Energy Calculations

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Angular Momentum Operator and Values

$$L^2 = L_x^2 + L_y^2 + L_z^2 = I_a^2\omega_x^2 + I_b^2\omega_y^2 + I_c^2\omega_z^2 \Rightarrow L^2 - L_z^2 = L_x^2 + L_y^2$$

$$\hat{H}_{rot} = \frac{L_x^2}{2I_a} + \frac{L_y^2}{2I_b} + \frac{L_z^2}{2I_c} = \frac{L_x^2}{2I_a} + \frac{L_y^2}{2I_a} + \frac{L_z^2}{2I_c} = \frac{1}{2I_a}\left(L_x^2 + L_y^2\right) + \frac{L_z^2}{2I_c}$$

$$H_{rot} = \frac{L^2 - L_z^2}{2I_a} + \frac{L_z^2}{2I_c} \Rightarrow \left\{\begin{matrix} switch \\ to \\ operators \end{matrix}\right\} \hat{H}_{rot} = \frac{\hat{L}^2 - \hat{L}_z^2}{2I_a} + \frac{\hat{L}_z^2}{2I_c}$$

$$\hat{L}^2|J,K\rangle = \hbar^2\left(J(J+1)\right)|J,K\rangle$$

$$\hat{L}_z^2|J,K\rangle = \hbar^2K^2|J,K\rangle$$

Energy of Quantum Numbers

$$\hat{H}_{rot}|J,K\rangle = E|J,K\rangle = \left(\frac{\hat{L}^2 - \hat{L}_z^2}{2I_a} + \frac{\hat{L}_z^2}{2I_c}\right)|J,K\rangle = \left(\frac{\hbar^2[J(J+1) - K^2]}{2I_a} + \frac{\hbar^2K^2}{2I_c}\right)|J,K\rangle$$

$$E(J,K) = \frac{\hbar^2[J(J+1) - K^2]}{2I_a} + \frac{\hbar^2K^2}{2I_c} = \frac{\hbar^2}{2I_a}(J(J+1) + \frac{\hbar^2K^2}{2}\left(\frac{I}{I_c} - \frac{1}{I_a}\right)$$

$$= \frac{\hbar^2}{2I_a}(J(J+1) + \frac{\hbar^2K^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)$$

$$E(J,K) = \frac{\hbar^2}{2I_a}\left(J(J+1)\right) + \frac{\hbar^2K^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)$$

<u>Energy of Transitions</u>

$$E(\mathrm{J} = \mathrm{J}' + 1, K'') - E(J = J', K') = \Delta E(\Delta J = 1, \Delta K)$$

$$E(\mathrm{J} = \mathrm{J}' + 1, K'') = \frac{\hbar^2}{2I_a}\left((\mathrm{J}' + 1)(\mathrm{J}' + 1 + 1)\right) + \frac{\hbar^2K''^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)$$

$$= \frac{\hbar^2}{2I_a}\left((\mathrm{J}' + 1)(\mathrm{J}' + 2)\right) + \frac{\hbar^2K''^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)$$

$$= \frac{\hbar^2}{2I_a}\left(J'^2 + 3J' + 2\right) + \frac{\hbar^2K''^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)$$

$$E(\mathrm{J} = \mathrm{J}' + 1, K'') - E(J = J', K') = \Delta E(\Delta J = 1, \Delta K)$$

$$E(J',K') = \frac{\hbar^2}{2I_a}\left(J'(J'+1)\right) + \frac{\hbar^2K'^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right) = \frac{\hbar^2}{2I_a}\left(J'^2 + J'\right) + \frac{\hbar^2K'^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)$$

$$\Delta E_{rot}(\Delta J = 1, \Delta K) = \frac{\hbar^2}{2I_a}\left(J'^2 + 3J' + 2\right) + \frac{\hbar^2K''^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right) - \frac{\hbar^2}{2I_a}\left(J'^2 + J'\right) - \frac{\hbar^2K'^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)$$

$$= \frac{\hbar^2}{2I_a}\left(J'^2 + 3J' + 2 - J'^2 - J'\right) + \frac{\hbar^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)\left(K''^2 - K'^2\right)$$

$$\Delta E_{rot}(\Delta J = 1, \Delta K) = \frac{\hbar^2}{I_a}(J' + 1) + \frac{\hbar^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)\left(K''^2 - K'^2\right)$$

$$\Delta E_{rot}(\Delta J = 0, \Delta K) = \frac{\hbar^2}{2}\left(\frac{I_a - I_c}{I_aI_c}\right)\left(K''^2 - K'^2\right)$$

$$\Delta E_{rot}(\Delta J = -1, \Delta K) = E(\mathrm{J} = \mathrm{J}' - 1, K'') - E(J = J', K')$$

