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Rotation harmonics for a numerical diatomic potential

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Abstract. — The problem of the determination of the rotation harmonics \( \phi_1, \phi_2, \ldots \) 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 \( \psi_{vJ} \) is the wave function of the vibration level \( v \) and the rotation level \( J \), and \( \lambda = J(J + 1) \)) are studied for the potential of Dunham, and for a potential numérique défini par les coordonnées de ses points de retour et par des interpolations et extrapolations polynomiales. The expressions analytiques des harmoniques \( \phi_1, \phi_2, \ldots \) 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 \( \psi_{vJ} \) calculée à partir des fonctions harmoniques reproduit sa valeur calculée directement jusqu’au huitième chiffre significatif.

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 \( \psi_{vJ}(r) \) \((v \text{ and } J \text{ being the vibration and rotation quantum numbers})\).

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 $\phi_1, \phi_2, \ldots$ are related to the wavefunction $\psi_{vJ}$ 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 $\phi_1(r), \phi_2(r), \phi_3(r), \ldots$ decrease in absolute values as the constants $B_v, D_v, H_v, \ldots$

iii) The computation of $\psi_{vJ}$ is reduced to that of computing $\psi_v, \phi_1$ and $\phi_2$ only (and probably $\phi_3$); 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 preceded 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 :

$$\frac{d^2\psi_j}{dx^2} = F_j(x) \psi_j(x)$$

where :

$\psi_x = \psi_{vJ}$ ($\psi_v$ stands for $\psi_{v0}$) 

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

$$F_j(x) = -\frac{2\mu}{h^2} [E_j - U(x)] + \lambda \frac{r^2}{2}$$

$$E_j = E_{v0} - E_v$$

The energy $E_j$ is usually represented by [8]

$$E_j = \sum_{i=1}^{\infty} \lambda^i e_i$$

where $e_0 = E_{v0}, e_1 = B_v$ (the rotation constant), $e_2 = -D_v, e_3 = H_v, \ldots$ (the distortion constants). The energy factor $F_j(x)$ becomes :

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

with

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

$$f_1(x) = -\frac{2\mu}{h^2} e_1 + \lambda \frac{r^2}{2}$$

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

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

$$\psi_j(x) = \sum_{i=0}^{\infty} \lambda^i \phi_i(x).$$

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

$$\phi_0' - f_0 \phi_0 = 0$$

$$\phi_1' - f_0 \phi_1 = f_1 \phi_0$$

$$\phi_2' - f_0 \phi_2 = f_1 \phi_1 + f_2 \phi_0$$

$$\cdots$$

$$\phi_i' - f_0 \phi_i = \sum_{j=1}^{i} f_j \phi_{i-j}.$$  

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 $\phi$ of equations 5 is continuous at any point as well as the wavefunction $\psi_j$ or $\psi_v = \psi_0$; ii) all the functions $\phi(x)$ obey the same boundary conditions as the wavefunctions $\psi_j$ and $\psi_v$ :

$$\phi(x) \rightarrow 0 \quad \text{as} \quad x \rightarrow \pm \infty$$

3. Rotation harmonics for numerical potentials.

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

$$y''(x) - f_0(x) y(x) = s(x)$$

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

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

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

$$y(x) = \sum_{s=0}^{\infty} H_s(x)$$

$$H_s(x) = \int_{0}^{x} (x - t) f_0(t) H_{s-1}(t) dt$$

$$H_0(x) = y(0) + xy'(0) + \int_{0}^{x} (x - t) s(t) dt$$
where the series $\phi(x)$ is absolutely and uniformly convergent \([11]\).

