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Breakdown of the adiabatic approximation for strong coupled oscillators

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Received 16 April 1984, in final form 28 August 1984

Abstract. We study the accuracy of the adiabatic approximation (AA) for coupled oscillators (CO). This accuracy is mainly determined by the strength of coupling between oscillators and, to a lesser degree, by the frequency ratio μ of the CO. The AA works very well for coupling which is not too strong even though the frequencies of the CO are comparable. However, for strong coupling the AA can fail, even if $\mu = 0$, giving completely inadequate energy spectrum and wavefunctions of the CO.

1. Introduction

To treat systems with many interacting degrees of freedom the approximate methods of separation of the variables are most often used. A method of this kind is the adiabatic separation method. The idea of this approach is as follows: in the first step the dynamical problem for one part of the system is solved with the variables of the other part of the system 'frozen'. Then, in the second step these variables are 'unfrozen' and the effective equation is solved for the 'unfrozen' part of the system.

The adiabatic approach was proposed at the beginning of the development of quantum mechanics by Slater (1927) who formulated a mathematical scheme for this approach and proposed it to separate electronic variables for two-electron atoms and to separate electronic and nuclear variables for molecules. Born and Oppenheimer (1927) have accepted this approach as the basis of quantum theory for molecules. The adiabatic separation of electronic and nuclear motions called the Born-Oppenheimer (BO) method was later slightly modified on the grounds of a variational method by Born (1951), and Born and Huang (1954). (In this work we use the abbreviations: (A) = adiabatic Born-Huang method and (AA) = adiabatic approximation = BO or A method.)

Only recently has the AA scheme been applied to separate low-frequency from high-frequency vibrations in molecules (Brickmann 1973, Russeger and Brickmann 1975, 1977, Holmgren *et al* 1977, Huston and Howard 1980, Makarewicz 1984). By analogy with the adiabatic electron-nuclear separation it is usually assumed that the accuracy of adiabatic separation of vibrations of one kind from another is high when the frequency ratio μ of the separated vibrations is small (see e.g., Christoffel and Bowman 1981).

However, the calculations performed for the CO model by Caswell and Danos (1970) proved that the accuracy of such separation is very high within a wide range of μ provided that the oscillator coupling constant is sufficiently small (in their model

this constant tended to zero when $\mu \rightarrow 0$). Further analysis of the AA for CO (Makarewicz 1979, Zhi-Ding *et al* 1982) proved that its accuracy strongly depends on the coupling of the CO.

For high coupling an improvement in the adiabatic results can be obtained by expanding the wavefunction of a system considered in a basis of adiabatic functions. However, this is possible only if this basis is complete. Recently, Woolley and Sutcliffe (1977) questioned the dogma of completeness of the adiabatic basis but so far the counter-example has not been found.

In this paper we consider the CO model and analyse the dependence of the accuracy of adiabatic eigenenergies on the model parameters. We show that this accuracy does not extend to zero when $\mu \rightarrow 0$ at any fixed coupling constant. We also study the adiabatic potentials and prove that for strong coupling they significantly depart from exact non-adiabatic potentials. This work also proves that in some cases the A method does not allow as to describe correctly the energy spectrum of CO because adiabatic functions cannot reflect adequately the properties of the exact wavefunctions.

2. Slow and fast motions, and accuracy of the adiabatic approximation

Let us consider the CO model described by the Hamiltonian

$$H(x_1, x_2) = -\frac{1}{2}(\partial^2/\partial x_1^2 + \partial^2/\partial x_2^2) + \sum_{n_1, n_2=0}^2 a_{n_1, n_2} x_1^{2n_1} x_2^{2n_2}. \quad (1)$$

