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LAMP
SERIES REPORT

(Laser, Atomic and Molecular Physics)

ROTATION EFFECT
IN THE VIBRATION-ROTATION WAVE FUNCTION
OF A DIATOMIC MOLECULE

Mahmoud Korek

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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS

Preface

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These reports aim at informing LAMP researchers on the activity carried out at ICTP in their field of interest, with the specific purpose of stimulating scientific contacts and collaboration of physicists from Third World Countries.

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I-THE ROTATION HARMONICS

1-Introduction

In the Born-Oppenheimer [1] approximation, the vibration-rotation motion of a diatomic molecule is described by the wave function ψ_{vJ} and the energy E_{vJ} which are respectively the eigenfunction and the eigenvalue of the radial Schrödinger equation [2]

$$d^2\psi_{vJ}(r)/dr^2 + [k(E_{vJ} - U(r)) - J(J+1)/r^2]\psi_{vJ}(r) = 0 \quad (1)$$

where v and J are the vibrational and rotational quantum numbers, r is the internuclear distance, and $k = 2U/r^2$.

The wave function ψ_{vJ} for a given potential $U(r)$ is usually calculated by numerical methods where the rotational effect appears implicitly. If we have to study some transitions and if the rotational effect is considered, it is necessary to repeat the calculation for every value of J , where J is variable.

The aim of this work is to dissociate, in the wave function ψ_{vJ} , the effect of the rotation from the pure vibration wave function ψ_v and to give the analytic expression of this rotational effect.

$$\psi_{vJ} = \psi_v + \phi_R$$

where ϕ_R represents the rotational effect. This separation is possible by using the vibration-rotation canonical functions α_{vJ} and β_{vJ} [3], that we present in section 2.

2-Vibration-rotation canonical functions

The Schrödinger equation (1) can be simply represented by

$$\psi''_{\lambda}(x) = f_{\lambda}(x)\psi_{\lambda}(x), \quad (2)$$

where $\lambda = J(J+1)$, $x = r - r_e$ (r_e being the value of r at the equilibrium) and

$$f_{\lambda}(x) = -k[E_{\lambda} - U(x)] + \lambda/(x+r_e)^2 \quad (3)$$

The equation (2) is equivalent to the integral equation [4]

$$\psi_{\lambda}(x) = \psi_{\lambda}(0) + x\psi'_{\lambda}(0) + \int_0^x (x-t)f_{\lambda}(t)\psi_{\lambda}(t)dt \quad (4)$$

in the sense that any solution of equation (4) is solution of equation (2) and vice versa.

Kobeissi et al [5] associated to a given energy factor $f_{\lambda}(x)$ two functions $\alpha(x)$ and $\beta(x)$ defined by

$$\begin{aligned} \alpha(x) &= \sum_{i=0}^{\infty} A_i(x) \\ A_i &= \int_0^x (x-t)f_{\lambda}(t)A_{i-1}(t)dt \\ A_0(x) &= 1 \end{aligned} \quad (5)$$

and

$$\begin{aligned} \beta(x) &= \sum_{i=0}^{\infty} B_i(x) \\ B_i(x) &= \int_0^x (x-t)f_{\lambda}(t)B_{i-1}(t)dt \\ B_0(x) &= x \end{aligned} \quad (6)$$

by using the properties of the Volterra integral equation (4), we obtain:

i) The wave function $\psi_{\lambda}(x)$ is related to the functions $\alpha(x)$ and $\beta(x)$ by the relation

$$\psi_{\lambda}(x) = \psi_{\lambda}(0)\alpha(x) + \psi'_{\lambda}(0)\beta(x) \quad (7)$$

ii) $\alpha(x)$ and $\beta(x)$ are two particular solutions of equation (2) with the well determined initial values

$$\begin{aligned} \alpha(0) &= 1, & \alpha'(0) &= 0, \\ \beta(0) &= 0, & \beta'(0) &= 1 \end{aligned} \quad (8)$$

iii) The initial values $\psi_{\lambda}(0)$ and $\psi'_{\lambda}(0)$ for the unnormalized wave function $\psi_{\lambda}(x)$ can be deduced from $\alpha(x)$ and $\beta(x)$ by using eq.(7) on one hand, and on the other hand, the boundary conditions

$$\psi_{\lambda}(x) \xrightarrow{x \rightarrow \infty} 0 \quad (9)$$

we find

$$\begin{aligned} \psi_{\lambda}(0)/\psi'_{\lambda}(0) &= \lim_{x \rightarrow \infty} \alpha(x)/\beta(x) \\ \psi'_{\lambda}(0)/\psi_{\lambda}(0) &= \lim_{x \rightarrow -r_e} -\alpha(x)/\beta(x) \end{aligned} \quad (10)$$

The canonical functions $\alpha(x)$ and $\beta(x)$ are well defined by the analytic expressions (5) and (6), or numerically as particular solutions of eq. (2) with the initial values (8) [6].

3-The rotational Schrödinger equations

The vibration-rotation energy E_{vJ} being related to the rotational constants by

$$E_{\lambda} = E_v + \lambda B_v - \lambda^2 D_v + \lambda^3 H_v + \dots \quad (11)$$

or

$$E_{\lambda} = \sum_{n=0}^{\infty} e_n \lambda^n \quad (12)$$

where $e_0 = E_v$, $e_1 = B_v$, $e_2 = -D_v$, ...

Therefore, we can expand the energy factor $f_{\lambda}(x)$ in the same manner

$$f_{\lambda}(x) = \sum_{n=0}^{\infty} \epsilon_n(x) \lambda^n \quad (13)$$

where

$$\epsilon_0 = -k(e_0 - U(x)) \quad (14-0)$$

$$\epsilon_1 = -k e_1 + 1 / (r_0 + x)^2 \quad (14-1)$$

$$\epsilon_n = k e_n \quad (\text{for } i \geq 2) \quad (14-n)$$

by replacing $f_{\lambda}(x)$ in relations (5) and (6) by its expression (14) we find //

$$\alpha_{\lambda}(x) = \sum_{n=0}^{\infty} C_n(x) \lambda^n \quad (15)$$

$$\beta_{\lambda}(x) = \sum_{n=0}^{\infty} G_n(x) \lambda^n \quad (16)$$

$$\psi'(0)/\psi(0) = \sum_{n=0}^{\infty} l_n \lambda^n$$

where l_n are constants determined by the values of $C_n(x)$ and $G_n(x)$ at the boundaries ($x=+\infty$ or $x=-r_e$).

By replacing $\alpha_{\lambda}(x)$, $\beta_{\lambda}(x)$ and $\psi'_{\lambda}(x)$ by their expressions (15), (16) and (17) in eq.(7), we find

$$\psi_{\lambda}(x) = \psi_v(x) + \sum_{n=1}^{\infty} \varphi_n(x) \lambda^n \quad (18)$$

where the rotation harmonics $\varphi_n(x)$ depend on $C_n(x)$, $G_n(x)$ and l_n , i.e., unequally on $C_n(x)$ and $G_n(x)$.

Thus the rotation effect in the vibration-rotation wave function $\psi_{\lambda}(x)$ is separated from the pure vibration wave function $\psi_v(x)$.

By replacing the wave function $\psi_{\lambda}(x)$ by its expression (18) in equation (2), we obtain the rotational Schrödinger equations

$$\varphi_0''(x) - \epsilon_0(x) \varphi_0(x) = 0 \quad (19-0)$$

$$\varphi_1''(x) - \epsilon_0(x) \varphi_1(x) = \epsilon_1(x) \varphi_0(x) \quad (19-1)$$

$$\varphi_2''(x) - \epsilon_0(x) \varphi_2(x) = \epsilon_1(x) \varphi_1(x) + \epsilon_2(x) \varphi_0(x) \quad (19-2)$$

$$\varphi_n''(x) - \epsilon_0(x) \varphi_n(x) = \sum_{m=1}^n \epsilon_m(x) \varphi_{n-m}(x) \quad (19-n)$$

The first of these equations is the radial Schrödinger equation of pure vibration. All the others are nonhomogeneous differential equations having the same homogeneous equation and differing only by the second member.

4. Analytic expressions of the rotation harmonics

4.1 Pure vibration $\psi_v(x)$

For one electronic state and for a given potential, the solution of the vibrational Schrödinger equation (19-0) is

$$\psi_v(x) = \psi_v(0) \alpha_v(x) + \psi_v'(0) \beta_v(x) \quad (20)$$

where $\alpha_v(x)$ and $\beta_v(x)$ are the pure vibration canonical functions defined by relations (5) and (6) in which we replace $f_{\lambda}(x)$ by $f_v(x)$ (i.e., we make $J=0$).

