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NEW PARTITIONING PERTURBATION THEORY:

II. EXAMPLE OF ALMOST DEGENERACY.

by

Phillip R. Certain, David R. Dion, and Joseph O. Hirschfelder

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NEW-PARTITIONING PERTURBATION THEORY: II.  
EXAMPLES OF ALMOST DEGENERACY

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page

- 1 Eq. (2) interchange  $\omega_+$  and  $\omega_-$ .
- 2 Line below (5) interchange  $\omega_+$  and  $\omega_-$ .
- 13 Six lines from the bottom (which now starts with (RS; $\beta$ )).  
This line should read: "(RS; $\alpha\beta$ ) gives good values for  $\Delta E$   
and fair values for  $\bar{E}$ . The. . ."

NEW PARTITIONING PERTURBATION THEORY:

II. EXAMPLE OF ALMOST DEGENERACY.\*

by

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ABSTRACT

A system of two coupled simple harmonic oscillators where many of the energy levels are almost degenerate doublets serves as an excellent "guinea pig" for testing many perturbation techniques including the Modified Kirtman, Kirtman, and DE-FOP-VIM treatments discussed by Certain and Hirschfelder in a companion paper. These methods are compared with the "usual" approach to almost degenerate problems which makes the zeroth order energies of the doublet pair degenerate by a suitable choice of the zeroth order hamiltonian. In addition, four types of Rayleigh-Schrödinger expansions are considered. The best values of the energy are given by the Kirtman treatment. However, the DE-FOP-VIM and the Modified Kirtman procedures give values almost as good, and have the added advantage that they give upper bounds to the energy of the states which are considered.

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## I. Introduction

In this paper, the perturbation techniques developed by Certain and Hirschfelder in a companion paper<sup>1</sup> (which we shall refer to as I), as well as various types of Rayleigh-Schrödinger expansions, are applied to a model problem where many of the energy levels are almost degenerate doublets. We consider the system<sup>2</sup> composed of two coupled simple harmonic oscillators as described by the hamiltonian

$$H = -\frac{1}{2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} (1 + \alpha)^2 x^2 + \frac{1}{2} (1 - \alpha)^2 y^2 + \lambda xy \quad (1)$$

### Exact Solution

The Schrödinger Equation for this case is exactly solvable. By rotating the coordinates so that  $x = \zeta \cos\theta + \eta \sin\theta$  and  $y = -\zeta \sin\theta + \eta \cos\theta$ , then setting  $\tan(2\theta) = -\lambda/(2\alpha)$ , the hamiltonian becomes

$$H = -\frac{1}{2} \left( \frac{\partial^2}{\partial \zeta^2} + \frac{\partial^2}{\partial \eta^2} \right) + \frac{1}{2} \omega_+^2 \zeta^2 + \frac{1}{2} \omega_-^2 \eta^2 \quad (2)$$

where

$$\omega_{\pm} = \left[ 1 + \alpha^2 \pm (4\alpha^2 + \lambda^2)^{1/2} \right]^{1/2} \quad (3)$$

This hamiltonian corresponds to a two dimensional simple harmonic oscillator with the energy levels

$$E_{nm} = (n + \frac{1}{2})\omega_+ + (m + \frac{1}{2})\omega_- \quad (4)$$

where the quantum numbers  $n$  and  $m$  are either zero or positive integers. The corresponding wave functions are

$$\Psi_{nm} = (\omega_+ \omega_-)^{1/4} U_m(\zeta') U_m(\eta') \quad (5)$$

where  $\zeta' = (\omega_+)^{-1/2} \zeta$  and  $\eta' = (\omega_-)^{-1/2} \eta$ . Letting  $H_n(q)$  be the  $n$ -th Hermite polynomial,

$$U_m(q) = (\pi)^{-1/4} (2^m m!)^{-1/2} H_m(q) e^{-q^2/2} \quad (6)$$

When  $\alpha$  and  $\lambda$  are small, the states  $nm$  and  $mn$  (with  $m \neq n$ ) are closely spaced doublets. By squaring the sum and difference of  $\omega_+$  and  $\omega_-$  and then taking the square root of the result, we obtain

$$\omega_+ \pm \omega_- = [2 + 2\alpha^2 \pm 2[(1-\alpha^2)^2 - \lambda^2]^{1/2}]^{1/2} \quad (7)$$