This Hamiltonian defines the Caswell-Danos model for the special case $a_{n_1, n_2} = 0$ for $n_1, n_2 > 1$. Another model can be obtained if the parameters a_{n_1, n_2} fulfil the following relations

$$\begin{aligned} a_{1,0} &= (\omega_1^2 - \gamma_1 \eta)/2 & a_{1,1} &= \eta(\omega_1 + \omega_2) \\ a_{0,1} &= (\omega_2^2 - \gamma_2 \eta)/2 & a_{2,1} &= a_{1,2} = \eta^2/2 \\ a_{2,0} &= a_{0,2} = a_{2,2} = 0 \end{aligned} \quad (2)$$

where ω_i and η are arbitrary positive parameters. For this model, eigenfunctions and eigenenergies for some states are known (Makarewicz 1983), for example

$$\psi_{p_1, p_2} = \exp[-(\omega_1 x_1^2 + \omega_2 x_2^2 + \eta x_1^2 x_2^2)/2] x_1^{p_1} x_2^{p_2} \quad (3)$$

$$E_{p_1, p_2} = (\gamma_2 \omega_1 + \gamma_1 \omega_2)/2; \quad \gamma_j = 2p_j + 1; \quad p_i = 0, 1. \quad (4)$$

The proposed model for $\eta \ll 1$ is close to the Caswell-Danos model (as $\eta^2 \ll \eta$) and is more convenient to analyse.

We now calculate the adiabatic eigenenergies for this model. In the BO approximation the wavefunction is represented as the product

$$\phi^{\text{BO}}(x_1, x_2) = \phi_1^{\text{BO}}(x_1, \tilde{x}_2) \phi_2^{\text{BO}}(x_2) \quad (5)$$

where ϕ_1^{BO} obeys the equation

$$[H_1(x_1, \tilde{x}_2) - \varepsilon^{\text{BO}}(\tilde{x}_2)] \phi_1^{\text{BO}}(x_1, \tilde{x}_2) = 0 \quad (6)$$

with the operator $H_1 = H - T_2$ ($2T_2 \equiv -\partial^2/\partial x_2^2$) obtained from the Hamiltonian (1) by fixing the x_2 variable. In equation (6) \tilde{x}_2 is the coordinate of the oscillator of a lower frequency and is treated as a parameter, which is marked by a tilde.

The function ϕ_2^{BO} is determined from the equation

$$[T_2 + \varepsilon^{\text{BO}}(x_2) - E^{\text{BO}}]\phi_2^{\text{BO}}(x_2) = 0. \quad (7)$$

The BO method can be corrected by including in equation (7) the diagonal adiabatic correction

$$A^{\text{BO}}(x_2) = \langle \phi_1^{\text{BO}} | T_2 \phi_1^{\text{BO}} \rangle_{x_1} \quad (8)$$

which takes into account some part of the dynamical correlation between (x_1) and (x_2) subsystems. Equation (7) with the potential $\varepsilon^{\text{A}} = \varepsilon^{\text{BO}} + A^{\text{BO}}$ defines the A method.

In our case the operator H_1 represents the anharmonic oscillator

$$H_1 = \frac{1}{2}[-\partial^2/x_1^2 + \omega^2(x_2)x_1^2] + v(x_2)x_1^4 + a_{0,1}x_2^2 \quad (9)$$

for which the eigenenergies can be calculated by applying perturbation theory

$$\varepsilon^{\text{BO}} = a_{0,1}x_2^2 + \omega(x_2) \sum_{k=0}^N u^k(x_2) E_k \quad (10)$$

where

$$\begin{aligned} \omega(x_2) &= [\tilde{\omega}_1^2 + ax_2^2 + (\eta x_2^2)^2]^{1/2}; & \tilde{\omega}_1 &= (2a_{1,0})^{1/2}, & \tilde{\omega}_2 &= (2a_{0,1})^{1/2}, \\ v(x_2) &= (\eta x_2^2)^2/2, & u(x_2) &= v(x_2)/\omega^3(x_2); & a &\equiv 2a_{1,1} \end{aligned}$$

and E_k are the standard perturbation coefficients (Caswell 1979).

