About the Dunham Coefficients Y_{20} and Y_{11} for Diatomic Molecules

(Dedicated to Prof. S.A. Suryawansi, Vice-Chancellor, SRTM University, Nanded on the occasion of his 60^{th} birth-day)

ARVIND K. SHARMA AND SURESH CHANDRA

School of Physical Sciences, S.R.T.M. University, Nanded 431 606, India

For a diatomic molecule, when the Dunham coefficients Y_{20} is negative, all features of potential-energy curve can be reproduced. When Y_{20} is positive, it is not possible to reproduce all features of the potential-energy curve. However, turning points for some lower vibrational states can be obtained.

Classical left- and right-hand turning points, r$_{min}$ and r$_{max}$, respectively, of Rydberg-Klein-Rees (RKR) potential-energy curve, for a diatomic molecule, are given by (Rydberg, 1931, 1933; Klein, 1932; Rees, 1947)

$$r_{\rm min} = (f/g + f^2)^{1/2} - f, \qquad r_{\rm max} = (f/g + f^2)^{1/2} + f,$$

where the Klein integrals f and g are defined as (Chandra et al., 1996)

$$f({\rm cm}) = \Big(\frac{h}{8\pi^2\mu c}\Big)^{1/2} \int_{-\Delta}^{t} [U - E(v,J)]^{-1/2} ds \tag{1}$$

and

$$g({\rm cm}^{-1}) = \Big(\frac{8\pi^2\mu c}{h}\Big)^{1/2} \int_{-\Delta}^{t} \frac{\partial E}{\partial[J(J+1)]} [U - E(v,J)]^{-1/2} ds \tag{2}$$

where

$$s = v + \frac{1}{2}, \qquad t = v' + \frac{1}{2},$$

h the Planck constant, c the speed of light in vacuum, μ the reduced mass of the molecule, v the vibrational quantum number, and v' the vibrational quantum number of the level (with the rotational quantum number $J = 0$) for which the turning points are to be calculated. The energy of the vib-rotational levels, in a diatomic molecule, can be expressed as

$$E(v,J)=\sum_{i,j}Y_{ij}\Big(v+\frac{1}{2}\Big)^i\Big[J(J+1)\Big]^j. \tag{3}$$

Here, Y_{ij} are referred to Dunham coefficients. The Dunham coefficient Y_{10} corresponds to the vibrational frequency of the molecule, and the Dunham coefficient Y_{01} is inversely proportional to the moment of inertia of the molecule about an axis perpendicular to the axis of the molecule and passing through the centre-of-mass of the molecule. Obviously, the Dunham coefficients Y_{10} and Y_{01} can never be negative. The energy of the level with the vibrational quantum number v', and the rotational quantum number $J = 0$, is given by

$$U=\sum_{i=0}Y_{i0}t^i. \tag{4}$$

In a large number of molecules, the energy $U = 0$ when $v' = -1/2$ (i.e., $t = 0$). However, in some molecules, $U = Y_{00}$ when $v' = -1/2$. (The value of Y_{00} may affect the results, but does not change the general behavior of the results.) Note that the lower limit of the integrals in the eqs. (1) and (2), following Kaiser (1970), has been taken as $-\Delta$, where Δ is the root of the equation

$$\sum_{i=0}Y_{i0}(-\Delta)^i=0. \tag{5}$$

For a large number of molecules, the value of the Dunham coefficient Y_{00} is zero, and then the lower limit of the integrals in the eqs. (1) and (2) becomes the same (i.e., zero) as used earlier (Klein, 1932; Rees, 1947).

With the advent of the high speed computers, the turning points of the potential energy curve can be obtained to great accuracy. But one cannot and should not forget about the basic requirements, which can only be derived analytically. Laboratory spectra of diatomic molecules are generally fitted in terms of the Dunham coefficients, which are later on used in the calculation of the potential energy curve. While fitting the laboratory spectrum, one way get any sign (positive or negative) for the Dunham coefficients Y_{20} and Y_{11}. The purpose of the present investigation is to discuss analytically the repercussions of the signs of Y_{20} and Y_{11}.

