Rotation harmonics for a numerical diatomic potential

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Résumé. — Le problème de la détermination des harmoniques de rotation ϕ_1, ϕ_2, ... dans le cas d'un potentiel diatomique *numérique* est considéré. Ces harmoniques récemment définies par $\psi_{vJ} = \psi_{v0} + \lambda\phi_1 + \lambda^2 \phi_2 + \cdots$ (où ψ_{vJ} est la fonction d'onde du niveau vibrationnel v et du niveau rotationnel J, avec $\lambda = J(J + 1)$) sont étudiées pour le potentiel de Dunham, et pour un potentiel numérique défini par les coordonnées de ses points de retour et par des interpolations et extrapolations polynomiales. Les expressions analytiques des harmoniques ϕ_1, ϕ_2, ... sont données sous forme de polynômes dont les coefficients sont simplement liés à ceux du potentiel dans le cas du potentiel de Dunham, et aux coordonnées du potentiel dans le cas du potentiel numérique. L'application numérique est simple. Les exemples présentés montrent que la fonction d'onde de vibration-rotation ψ_{vJ} calculée à partir des fonctions harmoniques reproduit sa valeur calculée directement jusqu'au huitième chiffre significatif.

Abstract. — The problem of the determination of the rotation harmonics ϕ_1, ϕ_2, ... for the case of a numerical diatomic potential is considered. These harmonics defined in a recent work by $\psi_{vJ} = \psi_{v0} + \lambda\phi_1 + \lambda^2 \phi_2 + \cdots$ (where ψ_{vJ} is the wave function of the vibration level v and the rotation level J, and $\lambda = J(J + 1)$) are *studied* for the case of the Dunham potential and for a numerical potential defined by the coordinates of its turning points with polynomial interpolations and extrapolations. It is proved that the analytic expressions of the harmonics ϕ_1, ϕ_2, ... reduce to polynomials where the coefficients are simply related to those of the potential in the case of the Dunham potential, and to the coordinates of the turning points in the case of the numerical potential. The numerical application is simple. The examples presented show that the vibration-rotation wave function ψ_{vJ} calculated by using two harmonics only is « exact » up to eight significant figures.

1. Introduction.

In the Born-Oppenheimer approximation [1], a given electronic state of a diatomic molecule is characterized by the potential $U(r)$, a function of the internuclear distance r.

The most commonly used method for the determination of $U(r)$, for two decades, is the well known semi-classical Rydberg-Klein-Rees (R.K.R.) method [2]. The R.K.R. potential is usually given in numerical form, i.e. $U(r)$ is defined by the coordinates of some points (turning points or others) with interpolations and extrapolations which are, usually, polynomials or can be reduced to polynomials.

A new trend in the treatment of the potential problem is the quantum mechanical (Q.M.) method [3-5]. This method replaces the semi-classical laws used for the R.K.R. method, by the properties of the wavefunction.

This method has already been applied to some states of the molecules N_2^+, Li_2, CO, I_2, H_2... These published results show that the Q.M. potential is generally in better agreement with the spectroscopic data than the R.K.R. potential [3-6]. Use of this method might become widespread in the coming years.

The Q.M. potential is given in a numerical form like the R.K.R. potential. Yet these two potentials differ from each other, not only in the theoretical approach, but also in the mathematical treatment (and numerical analysis). Unlike the R.K.R. method, the Q.M. method implies the computation of the wavefunction $\psi_{vJ}(r)$ (v and J being the vibration and rotation quantum numbers).

A highly accurate vibration-rotation wavefunction is required, not only to assure a good accuracy of the Q.M. potential, but more generally to assure good accurate vibrational and rotational characteristics for any numerical potential (mainly for energy expectation values, matrix elements and line intensities).

Therefore, the introduction of the rotation harmo-

nics is useful. These functions ϕ_1, ϕ_2, ... are related to the wavefunction ψ_{vJ} by $\psi_{vJ} = \psi_v + \lambda\phi_1 + \lambda^2 \phi_2 + \cdots$ (with $\lambda = J(J + 1)$). They present, in the main the following advantages [7] :

i) They are independent of J.

ii) For a given r, the functions $\phi_1(r)$, $\phi_2(r)$, $\phi_3(r)$... decrease in absolute values as the constants B_v, D_v, H_v, ...

iii) The computation of ψ_{vJ} is reduced to that of computing ψ_v, ϕ_1 and ϕ_2 only (and probably ϕ_3); it is greatly simplified when J has to vary.