Eq. (7) is convenient for expressing the mean energy of the doublet,

$$(E_{nm} + E_{mn})/2 = (\frac{1}{2})(n + m + 1)(\omega_+ + \omega_-) \quad (8)$$

and the energy splitting within the doublet

$$(E_{nm} - E_{mn}) = (n - m)(\omega_+ - \omega_-) \quad (9)$$

In the remainder of the paper we consider many different types of perturbation procedures for determining the mean energy and energy splitting of the 10,01 doublet. Tables 1 and 2 give the results which we obtained for  $\alpha = 0.1$  and  $\lambda$  varying from zero to 0.35.

## II. The Rayleigh-Schrödinger Expansions

The basic assumption of the Rayleigh-Schrödinger theory is that the exact wave function and the exact energy may be expanded in power series in the perturbation parameter. For the problem at hand, there are four types of Rayleigh-Schrödinger expansions which we might consider:

### 1) Expansion in Powers of $\lambda$ (RS; $\lambda$ )

The (RS; $\lambda$ ) energies are most easily obtained by expanding the expressions for the exact energies, Eqs. (7) - (9), in powers of  $\lambda$ . This involves: first, the expansion of the inner square root; and then the expansion of the outer square root in Eq. (7). Thus we obtain:

$$(E_{nm} + E_{mn})/2 = (n+m+1) \left[ 1 - \frac{\lambda^2}{8(1-\alpha^2)} - \frac{(5-\alpha^2)\lambda^4}{128(1-\alpha^2)^3} - O(\lambda^6) \right] \quad (10)$$

This series converges provided that:

$$\lambda^2 < (1-\alpha^2)^2 \quad \text{and} \quad 4\alpha^2 - \lambda^2 < 8 \quad (11)$$

Furthermore,

$$(E_{nm} - E_{mn}) = 2\alpha(n-m) \left[ 1 + \frac{\lambda^2}{8\alpha^2(1-\alpha^2)} + \frac{(5\alpha^2-1)\lambda^4}{128\alpha^4(1-\alpha^2)^3} + O(\lambda^6) \right] \quad (12)$$

and the series converges provided that

$$\lambda^2 < (1-\alpha^2)^2 \quad \text{and} \quad \lambda^2 < 4\alpha^2(1-2\alpha^2) \quad (13)$$

Thus, the range of convergence for the mean energy series is much greater than that for the energy splitting series. For example, if  $\alpha = 0.1$ , then the mean energy series converges if  $\lambda < 0.99$ ; whereas the energy splitting series converges if  $\lambda < 0.198$ . Of course, the first few terms in these series can be used as an asymptotic approximation to the energy outside of the range of convergence. Thus, in Table I it is seen that the first two terms in Eq. (10) give an excellent approximation to the mean energy for even the largest tabulated value of  $\lambda$  (0.35), whereas in Table 2, the first two terms of Eq. (12) give a very poor approximation to the energy splitting for even the smallest values of  $\lambda$ .

