INTERSTELLAR MEDIUM

- Stefano Bovino -

Molecular structure

Energy operator

Classical-mechanical observables and their corresponding quantum-mechanical operators.

| Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x	$\hat{X}$	Multiply by x
	$\mathbf{r}$	$\hat{\mathbf{R}}$	Multiply by $\mathbf{r}$
Momentum	p_x	$\hat{P}_x$	$-i\hbar \dfrac{\partial}{\partial x}$
	$\mathbf{p}$	$\hat{\mathbf{P}}$	$-i\hbar \left(\mathbf{i}\dfrac{\partial}{\partial x} + \mathbf{j}\dfrac{\partial}{\partial y} + \mathbf{k}\dfrac{\partial}{\partial z} \right)$
Kinetic energy	K_x	$\hat{K}_x$	$-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$
	K	$\hat{K}$	$-\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2} \right)$
			$= -\dfrac{\hbar^2}{2m}\nabla^2$
Potential energy	$V(x)$	$\hat{V}(\hat{x})$	Multiply by $V(x)$
	$V(x, y, z)$	$\hat{V}(\hat{x}, \hat{y}, \hat{z})$	Multiply by $V(x, y, z)$
Total energy	E	$\hat{H}$	$-\dfrac{\hbar^2}{2m}\left(\dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2} \right)$ $+ V(x, y, z)$
			$= -\dfrac{\hbar^2}{2m}\nabla^2 + V(x, y, z)$
Angular momentum	$L_x = yp_z - zp_y$	$\hat{L}_x$	$-i\hbar\left(y\dfrac{\partial}{\partial z} - z\dfrac{\partial}{\partial y} \right)$
	$L_y = zp_x - xp_z$	$\hat{L}_y$	$-i\hbar\left(z\dfrac{\partial}{\partial x} - x\dfrac{\partial}{\partial z} \right)$
	$L_z = xp_y - yp_x$	$\hat{L}_z$	$-i\hbar\left(x\dfrac{\partial}{\partial y} - y\dfrac{\partial}{\partial x} \right)$

Hamiltonian in quantum mechanics

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V \right) |\Psi\rangle = E|\Psi\rangle$$

Hydrogen atom

▸ Provided energy levels for Hydrogen atom fully in agreement with Rydberg's law

▸ The atomic SE can be solved analytically for H in spherical coordinates
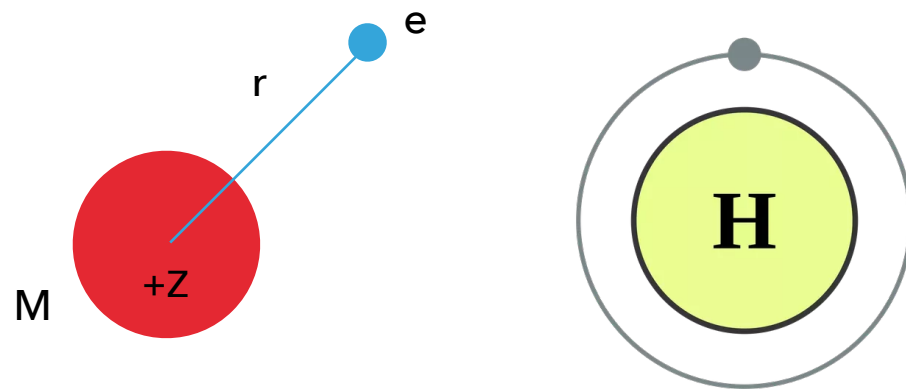
Hydrogen Electron Orbitals
Probability Density