The aim of this work is to derive simple analytic expressions for the rotation harmonics for the commonly used numerical potentials (R.K.R. potential and Q.M. potential). These expressions are simply related to the coordinates of the turning points of the given potential. The derivation of these new expressions is presented in section 3. This section is preceeded by the presentation of the rotation Schroedinger equations (section 2); it is followed by some examples of the numerical application along with a discussion of the results (section 4).

2. Rotational Schroedinger equations.

For a given vibrational level v, the radial Schroedinger equation can be written :

$$\frac{\mathrm{d}^2\psi_\lambda(x)}{\mathrm{d}x^2} = F_\lambda(x)\,\psi_\lambda(x) \qquad (1)$$

where :

$\psi_\lambda = \psi_{vJ}$ (ψ_0 stands for ψ_{v0})

$x = r - r_e$ (r_e being the value of r at the equilibrium geometry)

$$F_\lambda(x) = -\frac{2\mu}{\hbar^2}[E_\lambda - U(x)] + \frac{\lambda}{r^2}$$

$E_\lambda = E_{v\lambda}$ (E_v stands for E_{v0}).

The energy E_λ is usually represented by [8]

$$E_\lambda = \sum_{i=0}^{\infty} \lambda^i\, e_i \qquad (2)$$

where $e_0 = E_0$, $e_1 = B_v$ (the rotation constant), $e_2 = -D_v$, $e_3 = H_v$ ... (the distortion constants). The *energy factor* $F_\lambda(x)$ becomes :

$$F_\lambda(x) = \sum_{i=0}^{\infty} \lambda^i\, f_i(x)$$

with

$$f_0(x) = -\frac{2\mu}{\hbar^2}[e_0 - U(x)]$$

$$f_1(x) = -\frac{2\mu}{\hbar^2}e_1 + \frac{1}{r^2} \qquad (3)$$

$$f_i(x) = -\frac{2\mu}{\hbar^2}e_i; \quad i \geqslant 2$$

We already know that the wavefunction $\psi_\lambda(x)$ can be written :

$$\psi_\lambda(x) = \sum_{i=0}^{\infty} \lambda^i\, \phi_i(x). \qquad (4)$$

By substituting the above expressions for $\psi_\lambda(x)$ and $F_\lambda(x)$ into the radial equation 1 (which must be true for any λ), we deduce the following set of equations [7] :

$$\phi_0'' - f_0\cdot\phi_0 = 0 \qquad (5.0)$$

$$\phi_1'' - f_0\cdot\phi_1 = f_1\,\phi_0 \qquad (5.1)$$

$$\phi_2'' - f_0\cdot\phi_2 = f_1\,\phi_1 + f_2\,\phi_0 \qquad (5.2)$$

$$\cdots$$

$$\phi_i'' - f_0\,\phi_i = \sum_{j=1}^{i} f_j\,\phi_{i-j}. \qquad (5.i)$$

The first of these equations is nothing but the radial Schroedinger equation for pure vibration ($\lambda = 0$). The other equations are the *rotational* Schroedinger equations; they are inhomogeneous equations differing only by their second members. One of these second members is well defined by the solutions of the preceeding equations, i.e. the solution $\phi_0 = \psi_0$ of the first equation.

It has been shown [7, 9] that : i) any solution ϕ of equations 5 is continuous at any point as well as the wavefunction ψ_λ or $\psi_0 = \phi_0$; ii) all the functions $\phi(x)$ obey the same boundary conditions as the wavefunctions ψ_λ and ψ_0 :

$$\phi(x) \xrightarrow[x\to\infty]{} 0 \qquad (6)$$

$$\phi(x) \xrightarrow[x\to-r_e]{} 0. \qquad (6')$$

3. Rotation harmonics for numerical potentials.

3.1 The rotational Schroedinger equations 5, may be represented by :

$$y''(x) - f_0(x)\,y(x) = s(x) \qquad (7)$$

with

$$s(x) = s_0(x) = 0 \quad \text{for} \quad y = \phi_0$$

$$s(x) = s_1(x) = f_1\,\phi_0 \quad \text{for} \quad y = \phi_1$$

and

$$s(x) = s_i(x) = \sum_{j=1}^{i} f_j\,\phi_{i-j} \quad \text{for} \quad y = \phi_i \qquad (8)$$

By using the equivalence between the linear differential equation 7 and the corresponding Volterra (second kind) integral equation [10], we find :

$$y(x) = \sum_{n=0}^{\infty} H(x)$$

$$H_n(x) = \int_0^x (x - t)\,f_0(t)\,H_{n-1}(t)\,\mathrm{d}t \qquad (9)$$

$$H_0(x) = y(0) + xy'(0) + \int_0^x (x - t)\,s(t)\,\mathrm{d}t$$

where the series 9 is absolutely and uniformly convergent [11].