These formulas represent the solution $\phi_i$ ($i = 0, 1, 2, \ldots$) of any of the rotational Schrödinger 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 $F_r(x)$ 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:

$$a_n^0 = -\frac{2 \mu}{h^2} e_0 \quad a_0^0 = 0 \quad a_n^0 = \frac{2 \mu}{h^2} \gamma_n \quad n \geq 2$$

and:

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

with:

$$a_n^1 = -\frac{2 \mu}{h^2} e_1 + \theta_n \quad a_0^1 = \theta_n \quad n \geq 1$$

$\theta_n$ being the coefficients of the expansion

$$f(x) = \sum_{n=0}^{N} \theta_n x^n.$$

$N^1$ is the number of terms retained:

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

with:

$$a_n^0 = -\frac{2 \mu}{h^2} e_1 \quad a_0^0 = 0 \quad n \geq 1.$$

For the Dunham potential, and under the condition $|x| < 1$, the solution $\phi_0$ 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

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

$$\lambda_0^0 = \phi_0(0) \quad \lambda_1^0 = \phi_1(0).$$

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, $H_1(x), H_2(x), \ldots$ and their sum $\phi_1(x)$:

$$\phi_1(x) = \sum_{n=0}^{\infty} \lambda_1^1 x^n$$

with

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

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

We generalize for $\phi_0(x)$, and we write:

$$s_0(x) = \sum_{n=0}^{\infty} \delta_n^0 x^n \quad (10)$$

$$\delta_n^0 = \sum_{j=0}^{n} \sum_{m=0}^{j} a_m^0 \lambda_{j-m}^0 \quad (11)$$

$$\phi_0(x) = \sum_{n=0}^{\infty} \lambda_n^0 x^n \quad (12)$$

$$(n + 1)(n + 2) \lambda_{n+2}^0 = \sum_{m=0}^{n} (\lambda_m^0 a_{n-m}^0 + \delta_m^0) \quad (13)$$

When $|x| \geq 1$, 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:

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

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

On this interval the expressions for the functions $f_1, s_1$ and $\phi_1$ 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:

$$f_1(X) = \sum_{n=1}^{N^1} a_n^1(p) X^n \quad (14)$$

$$s_1(X) = \sum_{n=0}^{\infty} \delta_n^1(p) X^n \quad (15)$$

$$\phi_1(X) = \sum_{n=0}^{\infty} \lambda_n^1(p) X^n \quad (16)$$

Where $x_p$ is the origin of the interval $I_p$. 

With $|x| \geq 1$, we divide the x-axis into small intervals and we apply, for the Dunham potential function, the method detailed below.
We start at the origin \( x = 0 \) with interval \( I_0(x_p = 0) \), and with trial values of \( \psi_0(0) \) and \( \psi_0'(0) \). We deduce the values of \( \psi_1 \) and \( \psi_1' \) at the end of the interval :

\[
\begin{align*}
\psi_1(x_{p+1}) &= \sum_{n=0}^{\infty} a_n \psi_0(n) (x_{p+1} - x_p)^n \\
\psi_1'(x_{p+1}) &= \sum_{n=1}^{\infty} n a_n \psi_0(n) (x_{p+1} - x_p)^{n-1}.
\end{align*}
\]

These values of \( \psi_1 \) and \( \psi_1' \) 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 \( \psi_i(x) \) and \( \psi_i'(x) \) at any point \( x \).

### 3.4 The analytic expressions of the functions \( \psi_i(x) \)

The analytic expressions of the functions \( \psi_i(x) \) given above for a given numerical potential have no physical meaning, unless the values used for \( e_0, e_1, e_2, \ldots \) are the eigenvalues \( \lambda_v, \beta_v, \sigma_v, \ldots \) of the potential for the given vibrational level \( v \), and unless the initial values \( \psi_i(0) \) and \( \psi_i'(0) \) (for \( i \geq 0 \), 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] :

\[
y(x) = \psi(x) + y'(0) \beta(x) + \sigma(x)
\]

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

\[
\begin{align*}
\alpha(0) &= 1, \quad \alpha'(0) = 0 \\
\beta(0) &= 0, \quad \beta'(0) = 1
\end{align*}
\]

\( \sigma(x) \) 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 :

- \( y(0) = 1, \quad y'(0) = 0 \) for \( \alpha(x) \)
- \( y(0) = 0, \quad y'(0) = 1 \) for \( \beta(x) \)
- \( y(0) = 0, \quad y'(0) = 0 \) for \( \sigma(x) \).

Thus the expression of the \( i \)th harmonic is :

\[
\psi_i(x) = \psi_i(0) \alpha(x) + \psi_i'(0) \beta(x) + \sigma_i(x).
\]

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

\[
\psi_i(0) = \psi_i'(0) = 1
\]

and \( \psi_1(0) = \psi_2(0) = \ldots = \psi_i(0) = \ldots = 0 \).