The adiabatic correction is given by

$$A^{\text{BO}}(x_2) \equiv C[MC + Qu(x_2)(2/x_2 - 11C)] \quad (11)$$

where

$$\begin{aligned} C &= \frac{1}{4} \text{dln } \omega / \text{d}x_2 = x_2[a + 2(\eta x_2^2)^2] / (2\omega^2), \\ M &\equiv n_1^2 + n_1 + 1, & Q &\equiv 2n_1^3 + 3n_1^2 + 7n_1 + 3. \end{aligned}$$

Having defined ε^{BO} and ε^{A} potentials we solve equation (7) numerically by the Numerov-Cooley method (Cooley 1961). The energies E^{BO} and E^{A} obtained for various values of the parameter $\mu \equiv \tilde{\omega}_2/\tilde{\omega}_1$ and a are compared with the exact energies E (see equation (4)) in figure 1 where the dependences of $\Delta E^{\text{M}} = |E^{\text{M}} - E|/E$ (where $\text{M} = \text{BO}, \text{A}$) on these parameters are shown for the ground state.

Let us consider the following facts.

(i) For $a = \text{constant}$, ΔE^{M} does not tend to zero as $\mu \rightarrow 0$ but, on the contrary, increases.

(ii) ΔE^{A} changes very slowly with changing μ and is almost constant for a wide range of μ values.

(iii) For $\mu \ll 1$, ΔE^{BO} is significantly higher than ΔE^{A} and quickly increases as $\mu \rightarrow 0$, more quickly the higher is a . The property (i) is a direct contradiction to the usually accepted view that AA is best for $\mu \rightarrow 0$. The criterion of a small μ is not sufficient. This is not surprising; indeed, when $a = \text{constant}$ and $\mu \rightarrow 0$ the relative value of the coupling with respect to the energy of the slow oscillator increases and this is the reason why ΔE^{M} does not tend to zero. Thus, as can be seen in what follows, the existence of the high- and low-frequency oscillators in the system of CO is not sufficient for a good AA. More important are the couplings between them.

The property (ii) is important from a practical point of view as it allows us to apply this method for a very wide range of the parameter μ .

The property (iii) points to the fact that dynamical correlation of motions in the system taken into account significantly corrects E^{BO} in the range of low μ values.

3. Adiabatic and non-adiabatic potentials

Adiabatic potentials ε^{BO} and ε^{A} do not describe exactly the dynamics of the subsystem with x_2 coordinate (slow oscillator in our case). In order to show that adiabatic approximation can be essentially unsatisfactory let us consider ε^{A} in detail. The ε^{A} can be determined as (see equation (6))

$$\varepsilon^{\text{A}} = \langle \phi_1^{\text{BO}} | H \phi_1^{\text{BO}} \rangle_{x_1} \quad (12)$$

if the function ϕ_1^{BO} obeys the normalisation condition

$$\langle \phi_1^{\text{BO}} | \phi_1^{\text{BO}} \rangle_{x_1} = 1 \quad \text{for arbitrary } x_2.$$

By analogy with ε^{A} the non-adiabatic potential ε^{NA} taking into account the dynamics of the whole system exactly can be determined as

$$\varepsilon^{\text{NA}} = \langle \phi_1 | H \phi_1 \rangle_{x_1} \quad (13)$$

where the function ϕ_1 is determined by the relation

$$\psi(x_1, x_2) = \phi_1(x_1, x_2) \phi_2(x_2) \quad (14)$$

where ψ is the exact normalised wavefunction and

$$\phi_2(x_2) = \langle \psi | \psi \rangle_{x_1}^{1/2}. \quad (15)$$

Thus, knowing ψ , the function $\phi_2(x_2)$ can be calculated and then ϕ_1 and ε^{NA} can be determined.

The definitions (13)–(15) have been proposed by Hunter (1974, 1975, 1981). He showed that $|\phi_2(x_2)|^2$ has no nodes and, in consequence, ε^{NA} has spiky barriers in the vicinity of the nodes in the $\phi_2^{\text{A}}(x_2)$ function.