These formulas represent the solution ϕ_i ($i = 0$, 1, 2, ...) of any of the rotational Schroedinger equations 5. It is enough to replace in (7) or (9) $s(x)$ by the *convenient* value given by (8).

These formulas can be used for any diatomic potential without restriction.

3.2 When the potential $U(x)$ is given by the Dunham function :

$$U(x) = \sum_{n=2}^{N} \gamma_n x^n$$

the related energy factor $F_\lambda(x)$ can also be represented by a polynomial. We write by substituting into (3) the above expression for $U(x)$:

$$f_0(x) = \sum_{n=0}^{N} a_n^0 x^n$$

with :

$$a_0^0 = -\frac{2\mu}{\hbar^2} e_0, \quad a_1^0 = 0, \quad a_n^0 = \frac{2\mu}{\hbar^2} \gamma_n \text{ for } n \geqslant 2$$

$$f_1(x) = \sum_{n=0}^{N^1} a_n^1 x^n \text{ for } |x| < 1$$

with :

$$a_0^1 = -\frac{2\mu}{\hbar^2} e_1 + \theta_0, \quad a_n^1 = \theta_n \text{ for } n \geqslant 1;$$

θ_n being the coefficients of the expansion

$$\frac{1}{r^2} = \sum_{n=0}^{N^1} \theta_n x^n.$$

N^1 is the number of terms retained :

$$f_i(x) = \sum_{n=0}^{N^1} a_n^i x^n$$

with :

$$a_0^i = -\frac{2\mu}{\hbar^2} e_i, \quad a_n^i = 0 \text{ for } n \geqslant 1.$$

For the Dunham potential, and under the condition $|x| < 1$, the solution ϕ_0 of equation 5.0, can be deduced from equation 9 with $s(x) = 0$, and we find [13] :

$$\phi_0(x) = \sum_{n=0}^{\infty} \lambda_n^0 x^n$$

with

$$(n + 1)(n + 2) \lambda_{n+2}^0 = \sum_{m=0}^{n} \lambda_m^0 a_{n-m}^0;$$

$$\lambda_0^0 = \phi_0(0), \quad \lambda_1^0 = \phi_0^1(0).$$

Since $\phi_0(x)$ is a series, the second member $s_1(x) = f_1(x)\phi_0(x)$ of equation 5.1 is a series :

$$s_1(x) = \sum_{n=0}^{\infty} \delta_n^1 x^n; \quad \delta_n^1 = \sum_{m=0}^{n} a_m^1 \lambda_{n-m}^0.$$

For this case, the function $y(x)$ in equation 9 stands

for $\phi_1(x)$. The function $H_0(x)$ is a series, as well as, $H_1(x)$, $H_2(x)$, ... and their sum $\phi_1(x)$:

$$\phi_1(x) = \sum_{n=0}^{\infty} \lambda_n^1 x^n$$

with

$$(n + 1)(n + 2) \lambda_{n+2}^1 = \sum_{m=0}^{n} (\lambda_m^1 a_{n-m}^0 + \delta_m^1);$$

$$\lambda_0^1 = \phi_1(0); \quad \lambda_1^1 = \phi_1^1(0).$$

We generalize for $\phi_i(x)$, and we write :

$$s_i(x) = \sum_{n=0}^{\infty} \delta_n^i x^n \tag{10}$$

$$\delta_n^i = \sum_{j=1}^{i} \sum_{m=0}^{n} a_n^j \lambda_{n-m}^{i-j} \tag{11}$$

$$\phi_i(x) = \sum_{n=0}^{\infty} \lambda_n^i x^n \tag{12}$$

$$\left. \begin{array}{l} (n + 1)(n + 2) \lambda_{n+2}^i = \sum_{m=0}^{n} (\lambda_m^i a_{n-m}^0 + \delta_m^i) \\ \lambda_0^i = \phi_i(0) \\ \lambda_1^i = \phi_i^1(0) \end{array} \right\} \tag{13}$$

When $|x| \geqslant 1$, we divide the x-axis into small intervals and we apply, for the Dunham potential function, the method detailed below.

3.3 The numerical potential $U(x)$, as considered here, is determined by the coordinates of its turning points (and/or other points) with suitable interpolations and extrapolations; these interpolations (and extrapolations) are (or can be reduced to) polynomials.