$$E(\mathrm{J}=\mathrm{J}'-1,K'')=\frac{\hbar^2}{2I_a}\big((\mathrm{J}'-1)(\mathrm{J}'-1+1)\big)+\frac{\hbar^2K''^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)$$
$$=\frac{\hbar^2}{2I_a}\big((\mathrm{J}'-1)(\mathrm{J}')\big)+\frac{\hbar^2K''^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)=\frac{\hbar^2}{2I_a}\left(J'^2-J'\right)+\frac{\hbar^2K''^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)$$
$$E(J',K')=\frac{\hbar^2}{2I_a}\big(J'(J'+1)\big)+\frac{\hbar^2K^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)=\frac{\hbar^2}{2I_a}\left(J'^2+J'\right)+\frac{\hbar^2K'^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)$$
$$\begin{aligned}\Delta E_{rot}(\Delta J=-1,\Delta K)&=\frac{\hbar^2}{2I_a}\left(J'^2-J'\right)+\frac{\hbar^2K''^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)-\frac{\hbar^2}{2I_a}\left(J'^2+J'\right)-\frac{\hbar^2K'^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)\\&=\frac{\hbar^2}{2I_a}\left(J'^2-J'-J'^2-J'\right)+\frac{\hbar^2\left(K''^2-K'^2\right)}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)\\&=\frac{\hbar^2}{2I_a}(-2J')+\frac{\hbar^2\left(K''^2-K'^2\right)}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)\\&=\frac{\hbar^2}{I_a}(-J')+\frac{\hbar^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)\left(K''^2-K'^2\right)\end{aligned}$$

Summarized Results

$$E(J,K)=\frac{\hbar^2}{2I_a}\big(J(J+1)\big)+\frac{\hbar^2K^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)$$

P: $\Delta E_{rot}(\Delta J=1,\Delta K)=\frac{\hbar^2}{I_a}(J'+1)+\frac{\hbar^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)\left(K''^2-K'^2\right)$

Q: $\Delta E_{rot}(\Delta J=0,\Delta K)=\frac{\hbar^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)\left(K''^2-K'^2\right)$

R: $\Delta E_{rot}(\Delta J=-1,\Delta K)=-\frac{\hbar^2}{I_a}J+\frac{\hbar^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)\left(K''^2-K'^2\right)$

$$\frac{\hbar^2}{2I_a}=\frac{1}{2}\frac{h}{2\pi}\frac{h}{2\pi}\frac{1}{I_a}=hB_e\Rightarrow B_e=\frac{h}{8\pi^2I_a}\Rightarrow$$
$$\frac{\hbar^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)=h\left[\frac{h}{8\pi^2}\left(\frac{I_a-I_c}{I_aI_c}\right)\right]=hB_e'\Rightarrow B_e'=\frac{h}{8\pi^2}\left(\frac{I_a-I_c}{I_aI_c}\right)$$

In terms of B_e, B_e'

$$\begin{aligned}E(J,K)&=\frac{\hbar^2}{2I_a}\big(J(J+1)\big)+\frac{\hbar^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)K^2\\&=hB_e\big(J(J+1)\big)+hB_e'K^2\end{aligned}$$

Energy transitions

P: $\Delta E_{rot}(\Delta J=1,\Delta K)=2hB_e(J'+1)+hB_e'\left(K''^2-K'^2\right)$

Q: $\Delta E_{rot}(\Delta J=0,\Delta K)=hB_e'\left(K''^2-K'^2\right)$

R: $\Delta E_{rot}(\Delta J=-1,\Delta K)=-2hB_eJ+hB_e'\left(K''^2-K'^2\right)$

$$B_e=\frac{h}{8\pi^2I_a},\qquad B_e'=\frac{h}{8\pi^2}\left(\frac{I_a-I_c}{I_aI_c}\right)$$

In terms of $\widetilde{B}_e, \widetilde{B}_e'$

$$\begin{aligned}E(J,K)&=\frac{\hbar^2}{2I_a}\big(J(J+1)\big)+\frac{\hbar^2}{2}\left(\frac{I_a-I_c}{I_aI_c}\right)K^2\\&=h\widetilde{B}_e\big(J(J+1)\big)+h\widetilde{B}_e'K^2\end{aligned}$$

Energy transitions

R: $\Delta E_{rot}(\Delta J = 1, \Delta K) = 2h\tilde{B}_e(J' + 1) + h\tilde{B}_e'\left({K''}^2 - {K'}^2\right)$

Q: $\Delta E_{rot}(\Delta J = 0, \Delta K) = h\tilde{B}_e'\left({K''}^2 - {K'}^2\right)$

P: $\Delta E_{rot}(\Delta J = -1, \Delta K) = -2h\tilde{B}_e J + h\tilde{B}_e'\left({K''}^2 - {K'}^2\right)$