## 2) Expansion in Powers of $\alpha(\text{RS};\alpha)$

The  $(\text{RS};\alpha)$  energies are also obtained by expanding the inner and outer square roots in Eq. (7). We shall assume that  $\lambda^2 < 1$  so that  $c = (1 - \lambda^2)^{1/2}$  is real. Then,

$$(E_{nm} + E_{mn})/2 = (\frac{1}{2})(n+m+1) [2(1+c)]^{1/2} \left[ 1 - \frac{\alpha^2}{2} \frac{(1-c)}{(1+c)} - O(\alpha^4) \right] \quad (14)$$

and the series converges provided that  $\alpha^2 < 1 - |\lambda|$ . Furthermore,

$$(E_{nm} - E_{mn}) = (n-m) [2(1-c)]^{1/2} \left[ 1 + \frac{\alpha^2 (1+c)^2}{2\lambda^2 c} + O(\alpha^4) \right] \quad (15)$$

The convergence requirements of this series are that  $\alpha^2 < 1 - |\lambda|$  and that  $\alpha^2 < (-1+4c-3c^2)/4c \approx \lambda^2/4$ . From Tables 1 and 2, it is apparent that the  $(\text{RS};\alpha)$  series give a good approximation for the



mean energy but a poor approximation for the energy splitting. This behaviour is similar to that for the (RS; $\lambda$ ).

### 3) Double Power Series Expansion in $\alpha$ and $\lambda$ (RS; $\alpha\lambda$ )

There is no difficulty in obtaining the double power series for the mean energy by expanding the inner and outer square roots of Eq. (7),

$$(E_{nm} + E_{mn})/2 = (n+m+1) \left[ 1 - \frac{\lambda^2}{8} - \frac{5\lambda^4}{128} - \frac{\alpha^2\lambda^2}{8} - \frac{7\alpha^2\lambda^4}{64} - \frac{\alpha^4\lambda^2}{32} - \dots \right] \quad (16)$$

This series converges if

$$2\alpha^2 + \lambda^2 - \alpha^4 < 1 \quad \text{and} \quad 4\alpha^2 - \lambda^2 < 8$$

Note that Eq. (16) contains no terms in  $\alpha^n$  since the mean energy of the doublet is independent of the value of  $\alpha$  if  $\lambda = 0$ .

However, no double power series expansion can be obtained for the energy splitting. After expanding the inner square root in Eq. (7),

$$E_{nm} - E_{mn} = (n-m) \left[ \alpha^2 + \frac{1}{2} (2\alpha^2 + \lambda^2 - \alpha^4) + \frac{1}{8} (2\alpha^2 + \lambda^2 - \alpha^4)^2 + \dots \right] \quad (17)$$

A further expansion of Eq. (17) would lead to terms involving inverse powers of either  $\alpha$  or  $\lambda$ . There is a simple theoretical reason why this double power series cannot occur:<sup>2</sup> Let us resolve the hamiltonian into three parts,  $H = \tilde{H}^{(0)} + H^{(1,\alpha)} + H^{(1,\lambda)}$  where

$$\tilde{H}^{(0)} = -\frac{1}{2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} x^2 + \frac{1}{2} y^2 \quad (18)$$

$$H^{(1, \alpha)} = \left(\alpha + \frac{\alpha^2}{2}\right) x^2 - \left(\alpha - \frac{\alpha^2}{2}\right) y^2 \quad (19)$$

$$H^{(1, \lambda)} = \lambda xy \quad (20)$$

The zeroth order energy of the doublet states is degenerate,

$E_{nm}^{(0)} = E_{mn}^{(0)} = n+m+1$ . The zeroth order wave functions corresponding to these energy states are

$$\psi_1^{(0)} = \cos\theta u_n(x) u_m(y) + \sin\theta u_m(x) u_n(y) \quad (21)$$

$$\psi_2^{(0)} = -\sin\theta u_n(x) u_m(y) + \cos\theta u_m(x) u_n(y)$$

In order that a double Rayleigh-Schrodinger power series expansion be possible, it is necessary that  $\psi_1^{(0)}$  and  $\psi_2^{(0)}$  be simultaneously the "correct zeroth order" wave functions for the perturbations  $H^{(1, \alpha)}$  and  $H^{(1, \lambda)}$ . Unfortunately, it is impossible to find a value of  $\theta$  which permits both sets of conditions to be satisfied. This is easy to see in the special case that  $|n - m| = 1$  where the degeneracies are removed in the first order. Here  $\psi_1^{(0)}$  and  $\psi_2^{(0)}$  would be the "correct zeroth order" wave functions for the two perturbations if  $\langle \psi_1^{(0)} | H^{(1, \lambda)} | \psi_2^{(0)} \rangle = 0$  and  $\langle \psi_1^{(0)} | H^{(1, \alpha)} | \psi_2^{(0)} \rangle = 0$ .