The functions \( \psi_i(x) \) become :

\[
\begin{align*}
\psi_0(x) &= \alpha(x) + \psi_i(0) \beta(x) \\
\psi_1(x) &= \sigma_1(x) + \psi_i(0) \beta(x) \\
&\ldots \\
\psi_i(x) &= \sigma_i(x) + \psi_i(0) \beta(x)
\end{align*}
\]

In order to determine the initial value \( \psi_0(0) \) along with the eigenvalue \( \bar{e}_0 \) (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 :

\[
\begin{align*}
\lim_{x \to +\infty} \frac{\alpha(x)}{\beta(x)} &= l_+^+(e_0) \\
\lim_{x \to -\infty} \frac{\alpha(x)}{\beta(x)} &= l_-^-(e_0).
\end{align*}
\]

The continuity of \( \psi_0(x) \) at \( x = 0 \) implies :

\[
l_+^+(e_0) = l_-^-(e_0).
\]

The value \( \bar{e}_0 \) 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" \( \psi_0(x) \) is given by :

\[
l_+^+(e_0) = l_-^-(e_0) = \phi_0(0).
\]

Once the eigenvalue \( \bar{e}_0 \) and the eigenfunction \( \phi_0(x) \) are thus determined, \( \bar{e}_1 \) and \( \phi_1(x) \), \( \bar{e}_2 \) and \( \phi_2(x) \), \ldots 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 :

\[
\begin{align*}
&i) \lambda_0 = 1; \quad \lambda_1 = 0; \quad \delta_m = 0, \quad m \geq 0 \quad \text{for} \quad \alpha \\
&ii) \lambda_0 = 0; \quad \lambda_1 = 1; \quad \delta_m = 0, \quad m \geq 0 \quad \text{for} \quad \beta \\
&iii) \lambda_0 = 0; \quad \lambda_1 = 0; \quad \delta_m \neq 0, \quad \text{for} \quad \sigma_i
\end{align*}
\]

### 4. Numerical application.

The aim of the numerical application presented here is to give some examples of the computation of the rotation harmonics \( \psi_i(x) \) 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 $\bar{\varepsilon}_0, \bar{\varepsilon}_1, \bar{\varepsilon}_2$ 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 ($x = 0.1, 0.2, 0.3, 0.4, 0.5 \text{ Å}$) 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 $\psi_\lambda$ computed directly from the Schrödinger equation 1 by using the method described in [13] and [18].

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

In table II, we compare the new results to those obtained by using the Runge-Kutta difference equations with a mesh size $h = 0.005 \text{ Å}$ [7]. The agreement between $\psi_\lambda$ 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 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 $\psi_\lambda(x)$ [2] computed directly from the Schrödinger equation.

<table>
<thead>
<tr>
<th>$x = 0.1 \text{ Å}$</th>
<th>$v = 0$</th>
<th>$v = 10$</th>
<th>$v = 20$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_0$</td>
<td>0.933 9664</td>
<td>-0.143 3597</td>
<td>-1.081 8068</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>0.000 2736</td>
<td>0.000 0067</td>
<td>0.003 7062</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>0.000 0000</td>
<td>0.000 0000</td>
<td>0.000 0000</td>
</tr>
<tr>
<td>$\psi_0 + \lambda \phi_1 + \lambda^2 \phi_2$</td>
<td>0.934 5137</td>
<td>-0.137 3339</td>
<td>-1.074 4222</td>
</tr>
<tr>
<td>$\psi_\lambda$</td>
<td>0.934 5137</td>
<td>-0.137 3339</td>
<td>-1.074 4222</td>
</tr>
<tr>
<td>$x = 0.3 \text{ Å}$</td>
<td>$\psi_0$</td>
<td>0.429 1245</td>
<td>0.847 5791</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>0.000 3733</td>
<td>0.000 3578</td>
<td>0.000 6448</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>0.000 0000</td>
<td>0.000 0019</td>
<td>0.000 0117</td>
</tr>
<tr>
<td>$\psi_0 + \lambda \phi_1 + \lambda^2 \phi_2$</td>
<td>0.429 8717</td>
<td>0.844 8558</td>
<td>0.250 0883</td>
</tr>
<tr>
<td>$\psi_\lambda$</td>
<td>0.429 8717</td>
<td>0.844 8558</td>
<td>0.250 0883</td>
</tr>
<tr>
<td>$x = 0.5 \text{ Å}$</td>
<td>$\psi_0$</td>
<td>0.095 4102</td>
<td>-1.107 5704</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>0.000 1372</td>
<td>-0.000 4990</td>
<td>-0.000 5909</td>
</tr>
<tr>
<td>$\phi_2$</td>
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<td>0.000 0008</td>
</tr>
<tr>
<td>$\psi_0 + \lambda \phi_1 + \lambda^2 \phi_2$</td>
<td>0.095 6849</td>
<td>-1.108 5655</td>
<td>1.083 3004</td>
</tr>
<tr>
<td>$\psi_\lambda$</td>
<td>0.095 6849</td>
<td>-1.108 5655</td>
<td>1.083 3005</td>
</tr>
</tbody>
</table>

