)^3} + \dots \quad (94)$$

The substitutions  $a_k = 2E_k$ ;  $\alpha = S/4$  lead to the Slater's results [26]

$$a_k = k^2 + \frac{S^2}{32(k^2-1)} + \frac{(5k^2+7)S^4}{8192(k^2-4)(k^2-1)^3} + \dots \quad (95)$$

The denominators in both expressions are null when  $k$  reaches some of the Brillouin zones ( $k=1,2,\dots$ ) and in such cases the perturbative calculation is no longer possible.

Recently, Wigner and Lambin [30] and Killingbeck [31] performed the calculation of the 1D energy bands. They chose the Mathieu equation



$$-D^2\psi + 2\psi \cos 2x = E\psi \quad (96)$$

In Table II we compare the ground state energy ( $k=0$ ) calculated via the expression

$$2 E_O^N(\alpha=1) = \sum_{M=0}^N 2E_O^M(\alpha=1) \quad (97)$$

with the results reported in Refs. [30,31]. It can be seen that the present results are more exact than the other ones. The program is the same as that used in a).

The method given above seems to be useful to calculate up to a great degree of exactness the energies  $E_k$  when the wave vector  $k$  is far apart from the Brillouin's zones. Although the procedure has the same limitations as the PTWWF it is easier to programme for a computer machine.

#### NUMERICAL RESULTS

TABLE I. Autovalues for Mathieu's equation

1)					
S	0.2	1.0	2.0	4.0	
$b_o^a$	0.09875	0.46896	0.87822	1.54210	
$b_o^b$	0.09875	0.46896	0.87823	1.54486	
2)					
S	0.5	2.0	3.0		
$b_3^a$	36.25022	37.00357	51.81704		
$b_3^b$	36.25022	37.00357	51.82897		
3)					
N	10	20	30	40	50
$b_o^c$	1.5457399	1.5448553	1.5448615	1.5448614	1.5448614

a: Eqs. (69) and (71)

b: Ref. [25]

c: calculated by means of the computer machine

TABLE II. Ground state of an electron subjected to a periodical potential  $V(x) = \cos 2x$

N	$2E_O^N(1)$	N	$E_O^N$ <sup>a</sup>	N	$E_O^N$ <sup>b</sup>
10	-0.45426014	50	-0.4556	25	-0.455145
20	-0.45514472	100	-0.45527	50	-0.455139
30	-0.45513854	300	-0.455153	$\infty$	-0.455139
40	-0.45513860	exact	-0.455139		
50	-0.45513860				

a: Ref. [30]

b: Ref. [31]

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