The f and g can be expressed as

$$f=\frac{1}{2}(r_{\mathrm{max}}-r_{\mathrm{min}}), \qquad g=\frac{1}{2}(\frac{1}{r_{\mathrm{min}}}-\frac{1}{r_{\mathrm{max}}}).$$

Hence, the requirement for the shape of the potential-energy curve is that both f and g, and their gradients, $\partial f/\partial U$ and $\partial g/\partial U$, must be positive.

Before the development of the numerical techniques around 1963 analytical expressions for f and g (Rees, 1947) were in use for a long time to get rid of the singularity at the upper limit of the integrals in eqs. (1) and (2). For a limited number of Dunham coefficients, Y_{00}, Y_{10}, Y_{20}, Y_{01}, and Y_{11}, the f and g can be obtained analytically. The expressions for f and g are found to depend on the sign of Y_{20}. When Y_{20} has a negative value, the expressions for f and g are given by

$$f(\mathrm{cm}) = \Big(\frac{h}{8\pi^2\mu c(-Y_{20})}\Big)^{1/2} \ln\Bigg[\frac{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20} + 4UY_{20}}}{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20}} - \sqrt{4U(-Y_{20})}}\Bigg] \tag{6}$$

and

$$g(\mathrm{cm}^{-1}) = \Big(\frac{8\pi^2\mu c}{h(-Y_{20})}\Big)^{1/2} Y_{11}\Bigg(-\sqrt{\frac{U}{(-Y_{20})}} + \Big(\frac{Y_{01}}{Y_{11}} - \frac{Y_{10}}{2Y_{20}}\Big)\ln\Bigg[\frac{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20} + 4UY_{20}}}{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20}} - \sqrt{4U(-Y_{20})}}\Bigg]\Bigg). \tag{7}$$

When the Y_{20} has a positive value, the expressions for f and g are given by

$$f(\mathrm{cm}) = \Big(\frac{h}{8\pi^2\mu c Y_{20}}\Big)^{1/2}\Bigg[\frac{\pi}{2} - \arcsin\Big(\sqrt{\frac{Y_{10}^2 - 4Y_{00}Y_{20}}{Y_{10}^2 - 4Y_{00}Y_{20} + 4UY_{20}}}\Big)\Bigg] \tag{8}$$

and

$$g(\mathrm{cm}^{-1}) = \Big(\frac{8\pi^2\mu c}{hY_{20}}\Big)^{1/2} Y_{11}\Bigg(\sqrt{\frac{U}{Y_{20}}} + \Big(\frac{Y_{01}}{Y_{11}} - \frac{Y_{10}}{2Y_{20}}\Big)\Bigg[\frac{\pi}{2} - \arcsin\Big(\sqrt{\frac{Y_{10}^2 - 4Y_{00}Y_{20}}{Y_{10}^2 - 4Y_{00}Y_{20} + 4UY_{20}}}\Big)\Bigg]\Bigg). \tag{9}$$

However, the expressions for the gradients of f and g are found not to depend on the sign of Y_{20}, and are given by

$$\frac{\partial f}{\partial U} = \Big(\frac{h}{8\pi^2\mu c U}\Big)^{1/2} \frac{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20}}}{(Y_{10}^2 - 4Y_{00}Y_{20} + 4UY_{20})} \tag{10}$$

and

$$\frac{\partial g}{\partial U} = \Big(\frac{8\pi^2\mu c}{hU}\Big)^{1/2} Y_{11}\Big[\frac{1}{2Y_{20}} + \Big(\frac{Y_{01}}{Y_{11}} - \frac{Y_{10}}{2Y_{20}}\Big)\frac{\sqrt{Y_{10}^2 - 4Y_{00}Y_{20}}}{(Y_{10}^2 - 4Y_{00}Y_{20} + 4UY_{20})}\Big]. \tag{11}$$

