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The Analytic Representation of Radial Functions Determined from the Spectra of Diatomic Molecules

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An alternative approach to the derivation of the expressions for the function Z_{kl} (to take account of effects beyond the vibrational and rotational motions of the nuclei) in the term coefficients of diatomic molecules is outlined. Application of the resulting expressions is made to the spin–rotational coupling parameter of $^{12}C^{14}N$ in the $X^2\Sigma$ state and to the electric quadrupolar coupling parameter of the ^{35}Cl nucleus in $H^{35}Cl$. © 1988 Academic Press, Inc.

Recently Bessis *et al.* (*1*) proposed an analytic method to enable the determination of the radial dependence of certain functions of diatomic molecules in terms of vibration–rotational spectroscopic parameters. The purpose here is both to demonstrate a simpler and improved procedure to accomplish the same objective and to illustrate its applications.

The procedure is essentially an extension of the original method (*2*). In summary, Dunham proposed a general internuclear potential-energy function of a diatomic molecule in terms of the reduced internuclear separation $x \equiv (R - R_e)/R_e$,

$$V(x) = a_0 x^2 (1 + \sum_{j=1} a_j x^j). \tag{1}$$

Then the coefficients $Y_{k,0}$ in the energy term values (in wavenumber units)

$$E_v = \sum_{k=0} Y_{k,0}(v + 1/2)^k \tag{2}$$

were expressed as a sum of contributions

$$Y_{k,0} = Y_{k,0}^{(0)} = Y_{k,0}^{(2)} + Y_{k,0}^{(4)} + \cdots, \tag{3}$$

of which the parenthesized numeral in the superscript indicates the order of the integral (according to the BKW (*3–5*) theory) from which the contribution originates. (The first-order integral is evaluated directly and leads to the addend $\frac{1}{2}$ of the vibrational quantum number v; other integrals of odd order vanish.) In order to take account of the rotation of the nuclei about the center of molecular mass, Dunham (*2*) included a centrifugal term in an effective potential-energy function:

$$V_{\text{eff}}(x) = a_0 x^2 (1 + \sum_{j=1} a_j x^j) + B_e J(J + 1)/(1 + x)^2; \tag{4}$$

by forming the J-dependent potential-energy parameters $a_j(J)$ for substitution into the $Y_{k,0}$ expressions, he thus derived the vibration–rotational term coefficients Y_{kl},

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$l > 0$. Simply by adding a further term $K(x)$ to the effective potential energy in order to take account of effects beyond the vibrational and rotational motions of the nuclei,

$$V_{\mathrm{eff}}(x) = a_0 x^2 (1 + \sum_{j=1} a_j x^j) + B_e J(J+1)/(1+x)^2 + \sum_{j=0} k_j x^j, \tag{5}$$

one can use a procedure entirely analogous to Dunham's (*2*); by this means one can generate expressions for the additional coefficients Z_{kl} in the extended equation (*6*) for the term values

$$E_{vJ} = \sum_{k=0} \sum_{l=0} (Y_{kl} + Z_{kl})(v + 1/2)^k [J(J+1)]^l. \tag{6}$$

By means of computer algebra (*7*), we have derived (and checked) the analytic expressions for Y_{kl}, including all contributions $Y_{kl}^{(0)}$, $Y_{kl}^{(2)}$, $Y_{kl}^{(4)}$, and $Y_{kl}^{(6)}$, $(2k + l) \leqslant 12$, containing terms in the potential-energy coefficients up to a_{10}, plus $Y_{6,1}$ (a_{11}) and $Y_{7,0}$ (a_{12}), and Z_{kl}, $(2k + l) \leqslant 9$, containing terms up to a_7 and k_9. (Except for $Z_{0,0}^{(2)}$ and $Z_{1,0}^{(2)}$, the expressions derived for Z_{kl} are only the contributions $Z_{kl}^{(0)}$ obtained from the zero-order integral of the BKW procedure.) According to the simple and well established procedure just outlined, the expressions that have been derived are equivalent to those termed $\mathcal{Y}_{kl}$ and $\mathcal{Z}_{kl}$ of Bessis *et al.* (*1*) whose procedure was extraordinarily and unnecessarily complicated. Also, and perhaps for this reason, the expressions in their paper contain many errors (for instance, in $\mathcal{Y}_{3,1}$, $\mathcal{Y}_{4,1}$, and $\mathcal{Z}_{2,2}$).