#### 4) Expansion in Powers of $\alpha$ and $\beta$ (RS; $\alpha \beta$ )

Finally, as Saul T. Epstein suggested to us, let us consider a double Rayleigh-Schrödinger power series expansion which exists for both the mean energy and the energy splittings. Let us express the problem in the  $\zeta$  and  $\eta$  (instead of the  $x$  and  $y$ ) coordinates.

Then the hamiltonian, Eq. (2), can be expressed as the sum of three terms

$$\tilde{H}^{(0)} = -\frac{1}{2} \left( \frac{\partial^2}{\partial \zeta^2} + \frac{\partial^2}{\partial \eta^2} \right) + \frac{1}{2} (\zeta^2 + \eta^2)$$

$$\tilde{H}^{(1)} = \frac{\beta}{2} [\eta^2 - \zeta^2]$$

$$\tilde{H}^{(2)} = \frac{\alpha^2}{2} (\zeta^2 + \eta^2)$$

where  $\beta = \sqrt{4\alpha^2 + \lambda^2}$ . Then the exact energy is given by Eqs. (3) and (4) with

$$\omega_{\pm} = [1 + \alpha^2 \pm \beta]^{1/2}$$

Expanding  $\omega_{\pm}$  through terms of the third order ( $\alpha^i \beta^j$  where  $i+j \leq 3$ )

$$\omega_{\pm} = 1 \pm \frac{\beta}{2} + \frac{\alpha^2}{2} - \frac{\beta^2}{8} \mp \frac{\alpha^2 \beta}{4} \pm \frac{\beta^3}{16} + \dots$$

These series converges for  $(\alpha^2 - \beta)^2 < 1$ . The advantage of the (RS;  $\alpha \beta$ ) treatment is that the double power series expansion exists for both the mean energy and the energy splitting of a doublet.

### III. The Kirtman, Modified Kirtman, and De-FOP-VIM Approximations

Next, let us apply the Kirtman (K), Modified Kirtman (MK), and DE-FOP-VIM approximations developed in the companion paper I. Taking

$\lambda$  as the perturbation parameter, the unperturbed hamiltonian is

$$H^{(0)} = -\frac{1}{2} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{1}{2} (1+\alpha)^2 x^2 + \frac{1}{2} (1-\alpha)^2 y^2 \quad (23)$$

and the perturbation is

$$H^{(1)} = xy$$

The eigensolutions of the unperturbed problem are

$$E_{mm}^{(0)} = \left(m + \frac{1}{2}\right)(1+\alpha) + \left(m + \frac{1}{2}\right)(1-\alpha) \quad (24)$$

and

$$\phi_{mm}^{(0)} = (1-\alpha^2)^{1/4} u_m(x') u_m(y') \quad (25)$$

where  $x' = (1+\alpha)^{1/2} x$  and  $y' = (1-\alpha)^{1/2} y$ .

Let us apply each of the perturbation techniques to the doublet pair 10 and 01 :

Kirtman Approximation

In vector notation, the zeroth order function for the 10 and 01 states is

$$\Phi^{(0)} = (\phi_{10}^{(0)}, \phi_{01}^{(0)})$$

Using the full normalization condition, so that  $\langle \Phi^{(0)} | \Phi^{(1)} \rangle = 0$ ,

$$\epsilon^{(0)} = \begin{pmatrix} 2 + \alpha & 0 \\ 0 & 2 - \alpha \end{pmatrix}$$