4.2 Calculation of the rotation harmonics $\varphi_n(x)$

We found that, a rotational Schrödinger equation (19) is given by

$$\varphi_n''(x) - \epsilon_0(x) \varphi_n(x) = \sum_{m=1}^n \epsilon_m(x) \varphi_{n-m}(x),$$

we multiply this equation by $x-t$ and we integrate it between n zero and x , we obtain

$$\varphi_n(x) = \varphi_n(0) + \varphi_n'(0)x + \sum_{m=1}^n \int_0^x (x-t) \epsilon_m(t) \varphi_{n-m}(t) dt \quad (21)$$

by replacing $\epsilon_m(t)$ by its expression (14) in eq (21), we obtain

$$\varphi_n(x) = \varphi_n(0)\alpha_v(x) + \varphi'(0)\beta_v(x) + \sigma_n(x) \quad (22)$$

where
$$\sigma_n(x) = \sum_{m=0}^{\infty} K_m^n(x) \quad (23-0)$$

$$K_0^n(x) = \int_0^x (x-t)\epsilon_n(t)\varphi_0(t)dt \quad (23-1)$$

$$K_1^n(x) = \int_0^x (x-t) \int_0^t (t-t_1)\epsilon_n(t)\varphi_0(t)dt, dt \quad (23-2)$$

$$K_m^n(x) = \int_0^x (x-t)\epsilon_n(t)K_{m-1}(t)dt \quad (23-3)$$

for $x=0$
$$K_0^n(0) = K_1^n(0) = \dots = K_m^n(0) = \dots = 0$$

$$K_0^n'(0) = K_1^n'(0) = \dots = K_m^n'(0) = \dots = 0$$

therefore
$$\sigma_n(0) = \sigma_n'(0) = 0$$

for the derivation of order i we proved that

$$d^i K_m^n(0)/dx^i = 0 \text{ for } i \geq 2.$$

and
$$d^i \sigma_n(0)/dx^i \neq 0.$$

For the unnormalized wave function, we chose $\psi_v(0) = \varphi_0(0) = 1$; by using eq.(18) we obtain

$$\varphi_n(0) = 0$$

by replacing $\varphi_n(0)$ by its value in eq.(22) we find

$$\varphi_n(x) = \varphi_n'(0)\beta_v(x) + \sigma_n(x). \quad (24)$$

On the other hand, the rotation harmonics must be vanished at the boundaries.

$$\varphi_n(x) \rightarrow 0 \quad \begin{matrix} x \rightarrow \infty \\ x \rightarrow -r_e \end{matrix} \quad (25)$$

by using eq.(25) the eq.(24) becomes

$$\varphi_n'(0) = \lim_{x \rightarrow -r_e} \sigma_n(x)/\beta_v(x) = 1_n \quad (26)$$

Thus the rotation harmonic $\varphi_n(x)$ is given by

$$\varphi_n(x) = \sigma_n(x) + 1_n \beta_v(x),$$

this expression is valid without any restriction on the form of the given potential function.

5-Representation of a potential function

To simplify the numerical application, we have found a unified form of the potential function which is similar to the potential of Dunham for a diatomic molecule

$$U(x) = \sum_{n=0}^{\infty} \gamma_n x^n \quad (27)$$

where $x = r - r_e$ and $\gamma_0 = \gamma_1 = 0$

5.1 Morse Potential

The Morse potential function is given by /8/

$$U(r) = D[1 - \exp(-a(r - r_e))]^2 \quad (28)$$

this function can be written as

$$U(r) = D[1 - 2y_1(r) + y_2(r)]$$

where

$$y_1(r) = \exp(-a(r - r_e))$$

$$y_2(r) = \exp(-2a(r - r_e))$$

we divide the r -axis into intervals $I_i = [r_i, r_{i+1}]$, for this interval we take

$$x = r - r_i, \quad X = r_{i+1} - r_i \quad \text{and} \quad 0 \leq x \leq X$$

on one interval the function y_1 can be written as

$$y_1(r) = A_1 \exp(-ax) = A_1 \sum_{n=0}^{\infty} (-ax)^n / n! = \sum_{n=0}^{\infty} c_n x^n$$

with $A_1 = \exp(-a(r_i - r_e))$.

The coefficients are given by the recurrence relation

$$C_{n+1}/C_n = -a/n+1 \quad ; \quad C_0 = A_1$$

by using the same method, the function y_2 is given by

$$y_2(r) = A_2 \exp(-2ax) = A_2 \sum_{n=0}^{\infty} (-2ax)^n / n! = \sum_{n=0}^{\infty} d_n x^n$$

with $A_2 = \exp(-2a(r_i - r_e))$

$$d_{n+1}/d_n = -2a/n+1 \quad , \quad d_0 = A_2$$

we deduce for $U(x)$ the expansion

$$U(x) = \sum_{n=0}^{\infty} \gamma_n x^n$$

where $\gamma_0 = D[1 - 2C_0 + d_0]$ and $\gamma_n = D[-2C_n + d_n]$ for $n > 0$.

5.2 Lennard-Jones potential

The Lennard-Jones potential function is given by /9/

$$U(r) = D \left[1 - \left(r_e / r \right)^{-6} \right]^2 \quad (29)$$

This function can be written as

$$U(r) = D [1 - 2y_1(r) + y_2(r)]$$

where

$$y_1(r) = (r_e / r)^6$$

$$y_2(r) = (r_e / r)^{12}$$

whith $q = -6$.

In the interval $[r_i, r_{i+1}]$ the function $y_1(r)$ is given by

$$y_1(r) = A_1 (1 + x/r_i)^q = \sum_{n=0}^{\infty} [(q(q-1)...(q-n+1)(x/r_i)^n) / n!] = \sum_{n=0}^{\infty} C_n x^n \quad (30)$$

where $x = r - r_i$, $0 \leq x \leq r_{i+1} - r_i$ and $A_1 = (r_e / r_i)^q$.

The coefficients C_n can be obtained from the recurrence relation

$$C_{n+1}/C_n = (q-n)/(n+1)r_i \quad ; \quad C_0 = A_1$$

and y_2 has the form

$$y_2(r) = A_2 (1 + x/r_i)^{2q} = \sum_{n=0}^{\infty} [(2q(2q-1)...(2q-n+1)(x/r_i)^n) / n!] = \sum_{n=0}^{\infty} d_n x^n \quad (31)$$

with

$$A_2 = (r_e / r_i)^{2q}$$

$$d_{n+1}/d_n = (2q-n)/(n+1)r_i \quad ; \quad d_0 = A_2$$

Therefore the Lennard-Jones potential is given by /10/

$$U(x) = \sum_{n=0}^{\infty} \gamma_n x^n$$

with

$$\gamma_0 = D[1 - 2C_0 + d_0]$$

$$\gamma_n = D[-2C_n + d_n] \quad , \quad n > 0$$

5.3 Numerical potential.

A numerical potential is defined by the coordinates of its turning points with polynomial interpolations and extrapolations. For this potential, we divide the r -axis into intervals $I_i = [r_i, r_{i+1}]$ where r_i and r_{i+1} are the abscissas of two consecutive turning points. On one interval the polynomial form of the potential function, is given by

$$U(x) = \sum_{n=0}^N \gamma_n x^n \quad (32)$$

6-Numerical method

6.1 calculation of the vibrational wave function $\varphi_0(r)$

For one electronic state and for a given potential the vibrational wave function is given by (20)

$$\varphi_0(x) = \varphi_0(0) \alpha_v(x) + \varphi_0'(0) \beta_v(x) \quad (33)$$

where $x = r - r_i$

The determination of $\varphi_0(x)$, requires the calculation of $\alpha_v(x)$, $\beta_v(x)$ and $\varphi_0'(x)$.

6.1.1 Calculation of $\alpha_v(x)$ and $\beta_v(x)$

We found that, on one interval $I_i = [r_i, r_{i+1}]$, a given potential has the polynomial form

$$u(r) = \sum_{n=0}^N \gamma_n(i) (r-r_i)^n$$

The canonical functions $\alpha(x)$ and $\beta(x)$ are particular solutions of eq. (19-0); because $U(x)$ is polynomial; $\alpha(x)$ and $\beta(x)$ are polynomials

$$\alpha(r) = \sum_{n=0}^{\infty} a_n (r-r_i)^n \quad (34-1)$$

$$\beta(r) = \sum_{n=0}^{\infty} b_n (r-r_i)^n \quad (34-2)$$

We represent $\alpha(r)$ and $\beta(r)$ by the same function $y(r)$. For a given potential $U(r)$ and energy E , the function $y(r)$ is given by

$$y(r) = \sum_{n=0}^{\infty} C_n(i) (r-r_i)^n \quad (35)$$

by using eq. (19-0), we obtain the following relation

$$(n+2)(n+1)C_{n+2}(i) = -kEC_n(i) + k \sum_{m=0}^n C_m(i) \alpha_{n-m}(i)$$

with $C_0(i) = y(r_i)$, $C_1(i) = y'(r_i)$

The initial values $y(r_i)$ and $y'(r_i)$ are given by

$$y(r_i) = \sum_{n=0}^{\infty} C_n(i-1) (r_i - r_{i-1})^n \quad (36)$$

$$y'(r_i) = \sum_{n=1}^{\infty} n C_n(i-1) (r_i - r_{i-1})^{n-1} \quad (37)$$

where, for α

$$y(0) = 1, \quad y'(0) = 0$$

and for β

$$y(0) = 0, \quad y'(0) = 1$$

Therefore the canonical function $\alpha(r)$ and $\beta(r)$ are determined at any point r .

6.1.2 Calculation of $\varphi_0(0)$.

We found (7) that, the wave function $\varphi_0(x)$ is given by

$$\varphi_0(r) = \varphi_0(0) \alpha(r) + \varphi_0'(0) \beta(r) \quad (38)$$

and (9)

$$\varphi_0(r) \xrightarrow[r \rightarrow 0]{r \rightarrow \infty} 0$$

it is the same for the first derivative of $\varphi_0(x)$

$$\varphi_0'(r) \xrightarrow[r \rightarrow 0]{r \rightarrow \infty} 0$$

Therefore

$$\varphi_0'(0)/\varphi_0(0) = \lim_{r \rightarrow \infty} \alpha(r)/\beta(r) = \lim_{r \rightarrow \infty} \alpha'(r)/\beta'(r)$$

For the unnormalized wave function $\varphi_0(0) = 1$, the vibration wavefunction $\varphi_0(r)$ is determined at any point r .