The gradients of the turning points are given by

$$\frac{\partial r_{\mathrm{min}}}{\partial U} = \Big(\frac{f}{g} + f^2\Big)^{-1/2}\Big[\frac{1}{2g} + f\Big]\frac{\partial f}{\partial U} - \Big[\frac{f}{2g^2}\Big(\frac{f}{g} + f^2\Big)^{-1/2}\frac{\partial g}{\partial U} + \frac{\partial f}{\partial U}\Big] \tag{12}$$

$$\frac{\partial r_{\mathrm{max}}}{\partial U} = \Big(\frac{f}{g} + f^2\Big)^{-1/2}\Big[\frac{1}{2g} + f\Big]\frac{\partial f}{\partial U} + \frac{\partial f}{\partial U} - \frac{f}{2g^2}\Big(\frac{f}{g} + f^2\Big)^{-1/2}\frac{\partial g}{\partial U}. \tag{13}$$

For negative values of the Y_{20}, the Y_{11} may be positive as well as negative. Here, the gradients, $\partial f/\partial U$, $\partial g/\partial U$, and $\partial r_{\mathrm{max}}/\partial U$ are always positive, and the gradient $\partial r_{\mathrm{min}}/\partial U$ is always negative, up to the dissociation limit, when f (the half-width of the potential-energy curve) becomes infinite at the energy

$$U = Y_{00} + \frac{Y_{10}^2}{4(-Y_{20})}, \tag{14}$$

which corresponds to the vibrational quantum number

$$v'_{\mathrm{m}} = \frac{Y_{10} + Y_{20}}{2(-Y_{20})}. \tag{15}$$

This value of the energy U, for the quadratic case, may be taken equal to the dissociation energy of the molecule. For example, by using the Dunham coefficients for CO given by Farrenq et al. (1991), the value of the dissociation energy comes out to be 88578 cm^{-1}, which is within 2.3 % of the real value, 90674 cm^{-1}. In order to have a large value of v'_{m}, the value of (-Y_{20}) should be much smaller than that of Y_{10}. For CO, here, the value of v'_{m} is 81. It shows that the turning points, corresponding to the negative values of the Y_{20}, satisfy all the requirements for the shape of the potential-energy curve. Hence, all the features of the potential-energy curve can be reproduced when Y_{20} is negative.

For positive values of the Y_{20}, both $\partial f/\partial U$ and $\partial g/\partial U$ are always positive when Y_{11} is positive, but when Y_{11} is negative, $\partial g/\partial U$ becomes negative for the higher levels. Further, (i) when the value of Y_{11} is negative, the value of r_{min} starts to increase after some vibrational quantum number, (ii) when the value of Y_{11} is positive, the value of $r_{i\mathrm{max}}$ starts to decrease after some vibrational quantum number. Moreover, the value of f, corresponding to the positive value of Y_{20}, is always finite (never becomes infinite) with the largest value

$$f(\mathrm{cm}) = \Big(\frac{h}{8\pi^2 \mu c Y_{20}}\Big)^{1/2} \frac{\pi}{2}. \tag{16}$$

In order to show these effects explicitly, let us consider the Dunham coefficients for the A$^1\Sigma^+$ state of ^{7}LiH molecule, Y_{00} = 7.26 cm^{-1}, Y_{10} = 236.4717 cm^{-1}, Y_{20} = 26.8514 cm^{-1}, Y_{01} = 2.8418 cm^{-1}, and Y_{11} = 0.025116 cm^{-1}. The calculated values of the the turning points are given in the columns 3 and 4 of Table 1. Obviously, after v = 27, the value of r_{max} starts to decrease. When we changed the sign of Y_{11} (i.e., we took Y_{11} = - 0.025116 cm^{-1}), the values of the turning points are given in the columns 5 and 6 of Table 1. Now the value of r_{min} starts to increase after v = 13. Obviously, when Y_{20} is positive, it is not possible to get all turning points of the potential-energy curve up to the dissociation limit.