The solution of the first order equation (I-11)<sup>3</sup> is

$$\Phi^{(1)} = -[2\sqrt{2(1-\alpha^2)}]^{-1} (\phi_{21}^{(0)}, \phi_{12}^{(0)})$$

$$\epsilon^{(1)} = \begin{pmatrix} 0 & \frac{1}{2\sqrt{1-\alpha^2}} \\ \frac{1}{2\sqrt{1-\alpha^2}} & 0 \end{pmatrix}$$

$$\epsilon^{(2)} = \begin{pmatrix} -\frac{1}{4(1-\alpha^2)} & 0 \\ 0 & -\frac{1}{4(1-\alpha^2)} \end{pmatrix}$$

$$\epsilon^{(3)} = \begin{pmatrix} 0 & \frac{1}{16[1-\alpha^2]^{3/2}} \\ \frac{1}{16[1-\alpha^2]^{3/2}} & 0 \end{pmatrix}$$

To this order, the energy of the Kirtman formalism is given by the roots of the secular equation (I-29) which yields

$$E_{\substack{10 \\ 01}}(k) = 2 - \frac{\lambda^2}{4(1-\alpha^2)} \pm \sqrt{\alpha^2 + \left[ \frac{\lambda}{2(1-\alpha^2)^{1/2}} + \frac{\lambda^3}{16(1-\alpha^2)^{3/2}} \right]^2} \quad (27)$$

#### Modified Kirtman Approximation

Alternatively, the modified Kirtman secular equation (I-14) with  $N = 1$  reduces for this case to

$$\left| \left( \mathbb{1} + \lambda^2 \langle \phi^{(1)} | \phi^{(1)} \rangle \right) (\epsilon^{(0)} + \lambda \epsilon^{(1)} - E \mathbb{1}) + \lambda^2 \epsilon^{(2)} + \lambda^3 \epsilon^{(3)} \right| = 0$$

which has the roots

$$E_{\substack{10 \\ 01}}(MK) = 2 - \frac{2\lambda^2}{8(1-\alpha^2) + \lambda^2} \pm \sqrt{\alpha^2 + \left[ \frac{\lambda^2}{4(1-\alpha^2)} \right] \left[ 1 + \frac{\lambda^2}{8(1-\alpha^2) + \lambda^2} \right]^2} \quad (28)$$

Since the 10 and 01 states are the lowest energy states with their symmetry, the roots (28) are upper bounds to the exact energies. Clearly, the modified Kirtman roots (28) differ from the Kirtman roots (27) by terms of order  $\lambda^4$ .

#### DE-FOP-VIM Approximation

For the application of DE-FOP-VIM to this example, the secular equation to be solved is Eq. (I-28). Substitution of the proper

quantities and transforming to the orthonormal set of functions

$\phi_{10}^{(0)}, \phi_{01}^{(0)}, \phi_{21}^{(0)}, \phi_{12}^{(0)}$  yields the  $4 \times 4$  secular equation for the energy

$$0 = \begin{vmatrix} a + \alpha - E & \frac{\lambda}{2(1-\alpha^2)^{1/2}} & -\frac{\lambda}{[2(1-\alpha^2)]^{1/2}} & 0 \\ \frac{\lambda}{2(1-\alpha^2)^{1/2}} & a - \alpha - E & 0 & -\frac{\lambda}{[2(1-\alpha^2)]^{1/2}} \\ -\frac{\lambda}{[2(1-\alpha^2)]^{1/2}} & 0 & 4 + \alpha - E & \frac{\lambda}{(1-\alpha^2)^{1/2}} \\ 0 & -\frac{\lambda}{[2(1-\alpha^2)]^{1/2}} & \frac{\lambda}{(1-\alpha^2)^{1/2}} & 4 - \alpha - E \end{vmatrix}$$

Note that of the four energy roots, the only two which are significant approach  $\epsilon_{10}^{(0)}$  and  $\epsilon_{01}^{(0)}$  in the limit as  $\lambda \rightarrow 0$ .