$$\psi_{n\ell m}(r,\vartheta,\varphi) = \sqrt{\left(\frac{\rho}{r}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) \cdot Y_\ell^m(\vartheta,\varphi)$$
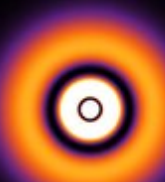
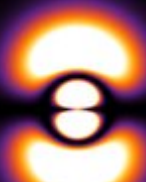$$\rho = 2r/na_0 \qquad darksilverflame.deviantart.com$$
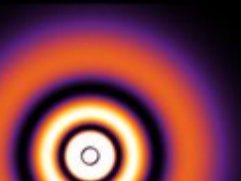
(2,0,0) (2,1,0) (2,1,1)
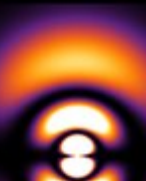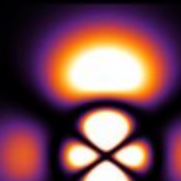
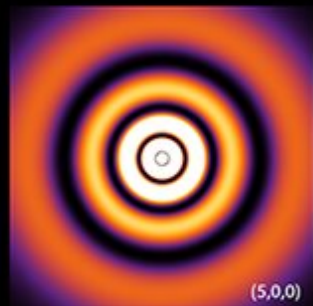(3,0,0) (3,1,0) (3,1,1) (3,2,0) (3,2,1) (3,2,2)

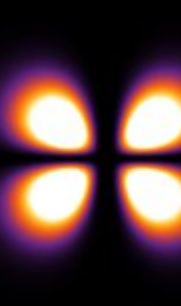(4,0,0) (4,1,0) (4,1,1) (4,2,0) (4,2,1) (4,2,2)
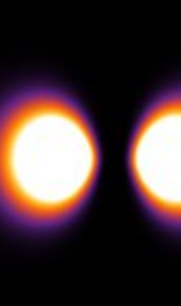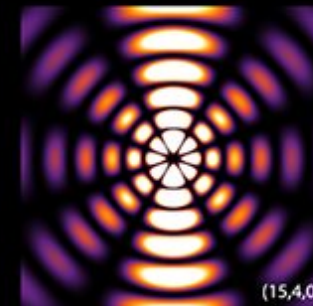
(5,0,0) (4,3,0) (4,3,1) (4,3,2) (4,3,3) (15,4,0)

Atomic structure

- Location/Energy is determined by a set of four quantum numbers

- n, l, m_l, m_s

- Configuration specifies the orbitals that electrons occupy (e.g. 1s)

- A single configuration (e.g. $2p^1$) can split in more levels or state

Term symbols and transitions

$$\text{multiplicity} \rightarrow 2S+1 \{L\} \underset{J \leftarrow \text{Level}}{\leftarrow} \text{orbital angular momentum}$$

Spin-orbit coupling

- Rotation of an electrical charge generates a magnetic dipole (classical electrodynamics)

- The spin and orbital angular momenta couple

- This generates a splitting of a given energetic level (fine structure)

- This can be further split by the presence of a magnetic field (hyperfine structure)

Atomic structure: selection rules

Type	Mechanism	Rules
"allowed"	electric dipole	1) Parity must change 2) $\Delta L = 0, \pm 1$ 3) $\Delta J = 0, \pm 1$ but not $J=0 \rightarrow 0$ 4) only one e- wavefunction nl changes with $\Delta l = \pm 1$ 5) $\Delta S = 0$
"semi-forbidden"	electric dipole but with $\Delta S \neq 0$ from configuration mixing due to relativistic effects	same as "allowed" except violates #5
"forbidden"	magnetic dipole or electric quadrupole	violates at least one other selection rule other than #5

config.	term	E/hc (cm^{-1})
1s^{2}2s^{2}2p3s	$^3D^o_1$	92252
1s^{2}2s^{2}2p3s	$^3D^o_2$	92250
1s^{2}2s^{2}2p3s	$^3D^o_3$	92237
1s^{2}2s2p^3	$^5S^o_2$	46785
1s^{2}2s^{2}2p^2	$^1S_0$	32689
1s^{2}2s^{2}2p^2	$^1D_2$	15316
1s^{2}2s^{2}2p^2	$^3P_2$	130.8
1s^{2}2s^{2}2p^2	$^3P_1$	48.7
1s^{2}2s^{2}2p^2	$^3P_0$	0