The potential-energy function $V(x)$ in the Dunham (*2*) treatment, also used by Bessis *et al.* (*1*), suffers from a finite region of convergence, $|x| \leqslant 1$ or $0 \leqslant R \leqslant 2R_e$. For this reason and because of other useful properties (*8*), the alternative series representation $V(z)$ (*9*), in which $z \equiv 2(R - R_e)/(R + R_e)$,

$$V(z) = c_0 z^2 (1 + \sum_{j=1} c_j z^j) \tag{7}$$

is preferable because its range of convergence $|z| \leqslant 2$ spans the entire range of molecular existence, $0 \leqslant R < \infty$. The expressions for Y_{kl}, all orders specified above, $(2k + l) \leqslant 12$, in terms of c_j with $j \leqslant 10$, as well as the derivatives of Y_{kl} with respect to their parameters (useful for purposes of fitting spectra), have already been published (*10*) in machine-readable form (FORTRAN code). Here we introduce a further series representation $K(z)$ corresponding to $K(x)$ in Eq. (5)

$$K(z) = \sum_{j=0} h_j z^j; \tag{8}$$

the expressions Z_{kl} in terms of c_j, h_j and $\gamma \equiv 2B_e/\omega_e$ to be applied in this paper are listed in Table I.

To demonstrate the application of these results, we consider first the spin–rotational interaction in the $X^2\Sigma$ state of $^{12}C^{14}N$ (*11*); although other sets ((*12*) and references therein) of spectroscopic data have since been published for this free radical, these data are convenient for the present illustrative purpose. The available values of γ_v and γ_J (*11*) for the vibrational states $0 \leqslant v \leqslant 3$ were separately fitted to quadratic and linear, respectively, dependences on $(v + \frac{1}{2})$; the resulting coefficients correspond to $Z_{0,0}$, $Z_{1,0}$, and $Z_{2,0}$ and to $Z_{0,1}$ and $Z_{1,1}$, respectively. (The correction term in $Z_{0,0}$, containing the factor γ^2 is negligible in comparison with experimental error.) The

TABLE I

Expressions for Z_{kl}

$$\begin{aligned}
Z_{0,0} &= h_0 + \gamma^2\,[(-\,3/32\ c_1 - 13/32\ c_1^2 - 21/32\ c_1^3 \\
&\quad + 23/16\ c_1c_2 + 5/8\ c_2 - 15/16\ c_3 + 1/32)\ h_1 \\
&\quad + (1/8\ c_1 - 3/8\ c_2 + 7/16\ c_1^2)\ h_2 \\
&\quad + (-\,7/16\ c_1 - 1/8)\ h_3 + 3/8\ h_4] \\
Z_{1,0} &= \gamma\ (h_1 + h_2 - 3/2\ c_1h_1) \\
Z_{2,0} &= \gamma^2\,[(9/8\ c_1 + 3/8\ c_1^2 - 45/8\ c_1^3 + 39/4\ c_1c_2 \\
&\quad - 3/2\ c_2 - 15/4\ c_3 - 3/8)\ h_1 + \\
&\quad (15/4\ c_1^2 - 3/2\ c_1 - 3/2\ c_2)\ h_2 + \\
&\quad (3/2 - 15/4\ c_1)\ h_3 + 3/2\ h_4] \\
Z_{0,1} &= \gamma^2\ h_1 \\
Z_{1,1} &= \gamma^3\,[(27/4\ c_1^2 + 9/2\ c_1 - 6\ c_2 + 3/4)\ h_1 \\
&\quad - 9/2\ c_1h_2 + 3\ h_3] \\
Z_{0,2} &= \gamma^4\ (h_2 - 2\ h_1 - 3/2\ c_1h_1)
\end{aligned}$$