#### IV. Reduction to Degenerate Perturbation

As explained in Paper I, the almost degeneracy of the doublet 10 and 01 can be transformed into a true degeneracy by using the zeroth order hamiltonian

$$\begin{aligned} \bar{H}^{(0)} = H^{(0)} &+ (\bar{E} - \epsilon_{10}^{(0)}) \phi_{10}^{(0)} \langle \phi_{10}^{(0)} | \\ &+ (\bar{E} - \epsilon_{01}^{(0)}) \phi_{01}^{(0)} \langle \phi_{01}^{(0)} | \end{aligned} \quad (30)$$

where  $H^{(0)}$  is the  $H^{(0)}$  of Eq. (23). Clearly,  $\bar{H}^{(0)} \phi_{10}^{(0)} = \bar{\epsilon} \phi_{10}^{(0)}$  and  $\bar{H}^{(0)} \phi_{01}^{(0)} = \bar{\epsilon} \phi_{01}^{(0)}$ . The energy  $\bar{\epsilon}$  is arbitrary. Thus, it may be taken to be the mean unperturbed energy of the doublet pair,  $\bar{\epsilon} = \frac{1}{2}(\epsilon_{10}^{(0)} + \epsilon_{01}^{(0)}) = 2$ , or  $\bar{\epsilon}$  may be considered to be a variational parameter. Corresponding to  $H^{(0)}$  is the first order perturbation potential  $\bar{H}^{(1)} = H - \bar{H}^{(0)}$ .

Having reduced the problem to a degenerate perturbation, we have a number of choices as to the method of solution. Let us use the modified Kirtman approach. Then, from Eq. (I-22) and the recursion relations for Hermite polynomials, it follows that

$$\begin{aligned}\bar{\Phi}_{10}^{(1)} &= 2(\bar{\epsilon} - \epsilon_{21}^{(0)})^{-1} \phi_{10}^{(1)} \\ \bar{\Phi}_{01}^{(1)} &= 2(\bar{\epsilon} - \epsilon_{12}^{(0)})^{-1} \phi_{01}^{(1)}\end{aligned}\tag{31}$$

Warning: In general, one should not expect a simple relationship such as (31) between the  $\bar{\Phi}_k^{(1)}$  and the  $\phi_k^{(1)}$  which results from the simple harmonic nature of both  $H^{(0)}$  and  $H$ . The energy is then given by

$$|\langle \bar{\Phi}^{(1)} | H - E | \bar{\Phi}^{(1)} \rangle| = 0$$



Evaluating the matrix elements leads to the 2 x 2 secular equation,

$$0 = \begin{vmatrix} \epsilon_{10}^{(0)} + \sqrt{2}rs + s^2\epsilon_{21}^{(0)} & r(\frac{1}{2} + st) \\ -E(1+s^2) & \\ r(\frac{1}{2} + st) & \epsilon_{01}^{(0)} + \sqrt{2}rs + t^2\epsilon_{12}^{(0)} \\ & -E(1+t^2) \end{vmatrix} \quad (32)$$

where

$$r = \lambda(1 - \alpha^2)^{-1/2}$$

$$s = r\sqrt{2}(\bar{\epsilon} - \epsilon_{21}^{(0)})^{-1}$$

$$t = r\sqrt{2}(\bar{\epsilon} - \epsilon_{12}^{(0)})^{-1}$$

Eq. (32) gives the two energy roots  $E_{10}(\bar{\epsilon})$  and  $E_{01}(\bar{\epsilon})$ . These energies are upper bounds to the exact energy for the states 10 and 01 since: (1) The approximate wave functions for the 10 and 01 states are orthogonal to the 00 ground state wave function; and (2) the H matrix component linking the approximate 10 (or 01) wave function with the 00 is zero. Thus,  $\bar{\epsilon}$  can be assigned a reasonable value such as  $\frac{1}{2}(\epsilon_{10}^{(0)} + \epsilon_{01}^{(0)}) = 2$  or  $\bar{\epsilon}$  can be taken as a variational parameter. The best (or lowest) value of  $E_{10}$  is obtained for a different value of  $\bar{\epsilon}$  than that which gives the best (or lowest) value of  $E_{01}$ .