N II

$g_8 = 3$ 8
$g_7 = 5$ 7
$g_6 = 7$ 6
$g_5 = 5$ 5
$g_4 = 1$ 4
$g_3 = 5$ 3
$g_2 = 5$ 2
$g_1 = 3$ 1
$g_0 = 1$ 0

1085.7Å 1084.6Å 1085.6Å 1084.0Å 1084.6Å 1085.5Å
2139.7Å 2143.4Å
5756.2Å 3063.7Å
6549.9Å 6585.3Å
122μm 205μm
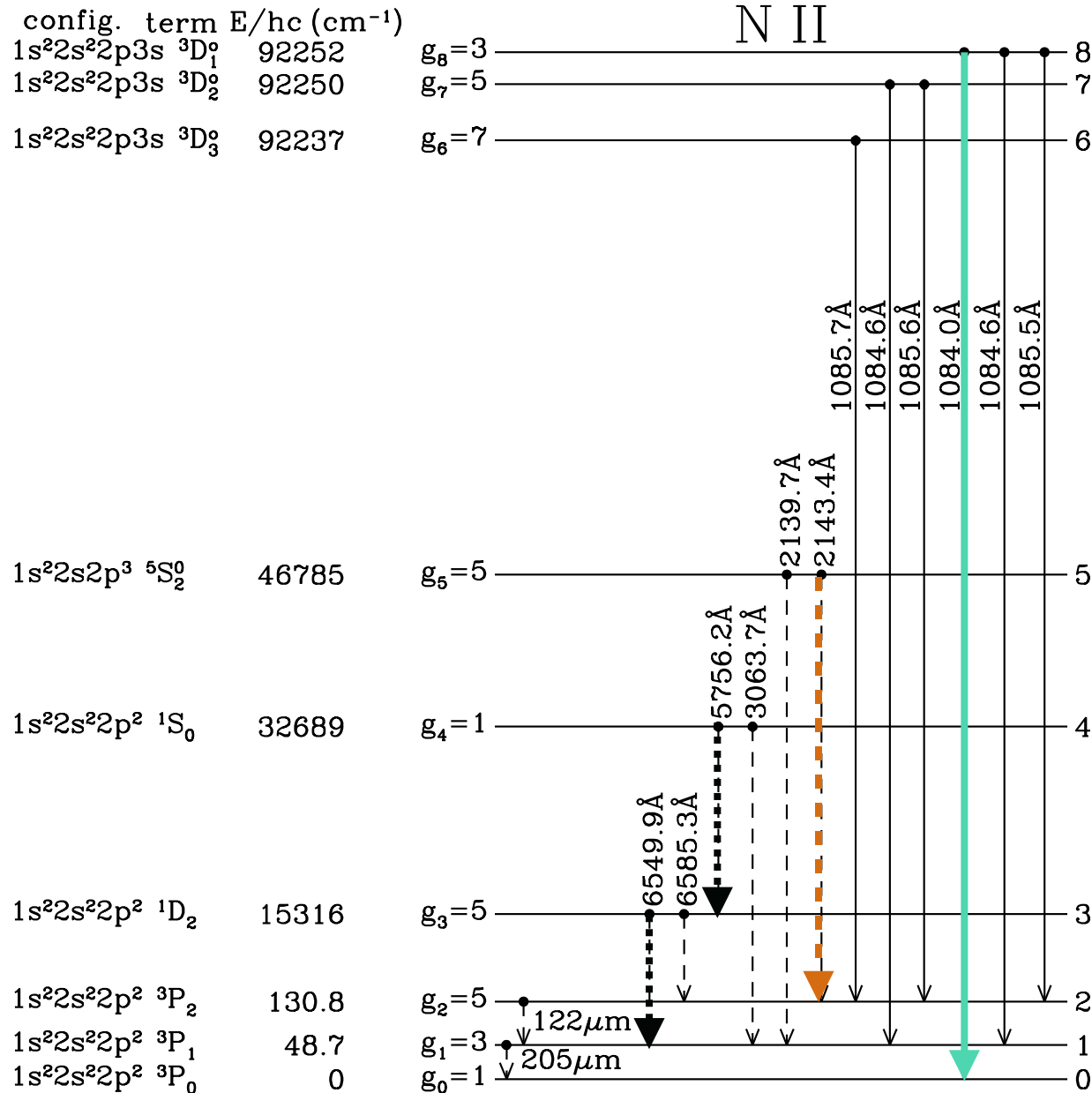
Allowed transition
$^3D_1$ - $^3P_0$
$A_{ul} = 2.18 \times 10^8$ s^{-1}