necessary data and parameters are given in Table II, with the values of the coefficients h_j obtained by applying serially the expressions in Table I. Because Bogey *et al.* (*13*) have shown that an extra power of reduced mass is necessary for the spin–rotational parameter, this factor is here taken into account by the insertion of B_e into each expression Z_{kl} in Table I. Because of the experimental error propagated from the input data (*11*), the values obtained for h_3 and h_4 are not very significant, but serve anyhow to indicate the use of the theory. The range of validity of the function $K(z)$ should be between the classical turning points for $v = 3$, namely $1.05 < R/10^{-10}\ \mathrm{m} < 1.33$.

The second application of this theory is to an experimental quantity not previously considered (*1*), namely the electric quadrupolar coupling parameter qQ of a nucleus

TABLE II

Data and Results for the Spin–Rotational Coupling Function of $^{12}C^{14}N$ in the $X^2\Sigma$ State

$/\mathrm{m}^{-1}$	
$Z_{0,0} = 0.7441 \pm 0.0020$	$c_1 = -1.6595$
$Z_{1,0} = -0.0039 \pm 0.0025$	$c_2 = 0.9997$
$Z_{2,0} = -0.00097 \pm 0.00062$	$c_3 = -0.3831$
$Z_{0,1} = (-0.72 \pm 0.14)\mathrm{x}10^{-5}$	$c_4 = 0.1266$
$Z_{1,1} = (-0.090 \pm 0.063)\mathrm{x}10^{-5}$	$h_0 = 0.003917 \pm .000010$
$Z_{0,2} = (4.9 \pm 1.6)\mathrm{x}10^{-11}$	$h_1 = -0.0113 \pm .0019$
$B_e = 189.9779$	$h_2 = 0.028 \pm .0053$
$\omega_e = 206868.09$	$h_3 = -0.303 \pm 0.13$
	$h_4 = 0.40 \pm 0.46$

with spin of magnitude greater than $\frac{1}{2}$ (in units of $h/2\pi$). For this application, the available eight data (*14, 15*) of the electric quadrupolar coupling parameter of the ^{35}Cl nucleus in $^{1}H^{35}Cl$ and $^{2}H^{35}Cl$ were fitted directly to the h_j parameters, $0 \leqslant j \leqslant 4$, through the expressions for Z_{kl} in Table I, by means of the method of multiple linear weighted regression (*16*). (The other necessary spectroscopic parameters of HCl were obtained from our previously published results (*17*).) As shown in Table III, the deduced values of the five parameters h_j reproduce the eight input data within an average of 1.02 experimental standard deviations. (In contrast, Kaiser's function (*14*) produces an average magnitude of difference between the eight observed and calculated values equal to ~150 times the experimental standard deviations.) In this case the correction term in $Z_{0,0}$ is significant, and its incorporation into the analysis permits the meaningful determination of values of h_3 and h_4. Because of this correction term, the data of $^{2}H^{35}Cl$ fit as well as those of $^{1}H^{35}Cl$; the invocation (*14*) of the breakdown of the Born–Oppenheimer approximation is superfluous. The range of validity of this function $K(z)$ should be between the classical turning points for $v = 2$, namely $1.08 < R/10^{-10}$ m < 1.58.