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.

$$x = 0.1 \text{ Å}$$

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\psi_0$</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\psi_\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.933 9664</td>
<td>0.000 2736</td>
<td>0.000 0000</td>
<td>0.934 5137</td>
</tr>
<tr>
<td>5</td>
<td>1.297 9359</td>
<td>0.000 1373</td>
<td>0.000 0000</td>
<td>1.308 7100</td>
</tr>
<tr>
<td>10</td>
<td>-0.143 3561</td>
<td>0.000 0024</td>
<td>0.000 0000</td>
<td>-0.137 2445</td>
</tr>
</tbody>
</table>

$$x = 0.3 \text{ Å}$$

<table>
<thead>
<tr>
<th>$v$</th>
<th>$\psi_0$</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$\psi_\lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.933 9664</td>
<td>0.000 2736</td>
<td>0.000 0000</td>
<td>0.934 5137</td>
</tr>
<tr>
<td>5</td>
<td>1.297 9359</td>
<td>0.000 1373</td>
<td>0.000 0000</td>
<td>1.308 7100</td>
</tr>
<tr>
<td>10</td>
<td>-0.143 3561</td>
<td>0.000 0024</td>
<td>0.000 0000</td>
<td>-0.137 2445</td>
</tr>
</tbody>
</table>
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 \( \lambda \), compared to the wavefunction \( \psi_\lambda(x) \) (2nd line). The mean value \( \bar{\Delta} \) of the difference in absolute value for the five considered points is given in the last line.

<table>
<thead>
<tr>
<th>( x ) (( \text{Å} ))</th>
<th>2</th>
<th>6</th>
<th>12</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-0.137 333 9</td>
<td>-0.125 222 1</td>
<td>-0.106 894 6</td>
<td>-0.082 159 8</td>
<td>-0.050 762 1</td>
</tr>
<tr>
<td>0.2</td>
<td>-0.910 136 0</td>
<td>-0.920 168 7</td>
<td>-0.935 312 7</td>
<td>-0.955 681 5</td>
<td>-0.981 426 9</td>
</tr>
<tr>
<td>0.3</td>
<td>0.844 855 8</td>
<td>0.839 363 4</td>
<td>0.831 010 1</td>
<td>0.819 657 9</td>
<td>0.805 123 4</td>
</tr>
<tr>
<td>0.4</td>
<td>0.388 680 1</td>
<td>0.403 239 9</td>
<td>0.425 246 4</td>
<td>0.454 899 8</td>
<td>0.492 466 9</td>
</tr>
<tr>
<td>0.5</td>
<td>-1.108 565 5</td>
<td>-1.110 538 2</td>
<td>-1.113 453 5</td>
<td>-1.117 258 7</td>
<td>-1.121 883 9</td>
</tr>
<tr>
<td>( \bar{\Delta} )</td>
<td>0</td>
<td>1</td>
<td>9</td>
<td>51</td>
<td>180</td>
</tr>
</tbody>
</table>

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.

5. Conclusion.

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

References