Finally, it can be concluded that when the Dunham coefficient Y_{20} is negative, all the features of the potential-energy curve can be obtained. But when Y_{20} is positive, it is not possible to reproduce all the features of the potential-energy curve. However, the turning points for some lower vibrational states can be obtained. Thus, while fitting the observed spectrum, one should take care that the fitting is done in such a fashion that proper sign of Y_{20} is obtained. Otherwise it would lead to a situation where it would not be possible to obtain a proper potential energy curve for the molecule.

Acknowledgments

We are grateful to Professor J.V. Narlikar, Director, IUCAA, Pune for his encouragement. AKS is thankful to IUCAA, Pune for providing financial support for his visit to IUCAA.

References

Chandra, S., Sharma, A. K., and Khan, Z. H., 1996 *Pramana*, **47**, 65.

Farrenq, R., Guelachvili, G., Sauval, A. J., Grevesse, N., and Farmer, C. B., 1991 *J. Mol. Spectrosc.*, **149**, 375.

Kaiser, E. W., 1970 *J. Chem. Phys.*, **53**, 1686.

Klein, O., 1932 *Z. Physik*, **76**, 221.

Rees, A. L. G., 1947 *Proc. Phys. Soc. (London)*, **59**, 998.

Rydberg, R., 1931 *Z. Physik*, **73**, 376.

Rydberg, R., 1933 *Z. Physik*, **80**, 514.

Table 1: Values of the turning points when Y_{20} is positive

		$Y_{11} = 0.025116$		$Y_{11} = - 0.025116$	
v'	$U(\mathrm{cm}^{-1})$	$r_{\mathrm{min}}(\mathring{A})$	$r_{\mathrm{max}}(\mathring{A})$	$r_{\mathrm{min}}(\mathring{A})$	$r_{\mathrm{max}}(\mathring{A})$
0	132.21	2.224598	3.017344	2.231891	3.024638
1	422.38	2.035308	3.278936	2.057169	3.300797
2	766.26	1.935193	3.428936	1.971198	3.464941
3	1163.84	1.868788	3.530786	1.918671	3.580669
4	1615.12	1.820051	3.605113	1.883635	3.668697
5	2120.11	1.781999	3.661729	1.859161	3.738891
6	2678.80	1.750990	3.706121	1.841645	3.796775
7	3291.19	1.724906	3.741664	1.828991	3.845749
8	3957.28	1.702416	3.770573	1.819888	3.888045
9	4677.08	1.682642	3.794367	1.813472	3.925197
10	5450.58	1.664976	3.814134	1.809143	3.958301
11	6277.78	1.648982	3.830669	1.806476	3.988163
12	7158.69	1.634343	3.844571	1.805159	4.015388
13	8093.30	1.620816	3.856301	1.804956	4.040442
14	9081.61	1.608218	3.866218	1.805688	4.063689
15	10123.62	1.596404	3.874607	1.807216	4.085419
16	11219.34	1.585259	3.881697	1.809427	4.105865
17	12368.76	1.574693	3.887674	1.812235	4.125215
18	13571.88	1.564629	3.892690	1.815567	4.143628
19	14828.70	1.555007	3.896874	1.819364	4.161232
20	16139.23	1.545775	3.900331	1.823580	4.178136
21	17503.46	1.536890	3.903150	1.828173	4.194433
22	18921.39	1.528316	3.905407	1.833109	4.210201
23	20393.03	1.520022	3.907168	1.838361	4.225507
24	21918.37	1.511983	3.908488	1.843906	4.240410
25	23497.41	1.504175	3.909415	1.849721	4.254961
26	25130.16	1.496578	3.909991	1.855791	4.269204
27	26816.60	1.489175	3.910252	1.862100	4.283176
28	28556.75	1.481952	3.910231	1.868635	4.296914
29	30350.61	1.474895	3.909955	1.875387	4.310447
30	32198.16	1.467992	3.909450	1.882344	4.323803