The degenerate problem can also be treated by the usual Rayleigh-Schrodinger treatment. Since the degeneracy of the 01 and 10 states is resolved in the first order, it is not difficult to determine the wave functions accurate through the first order. These wave functions are then used to determine the energy correct through the third order. Numerical results corresponding to  $\bar{\epsilon} = 2$  are given in Tables I and II

If we had used the DE-FOP-VIM method of approximating the energies of the degenerate perturbation, we would have obtained the secular equation (29) and the same energies which result from using the DE-FOP-VIM approximation without making the reduction to the degenerate problem. However, this equality is not general, but rather it is a result of the proportionality of the  $\bar{\phi}_k^{(1)}$  and the  $\phi_k^{(1)}$  as given by Eq. (31).

#### V. Numerical Calculations

The results of the various perturbation treatments are compared numerically in Tables I, II, and III for  $\alpha = 0.1$  and  $0 < \lambda < 0.35$ . The mean energy of the doublet,  $\bar{E} = \frac{1}{2}(E_{10} + E_{01})$  is given in Table I; the energy splitting,  $\Delta E = E_{10} - E_{01}$ , is shown in Table II; and the optimum values of  $\bar{\epsilon}$  for the two states appear in Table III.

First, let us consider the Rayleigh-Schrodinger expansions. The (RS; $\alpha$ ) gives excellent values for  $\bar{E}$  but poor values for  $\Delta E$ . The (RS; $\beta$ ) gives excellent values for  $\Delta E$  but poor values for  $\bar{E}$ . The (RS; $\lambda$ ) gives fair values for  $\bar{E}$  but very poor values for  $\Delta E$ . The (RS; $\lambda\alpha$ ) gives almost the same fair values for  $\bar{E}$  as does (RS; $\lambda$ ), but the (RS; $\lambda\alpha$ ) perturbation series for  $\Delta E$  does not exist.

All of the rest of the perturbation procedures (K, MK, DE-FOP-VIM, and the reductions to a degenerate problem) give essentially the same

results: good to very good values of the splitting  $\Delta E$ , and fair values of the mean energy  $\bar{E}$ . Although the DE-FOP-VIM gives slightly better energies than the MK (as it must) for both the 10 and 01 states, the DE-FOP-VIM values for  $\Delta E$  are not as good as the MK values. Thus, as far as this example is concerned, DE-FOP-VIM is not worth the extra effort. The Kirtman (K) values are slightly better than the Modified Kirtman (MK) values for both  $\bar{E}$  and  $\Delta E$ . However, the Kirtman values for the energies of the 10 and of the 01 states, individually, are not upper bounds. This is the big advantage of the Modified Kirtman treatment. The reduction to a degenerate problem required considerably more work and the results were about the same.

It is difficult to generalize these results to other problems. However, we are disappointed that no one method showed itself to be outstandingly better than the others.

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Table I

Mean Energy,  $\bar{E} = \frac{1}{2}(E_{10} + E_{01})$ , for  $\alpha = 0.1$

The accuracy of the (RS; $\lambda$ ) is through  $\lambda^3$ ; the (RS; $\alpha$ ) is through  $\alpha^3$ ;

the (RS; $\lambda\alpha$ ) is through  $\lambda^3$  and  $\alpha^3$ ; and the (RS; $\alpha\beta$ ) is through  $\alpha^3$  and  $\beta^3$ .

