Solution of the rigid rotor Schrödinger equation

Chemistry BC3253x

$$-\frac{\hbar^2}{2\mu}\nabla^2\,\Psi \;=-\frac{\hbar^2}{2\mu R^2}\Lambda^2\,\Psi \;=-B\Lambda^2\,\Psi \;=\; E\Psi$$

1. Classical rigid rotor $E \;=\; \frac{L^2}{2I} \;= \frac{L^2}{2\mu R^2}$. Quantum mechanical operator $\hat{L}^2 \;\rightarrow\; -\hbar^2\Lambda^2$.

$$\Lambda^2 \;=\; \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right].$$

Let $\Psi(\theta,\phi) \;=\; \Theta(\theta)\,\Phi(\phi)$ and $\varepsilon \;=\; \frac{E}{B}$.

2. Substitute $\Psi(\theta,\phi) \;=\; \Theta(\theta)\,\Phi(\phi)$ into the eigenvalue equation $\Lambda^2\,\Psi \;=\; -\varepsilon\Psi$.

Rearrange the equation so the variables are separated:

$$\frac{\sin\theta}{\Theta(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\varepsilon\sin^2\theta \;=\; -\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2} \;=\; M^2,\ \text{a constant.}$$

3. $-\frac{1}{\Phi(\phi)}\frac{\partial^2\Phi(\phi)}{\partial\phi^2} \;=\; M^2\ ;\ \ \Phi(\phi) \;=\; \frac{1}{\sqrt{2\pi}}e^{iM\phi}$, $M = 0 , \pm1 , \pm2 , \pm3 , ...$.

4. $\sin\theta\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta(\theta)}{\partial\theta}\right)+\left(\varepsilon\sin^2\theta - M^2\right)\Theta(\theta) \;=\; 0$.

$$\sin^2\theta\,\frac{\partial^2\Theta(\theta)}{\partial\theta^2}+\sin\theta\cos\theta\,\frac{\partial\Theta(\theta)}{\partial\theta}+\left(\varepsilon\sin^2\theta - M^2\right)\Theta(\theta) \;=\; 0\,.$$

5. As $\theta \;\rightarrow\; 0$, $\sin\theta \;\rightarrow\; 0$, and so the above equation reduces to $M^2\,\Theta(\theta) \;\rightarrow\; 0$.

Therefore, unless $M \;=\; 0$, the functions $\Theta(\theta) \;=\; 0$ when $\theta \;=\; 0$.

This condition is guaranteed if we choose a function of the form $\Theta(\theta) \;=\; (\sin\theta)^{|M|}\,K(\theta)$.

6. Assume that the functions $K(\theta)$ can be expanded in a series of powers of $\cos\theta$:

$$K(\theta) \;=\; \sum_{j=0}^{j=\infty} a_j\,(\cos\theta)^{\,j}. \qquad \text{Therefore}\ \ \Theta(\theta) \;=\; (\sin\theta)^{|M|}\sum_{j=0}^{j=\infty} a_j\,(\cos\theta)^{\,j}\ .$$

7. Substituting this form into the differential equation for $\Theta(\theta)$, we obtain

$$\begin{aligned}
\Big\{ -|M|(\sin\theta)^{(|M|+2)}\sum (j+1)\,a_j\,(\cos\theta)^{\,j} \;+\; |M|(|M|-1)\,(\sin\theta)^{|M|}\sum a_j\,(\cos\theta)^{\,j+2} \\
+\;(\sin\theta)^{(|M|+4)}\sum j(j-1)\,a_j\,(\cos\theta)^{\,j-2} \;-\; (|M|+1)\,(\sin\theta)^{(|M|+2)}\sum j a_j\,(\cos\theta)^{\,j} \\
+\;|M|(\sin\theta)^{|M|}\sum a_j\,(\cos\theta)^{\,j+2} \;-\; (\sin\theta)^{(|M|+2)}\sum j a_j\,(\cos\theta)^{\,j} \\
+\;\varepsilon\,(\sin\theta)^{(|M|+2)}\sum a_j\,(\cos\theta)^{\,j} \;-\; M^2\,(\sin\theta)^{|M|}\sum a_j\,(\cos\theta)^{\,j}\Big\} \;=\; 0\ .
\end{aligned}$$

