Angular Momentum in 3 Dimensions

CLASSICAL, 3 numbers: $(L_x,\ L_y,\ L_z)$; $(|\vec{L}|,\ \theta,\ \phi)$

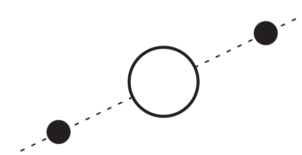
QUANTUM, 2 numbers: magnitude and 1 component

$$\hat{\vec{L}} \cdot \hat{\vec{L}}\, \psi_{l,m} \equiv \widehat{L^2}\, \psi_{l,m} \ = \ l(l+1)\hbar^2\, \psi_{l,m} \quad l = 0, 1, 2 \cdots$$

$$\hat{L}_z\, \psi_{l,m} \ = \ m\hbar\, \psi_{l,m} \qquad m = \underbrace{l, l-1, \cdots - l}_{2l+1 \text{ values}}$$

Specification: 2 numbers l & m $\rightarrow$ $\psi_{l,m}$ or $|l, m>$

<u>Molecular rotation</u>



In general

$$\mathcal{H}_{\text{rot}} = \frac{1}{2I_1}L_1^2 + \frac{1}{2I_2}L_2^2 + \frac{1}{2I_3}L_3^2$$

$$\begin{aligned} I_3 &= 0 \\ L_3 &= I_3\,\dot{\theta}_3 \\ &= 0 \\ I_1 &= I_2 \equiv I_\perp \end{aligned}$$

For a linear molecule

$$\mathcal{H}_{\text{rot}} = \frac{1}{2I_\perp}(L_1^2 + L_2^2) = \frac{1}{2I_\perp}\vec{L}\cdot\vec{L}$$

$$\hat{\mathcal{H}}_{\text{rot}} = \frac{1}{2I_\perp}\hat{L}^2$$

$$\hat{\mathcal{H}}_{\text{rot}}\,|l,m> \;=\; \epsilon_l|l,m>$$

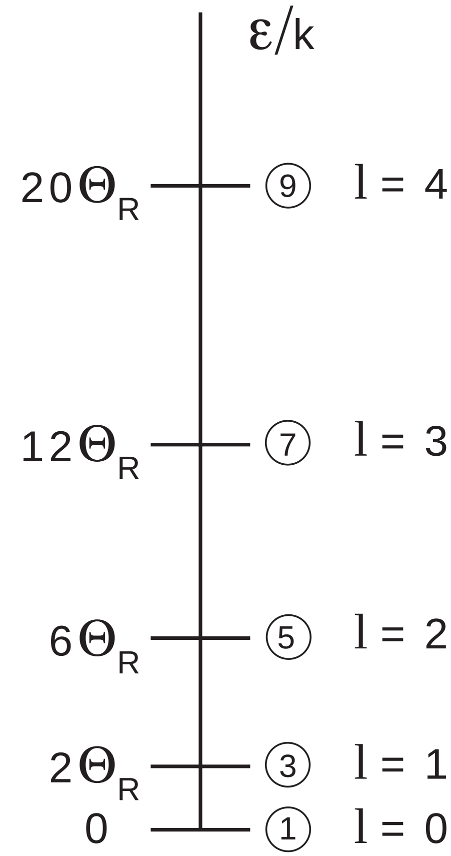
$$=\; \frac{\hbar^2}{2I_\perp}l(l+1)|l,m>$$

ϵ_l depends on l only;

it is $2l+1$ fold degenerate.

$$\epsilon_l = k\Theta_R\, l(l+1)$$

$$\Theta_R \equiv \frac{\hbar^2}{2I_\perp k} \quad \text{(rotational temp.)}$$



$$p(l,m) = \frac{1}{Z_R} e^{-l(l+1)\Theta_R/T}$$

$$Z_R = \sum_{l,m} e^{-l(l+1)\Theta_R/T} = \sum_l (2l+1) e^{-l(l+1)\Theta_R/T}$$

For $T \ll \Theta_R$ $\quad Z_R \approx 1 + 3e^{-2\Theta_R/T} = 1 + 3e^{-2\Theta_R k\beta}$

$$< \epsilon >= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{6\Theta_R\, k\, e^{-2\Theta_R k\beta}}{1 + 3e^{-2\Theta_R k\beta}} \approx 6\Theta_R\, k\, e^{-2\Theta_R/T}$$

$$C_V|_{\text{rot}} = N\frac{\partial < \epsilon >}{\partial T} = 6\Theta_R Nk \left(\frac{2\Theta_R}{T^2}\right) e^{-2\Theta_R/T}$$

$$= \underline{3Nk \left(\frac{2\Theta_R}{T}\right)^2 e^{-2\Theta_R/T}} \qquad \text{(energy gap behavior)}$$