It is interesting to compare ε^{A} and ε^{BO} with ε^{NA} for our model. Knowing the exact ψ (see equation (3)) ϕ_2 and ε^{NA} can be easily calculated. For the ground state they have the form

$$\phi_2^{(0,0)}(x_2) = N_0 F^{1/4} \exp(-\omega_2 x_2^2 / 2), \quad (16)$$

$$\varepsilon_{(0,0)}^{\text{NA}} = \frac{1}{2} [(\omega_2 x_2)^2 + F((\omega_2 + 5F/4)x_2^2 - \frac{1}{2}) + \omega_1] \quad (17)$$

and for the first excited state

$$\phi_2^{(0,1)}(x_2) = N_1 x_2 \phi_2^{(0,0)}(x_2), \quad (18)$$

$$\varepsilon_{0,1}^{\text{NA}} = \varepsilon_{0,0}^{\text{NA}} - F/2 \quad (19)$$

where $F = (x_2^2 + \omega_1 / \eta)^{-1}$.

Let us note that the form of ε^{A} and ε^{BO} is the same for a given value of the quantum number n_1 and for various values of n_2 . The non-adiabatic potential ε^{NA} , contrary to ε^{A} and ε^{BO} , changes with n_2 , e.g. $\varepsilon_{0,0}^{\text{NA}}$ and $\varepsilon_{0,1}^{\text{NA}}$ have different functional forms. (In equations (16)–(17) and (18)–(19) the values of η are different because they are determined from equations (2) for a given $a_{1,0}$ and $a_{1,1}$, and for different p_i , but this difference is unimportant.)

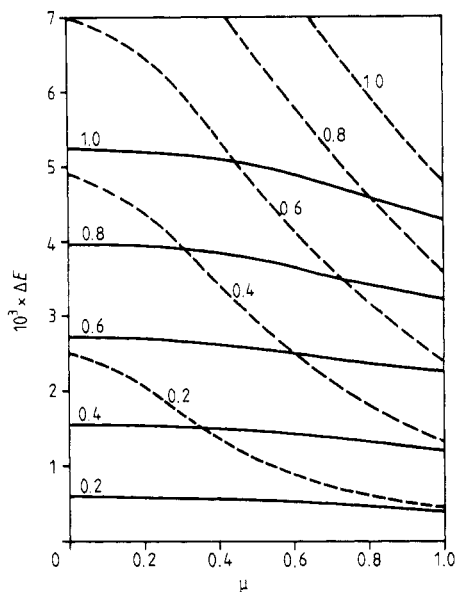


Figure 1. The ΔE^{BO} (broken curves) and ΔE^{A} (full curves) as functions of the frequency ratio μ for various values of the coupling constant a indicated above the lines for the ground state of CO with $\tilde{\omega}_1 = 1$.

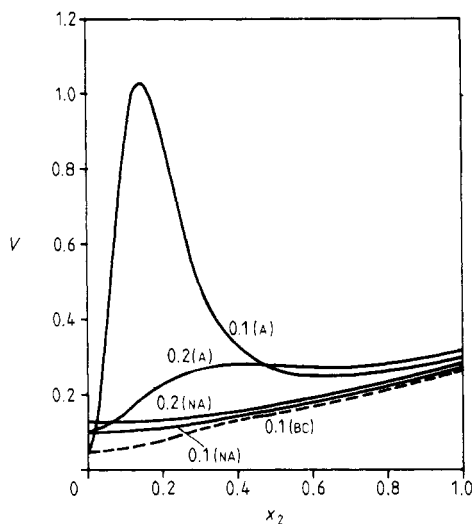


Figure 2. The Born-Oppenheimer, adiabatic and exact non-adiabatic potentials ($V = \epsilon^{\text{BO}}, \epsilon^{\text{A}}$ and ϵ^{NA}) for CO with $a = 0.2, \mu = 0$ and $\tilde{\omega}_1 = 0.1$ and 0.2 (the values in the figure). The line 0.2 (BO) lies close to the line 0.1 (NA), so it is not shown.