For this potential, we divide the x-axis into intervals $I_p = [x_p, x_{p+1}]$ where x_p and x_{p+1} are the abscissae of two consecutive turning points. For this interval we take :

$$x = x_p + X \text{ with } 0 < X < x_{p+1} - x_p$$

$$U(X) = \sum_{n=0}^{\infty} \gamma_n(p) X^n.$$

On this interval the expressions for the functions f_i, s_i and ϕ_i can be determined in the same way used above for the Dunham potential; the results are similar with slight differences. We summarize these results as follows :

$$f_i(X) = \sum_{n=0}^{N^1} a_n^i(p) X^n \tag{14}$$

$$s_i(X) = \sum_{n=0}^{\infty} \delta_n^i(p) X^n \tag{15}$$

$$\left. \begin{array}{l} \phi_i(X) = \sum_{n=0}^{\infty} \lambda_n^i(p) X^n \\ (n + 1)(n + 2) \lambda_{n+2}^i(p) = \\ = \sum_{m=0}^{n} (\lambda_m^i(p) a_{n-m}^0(p) + \delta_m^i(p)) \\ \lambda_0^i(p) = \phi_i(x_p) \\ \lambda_1^i(p) = \phi_i^1(x_p) \end{array} \right\} \tag{16}$$

where x_p is the origin of the interval I_p.

We start at the origin $x = 0$ with interval $I_0(x_p = 0)$, and with *trial values* of $\phi_i(0)$ and $\phi_i^1(0)$. We deduce the values of ϕ_i (and ϕ_i^1) at the end of the interval :

$$\phi_i(x_{p+1}) = \sum_{n=0}^{\infty} \lambda_n^i(p) (x_{p+1} - x_p)^n$$

$$\phi_i^1(x_{p+1}) = \sum_{n=1}^{\infty} n\lambda_n^i(p) (x_{p+1} - x_p)^{n-1} \,.$$

These values of ϕ_i and ϕ_i^1 are taken now as the origin of the second interval. We can use the same relations to get the values of the same functions at the origin of the third interval, and so on... we can reach like this the values of $\phi_i(x)$ and $\phi_i^1(x)$ ($i \geqslant 0$) at any point x.

3.4 The analytic expressions of the functions $\phi_i(x)$ given above for a given numerical potential have no physical meaning, unless the values used for e_0, e_1, e_2, ... are the eigenvalues E_v, B_v, D_v, ... of the potential for the given vibrational level v, and unless the initial values $\phi_i(0)$ and $\phi_i^1(0)$ (for $i \geqslant 0$), generate the eigenfunctions of the rotational Schroedinger equations 5.

The problem of the determination of the eigenvalues along with that of the initial values has been solved recently for any potential [14]. We give, in the following an outline of the solution of this problem applied to the numerical potential.

We know that the general solution of one of the rotational Schroedinger equation 7 can be written [15] :

$$y(x) = y(0) \, \alpha(x) + y'(0) \, \beta(x) + \sigma(x) \qquad (17)$$

where $\alpha(x)$ and $\beta(x)$ are two particular solutions of the homogeneous equation with :

$$\alpha(0) = 1 \,, \quad \alpha'(0) = 0 \qquad (18)$$

$$\beta(0) = 0 \,, \quad \beta'(0) = 1 \qquad (18')$$

$\sigma(x)$ being a particular solution of the inhomogeneous equation.

By comparing the expression of $y(x)$ given by equation 17 to that given by equation 9, we deduce that the functions $\alpha(x)$, $\beta(x)$ and $\sigma(x)$ are given by equation 9, in which we take :

i) $y(0) = 1$, $y'(0) = 0$, $s(x) = 0$ for $\alpha(x)$

ii) $y(0) = 0$, $y'(0) = 1$, $s(x) = 0$ for $\beta(x)$

iii) $y(0) = 0$, $y'(0) = 0$, $s(x) \neq 0$ for $\sigma(x)$.