6.2 calculation of the rotational harmonic function $\varphi_n(r)$

A rotational Schrödinger equation (19) can be written as

$$y''(r) - \epsilon_0(r)y(r) = s(r) \quad (39)$$

where $y(r)$ is a rotational harmonic function

and $s(r)$, for $y(r) = \varphi_n(r)$, is given by

$$s(r) = \sum_{m=1}^n \epsilon_m(r) \varphi_{n-m}(r)$$

The solution of the equation (39) is (24)

$$y(r) = y(0) \alpha_0(r) + y'(0) \beta_0(r) + \sigma(r)$$

6.2.1 calculation of the canonical function $\varphi_1(r)$

The first rotational Schrödinger equation (19-2) is given by

$$\varphi_1''(r) - \epsilon_0(r) \varphi_1(r) = \epsilon_1(r) \varphi_0(r)$$

where

$$x = r - r_i \quad \text{and} \quad \epsilon_1(r) = -k B_v + 1/r^2.$$

by replacing eq.(26-36-45) in eq.(46) we obtain

$$\varphi_1(x) = \sum_{n=0}^{\infty} C_n(i)x^n \quad (40)$$

where, the coefficients $C_n(i)$ are determined from those of $\sigma_1(r)$ and $\beta_0(r)$.

Having the rotation harmonics φ_1 we find φ_2 , by the same method by using eq. (19-2) and so on for the other harmonics.

6.2.2. Calculation of φ_n .

The n^{th} rotational Schrödinger equation (19-n) is given by

$$\varphi_n''(x) - \epsilon_0(x)\varphi_n(x) = \sum_{m=1}^n \epsilon_m(x)\varphi_{n-m}(x). \quad (41)$$

The second member can be written as

$$s_n(x) = \sum_{m=1}^n \epsilon_m(x)\varphi_{n-m}(x) = \sum_{n=0}^{\infty} \delta_n^n(i)x^n \quad (42)$$

The rotation harmonics is given by (23).

$$\varphi_n = \sum_{p=0}^{\infty} C_p^n(i)x^p \quad (43)$$

By replacing eq. (43-42) in eq.(41) we obtain the recurrence relation

$$C_{n+2}^n(i) = \left(\sum_{m=0}^n [C_m^n(i)\gamma_{n-m}(i) + \delta_m^n(C)] - kE_v C_n^n(i) \right) / ((n+1)(n+2))$$

with the initial values

$$C_0^n = \sigma_n(0) = 0$$

$$C_1^n = \sigma_n'(0) = 0$$

Thus, we can calculate the rotation harmonic φ_n at any point r .

On the interval $[r_i, r_{i+1}]$, $\epsilon_1(x)$ is given by

$$\epsilon_1(x) = \sum_{n=0}^N \gamma_n^1(i)x^n$$

where $\gamma_1^1(i), \gamma_2^1(i), \dots$ are the coefficients of expansion of $1/r^2$.

By using eq.(36) the vibrational Schrödinger equation is given by

$$\varphi_0(x) = \sum_{n=0}^N C_n^0(i)x^n$$

with
$$C_{n+2}^0(i) = \left(k \sum_{m=0}^n C_m^0(i)\gamma_{n-m}^0(i) - kE_v C_n^0(i) \right) / ((n+1)(n+2)). \quad (42)$$

The second member $s_1(i)$ of the eq.(41) is given by

$$s_1(x) = \epsilon_1(x)\varphi_0(x) = \left(\sum_{n=0}^N \gamma_n^1(i)x^n \right) \left(\sum_{n=0}^N C_n^0(i)x^n \right) = \sum_{n=0}^N \delta_n^1(i)x^n \quad (43)$$

with

$$\delta_n^1(i) = \sum_{m=0}^n \gamma_m^1(i)C_{n-m}^0(i) \quad (44)$$

We found that, eq.(23) the canonical function $\sigma_1(x)$ can be written as

$$\sigma_1(x) = \sum_{n=0}^{\infty} C_n^1(i)x^n \quad (45)$$

By replacing eq. (44-45) in eq.(24) we obtain the relation of recurrence

$$C_{n+2}^1(i) = \left(\sum_{m=0}^n [kC_m^1(i)\gamma_{n-m}^0(i) + \delta_m^1(i)] - kE_v C_n^1(i) \right) / ((n+1)(n+2))$$

with

$$C_0^1(0) = 0 \quad \text{and} \quad C_1^1(i) = 0.$$

Thus, the canonical function $\sigma_1(r)$ is determined at any point r .

The rotational harmonics φ_1 is given by (24)

$$\varphi_1(x) = \sigma_1(x) + \varphi_1'(0)\beta(x) \quad (46)$$

II. Numerical Application

In order to present examples of numerical application, we chose
i) The Morse potential, used by Cashion /11/, with the constants

$$2\mu/\hbar^2 = 1; D = 605.559 \text{ cm}^{-1}, a = 0.988 \text{ 879 \AA}, r_e = 2.408 \text{ 73 \AA}$$

and the eigenvalue of energy

$$E_v = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2$$

where

$$\omega_e = 48.668 \text{ 883} \quad \text{and} \quad \omega_e x_e = 0.977 \text{ 881 676 641 cm}^{-1}$$

ii) The Lennard-Jones potential, characterized by

$$2\mu/\hbar^2 = 10 \text{ 000}, D = 1 \text{ cm}^{-1} \quad \text{and} \quad r_e = 1 \text{ \AA}.$$

iii) A numerical potential of the ground state $X_1^+\Sigma^+$ of I_2 /12/, the constants of this potential are

$$2\mu/\hbar^2 = 3.764 \text{ 004 7} \quad \text{and} \quad r_e = 2.666 \text{ 399 954 \AA}$$

In tables (1-3) we give α/β and α'/β' for the three potentials. We notice that

$$\lim_{r \rightarrow 0} \frac{\alpha(r)}{\beta(r)} = \lim_{r \rightarrow 0} \frac{\alpha'(r)}{\beta'(r)} = \alpha'(0)/\beta'(0).$$

In tables (4-6) we give the pure vibrational wave function φ_0 for the three potentials (Morse, Lennard-Jones, and numerical). In tables (7-9) we give the rotational harmonics $\varphi_1, \varphi_2, \varphi_3$ and φ_4 for the vibrational level $v=5$ of Morse potential. We notice that, the convergence of all these functions at infinity.

In figures (1-5) we show the continuity of the functions $\varphi_0, \varphi_1, \varphi_2, \varphi_3$ and φ_4 for the Morse potential for the vibrational level $v=5$.

In table 10 we give $\alpha(r)/\beta(r)$ and $\alpha'(r)/\beta'(r)$, we find

$$\lim_{r \rightarrow 0} \frac{\alpha(r)}{\beta(r)} = \lim_{r \rightarrow 0} \frac{\alpha'(r)}{\beta'(r)} = \alpha'(0)/\beta'(0)$$

In table 11 we give the function φ_0, φ_1 and φ_2 of the Morse potential at several points ($x=0.1, 0.2, 0.3, 0.4, 0.5 \text{ \AA}$) and for several vibrational levels ($v=0, 10, 20$). The last level is at few cm^{-1} from the dissociation.

At each x the vibration-rotation wavefunction is deduced from its expression $\varphi_0 + \lambda \varphi_1 + \lambda^2 \varphi_2$ (with $J=1, \lambda=2$) and compared to its value ψ_λ computed directly from the Schrödinger equation (1) by using the method described in /3/ and /13/.

We notice that the agreement between the directly calculated vibration-rotation wave function ψ_λ and $\sum_{n=0}^2 \lambda^n \varphi_n$ is satisfactory to the 7th (or the 8th) significant figure.

In table 12, we compare the new results to those obtained by using the Runge-Kutta difference equation with a mesh size $h=0.005 \text{ \AA} / 14/$. The agreement between ψ_λ and $\sum_{n=0}^2 \lambda^n \varphi_n$ is much more satisfactory with the expressions of the rotation harmonics derived in this work, than with the Runge-Kutta numerical treatment.

In table 13 we finally give (for $v=10$) the values of $\sum_{n=0}^m \lambda^n \varphi_n$ and ψ_λ at several points and for several values of λ . We notice that the difference

$$\Delta = \left| \psi_\lambda - \sum_{n=0}^2 \lambda^n \varphi_n \right|$$

increases, at point x with λ . The mean value Δ for the five points considered here increases like λ^3 . This means that when J increases, we need higher harmonics ($\varphi_3, \varphi_4, \dots$) to obtain a desired accuracy. This results confirms the validity of the present method.

III. Conclusion

We proved that the vibration rotation wave function $\psi_{v,J}$ of any electronic diatomic potential can be written $\psi_{v,J} = \psi_v \varphi$ where ψ_v is the pure vibration wave function of the level v .

We defined a set of "rotation harmonics" $\varphi_n(r)$, and proved that the rotation effect ϑ_R is $\vartheta_R = \sum_{n=1}^{\infty} \lambda^n \varphi_n$, with $\lambda = J(J+1)$. The n harmonics $\varphi_1, \varphi_2, \dots$ are the eigenfunctions of some simple differential equations having as eigenvalues the rotational constants B_v, D_v, \dots respectively. The analytic expression of each harmonic φ_n is given in terms of the potential $U(r)$.

The harmonics φ_n are calculated by using these new expressions for many examples and compared to the values found by direct numerical integration of the rotation Schrödinger equations. The vibration-rotation wavefunction deduced from the harmonics is better approached by using the expressions found in the present work (up to eight significant figures) than by using numerical integration.