Other experimental data, for instance, the spin–orbital coupling parameter and other parameters discussed by Bessis *et al.* (*1*), as well as adiabatic and nonadiabatic corrections (*18*)—in fact, any applicable data with both vibrational and rotational

TABLE III

Data and Results for the Nuclear Quadrupole Coupling Function of the ^{35}Cl Nucleus in HCl in the $X^1\Sigma$ State[a]

$/m^{-1}$	$c_1 = -1.36337$
$h_0 = -0.2228391 \pm 1.3x10^{-6}$	$c_2 = 0.86552$
$h_1 = -0.30687 \pm 0.0011$	$c_3 = -0.47312$
$h_2 = 0.14713 \pm 0.0035$	$c_4 = 0.08959$
$h_3 = -1.7117 \pm 0.015$	$B_e = 1059.34994\ m^{-1}$
$h_4 = 7.6208 \pm 0.084$	$\omega_e = 299099.77\ m^{-1}$

v	J	observed[a] qQ/m^{-1}	calculated qQ/m^{-1}
			$^{1}H^{35}Cl$
0	1	$-0.2255521 \pm 5x10^{-7}$	$-0.2255524 \pm 4x10^{-7}$
0	2	$-0.2256179 \pm 5x10^{-7}$	$-0.2256175 \pm 4x10^{-7}$
1	1	$-0.2310695 \pm 3x10^{-6}$	$-0.2310697 \pm 4x10^{-7}$
2	1	$-0.2365240 \pm 8x10^{-6}$	$-0.2365237 \pm 4x10^{-7}$
			$^{2}H^{35}Cl$
0	1	$-0.2248001 \pm 3x10^{-7}$	$-0.2248000 \pm 4x10^{-7}$
0	2	$-0.2248333 \pm 1x10^{-6}$	$-0.2248330 \pm 4x10^{-7}$
0	3	$-0.2248822 \pm 3x10^{-7}$	$-0.2248824 \pm 4x10^{-7}$
1	1	$-0.2287686 \pm 3x10^{-6}$	$-0.2287684 \pm 4x10^{-7}$

[a] Note that all uncertainties given in this table correspond to ~3 standard deviations (14) or errors.

dependence—may be similarly treated to yield a radial dependence of the appropriate molecular property, according to the simple method here described and illustrated. A further advantage of this approach is the prediction of other values of Z_{kl} not measured; for instance, the value of $Z_{0,2}$ that appears in Table II was obtained in this way. This value of $Z_{0,2}$ for the spin–rotational coupling expansion of $^{12}C^{14}N$ is estimated to be $(4.9 \pm 1.6) \times 10^{-11}$ m^{-1} for comparison with the experimental value $(16 \pm 8) \times 10^{-11}$ m^{-1} for the state $v = 0$; the agreement is only moderate, and possible deficiencies in the spectral analysis (*11*) have already been discussed (*12*). It should be noted that, contrary to the usage of Bessis *et al.* (*1*), the factor B_e is here omitted in the function $K(x)$ or $K(z)$; the incorporation of this quantity would in general produce an incorrect mass dependence for isotopic molecules, although it is necessary, and has been incorporated within Z_{kl}, in the analysis of the data for the spin–rotational parameter. There however remains within the factor γ (proportional to $\mu^{-1/2}$) the effect of the reduced mass μ to bestow the proper mass dependence on isotopic molecules for the nuclear quadrupolar or other interaction.

In conclusion, we have demonstrated that one can conveniently derive expressions for Z_{kl} in a simpler and more direct way than that of Bessis *et al.* (*1*). Because these expressions given in Table I are in terms of the potential-energy coefficients c_j and h_j rather than of a_j and k_j, additional conditions can be applied to generate the correct long-range (and also short-range) behavior of $K(z)$ toward the limit of the separate atoms (and the united atom) (*9*); thus by comparison with $K(x)$, $K(z)$ is an improved representation. There is no necessity to introduce the $v!$ dependence (*1*) of vibrational terms (instead of the conventional dependence on $(v + \frac{1}{2})^k$), which results in inconsistent differences of vibrational terms relative to the Dunham formula in Eq. (2).

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