The potentials $\epsilon^{\text{A}}, \epsilon^{\text{BO}}$ and ϵ^{NA} for the ground state are shown in figure 2 for the most interesting case $\mu = 0$. These potentials differ from one another significantly for small values of ω_1 because then the coupling between the oscillators is relatively strong. Let us note that for sufficiently small values of $\tilde{\omega}_1, \epsilon^{\text{A}}$ have two barriers (in figure 2 $\epsilon^{\text{A}}(x_2)$ is illustrated only for $x_2 \geq 0$ as $\epsilon^{\text{A}}(x_2)$ is the even function of x_2). These barriers are due to the property of the A^{BO} correction which has two maxima at x_m and $-x_m$ where

$$x_m = k^{-1/2} \quad \text{and} \quad A^{\text{BO}}(x_m) = Mk/64; \quad k \equiv a/(2a_{1,0}).$$

We see that if k increases, both barriers approach each other and their heights increase. Such barriers do not occur in the ϵ^{NA} potential. Thus, for high values of k the A method evidently fails. In the A method the dynamical correlation of motions is overestimated because the correction A^{BO} is too high. On the other hand, in the BO method this correlation is neglected and as a consequence the potential ϵ^{BO} is lower than ϵ^{NA} .

In the first excited state $(0, 1) \epsilon^{\text{NA}}$ also has no barriers, which at a glance contradicts Hunter's statement (Hunter 1981) that the exact potential ϵ^{NA} must have spiky barriers in the vicinity of the nodes in the adiabatic function ϕ_2^{A} . He derived his theorem considering $|\phi_2|^2$ which has no nodes because, as he stated, 'for $|f(y)|^2 (= |\phi_2(x_2)|^2)$ to have a node $|\psi(x, y)|^2 (= |\psi(x_1, x_2)|^2)$ in our notation) must be zero at all points in the x subspace for the point in the y subspace where the node occurs. Excepting the case where the total wavefunction $\psi(x, y)$ is expressible as a single product (i.e., x and y are separable in the Hamiltonian $H(x, y)$) it is very unlikely that $|\psi(x, y)|^2$ could have such a node'.

For our model exactly this 'unlikely' case is realised. For the state $(0, 1)$ there is the nodal line $x_2 = 0$ on which $\psi(x_1, x_2) = 0$ for arbitrary x_1 . As a consequence $|\phi_2|^2$ has the node at $x_2 = 0$.

We see that Hunter's theorem (Hunter 1981) is valid for the less general case, namely when x_1 represents all variables of a particle or group of particles. Then x_2 for which $\psi = 0$ in the whole space of x_1 does not exist because it would indicate that for this x_2 the particles described by x_1 do not exist. This would lack physical sense.

4. Failure of the adiabatic separation method for strong coupled oscillators

As mentioned previously, for strong coupling, adiabatic potentials ε^A and ε^{BO} differ significantly from the exact potential ε^{NA} . Here we will analyse the adiabatic wavefunctions.

We now consider the model of strong coupled quadratic and quartic oscillators defined by the Hamiltonian (1) with $a_{n_1, n_2} = 0$ except $a_{1, 2} = \frac{1}{2}$. Let us calculate the potential ε^{BO} and adiabatic correction A^{BO} from equations (6) and (8):

$$\varepsilon^{BO} = (n_1 + \frac{1}{2})x_2^2, \quad A^{BO} = M/(2x_2)^2. \quad (20, 21)$$

Solving equation (7) with the potential (20) we obtain

$$E^{BO} = (n_2 + \frac{1}{2})\omega_A; \quad \omega_A \equiv (2n_1 + 1)^{1/2}.$$

Equation (7) with the potential ε^A , after introducing the variable $x = x_2\omega_A^{1/2}$, takes the form

$$[\frac{1}{2}(-d^2/dx^2 + x^2) + \lambda x^{-2} - e^A]\phi_2^A(x) = 0 \quad (22)$$

where

$$e^A\omega_A \equiv E^A, \quad \lambda \equiv M/4.$$

This equation has been analysed by Zirilli (1974) and Lathouwers (1975) who have found its solutions for $x \geq 0$:

$$\phi^A(x) = \phi_n^{(\alpha)}(x) \equiv x^{\alpha+1/2} \exp(-x^2/2) L_n^{(\alpha)}(x^2); \quad x \geq 0 \quad (23)$$

where $L_n^{(\alpha)}$ is the generalised Laguerre polynomial and $\alpha = \pm(1+8\lambda)^{1/2}/2$; $\alpha > -1$. The authors suggested, however, different solutions for $x < 0$. Zirilli (1974) considered only $\alpha > 0$ and for $x < 0$ he adopted:

$$\phi_2^A(x) = \begin{cases} +\phi_n^{(\alpha)}(|x|) & \text{for even states} \\ -\phi_n^{(\alpha)}(|x|) & \text{for odd states} \end{cases} \quad x < 0 \quad (24)$$

which gives doubly-degenerate states with the energies

$$e_n^\pm = 2n + \alpha + 1. \quad (25)$$

However, as Lathouwers (1975) noticed, this degeneracy is not removed when $\lambda \rightarrow 0$ ($|\alpha| \rightarrow \frac{1}{2}$). He recognised that such a solution of the problem is unsatisfactory because for $\lambda = 0$ we should have eigenenergies of the harmonic oscillator i.e.

$$e_n^+ = 2n + \frac{1}{2} \quad \text{and} \quad e_n^- = 2n + \frac{3}{2}.$$

He then rejected such constructed even solutions but he permitted square-integrable singular even solutions

$$\phi_2^A(x) = \phi_n^{(-\alpha)}(|x|) \quad \text{for } x < 0 \quad (26)$$

which correspond to the eigenvalues

$$e_n^+ = 2n - |\alpha| + 1. \quad (27)$$

However, such solutions exist only for $\alpha < 1$ ($\lambda < \frac{3}{8}$).

Now, let us consider the solutions of equation (22) for our problem. If we take the solutions (26)–(27) then for $n_1 \geq 1$ we will not obtain the even square-integrable solutions. We see that the adiabatic basis is not complete, as is also shown by the results contained in table 1. Comparing adiabatic energies E^A with the ‘exact’ ones (calculated by the variational method described in the appendix) we see that the A method gives an energy spectrum which is completely wrong because energies of the even states for $n_1 \geq 1$ are absent from this spectrum. Note that the ground state energy E_0^- lies below the bottom of the potential ($E_0^- < \varepsilon^A(x_{\min}) = (2\lambda)^{1/2}$) which means that $\langle T_2 \rangle < 0$. This non-physical result is due to the singularity of the adiabatic wavefunction at $x = 0$.

Table 1. The Born-Oppenheimer (E^{BO}), adiabatic (E^A) and ‘exact’ (E) energies of CO with potential $V = \frac{1}{2}x_1^2 x_2^4$. The minus sign denotes energies corresponding to the adiabatic singular wavefunctions for $\alpha < 0$.

n_1, n_2	0, 0	0, 1	1, 0	1, 1	0, 2	2, 0
E^{BO}	0.500	1.500	0.866	2.598	2.500	1.118
E^A	0.134 ⁻	1.866	—	—	2.134 ⁻	—
E	0.588	1.578	1.068	2.810	2.612	1.353

If we take the solutions by Zirilli (24)–(25) then we will not obtain the new energy levels due to degeneracy $e_n^+ = e_n^-$. Thus the structure of the energy spectrum is also incorrectly reflected.

We see that the A method for the CO model considered completely fails. In order to understand better this important fact let us consider the properties of the ϕ_1^{BO} function which determine the features of the A^{BO} correction. For a fixed value of x_1 (let us take $x_1 = 1$) $\phi_1^{\text{BO}}(x_1, x_2)$ becomes, for $n_1 = 0$:

$$\phi_1^{\text{BO}}(x_1, x_2) = |x_2|^{1/2} \exp(-x_2^2/2) \equiv |x_2|^{1/2} \quad \text{for } x_2 \ll 1.$$

The A^{BO} term is determined by the term $\phi_1^{\text{BO}} \partial^2 / \partial x_2^2 \phi_1^{\text{BO}} \sim |x_2|^{-1}$ which has a singularity at $x_2 = 0$ which decides the properties of A^{BO} . Such a typical behaviour of A^{BO} is a consequence of the fact that the potential $V(x_1, x_2)$ becomes zero on the line $x_1 = 0$. Due to the slow variation of $V(x_1, x_2)$ near the line $x_1 = 0$ the function ϕ_1^{BO} is very diffuse, so it feels the shape of $V(x_1, x_2)$ in the large domain of x_1 . However, for $x_1 \gg 1$ the potential is a fast varying function of x_2 which causes fast variation of ϕ_1^{BO} for $x_2 \sim 0$. It is now clear that A^{BO} will have large values near $x_2 = 0$.