Thus the expression of the ith harmonic is :

$$\phi_i(x) = \phi_i(0) \, \alpha(x) + \phi_i'(0) \, \beta(x) + \sigma_i(x) \,.$$

In order to make $\phi_i(x)$ obey equation 4, one can always write — without any loss of generality — for the unnormalized wavefunctions $\psi_\lambda(x)$ and $\psi_0(x)$:

$$\psi_\lambda(0) = \psi_0(0) = 1$$

and

$$\phi_1(0) = \phi_2(0) = \cdots = \phi_i(0) = \cdots = 0 \,.$$

The functions $\phi_i(x)$ become :

$$\phi_0(x) = \alpha(x) + \phi_0'(0) \, \beta(x)$$
$$\phi_1(x) = \sigma_1(x) + \phi_1'(0) \, \beta(x)$$
$$\cdots$$
$$\phi_i(x) = \sigma_i(x) + \phi_i'(0) \, \beta(x) \,.$$

In order to determine the initial value $\phi_0^1(0)$ along with the eigenvalue $\tilde{e}_0$ (included in $f_0(x)$), one can use a trial value e_0 and compute the functions $\alpha(x)$ and $\beta(x)$. From the boundary conditions (6)-(6'), one can have :

$$\lim_{x \to \infty} - \frac{\alpha(x)}{\beta(x)} = l^+(e_0)$$

$$\lim_{x \to -r_e} - \frac{\alpha(x)}{\beta(x)} = l^-(e_0) \,.$$

The continuity of $\phi_0(x)$ at $x = 0$ implies

$$l^+(e_0) = l^-(e_0) \,.$$

The value $\tilde{e}_0$ of the parameter e_0 satisfying this « eigenvalue equation » is the eigenvalue of equation 5.0 for the given potential. The initial value $\phi_0'(0)$ of the « eigenfunction » $\phi_0(x)$ is given by :

$$l^+(e_0) = l^-(e_0) = \phi_0'(0) \,.$$

Once the eigenvalue $\tilde{e}_0$ and the eigenfunction $\phi_0(x)$ are thus determined, $\tilde{e}_1$ and $\phi_1(x)$, $\tilde{e}_2$ and $\phi_2(x)$, ... are successively determined in the same manner.

This method can be applied to the numerical potential. The functions $\alpha(x)$, $\beta(x)$ and $\sigma_i(x)$ are derived from equation 9 in the same manner presented above for the derivation of $\phi_i(x)$ given by equations 16. These equations give the expressions for $\alpha(x)$, $\beta(x)$ and $\sigma_i(x)$ in which we take :

i) $\lambda_0 = 1$; $\lambda_1 = 0$; $\delta_m = 0$, $\quad m \geqslant 0$ for α
ii) $\lambda_0 = 0$; $\lambda_1 = 1$; $\delta_m = 0$, $\quad m \geqslant 0$ for β
iii) $\lambda_0 = 0$; $\lambda_1 = 0$; $\delta_m \neq 0$, $\quad\quad$ for σ_i.

4. Numerical application.

The aim of the numerical application presented here is to give some examples of the computation of the rotation harmonics $\phi_i(x)$ from the analytic expressions derived in this paper.

For this purpose, we consider the same potential function used already [7] to compute the harmonics $\phi_i(x)$ with the Runge-Kutta difference equations of the 5th order [16]. This potential is the Morse function used by Cashion [17], that we treat like a numerical potential by taking several points (turning points or others) and by using polynomial interpolations.

We compute first the eigenvalues $\tilde{e}_0$, $\tilde{e}_1$, $\tilde{e}_2$ along with the initial values $\phi'_0(0)$, $\phi'_1(0)$, $\phi'_2(0)$ by using the method outlined in § 3.4 and detailed in reference 14. The results are used to compute the functions $\phi_0(x) = \psi_0(x)$, $\phi_1(x)$ and $\phi_2(x)$ given by the analytic expressions (§ 3.3). In table I, we give the results at several points ($x = 0.1, 0.2, 0.3, 0.4, 0.5$ Å) and for several vibrational levels ($v = 0, 10, 20$). The last level is a few cm^{-1} from the dissociation.

At each x the vibration-rotation wavefunction is deduced from its expression $\psi_0 + \lambda\phi_1 + \lambda^2 \phi_2$ (with $J = 1$, $\lambda = 2$) and compared to its value ψ_λ computed directly from the Schroedinger equation 1 by using the method described in [13] and [18].

We notice that the agreement between the directly calculated vibration-rotation wavefunction ψ_λ and $\sum_{i=0}^{2} \lambda^i \phi_i$ is satisfactory to the 7th (or the 8th) signifiant figure.

In table II, we compare the new results to those obtained by using the Runge-Kutta difference equations with a mesh size $h = 0.005$ Å [7]. The agreement between ψ_λ and $\sum_{i=0}^{2} \lambda^i \phi_i$ is much more satisfactory with the expressions of the rotation harmonics derived here, than with the Runge-Kutta numerical treatment.