Spin forbidden transition
$^5S_2$ - $^3P_2$
$A_{ul} = 1.27 \times 10^2$ s^{-1}

Forbidden transition
$^1D_2$ - $^3P_1$
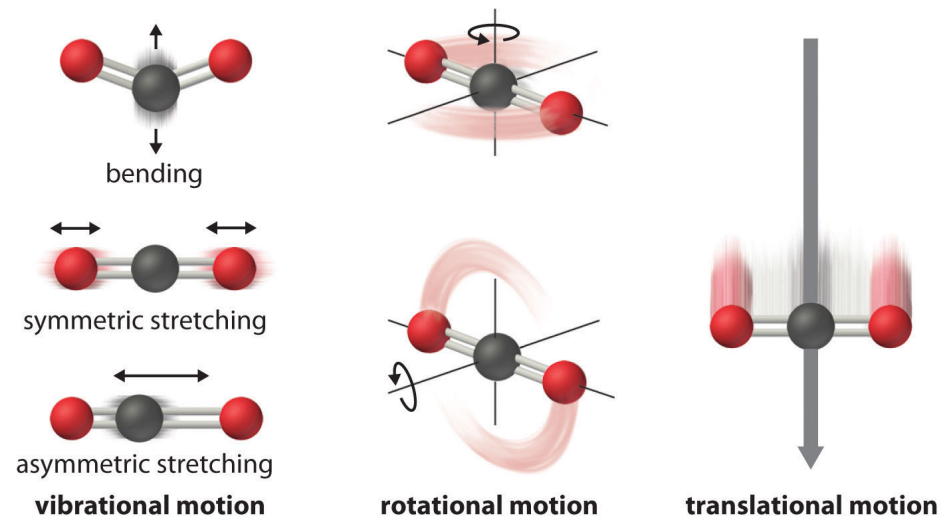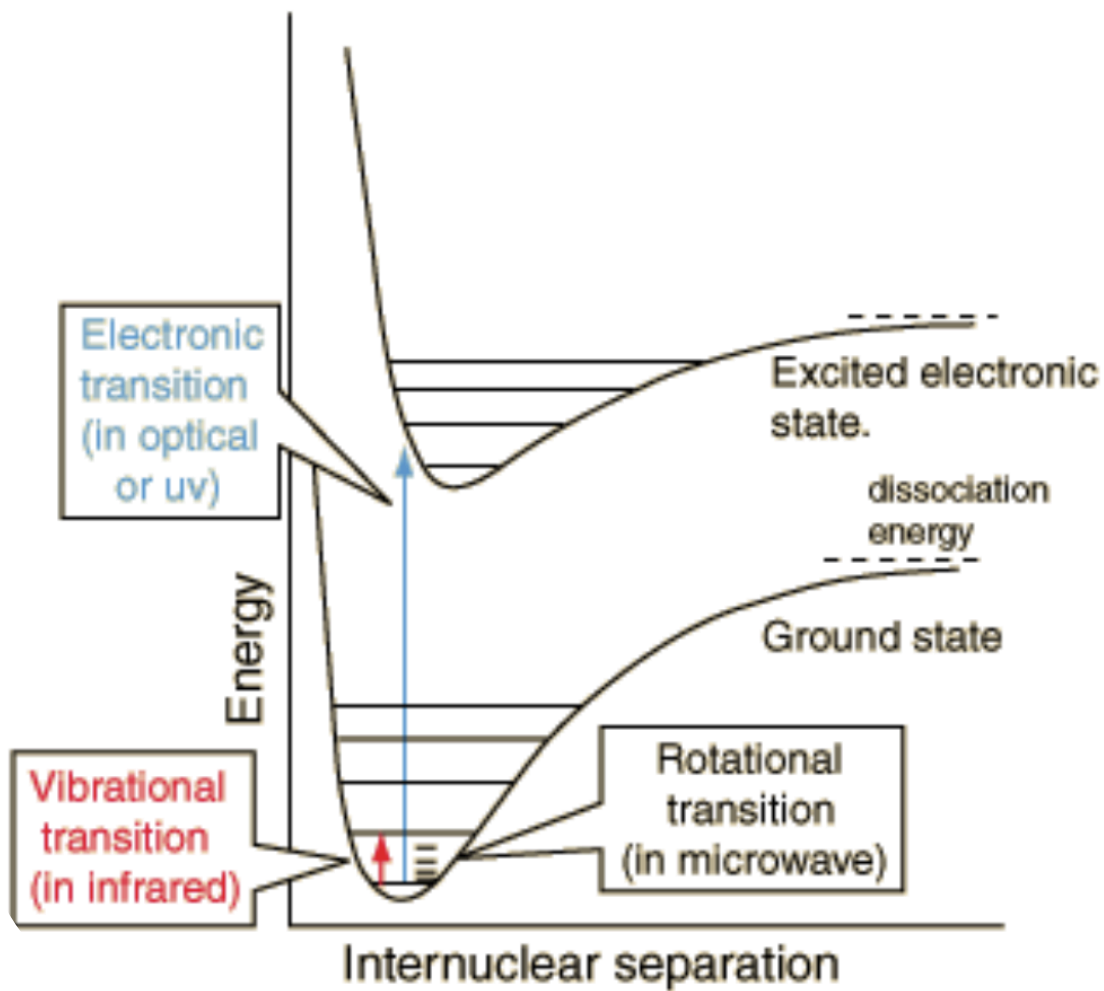## $A_{ul} = 1.17 \times 10^0$ s^{-1}