$\lambda$	$\bar{E}_{\text{approx.}} - \bar{E}_{\text{exact}}$							
	Rayleigh-Schrödinger Expansions		Using $H^{(0)}$ of (23)		Reduction to Degenerate Using $\bar{H}^{(0)}$ of (30)			
	(RS; $\lambda$ ) and (RS; $\lambda\alpha$ )	(RS; $\alpha$ ) (RS; $\alpha\beta$ )	KIRTMAN MODIFIED KIRTMAN	DE-FOP-VIM	MK $\bar{E}_{(\text{opt})}$	MK $\bar{E}_{=2}$	RS $\bar{E}_{=2}$	
.00	.00000	.00000	.00000	.00000	.00000	.00000	.00000	.00000
.05	.00000	.00000	.00001	.00000	.00000	.00000	.00000	.00000
.10	.00000	.00000	.00003	.00000	.00002	.00002	.00002	.00002
.15	.00004	.00000	.00009	.00004	.00006	.00005	.00009	.00006
.20	.00013	.00000	.00023	.00013	.00019	.00016	.00020	.00015
.25	.00033	.00001	.00049	.00033	.00045	.00039	.00048	.00036
.30	.00068	.00001	.00091	.00068	.00094	.00081	.00097	.00074
.35	.00130	.00003	.00161	.00130	.00177	.00154	.00176	.00137

Table II

Energy Difference,  $\Delta E = E_{10} - E_{01}$ , for  $\alpha = 0.1$

The accuracy of the (RS; $\lambda$ ) is through  $\lambda^3$ ; the (RS; $\alpha$ ) is through  $\alpha^3$ ; and the (RS; $\alpha\beta$ ) is through  $\alpha^3$  and  $\beta^3$ .

$\lambda$	$\Delta E_{\text{approx.}} - \Delta E_{\text{exact}}$								
	Rayleigh-Schrödinger Expansions		Using $H^{(0)}$ of Eq. (23)		Reduction to Degenerate Using $\bar{H}^{(0)}$ of (30)				
	(RS; $\lambda$ )	(RS; $\alpha$ )	(RS; $\alpha\beta$ )	KIRTMAN	MODIFIED KIRTMAN	DE-FOP-VIM	MK $\bar{\epsilon}_{\text{(opt)}}$	MK $\bar{\epsilon} = 2$	RS $\bar{\epsilon} = 2$
.00	.20000	.00000	$\infty$	.00000	.00000	.00000	.00000	.00000	.00000
.05	.20622	.00009	.24392	.00000	.00000	.00000	.00000	.00000	.00000
.10	.22389	.00136	.07649	.00000	.00000	.00000	.00000	.00000	.00000
.15	.25072	.00160	.03342	-.00001	-.00001	-.00001	.00000	-.00001	.00000
.20	.28430	.01671	.01724	-.00002	-.00002	-.00003	-.00003	-.00004	-.00002
.25	.32276	.03507	.00991	-.00006	-.00008	-.00010	-.00010	-.00009	-.00006
.30	.36483	.06244	.00617	-.00016	-.00019	-.00024	-.00028	-.00023	-.00017
.35	.40971	.00963	.00409	-.00033	-.00041	-.00053	-.00059	-.00040	-.00036

Table III

The Optimum Values of  $\bar{\epsilon}$  for  $\alpha = 0.1$  using  $\bar{H}^{(0)}$  of Eq. (30)  
followed by MK treatment.

$\lambda$	State	10	01
.05		2.096	1.915
.10		2.057	1.929
.15		2.013	1.949
.20		1.970	1.972
.25		1.933	1.996
.30		1.901	2.022
.35		1.873	2.046

## Footnotes

- 1.) P. R. Certain and J. O. Hirschfelder, *J. Chem. Phys.* (preceding companion paper; Part I).
- 2.) J. O. Hirschfelder, W. Byers Brown and S. T. Epstein, Adv. in Quant. Chem. 1, (P. O. Löwdin, Ed., Academic Press, New York, 1964). See p. 297.
- 3.) The notation (I-11) should be read: "Paper I; equation (11)".
- 4.) See, for example, A. Messiah, Quantum Mechanics, (Wiley, New York, 1964), Vol. 2, p. 711.