In table III, we finally give (for $v = 10$) the values of

Table I. — *Values of the rotation harmonics for some values of x of a numerical potential* [17] ($v = 0, 10, 20$). *The sum of the harmonics is compared, at every point and for every v, to the vibration-rotation wavefunction* $\psi_\lambda(x)$ [$\lambda = 2$] *computed directly from the Schroedinger equation.*

		$v = 0$	$v = 10$	$v = 20$
$x = 0.1$ Å	ψ_0	0.933 966 4	− 0.143 357 9	− 1.081 806 8
	ϕ_1	0.000 273 6	0.000 006 7	0.003 706 2
	ϕ_2	0.000 000 0	0.000 002 7	− 0.000 006 9
$\psi_0 + \lambda\phi_1 + \lambda^2\phi_2$		0.934 513 7	− 0.137 333 9	− 1.074 422 2
ψ_λ		0.934 513 7	− 0.137 333 9	− 1.074 422 2
$x = 0.3$ Å	ψ_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
$\psi_0 + \lambda\phi_1 + \lambda^2 \phi_2$		0.429 871 7	0.844 855 8	0.250 088 3
ψ_λ		0.429 871 7	0.844 855 8	0.250 088 3
$x = 0.5$ Å	ψ_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
$\psi_0 + \lambda\phi_1 + \lambda^2 \phi_2$		0.095 684 9	− 1.108 565 5	1.083 300 4
ψ_λ		0.095 684 9	− 1.108 565 5	1.083 300 5

Table II. — *Values of the rotation harmonics for some values of x of a numerical potential* [17] ($v = 0, 5, 10$). *The results of the present work* ($P.W.$) *are compared to those obtained by the Runge-Kutta* ($R.K.$) *difference equations. The wavefunction* $\psi_\lambda(x)$ *is also compared to the sum of harmonics* ($\lambda = 2$) *for both methods.*

		$x = 0.1$ Å		$x = 0.3$ Å	
		R.K.	P.W.	R.K.	P.W.
$v = 0$	ψ_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
$\psi_0 + \lambda\phi_1 + \lambda^2 \phi_2$		0.934 513 7	0.934 513 7	0.429 870 2	0.429 871 7
ψ_λ		0.934 514 2	0.934 513 7	0.429 872 3	0.429 871 7
$v = 5$	ψ_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
$\psi_0 + \lambda\phi_1 + \lambda^2 \phi_2$		1.308 708 8	1.308 691 0	− 1.524 846 8	− 1.524 828 9
ψ_λ		1.308 711 0	0.308 691 0	− 1.524 848 0	− 1.524 828 9
$v = 10$	ψ_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
$\psi_0 + \lambda\phi_1 + \lambda^2 \phi_2$		− 0.137 244 5	− 0.137 333 9	0.844 821 3	0.844 855 8
ψ_λ		− 0.137 253 2	− 0.137 333 9	0.844 824 6	0.844 855 8

Table III. — *Values of the sum of harmonics* $\psi_0 + \lambda\phi_1 + \lambda^2 \phi_2$ *(1st line) for some values of x of a numerical potential* [17] *(v = 10) and for some values of λ, compared to the wavefunction* $\psi_\lambda(x)$ *(2nd line). The mean value* $\overline{\Delta}$ *of the difference in absolute value for the five considered points is given in the last line.*

λ

x (Å)	2	6	12	20	30
0.1	− 0.137 333 9	− 0.125 222 1	− 0.106 894 6	− 0.082 159 8	− 0.050 762 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
$\overline{\Delta}$	0	1	9	51	180

$\sum_{i=0}^{2} \lambda^i \phi_i$ and ψ_λ at several points and for several values of λ. We notice that the difference

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

increases, at a point x, with λ. The mean value $\overline{\Delta}$ for the five points considered here increases like λ^3. This means that when J increases, we need higher harmonics (ϕ_3, ...) to obtain a desired accuracy. This result confirms the validity of the present method.

5. Conclusion.

The problem of the determination of the rotation harmonics was considered for the case of a numerical potential.

It is proved that when the interpolations in the potential are polynomials, the rotation harmonics are simply expressed by polynomials where the coefficients are simply related to the coordinates of the turning points of the potential.

The harmonics are calculated by using these new expressions for many examples and compared to the values found by a direct numerical integration of the rotation Schroedinger equations. The vibration-rotation wavefunctions 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 details of the numerical treatment of these new analytic expressions of the rotation harmonics will appear in a forthcoming paper.

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