General rules

- Intersystem lines are 10^6 times weaker than permitted transitions

- Forbidden transition are 10^2-10^6 times weaker than intersystem ones

- **Forbidden transitions** are important in astrophysics in particular in the low-dense environment where timescales are much longer and slow decay could occur (e.g. [CII] 158 micron $^2P_{1/2}$ - $^2P_{3/2}$)

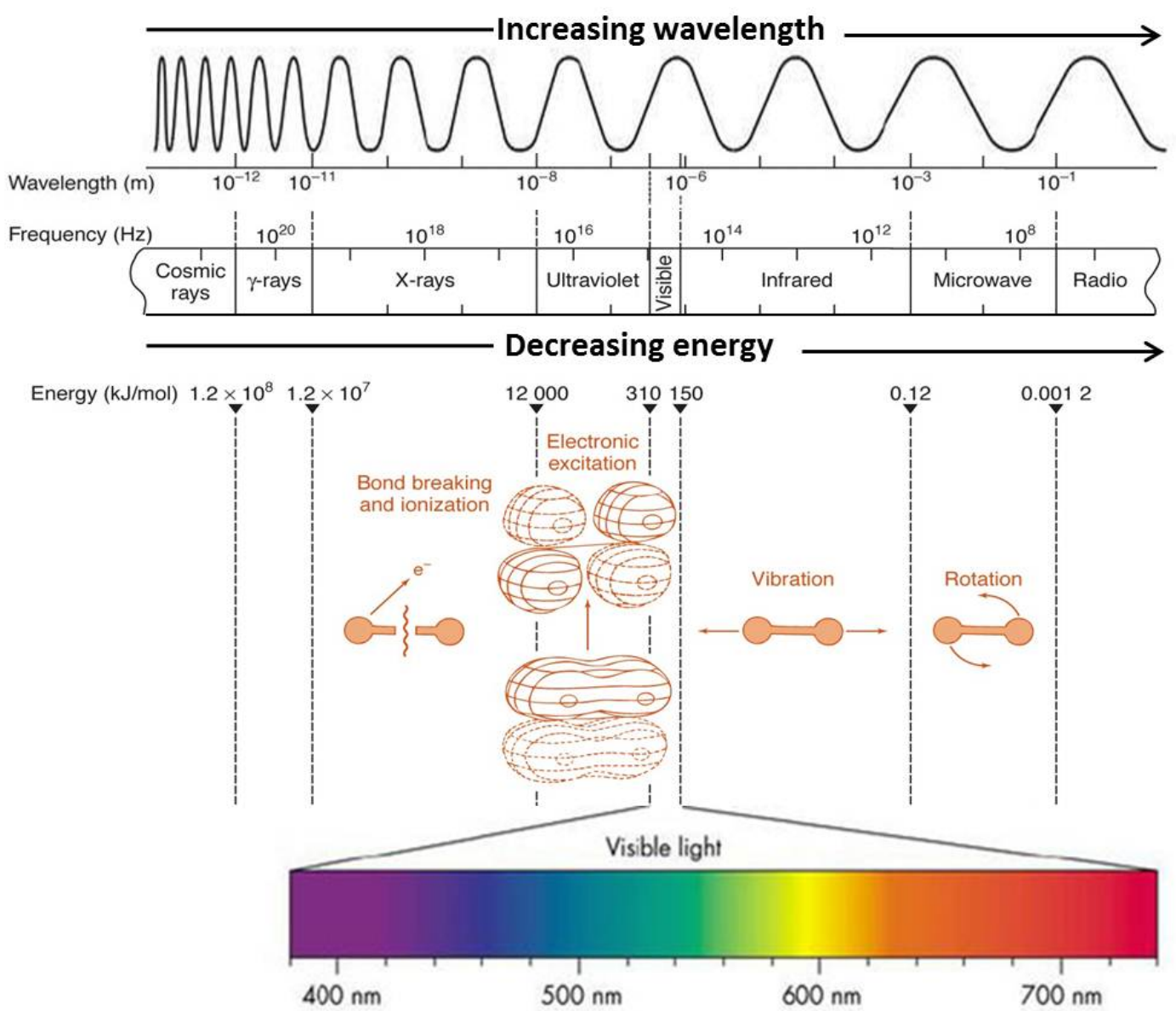# Molecules: adding degrees of freedom

bending

symmetric stretching

asymmetric stretching

vibrational motion   **rotational motion**   **translational motion**

