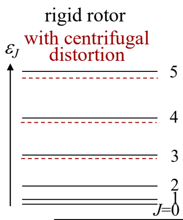
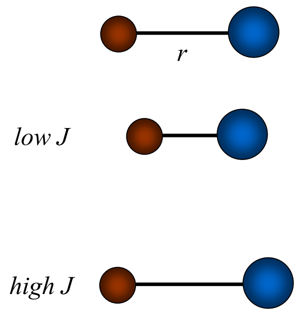
Corrections to Simple Energy Models

- In previous models used for diatomic energy modes, we made some simplifying assumptions that are not strictly accurate

1) Non-rigid rotor ($I \neq$ constant)

- as molecule rotates faster, internuclear distance r stretches, known as **centrifugal distortion**
  - $I \propto r^2$, so I increase with J
  - $\varepsilon_J \propto 1/I$, so energy level spacing $(\varepsilon_{J+1} - \varepsilon_J)$ decreases with J





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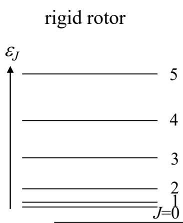
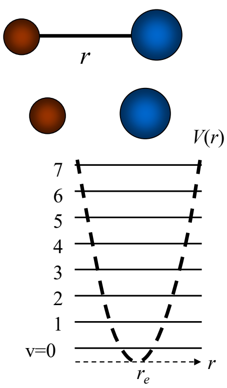
Corrections to Simple Energy Models

- In previous models used for diatomic energy modes, we made some simplifying assumptions that are not strictly accurate

1) Non-rigid rotor ($I \neq$ constant)

- vibrating molecule also means $r \neq$ constant, known as **vibration-rotation coupling**
  - not issue for harmonic oscillator, average r^2 does not change with v, $\langle r^2 \rangle = r_e^2$

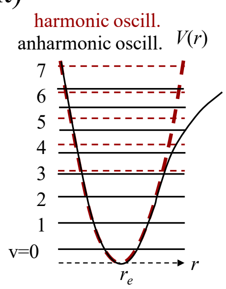




Corrections to Simple Energy Models

2) Anharmonic Oscillator ($k \neq$ constant)

- nonsymmetric potential between nuclei
- repulsion increases rapidly for decreasing r, attraction decreases for larger r
- energy levels get closer together



3) Interaction of Rotations-Electronic

- due to angular momentum coupling
- complex and usually very small change in energies

R-V Energy Corrections

- Rigid rotor model $\varepsilon_{rot}(J) = hc\underset{\text{in cm}^{-1}}{B}J(J+1)$
- With corrections

essentially Taylor series expansion in J(J+1)

$$\varepsilon_{rot}(\mathrm{v},J)/hc = B_v J(J+1) - D_v\underbrace{[J(J+1)]^2}_{\text{centrifugal distortion in harmonic force field}} + \underbrace{H_v[J(J+1)]^3}_{1^{\text{st}}\text{ anharmonic term}} + \ldots$$

$$B_v = \boxed{B_e} - \boxed{\alpha_e}(\mathrm{v}+½) + \ldots$$

$$D_v = \boxed{D_e} - \boxed{\beta_e}(\mathrm{v}+½) + \ldots$$

values at r_e rot.-vib. coupling

vib. freq. (cm^{-1})

$$D_e \cong 4B_e^3/\nu_e^2$$

$$\Rightarrow D_e << B_e$$

$$\Rightarrow D_v << B_v$$

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R-V Energy Corrections

- Harmonic oscillator model $\varepsilon_{vib}(\text{v}) = hc\nu(\text{v}+½)$
- With corrections

essentially Taylor series expansion in (v+1/2)

$$\varepsilon_{vib}(\text{v})/hc = \nu_e(\text{v}+½) - \underbrace{\nu_e x_e}_{\text{small}}(\text{v}+½)^2 + \underbrace{\nu_e y_e}_{\text{very small}}(\text{v}+½)^3 + \ldots$$

- Generally, molec. constants from spectroscopic data

(cm^{-1})	ν_e	$\nu_e x_e$	B_e	D_e	α_e
H_2	4380	118	60	0.046	3.1
O_2	1580	12	1.5	5×10^{-6}	0.016
NO	1905	14	1.7	5×10^{-6}	0.018

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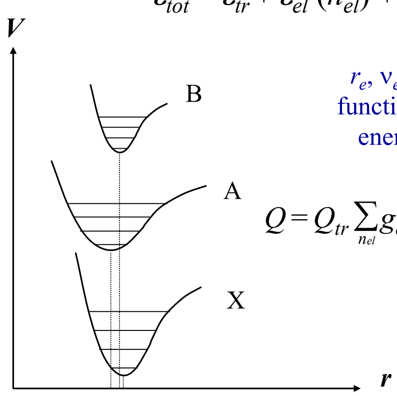
Energy Mode Coupling

- Internal energy modes now coupled

$$\varepsilon_{tot} = \varepsilon_{tr} + \varepsilon_{el}(n_{el}) + \varepsilon_{vib}(n_{el},\text{v}) + \varepsilon_{rot}(n_{el},\text{v},J)$$

r_e, ν_e and $\nu_e x_e$ function of elec. energy level

B_v, D_v change with elec. energy level and vib. energy level



$$Q = Q_{tr}\sum_{n_{el}} g_e\, e^{-\varepsilon_{el,i}/kT} \sum_{\text{v}} e^{-\varepsilon_{vib}(n_{el},\text{v})/kT} \sum_J (2J+1) e^{-\varepsilon_{rot}(n_{el},\text{v},J)/kT}$$

Corrected Partition Functions

- Can use new expressions to find Q, but in general case they do not reduce to simple analytic expressions
  - must use full summations
- For $\nu_e y_e = \beta_e = H_v = 0$

$$\varepsilon_{vib}(\mathrm{v},J)/hc = \nu_e(\mathrm{v}+½) + B_e J(J+1) - \nu_e x_e\,(\mathrm{v}+½)^2 - D_e[J(J+1)]^2 - \alpha_e(\mathrm{v}+½)J(J+1)$$

- If corrections small $Q_{rot,vib} \approx Q_{rigid\ rotor}\, Q_{HO}\, Q_{corr}$
  - with

$$Q_{\mathrm{corr}} \cong 1 + 2\frac{T}{\theta_r}\frac{D_e}{B_e} + \frac{\alpha_e}{B_e}\left(\frac{1}{2} + \frac{1}{e^{\theta_v/T}-1}\right) + \frac{\theta_{v_x}}{T}\left(\frac{1}{4} + \frac{2}{e^{\theta_v/T}-1} + \frac{2}{\left(e^{\theta_v/T}-1\right)^2}\right)$$

$$\theta_{v_x} \equiv \frac{hc}{k}\nu_e x_e$$