5. Conclusions

We have studied the AA for CO. We found that for coupling between oscillators which is not too strong the accuracy of adiabatic energies weakly depend on the frequency ratio μ . The BO and A methods work very well for a wide range of the parameters μ and a_{n_1, n_2} , and a hierarchy of slow and fast motions in the CO system is not required.

We have analysed the adiabatic potentials and we conclude that for strong coupling they significantly differ from the non-adiabatic potentials which means that they describe the dynamics of the system inadequately. Even for $\mu = 0$ the A method may turn out to be a failure giving an energy spectrum not corresponding to the real one.

The study of the CO model led to an important and rather general conclusion. If the potential of the system is a slowly varying function in some region along dynamical variables x_1 , then adiabatic wavefunctions will evidently differ from the exact wavefunctions (in our example in § 4 all adiabatic wavefunctions $\phi^A(x_1, x_2)$ have the nodal line $x_2 = 0$ which does not hold for the exact wavefunctions of even parity with respect to the reflection $x_2 \rightarrow -x_2$), then they will not be able to serve as the basis for expansion of the exact wavefunctions.

Acknowledgment

I wish to thank Dr A Wierzbicki for his help in numerical calculations. I also wish to thank the referee for his interesting suggestions and constructive comments which made the work clearer and helped in eliminating some errors.

Appendix

Calculation of eigenenergies for CO with potential $V = \frac{1}{2}x_1^2x_2^4$ is not a trivial problem due to strong coupling and anharmonicity. In the first step we look for the wavefunctions of CO in the form

$$\phi_{n_1, n_2}^H(x_1, x_2) = \phi_{n_1}^H(x_1)\phi_{n_2}^H(x_2). \quad (\text{A1})$$

We can obtain the best one-coordinate functions $\phi_{n_i}^H$ from the Hartree equations

$$(-d^2/dx_1^2 + \langle x_2^4 \rangle x_1^2 - 2e_{n_1}^H)\phi_{n_1}^H(x_1) = 0, \quad (\text{A2})$$

$$(-d^2/dx_2^2 + \langle x_1^2 \rangle x_2^4 - 2e_{n_2}^H)\phi_{n_2}^H(x_2) = 0. \quad (\text{A3})$$

The eigenvalues of these equations are well known:

$$e_{n_1}^H = w(n_1 + \frac{1}{2}), \quad w = \langle x_2^4 \rangle^{1/2}, \quad (\text{A4})$$

$$e_{n_2}^H = v^{1/3} N_2, \quad v = \langle x_1^2 \rangle / 2, \quad (\text{A5})$$

where N_2 are the eigenenergies of the one-dimensional quartic oscillator calculated by Bell *et al* (1970).

From the Hellmann-Feynman theorem (Hellmann 1937, Feynman 1939) we obtain

$$\langle x_1^2 \rangle = d \ln e_{n_1}^H / dw, \quad \langle x_2^4 \rangle = de_{n_2}^H / dv. \quad (\text{A6, 7})$$

Solving equations (A4)-(A7) we find

$$v = [(n_1 + \frac{1}{2})(3/N_2)^{1/2}]^{3/2}, \quad (\text{A8})$$

$$w = (n_1 + \frac{1}{2})/2v. \quad (\text{A9})$$

The eigenenergies of CO in the Hartree approximation are given by

$$E_{n_1, n_2}^H = e_{n_1}^H + e_{n_2}^H - \langle x_1^2 \rangle \langle x_2^4 \rangle = e_{n_1}^H + e_{n_2}^H - vw^2. \quad (\text{A10})$$

However, the values of E_{n_1, n_2}^H are not sufficiently accurate. The improvement of these energies can be obtained by diagonalisation of the Hamiltonian matrix in the basis of the Hartree wavefunctions (A1). This matrix can be factorised due to symmetry on four blocks. Diagonalisation of each block of dimension 10^2 gives energies of ∞ with accuracy of order 10^{-3} which is sufficient for our purpose.

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