Electronic transition (in optical or uv)

Excited electronic state.

dissociation energy

Ground state

Vibrational transition (in infrared)

Rotational transition (in microwave)

Energy

Internuclear separation

fact to know:

▶ the internal energy is *quantized*

$$E_t = E_{el} + E_{vib} + E_{rot}$$

Molecular structure

$$E_{tot} \sim E_{el} + E_{vib} + E_{rot}$$

Order of magnitudes
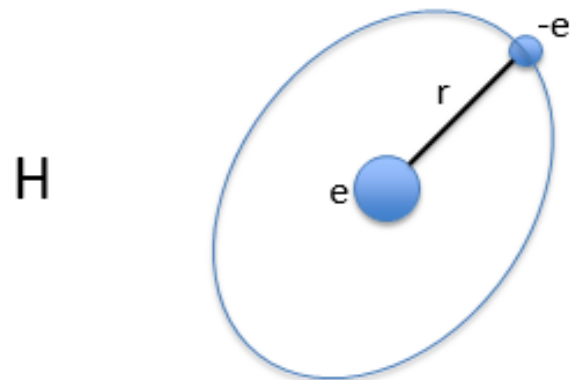
$E_{el} \sim 1\text{-}10$ eV
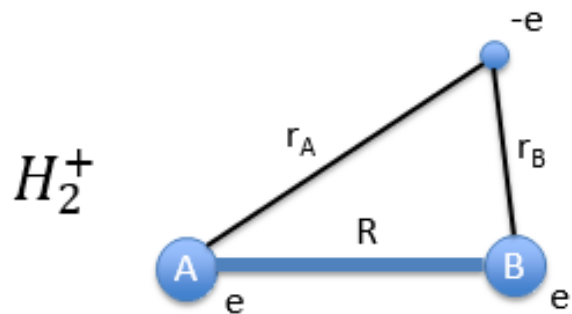
$E_{vib} \sim 10^{-2}\text{--}10^{-1}$ eV

