8.044 Statistical Physics I
Spring 2008

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

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

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

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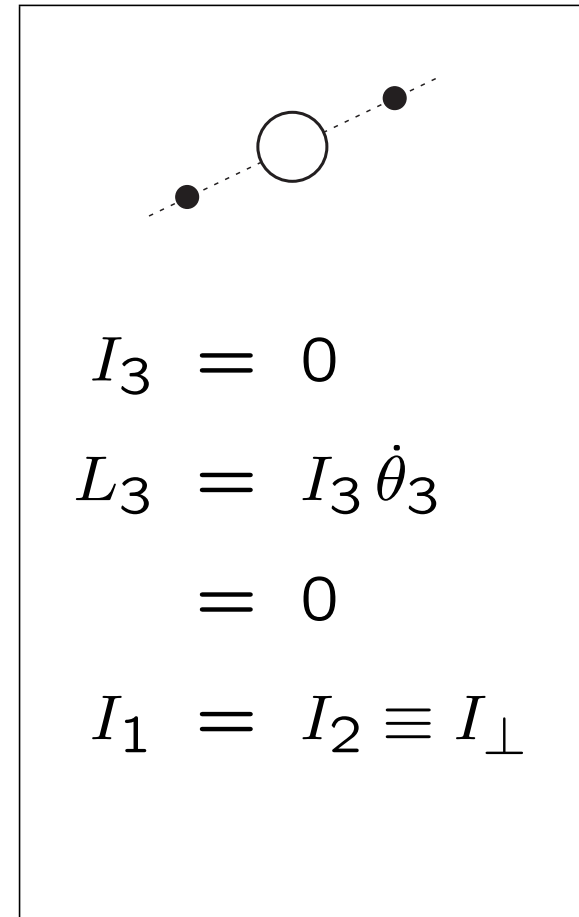
Molecular rotation

In general

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

For a linear molecule

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

$$I_3 = 0$$

$$L_3 = I_3 \dot{\theta}_3$$

$$= 0$$

$$I_1 = I_2 \equiv I_\perp$$

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

$$\widehat{\mathcal{H}}_{\text{rot}}\,|l,m> \;=\; \epsilon_l|l,m>$$
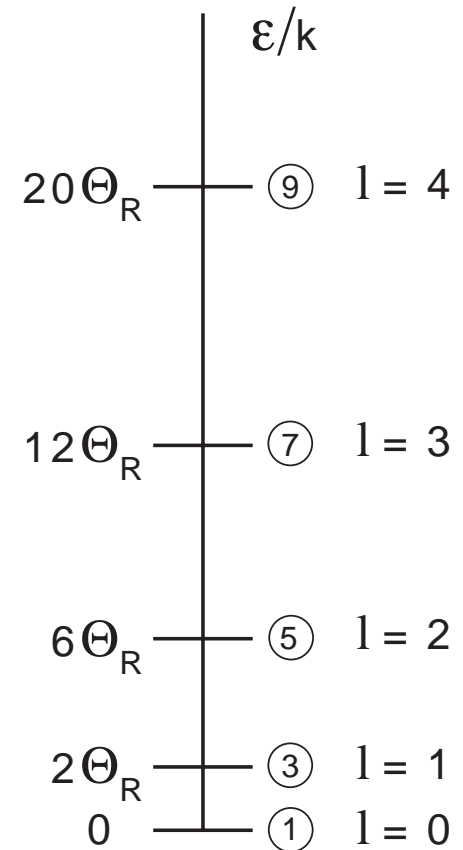
$$=\; \frac{\hbar^2}{2I_\perp}l(l+1)|l,m>$$

ϵ_l depends on l only;

it is $2l+1$ fold degenerate.

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

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

ϵ/k

$20\Theta_R$ —— ⑨ l = 4

$12\Theta_R$ —— ⑦ l = 3

$6\Theta_R$ —— ⑤ l = 2

$2\Theta_R$ —— ③ l = 1

0 —— ① l = 0

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

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

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

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

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

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

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.

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

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

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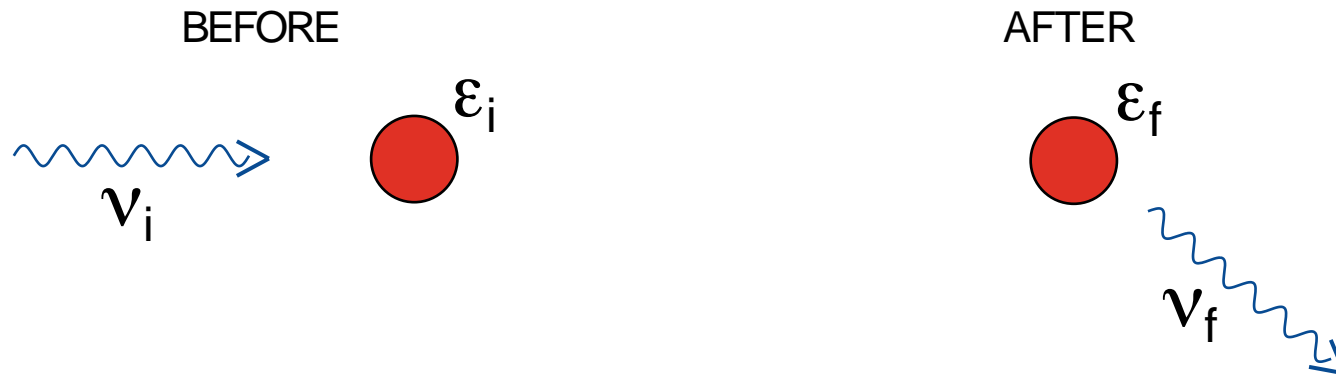Reading, MA: Addison-Wesley Pub. Co., 1975. ISBN: 020106894X.

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Figure 12-2 from
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Raman Scattering

BEFORE

ε_i

ν_i

AFTER

ε_f

ν_f

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

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

Example 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

$I(\Delta\nu)$

BOLTZMANN FACTOR

LEVEL DEGENERACY

$\Delta\nu$

$4(k\Theta_R/h)$

$-6(k\Theta_R/h)$

0

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