The use of the rotation harmonics approach for the calculation of the rotational and distortion constants, and the Franck-Condon factors will be in a forthcoming second report.

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Table 1

Values of $\alpha(r)/\beta(r)$ and $\alpha'(r)/\beta'(r)$ for the vibrational level $v=5$ of Morse potential.

Positive Branch ($r > r_e$)		Negative Branch ($r < r_e$)		
i	$-\alpha(r)/\beta(r)$	$-\alpha'(r)/\beta'(r)$	$-\alpha(r)/\beta(r)$	$-\alpha'(r)/\beta'(r)$
1	-5.40960675546	43.3837748426	5.41083336559	-43.286386937
2	18.7139283585	-13.0770404689	-18.5883293431	13.3315040416
3	-28.729855314	8.01266460999	30.5071786938	-7.18977360035
4	997223041033	-364.403297404	404770929655	-165.542786433
5	34.6831616856	-7.42924648979	-19.8514122781	16.2650736984
6	-22.4043276515	9.86404059676	259.081910301	5.59152563375
7	-.224101796083	245.365772336	28.9069385527	10.639113445
8	17.8494535186	-15.2766994226	20.568344066	18.158725832
9	-228.092337865	-364917383574	19.5677865145	19.4316661978
10	-16.5811801997	10.9001612577	19.5066816296	19.5031948863
11	-3.89198490952	30.5240074553	19.5050445282	19.5050044640
12	3.25162638255	80.8339987398	19.5050253026	19.5050251024
13	9.14585430269	76.9821070214	19.5050252054	19.505025205
14	14.0635287397	34.3543794383	19.5050252052	19.5050252052
15	17.3199715537	23.1546520549		
16	18.8382338666	20.3758949585		
17	19.3430484524	19.6941575132		
18	19.4720994434	19.5415107097		
19	19.49922973	19.5112720057		
20	19.5041223568	19.505982074		
21	10.5048987994	19.5051576496		
22	19.5050091099	19.5050419302		
23	19.505023323	19.5050271488		
24	19.5050250014	19.5050254146		
25	19.5050251846	19.5050252263		
26	19.5050252032	19.5050252072		
27	19.505025205	19.5050252054		
28	19.5050252052	19.5050252052		
29	19.5050252052	19.5050252052		
30	19.5050252052	19.5050252052		

Table 2

Values of $\alpha(r)/B(r)$ and $\alpha'(r)/B'(r)$ for the vibrational level $v=5$ of Lennard-Jones potential.

Positive Branch ($r > r_e$)		Negative Branch ($r < r_e$)	
i	$-\alpha(r)/B(r)$	$-\alpha'(r)/B'(r)$	$-\alpha(r)/B(r)$
1	-8.53309527876	582.583730972	8.55793146318
2	268.160957097	-20.9760909598	-253.872642468
3	-37.0489910474	137.082303662	46.5469314447
4	79.3862740149	-70.7839656618	-37.1390335454
5	-143.514799368	34.1838277369	-139.775191416
6	1.74401868489	3812.27847623	-227.991550406
7	126.902268258	-47.6083501307	-237.799247853
8	-174.102172388	24.3995687793	-237.94067235
9	-28.0186537156	142.595446433	-237.941053102
10	24.252442052	-461.074189181	-237.941053273
11	88.187659301	-105.457221124	-237.941053273
12	265.548902569	-70.614113349	-237.941053273
13	-3882.0274846	-88.27065969	-237.941053273
14	-392.641470934	-145.4688626	-237.941053273
15	-274.465371074	-201.683469141	-237.941053273
16	-246.927081742	-227.97622409	-237.941053273
17	-239.941246896	-235.72861161	-237.941053273
18	-238.335478945	-234.513925032	-237.941053273
19	-238.010565664	-237.867131058	-237.941053273
20	-237.952156149	-237.929399715	-237.941053273
21	-237.942681147	-237.939360635	-237.941053273
22	-237.941274701	-237.940824625	-237.941053273
23	-237.941081464	-237.941024316	-237.941053273
24	-237.941056657	-237.941049811	-237.941053273
25	-237.941053659	-237.94105288	-237.941053273
26	-237.941053315	-237.941053231	-237.941053273
27	-237.941053278	-237.942053269	-237.941053273
28	-237.941053274	-237.941053273	-237.941053273
29	-237.941053273	-237.941053273	-237.941053273

Table 3

Values of $\alpha(r)/B(r)$ and $\alpha'(r)/B'(r)$ for the vibrational level $v=5$ of the electronic state X_{1g}^+ of the molecule I_2 .

Positive Branch ($r > r_e$)		Negative Branch ($r < r_e$)	
i	$-\alpha(r)/B(r)$	$-\alpha'(r)/B'(r)$	$-\alpha(r)/B(r)$
1	24.6411534498	-13.0944868232	-22.9380055239
2	14.7051288081	-15.3726007682	-12.7843419837
3	7.11398344363	-10.5608527087	-4.91376615078
4	3.86838615473	-4.76070517287	-1.64768008197
5	2.27284104229	-1.70757479909	-0.209196082303
6	1.4794478188	-0.343501519824	-0.384187218196
7	1.09061089185	0.25252056711	0.610769102809
8	0.903003301478	0.516102895015	0.691895357669
9	0.813472413974	0.633818768792	0.719533319326
10	0.771002675241	0.687124505501	0.728587161413
11	0.750900986071	0.711519269812	0.73145957588
12	0.74138201921	0.722785865187	0.732346250688
13	0.736864260516	0.728032044901	0.732613389938
14	0.734712790594	0.730493362138	0.732692115173
15	0.733683939832	0.731656352133	0.73271484408
16	0.733189649265	0.73220961601	0.732721281275
17	0.73295100184	0.732474547962	0.732723071027
18	0.73283518921	0.732602221087	0.73272392466
19	0.732778692256	0.732664120533	0.732723691312
20	0.732750985472	0.732694333106	0.73272372601
21	0.73273732567	0.732709154973	0.732723735032
22	0.732730555593	0.732716471044	0.732723737341
23	0.732727182567	0.73272010283	0.732723737923
24	0.732725493284	0.732721915748	0.732723738067
25	0.732724642892	0.732722825674	0.732723738103
26	0.732724212621	0.732723284828	0.732723738111
27	0.732723993821	0.732723517739	0.732723738113
28	0.732723882006	0.732723636498	0.732723738114
29	0.732723824584	0.732723697359	0.732723738114
30	0.732723794952	0.732723728705	0.732723738114
31	0.732723779589	0.732723744928	0.732723738114
32	0.732723771585	0.732723753366	0.732723738114
33	0.732723767396	0.732723757775	0.732723738114
34	0.732723765194	0.7327236009	0.732723738114
35	0.732723764031	0.73272361311	0.732723738114
36	0.732723763414	0.732723761958	0.732723738114
37	0.732723763085	0.732723762302	0.732723738114
38	0.732723762909	0.732723762486	0.732723738114
39	0.732723762814	0.732723762585	0.732723738114
40	0.732723762763	0.732723762638	0.732723738114
41	0.732723762735	0.732723762667	0.732723738114
42	0.73272376272	0.732723762683	0.732723738114
43	0.732723762712	0.732723762691	0.732723738114
44	0.732723762708	0.732723762696	0.732723738114
45	0.732723762705	0.732723762699	0.732723738114
46	0.732723762704	0.7327237627	0.732723738114
47	0.732723762703	0.732723762701	0.732723738114
48	0.732723762703	0.732723762701	0.732723738114

Table 4

Values of the functions $\varphi_0(r)$ and $\varphi'_0(r)$ of pure vibration for the vibrational level $v=5$ of Morse potential.

Positive Branch ($r > r_e$)		
i	$\varphi_0(r)$	$\varphi'_0(r)$
1	1.5261152169	-7.98946719441
2	.0330536947943	-24.5292625815
3	-1.5236110661	-9.90210198121
4	-1.2573677786	15.4638044313
5	.432513921826	22.4446334921
6	1.72150483251	7.27356113694
7	1.48465319309	-12.2211804232
8	.0856932779427	-20.2852957784
9	-1.40619320835	-15.3632219407
10	-2.24010773249	-5.06665639796
11	-2.27315667097	3.29533067773
12	-1.82979461339	7.02173584957
13	-1.24985232285	7.02261980933
14	-.751598814365	5.29833699026
15	-.407091981031	3.35738341448
16	-.201769533343	1.87165983409
17	-.0926005392457	.942242865515
18	-.0397194315432	.435735752679
19	-.0160439282221	.187381801915
20	-.00614161992026	.0756375403017
21	-.00224006022255	.02087302988
22	-.000782104053378	.0104871437014
23	-.000262463122739	.00364313021699
24	-8.49653786107E-5	.00121578833507
25	-2.66234840576E-5	.000391189093283
26	-8.11618156972E-6	.000121497115259
27	-2.47436300858E-6	3.56086494216E-5
28	-9.64879825045E-7	6.59382996099E-6
29	-1.15025729297E-6	-1.19385618349E-5
Negative Branch ($r < r_e$)		
i	$\varphi_0(r)$	$\varphi'_0(r)$
1	-.863444597076	21.0475611782
2	-1.60375898079	-4.49390958135
3	-.337121318153	-23.1106358779
4	1.36254014611	-15.6315819184
5	1.89472605084	1.86240111617
6	1.34051793144	9.80959685265
7	.606908242633	7.51847513619
8	.186431691262	3.18667065118
9	.039434816618	.857714328413
10	.00572649806442	.151841079231
11	.000563677430922	.0177468245691
12	3.68957626316E-5	.00135515591133
13	1.51175780184E-6	6.86081720271E-5
14	-1.79526505898E-6	8.76497202941E-5

Table 5

Values of the functions $\varphi_0(r)$ and $\varphi'_0(r)$ of pure vibration for the vibrational level $v=5$ of Lennard-Jones potential.