$E_{rot} \sim 10^{-3}\text{--}10^{-2}$ eV
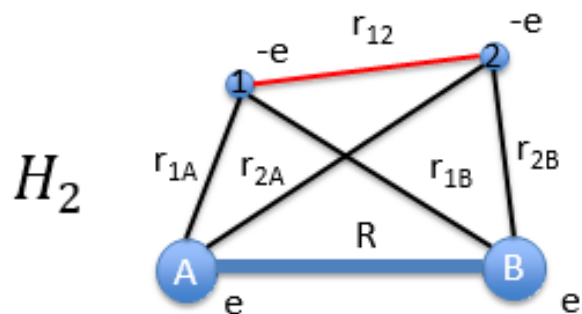
Molecules Hamiltonian

H

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}$$
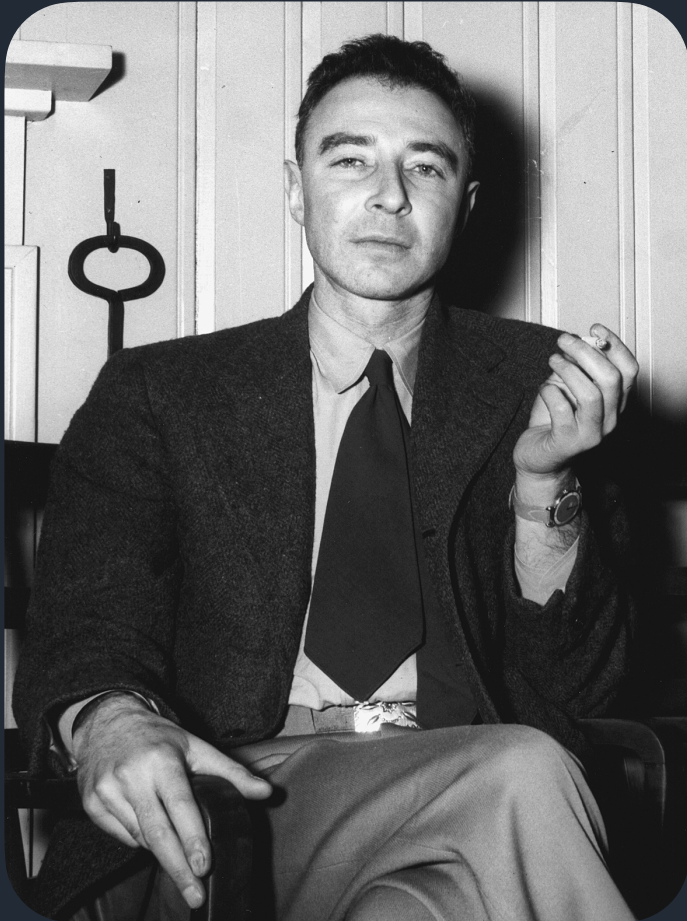
H$_2^+$ simplest molecule (1 electron)

H_2^+

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{\hbar^2}{2m_p}(\nabla_A^2 + \nabla_B^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_A} + \frac{1}{r_B}\right) + \frac{e^2}{4\pi\epsilon_0 R}$$

H_2

$$\widehat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{\hbar^2}{2m_p}(\nabla_A^2 + \nabla_B^2) - \frac{2e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{1A}} + \frac{1}{r_{1B}} + \frac{1}{r_{2A}} + \frac{1}{r_{2B}}\right) + \frac{e^2}{4\pi\epsilon_0 R} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Born-Oppenheimer approximation (1)