For $T \gg \Theta_R$, convert the sum to an integral.

$$Z_R \approx \int_0^\infty (2l+1)e^{-l(l+1)\Theta_R/T}\, dl$$

$$x \equiv (l^2 + l)\Theta_R/T \qquad dx = (2l + 1)\Theta_R/T\, dl$$

$$Z_R \approx \frac{T}{\Theta_R} \int_0^\infty e^{-x}\, dx = \frac{T}{\Theta_R} = \frac{1}{k\Theta_R}\beta^{-1}$$

$$< \epsilon >= -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{(-1)(-1)Z/\beta}{Z} = \beta^{-1} = kT$$

$$C_V|_{\text{rot}} = N\frac{\partial < \epsilon >}{\partial T} \to Nk \qquad \text{(classical result)}$$

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Figure 22-1 from
Morse, P. M. *Thermal physics*. 2nd ed. New York, NY: W. A. Benjamin, 1969. ISBN: 0805372024.

$$\mathcal{H} = \mathcal{H}_{\text{CM}} + \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{vib}}$$

$$C_V(T) = \underbrace{C_V\big|_{\text{CM}}}_{\text{all } T} \quad + \quad \underbrace{C_V\big|_{\text{rot}}}_{\text{appears at modest } T} \quad + \quad \underbrace{C_V\big|_{\text{vib}}}_{\text{only at highest } T}$$

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Figure 12-16 from
F. W. Sears, and G. L. Salinger.
Thermodynamics, Kinectic Theory, and Statistical Physics. 3rd ed.
Reading, MA: Addison-Wesley Pub. Co., 1975. ISBN: 020106894X.

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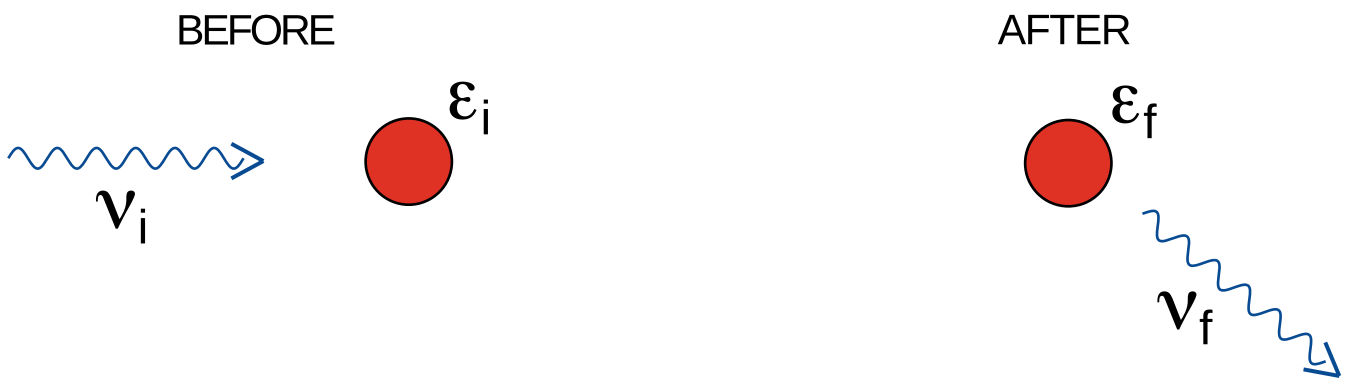
Figure 12-2 from
F. W. Sears, and G. L. Salinger.
Thermodynamics, Kinectic Theory, and Statistical Physics. 3rd ed.
Reading, MA: Addison-Wesley Pub. Co., 1975. ISBN: 020106894X.

Raman Scattering



$$\Delta\varepsilon = \varepsilon_f - \varepsilon_i = h(\nu_i - \nu_f)$$

FREQUENCY CHANGES IN THE SCATTERED LIGHT CORRESPOND TO ENERGY LEVEL DIFFERENCES IN THE SCATTERER.

WHICH ENERGY LEVEL CHANGES OCCUR DEPEND ON SELECTION RULES GOVERNED BY SYMMETRY AND QUANTUM MECHANICS

<u>Example</u> Rotational Raman Scattering

Selection rule: $\Delta l = \pm 2$

$$\Delta\nu_{l\uparrow} = -(k\Theta_R/h)[(l+2)(l+3) - l(l+1)]$$
$$= -(4l+6)(k\Theta_R/h)$$

$\Rightarrow$ uniform spacing between lines of $4(k\Theta_R/h)$

$I_{l\uparrow} \propto$ number of molecules with angular momentum l

$$\propto (2l+1)e^{-l(l+1)\Theta_R/T}$$

ROTATIONAL RAMAN SPECTRUM OF A DIATOMIC MOLECULE