Positive Branch ($r > r_e$)		
i	$\varphi_0(r)$	$\varphi'_0(r)$
1	-3.13962075802	-101.42608662
2	-1.86202653869	203.956738468
3	2.56633553125	168.58239264
4	3.17140234921	-111.377394027
5	-.654967008303	-220.778874907
6	-3.82354326992	-66.6296676653
7	-3.0530310793	130.33670383
8	.439476589583	191.977681701
9	3.74888277176	124.893064205
10	5.21265423891	23.1255963384
11	4.90867522096	-45.4549934818
12	3.71101209545	-67.532742457
13	2.40668993004	-59.7358350781
14	1.38768702759	-41.7071739587
15	.727793535103	-25.0004396061
16	.352794827283	-13.3932683435
17	.15996600748	-6.56690432643
18	.0684827339058	-2.9943757915
19	.0278890457674	-1.28454581564
20	.0108708280681	-.523030721294
21	.00407665463815	-.20355221391
22	.00147723731968	-.076148900588
23	.000519179042376	-.0275131411045
24	.000177526829655	-.00963971503442
25	5.91779475849E-5	-.0032888229932
26	1.91341281403E-5	-.00110380287111
27	5.563403975453E-6	-.00039070066974
28	-8.85582554629E-9	-.000225758623334
Negative Branch ($r < r_e$)		
i	$\varphi_0(r)$	$\varphi'_0(r)$
1	3.3756283036	41.9720591946
2	-.0624704046312	240.383914149
3	-3.64539685385	78.1286172484
4	-3.19707609503	-92.9480142721
5	-1.24408715771	-80.3205908826
6	-.243401663913	-24.0368012007
7	-.023611230964	-3.19206493108
8	-.00106024183462	-.186593069381
9	-1.99028081696E-5	-.00442596299465
10	-2.25492576952E-6	.000526717130805

Table 6

Values of the functions $\varphi_0(r)$ and $\varphi_0'(r)$ of pure vibration for the vibrational level $v=5$ of the electronic state $X_1^1\Sigma_g^+$ of the molecule I_2 .

Positive Branch ($r > r_e$)		
i	$\varphi_0(r)$	$\varphi_0'(r)$
1	.765943348047	11.4376628555
2	.599618659151	12.4772954289
3	.374287020714	10.893758705
4	.237273757188	8.41313943767
5	.152124712517	6.20681128366
6	.0984347760566	4.47857834452
7	.0641994956137	3.19296457863
8	.0421654704651	2.2610316368
9	.0278698001447	1.59508418761
10	.0185283597037	1.12313365418
11	.0123847073432	.790269184369
12	.00832016414896	.556121816429
13	.00561630735131	.391619143028
14	.00380834596402	.276079218929
15	.00259355875194	.294897881246
16	.00177357195313	.137809007678
17	.00121764937602	.0976143669794
18	.000839172614119	.0692732751013
19	.000580466293391	.0492572470533
20	.000402944675404	.0350956376776
21	.000280677119978	.0250572256282
22	.000196962552525	.0179275891242
23	.000137540428117	.0128536767802
24	9.67410251889E-5	.00923535306264
25	6.82528085534E-5	.0066396910822
26	4.82976590348E-5	.00479811404784
27	3.42764634951E-5	.00346943433215
28	2.43950087214E-5	.00251398340697
29	1.74106071427E-5	.00182548314478
30	1.24597587501E-5	.00132831329393
31	8.94055813205E-6	.000962558211753
32	6.4321636728E-6	.000707699201213
33	4.63944968487E-6	.000518161134096
34	3.35485310643E-6	.000380162964575
35	2.43197837335E-6	.000279485917417
36	1.76728394763E-6	.000205888674827
37	1.28734427562E-6	.000151980028022
38	9.39945493883E-7	.000112415174954
39	6.87867213855E-7	8.33212397993E-5
40	5.04503077536E-7	6.18867343292E-5
41	3.70786437998E-7	4.60667070001E-5
42	2.73019395536E-7	3.43713909388E-5
43	2.2033848011E-7	2.56126421319E-5
44	1.68607796291E-7	1.9297003746E-5
45	1.0967050911E-7	1.45421363413E-5
46	8.07704054751E-8	1.10222026706E-5
47	5.01688843185E-8	8.4275373777E-6
48	4.28481143899E-8	6.52857124805E-6
49	3.03116394207E-8	5.16697764397E-6
50	2.04308889806E-8	4.22634184361E-6
51	1.23400241137E-8	3.61725687981E-6
52	5.29689714313E-9	3.28943133354E-6

Continuing of table 6

Negative Branch ($r < r_e$)		
i	$\varphi_0(r)$	$\varphi_0'(r)$
1	.792786740751	-10.6754733904
2	.614444341527	-11.8835079538
3	.361605169335	-9.99286213227
4	.20893953208	-7.10088788664
5	.119024476452	-4.68094260476
6	.0669843979369	-2.94890892323
7	.0372891767298	-1.79958232818
8	.0205513860433	-1.07169795049
9	.0112208194416	-.625640235234
10	.00607216340443	-.359106908141
11	.00325808829335	-.203083387493
12	.00173386524247	-.113327684315
13	.00091539640482	-.0624748922767
14	.000479550561419	-.0340539533269
15	.000249325198045	-.0183665000711
16	.000128667382626	-.00980680141083
17	6.59167691168E-5	-.00518646114779
18	3.35270680125E-5	-.00271783993048
19	1.69320055079E-5	-.00141164147863
20	8.49124648994E-6	-.000726923171896
21	4.22885659646E-6	-.000371200279914
22	2.09180893762E-6	-.000187991041457
23	1.0280814422E-6	-9.44094499573E-5
24	5.02719558426E-7	-4.69626393169E-5
25	2.45931005338E-7	-2.30160076171E-5
26	1.23109202832E-7	-1.08480453491E-5
27	6.85977283864E-8	-4.33623790741E-6
28	5.28525561094E-8	-8.75443220139E-6
29	6.7288056016E-8	4.21702861786E-6

Table 7

Values of the rotation harmonics for some values of x in the case of the Morse potential. The sum of the harmonics is compared at every point and for every v , to the vibration-rotation wavefunction $\psi_v(r)$ computed directly from the Schrödinger equation.

J=1, $\lambda=2$				
	x=0.1A		x=0.3A	
	R.K	F.C.*	R.K	F.C.*
$v=0$				
φ_0	0.933 966 4	0.933 966 4	0.424 124 4	0.429 124 5
φ_1	0.000 273 6	0.000 273 6	0.000 372 3	0.000 373 3
φ_2	0.0	0.0	0.000 000 3	0.000 000 2
$\varphi_0 + \lambda\varphi_1 + \lambda^2\varphi_2$	0.934 513 6	0.934 513 6	0.429 870 2	0.429 871 9
ψ_λ	0.934 514 2	0.934 513 7	0.429 872 3	0.429 871 7
$v=5$				
φ_0	1.297 935 9	1.297 935 5	-1.513 973 6	-1.513 972 7
φ_1	0.005 359 9	0.005 350 9	-0.005 410 2	-0.005 401 2
φ_2	0.000 013 3	0.000 013 4	-0.000 013 2	-0.000 013 5
$\varphi_0 + \lambda\varphi_1 + \lambda^2\varphi_2$	1.308 708 9	1.308 691 1	-1.524 846 8	-1.524 829 1
ψ_λ	1.308 711 0	1.308 691 0	-1.524 848 0	-1.524 828 9
$v=10$				
φ_0	-0.143 356 1	-0.143 357 9	0.847 575 7	0.847 579 1
φ_1	0.003 050 4	0.003 006 7	-0.001 373 4	-0.001 357 8
φ_2	0.000 002 4	0.000 002 7	-0.000 001 9	-0.000 001 9
$\varphi_0 + \lambda\varphi_1 + \lambda^2\varphi_2$	-0.137 244 5	-0.137 333 7	0.844 821 3	0.844 855 9
ψ_λ	-0.137 253 2	-0.137 333 9	0.844 824 6	0.844 855 8

* Canonical formulation

Table 8

Values of the rotation harmonics for some values of x in the case of the Morse potential. The results of the present work (canonical formulation) are compared to those obtained by the Runge-Kutta (R.K) difference equations. The wavefunction $\psi_v(x)$ is also compared to the sum of harmonics ($\lambda=2$) for both methods.