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8. Using the relation $(\cos\theta)^{j+2} = (\cos^2\theta)(\cos\theta)^{j} = (1-\sin^2\theta)(\cos\theta)^{j}$ and the relation $(\sin\theta)^{(|M|+4)} = (\sin^2\theta)(\sin\theta)^{(|M|+2)} = (1-\cos^2\theta)(\sin\theta)^{(|M|+2)}$ and collecting terms,

$$(\sin\theta)^{(|M|+2)}\Big[\sum\Big\{(-|M|)(j+1)a_j - M^2 a_j - j(j-1)a_j - (|M|+2)\,ja_j + \varepsilon a_j\Big\}(\cos\theta)^{j} + \sum j(j-1)a_j(\cos\theta)^{j-2}\Big] = 0 .$$

9. This will be true if the coefficient of each term in $(\cos\theta)^{j}$ equals zero. Therefore

$$a_j\Big[\varepsilon - M^2 - |M|(j+1) - (|M|+2)\,j - j(j+1)\Big] + a_{j+2}\big[(j+2)(j+1)\big] = 0,$$

which gives the recursion relation: $a_{j+2} = a_j\left[\frac{(j+|M|+1)(j+|M|) - \varepsilon}{(j+2)(j+1)}\right]$.

10. As $j \to \infty$, $a_{j+2} \to a_j$, so the series will not converge and remain finite as $\theta \to 0$. Therefore either a_0 or a_1 must be chosen as zero, and the other series must terminate.

11. Let the terminal value of $(j+|M|) = J$. Then $\varepsilon = J(J+1)$, where the integer $J = 0 , 1 , 2 , 3 , ...$. For a given value of J , $M = 0 , \pm1 , \pm2 , \pm3 , ... , \pm J$.

Thus the quantization condition on total energy E and angular momentum squared L^2 is

$$\underline{E = BJ(J+1)} = \frac{\hbar^2}{2\mu R^2}J(J+1) \ ; \ L^2 = \hbar^2 J(J+1) \ ; J = 0 , 1 , 2 , ... ; \ J \geq |M| .$$

The angular momentum component $L_z = M\hbar$, $M = 0 , \pm1 , ... , \pm J$.

12. The polynomial solutions to the equation for Θ are the **associated Legendre functions**. The associated Legendre function of degree J and order |M| can be defined by

$$P_J^{|M|}(x) = (1-x^2)^{\frac{|M|}{2}}\frac{d^{|M|}P_J(x)}{dx^{|M|}} .$$ $P_J(x)$ is the **Legendre polynomial of degree J**:

$$P_J(x) = \frac{1}{2^J J!}\frac{d^J(x^2-1)^J}{dx^J}$$. Here $x = \cos\theta$, and the normalized functions $\Theta(\theta)$ are

$$\Theta(\theta) = \sqrt{\frac{(2J+1)}{2}\frac{(J-|M|)!}{(J+|M|)!}}\,P_J^{|M|}(\cos\theta) .$$ (See McQuarrie, pages 212–217 .)

13. The complete wavefunctions for the rigid rotor are the **normalized spherical harmonics** $\Psi(\theta,\phi) = Y_{J,M}(\theta,\phi) = \Theta_{J,M}(\theta)\Phi_M(\phi)$, with J = 0 , 1, 2, 3, ... and $M = 0 , \pm1, \pm2, ... , \pm J$. The quantized energy levels for the rigid rotor are $E = BJ(J+1)$, J = 0, 1, 2, 3, ...Each energy level is (2J+1)-fold degenerate.

The angular momentum is space-quantized: L_z has (2J+1) values for each L^2.