J=1 ; $\lambda=2$				
		v=0	v=10	v=20
		$x=0.1A$	φ_0	0.933 966 4
	φ_1	0.000 273 6	0.003 010 6	0.003 706 2
	φ_2	0.000 000 0	0.000 000 7	-0.000 006 9
	$\varphi_0 + \lambda\varphi_1 + \lambda^2\varphi_2$	0.934 513 6	-0.137 333 9	-1.074 422 2
	ψ_λ	0.934 513 7	-0.137 333 9	-1.074 422 2
$x=0.3A$	φ_0	0.429 124 5	0.847 579 1	0.240 006 2
	φ_1	0.000 373 3	-0.001 357 8	0.005 064 4
	φ_2	0.000 000 2	-0.000 001 9	-0.000 011 7
	$\varphi_0 + \lambda\varphi_1 + \lambda^2\varphi_2$	0.429 871 9	0.844 855 9	0.250 088 2
	ψ_λ	0.429 871 7	0.844 855 8	0.250 088 3
$x=0.5A$	φ_0	0.095 410 2	-1.107 570 4	1.092 463 0
	φ_1	0.000 137 2	-0.000 499 0	-0.004 590 9
	φ_2	0.000 000 0	0.000 000 7	0.000 004 8
	$\varphi_0 + \lambda\varphi_1 + \lambda^2\varphi_2$	0.095 684 6	-1.108 565 6	1.083 300 4
	ψ_λ	0.095 684 9	-1.108 565 5	1.083 300 5

Table 9

Values of the sum of harmonics $\psi_0 + \lambda\psi_1 + \lambda^2\psi_2$ (1st line) for some values of x of Morse potential ($v=10$) and for some values of λ , compared to the wavefunction $\psi_\lambda(x)$ (2nd line). The mean value Δ of the difference in absolute value for the five considered points is given in the last line.

v=10					
λ $x(\text{\AA})$	2	6	12	20	30
0.1	-0.137 333 9	-0.125 222 1	-0.106 894 6	-0.082 159 8	-0.050 162 1
	-0.137 333 9	-0.125 222 0	-0.106 894 0	-0.082 157 0	-0.050 752 7
0.2	-0.910 136 0	-0.920 168 7	-0.935 312 7	-0.955 681 5	-0.981 426 9
	-0.910 136 0	-0.920 168 7	-0.935 311 9	-0.955 678 1	-0.981 415 3
0.3	0.844 855 8	0.839 363 4	0.831 010 1	0.819 657 9	0.805 123 4
	0.844 855 8	0.839 363 4	0.831 008 3	0.819 650 0	0.805 096 4
0.4	0.388 680 1	0.403 239 9	0.425 246 4	0.454 899 8	0.492 466 9
	0.388 680 1	0.403 239 9	0.425 246 3	0.454 899 0	0.492 464 1
0.5	-1.108 565 5	-1.110 538 2	-1.113 453 5	-1.117 258 7	-1.121 883 9
	-1.108 565 5	-1.110 537 9	-1.113 451 0	-1.117 247 3	-1.121 845 0
Δ	0	1	9	51	180

Table 10

Values of $\alpha_1(r)/\beta(r)$ and $\alpha'_1(r)/\beta'(r)$ for the vibrational level $v=5$ of Morse potential.

Positive Branch ($r > r_e$)		Negative Branch ($r < r_e$)		
i	$-\alpha_1(r)/\beta(r)$	$-\alpha'_1(r)/\beta'(r)$	$-\alpha_1(r)/\beta(r)$	$-\alpha'_1(r)/\beta'(r)$
1	-.00154359667757	-.00605259550985	.000488936972069	-.0007193178146
2	-.00490772666213	3.74326024066E-5	-.00411341728646	.00665028914915
3	.00229731132734	-.00335336291984	.0195071721751	.00529673578339
4	-.00199805829652	.0398409009613	.00637880364086	-.10141357493
5	-.00503862172098	-.00134762437582	-.0163381377891	.0375176664835
6	.00136156270583	-.000498787655742	.5083686764	.042317760753
7	.00191040021614	.0459861142443	.0924403119269	.0647748087264
8	.00712464593176	-.00393231042233	.0811907728676	.0786894138897
9	-.0654618853981	.00379328978873	.0802912896981	.0802089776927
10	.0026682936345	.0179298788029	.0802608413421	.0802601122871
11	.0132847941346	.0578202846496	.0802606397047	.0802606444801
12	.0257143755615	.198938739004	.0802606443473	.0802606444557
13	.0413474082112	.248704650496	.0802606444061	.0802606444064
14	.0579107570647	.132465594703	.0802606444063	.0802606444063
15	.0705847386187	.0947082953814		
16	.077107096476	.0840348267687		
17	.0794480127039	.0811439761154		
18	.0800863153761	.0804424454747		
19	.0802283930917	.0802936203781		
20	.0802553811185	.0802659677734		
21	.080259874593	.0802614178021		
22	.0802605422612	.0802607465942		
23	.0802606319975	.0802606568111		
24	.0802606430262	.080260645813		
25	.0802606442771	.0802606445686		
26	.080260644409	.0802606444376		
27	.080260644422	.0802606444247		
28	.0802606444232	.0802606444235		
29	.0802606444234	.0802606444234		
30	.0802606444234	.0802606444234		
31	.0802606444234	.0802606444234		

Table 11

Values of the first harmonic rotation $\varphi_1(r)$ and $\varphi_1'(r)$ for the vibrational level $v=5$ of Morse potential

Positive Branch ($r > r_e$)		
i	$\varphi_1(r)$	$\varphi_1'(r)$
1	.0050108184351	.0288791000062
2	.00355851417604	-.0603956866106
3	-.00246265349384	-.0720438956644
4	-.00558886826473	-.00162810486412
5	-.00243068083308	.0680050941637
6	.00324092693341	.0609282858957
7	.0058960003764	.00185457288561
8	.00378555848491	-.0491027690407
9	-.000827609911226	-.0591237209198
10	-.00479516478683	-.0367011697466
11	-.00650709642424	-.00671120511304
12	-.00614077523225	.0135878065961
13	-.0046949508914	.0205806936653
14	-.00308704580523	.0186270335234
15	-.00180269425384	.0132907570269
16	-.00095425644033	.00811141445038
17	-.000464573675649	.00440069173551
18	-.000210298874917	.00217119700082
19	-8.92831100045E-5	.000989161387976
20	-3.58035942111E-5	.00042079444198
21	-1.36423100298E-5	.00016859741402
22	-4.96428340995E-6	6.40646689158E-5
23	-1.73277972497E-6	2.32199028739E-5
24	-5.82422879383E-7	8.06607705674E-6
25	-1.89231969507E-7	2.69561442346E-6
26	-5.98569330401E-8	8.66222545128E-7
27	-1.92947220369E-8	2.56387117455E-7
28	-9.06244593932E-9	2.75700630866E-8
29	-1.40124218373E-8	-1.68219333551E-7

Negative Branch ($r < r_e$)		
i	$\varphi_1(r)$	$\varphi_1'(r)$
1	-.00488700952643	.0271443283565
2	-.0035522116862	-.0547757604391
3	.00186157106998	-.0657646549401
4	.0052704520403	-.0153466037619
5	.00465298283098	.0245696794003
6	.00239541679114	.0267510682927
7	.000786216628273	.0131323064879
8	.000163079419125	.00371907933209
9	1.92553577861E-5	.000604087788066
10	6.80835754258E-7	4.41439729793E-5
11	-1.37150276317E-7	-1.77446420678E-6
12	-2.2316990314E-8	-6.52530746617E-7
13	-1.39582144104E-9	-6.20674568024E-8
14	3.38480870218E-9	-1.53903603536E-7

Table 12

Values of the second harmonics rotation $\varphi_2(r)$ and $\varphi_2'(r)$ for the vibrational level $v=5$ of Morse potential.

Positive branch ($r > r_e$)		
i	$\varphi_2(r)$	$\varphi_2'(r)$
1	1.25682198578E-5	7.27335105077E-5
2	9.06084784913E-6	-.000148037199808
3	-5.93904221203E-6	-.000181568321195
4	-1.40112603842E-5	2.24342080033E-7
5	-6.25194295101E-6	.000171488371967
6	8.29823929028E-6	.000158993010532
7	1.53438618518E-5	6.23039809326E-6
8	9.70908204269E-6	-.000133632930182
9	-3.09089580872E-6	.00016707871118
10	-1.45330521517E-5	-.000108800316725
11	-1.98100304556E-5	-2.39700998396E-5
12	-1.90350422133E-5	3.72103508893E-5
13	-1.487104449E-5	6.09280417641E-5
14	-1.00165405581E-5	5.74102859779E-5
15	-5.99433982994E-6	4.23390261813E-5
16	-3.25317132968E-6	2.66345784152E-5
17	-1.62403896658E-6	1.68735243238E-5
18	-7.5386566725E-7	7.54648940772E-6
19	-3.28182427407E-7	3.5332758736E-6
20	-1.34929466954E-7	1.54386607432E-6
21	-5.27019860051E-8	6.35058494448E-7
22	-1.96546123557E-8	2.47637305779E-7
23	-7.02942505968E-9	9.20692842925E-8
24	-2.42035533288E-9	3.27944146837E-8
25	-8.05408324186E-10	1.12327431125E-8
26	-2.60968201149E-10	3.69674783902E-9
27	-8.62800086126E-11	1.11878747585E-9
28	-4.114064684E-11	1.29621579764E-10
29	-6.12913090012E-11	-6.97338540886E-10

Negative branch ($r < r_e$)		
i	$\varphi_2(r)$	$\varphi_2'(r)$
1	-1.25914005187E-5	7.50792637403E-5
2	-9.70789137941E-6	-.000135920607328
3	4.489646265E-6	-.000182347824062
4	1.48590606861E-5	-6.24420614969E-5
5	1.46667464717E-5	5.43589994318E-5
6	8.76107106241E-6	7.86241929945E-5
7	3.55543227355E-6	4.80240903953E-5
8	1.01488480544E-6	1.80868925043E-5
9	2.0533839233E-7	4.5456741667E-6
10	2.92865498531E-8	7.78433928102E-7
11	2.90416655078E-9	9.07162036954E-8
12	1.96263764788E-10	7.10000263128E-9
13	8.97247922872E-12	3.58336513264E-10
14	6.94601643592E-12	-3.16924008053E-10

Table 13

Values of the third harmonic rotation $\varphi_3(r)$ and $\varphi_3'(r)$ for the vibrational level $v=5$ of Morse potential.

Positive Branch ($r > r_e$)		
i	$\varphi_3(r)$	$\varphi_3'(r)$
1	3.87998118074E-8	2.220720851523-7
2	2.77418714138E-8	-4.61438707527E-7
3	-1.84508492047E-8	-5.56368228253E-7
4	-4.30451897477E-8	2.88764183374E-9
5	-1.92270648376E-8	5.24064656499E-7
6	2.52011308384E-8	4.86016954427E-7
7	4.69544757167E-8	2.50110198883E-8
8	3.04350721326E-8	-3.9774551686E-7
9	-7.87699913267E-8	-5.02346627195E-7
10	-4.24662434581E-8	-3.31633775749E-7
11	-5.8807403984E-8	-7.89239007317E-8
12	-5.70151323758E-8	1.05738092333E-7
13	-4.4909344773E-8	1.79582885252E-7
14	-3.04761526635E-8	1.7159087723E-7
15	-1.83918085549E-8	1.27906776903E-7
16	-1.00717888007E-8	8.12830101406E-8
17	-5.07695405067E-9	4.58606417819E-8
18	-2.38118449629E-9	2.35192165298E-8
19	-1.04804048082E-9	1.11358136723E-8
20	-4.35898309552E-10	4.92313453876E-9
21	-1.72326725059E-10	2.0499696268E-9
22	-6.50800811071E-11	8.09565231983E-10
23	-2.35804264557E-11	3.04955617204E-10
24	-0.22869877197E-12	1.10096455091E-10
25	-2.77618292737E-12	3.82343527315E-11
26	-9.12404952641E-13	1.27620017714E-11
27	-3.05552241057E-13	3.92522847588E-12
28	-1.44839914303E-13	5.09775635444E-13
29	-2.07176682642E-13	-2.26268996116E-12
Negative Branch ($r < r_e$)		
i	$\varphi_3(r)$	$\varphi_3'(r)$
1	-3.89756900814E-8	2.30317570419E-7
2	-2.96384807353E-8	-4.27683985394E-7
3	1.46041411747E-8	-5.6220625012E-7
4	4.58960205804E-8	-1.76740201771E-7
5	4.39459069368E-8	1.82077851529E-7
6	2.51646593083E-8	2.41753482771E-7
7	9.60785719374E-9	1.38482139391E-7
8	2.51577395618E-8	4.80238533775E-8
9	4.51690059607E-10	1.07856320398E-8
10	5.37159958816E-11	1.5842839739E-9
11	4.33842308407E-12	1.49731681114E-10
12	2.14040300404E-13	9.75303157767E-12
13	6.73149695235E-15	2.5959548647E-13
14	2.80264303075E-14	-1.33069792038E-12

Table 14

Values of the fourth harmonic rotation $\varphi_4(r)$ and $\varphi_4'(r)$ for the vibrational level $v=5$ of Morse potential.

Positive Branch ($r > r_e$)		
i	$\varphi_4(r)$	$\varphi_4'(r)$
1	1.15923650733E-10	6.63689656706E-10
2	8.28841963347E-11	-1.37903336751E-9
3	-5.51619818073E-11	-1.66235259776E-9
4	-1.28560745891E-10	1.08522061891E-11
5	-5.71823658161E-11	1.56822080984E-9
6	7.56097238718E-11	1.45036004814E-9
7	1.40247582042E-10	6.78534425393E-11
8	9.02421403482E-11	-1.19698782733E-9
9	-2.48469239607E-11	-1.5073106137E-9
10	-1.28552055E-10	-9.9337658851E-10
11	-1.77433842975E-10	-2.34913618829E-10
12	-1.71913084455E-10	3.18949196962E-10
13	-1.35458198911E-10	5.40483262036E-10
14	-9.20159024042E-11	5.16602844305E-10
15	-5.56161461629E-11	3.85524733847E-10
16	-3.05198215729E-11	2.45419078241E-10
17	-1.54240593781E-11	1.387809527E-10
18	-7.25653228288E-12	7.13705595529E-11
19	-3.20534264231E-12	3.39038366084E-11
20	-1.3386323775E-12	1.504604474E-11
21	-5.31649979882E-13	6.29221149523E-12
22	-2.01805257614E-13	2.49690311239E-12
23	-7.35287956092E-14	9.45572856333E-13
24	-2.58145473771E-14	3.43358836793E-13
25	-8.7663646469E-15	1.19987654203E-13
26	-2.90152652382E-15	4.03102865493E-14
27	-9.80438086465E-16	1.24637971206E-14
28	-4.71019835443E-16	1.5727169895E-15
29	-6.79541975394E-16	-7.43957279278E-15
Negative Branch ($r < r_e$)		
i	$\varphi_4(r)$	$\varphi_4'(r)$
1	-1.1646829327E-10	6.8929005216E-10
2	-8.87484902587E-11	-1.27519502866E-9
3	4.34014343989E-11	-1.68285043765E-9
4	1.37513701763E-10	-5.3968885104E-10
5	1.32627546081E-10	5.34409218573E-10
6	7.68538553976E-11	7.23783308112E-10
7	2.99216941716E-11	4.22063127663E-10
8	8.08492210088E-12	1.50366227283E-10
9	1.52564831401E-12	3.52489170392E-11
10	1.99898064026E-13	5.54347342888E-12
11	1.79599543542E-14	5.8451022307E-13
12	1.08819856094E-15	4.08973116276E-14
13	4.55681009433E-17	1.78570023968E-15
14	7.58382816381E-17	-3.56262365212E-15

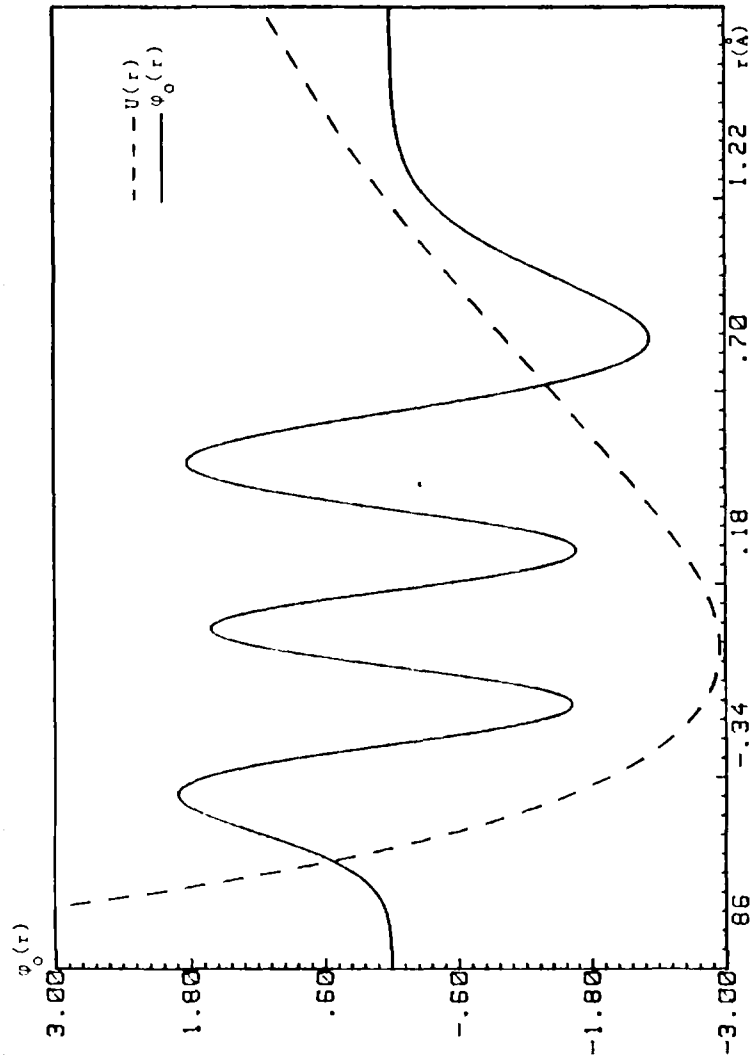


Fig. 1

- Variation of the potential function $U(r)$ in terms of r for the vibrational level $v=5$ of Morse potential.
- Variation of the function $\varphi_0(r)$ in terms of r for the level $v=5$ of Morse potential.

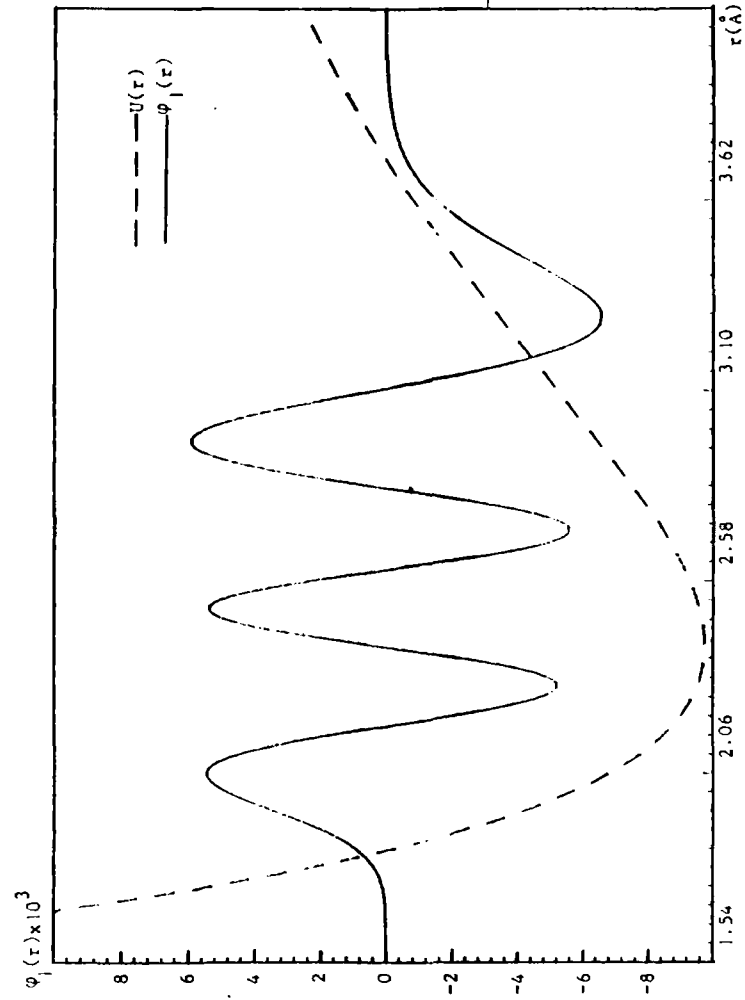


Fig. 2

- Variation of the potential function $U(r)$ in terms of r for the level $v=5$ of Morse potential.
- Variation of the first harmonic rotation $\varphi_1(r)$ in terms of r for the level $v=5$ of Morse potential.

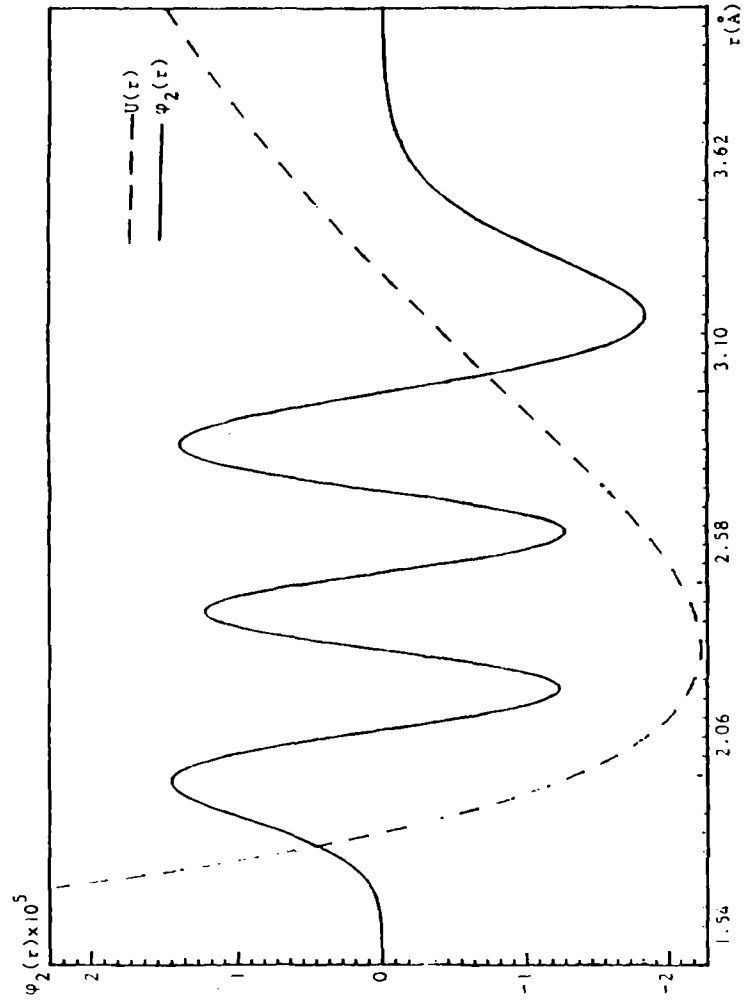


Fig. 3

-- -- Variation of the potential function $U(r)$ in terms of r for the level $v=5$ of Morse potential.
 ——— Variation of the second harmonic rotation $\varphi_2(r)$ in terms of r for the level $v=5$ of Morse potential.

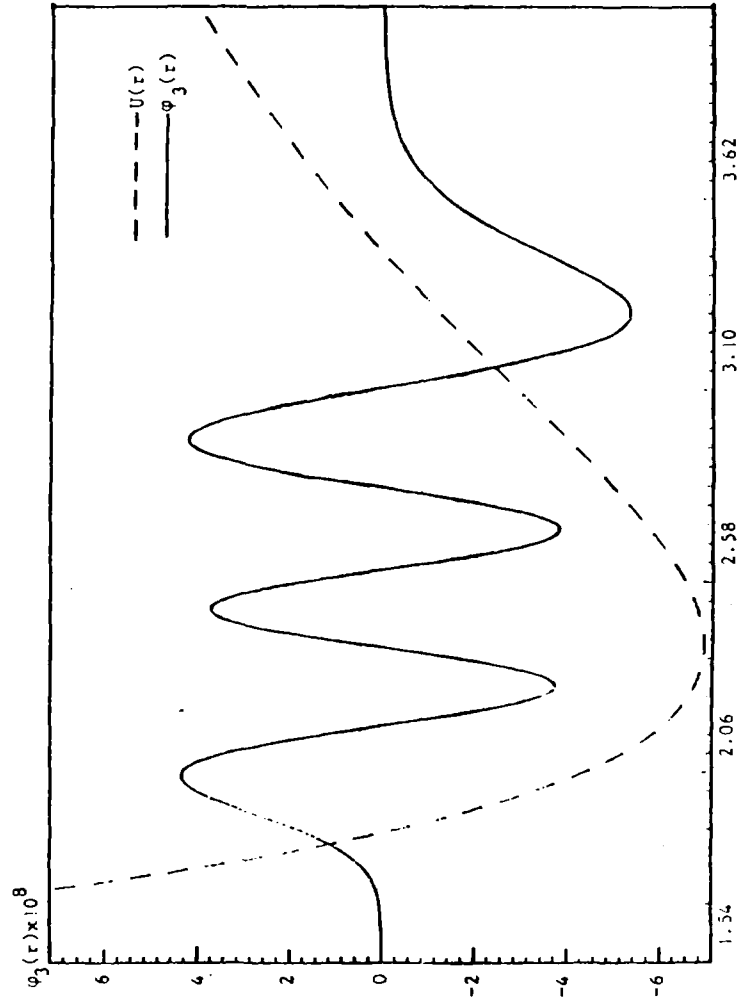


Fig. 4

-- -- Variation of the potential function $U(r)$ in terms of r for the level $v=5$ of Morse potential.
 ——— Variation of the third harmonic rotation $\varphi_3(r)$ in terms of r for the level $v=5$ of Morse potential.

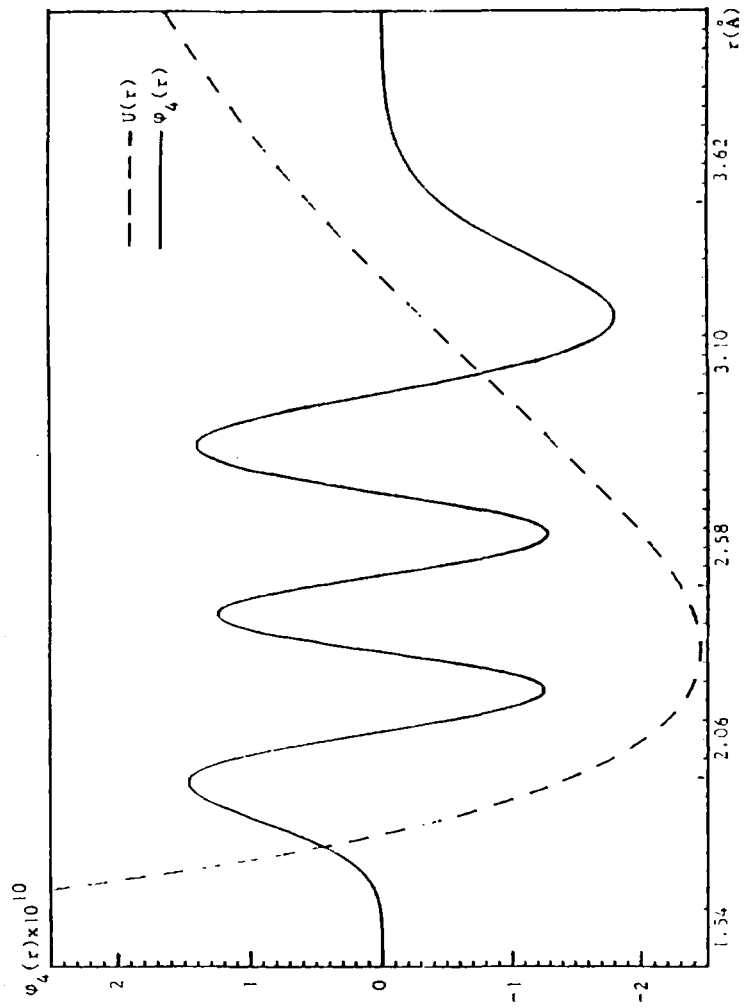


Fig. 5

- -- Variation of the potential function $U(r)$ in terms of r for the level $v=5$ of Morse potential.
- Variation of the fourth harmonic rotation $\phi_4(r)$ in terms of r for the level $v=5$ of Morse potential.