ROBERT OPPENHEIMER

MAX BORN

Born-Oppenheimer approximation (2)
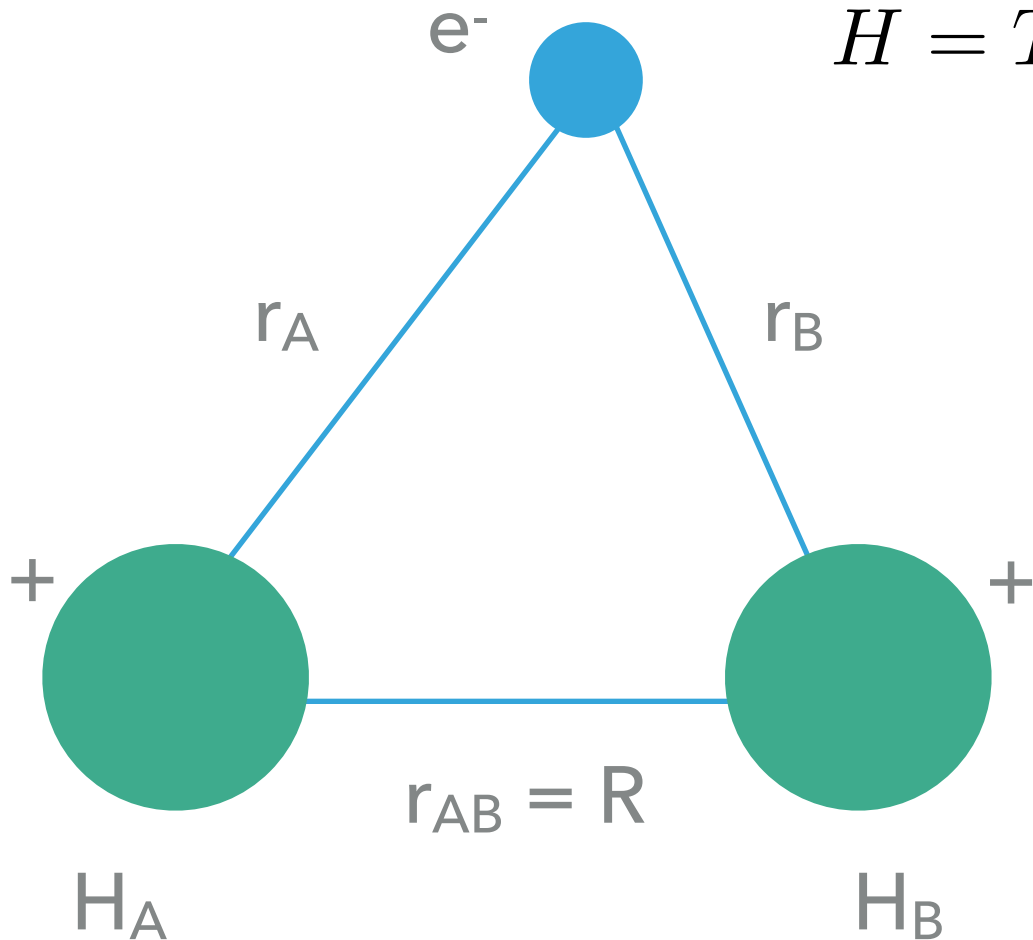
$$M_{nuclei} >> m_e$$
$$v_{nuclei} << v_e$$

- Electrons can respond almost instantaneously to displacement of nuclei (like flies)

Born-Oppenheimer approximation (3)

- We can treat them as stationary while the electrons move

- Solve the SE considering the nuclei as being fixed (R parameter)

- Nuclei provide a static potential at fixed geometry

- Different nuclei arrangements may then be adopted and the calculations repeated

- The set of solutions provide the molecular potential energy curve (diatomic molecule) or a surface in general
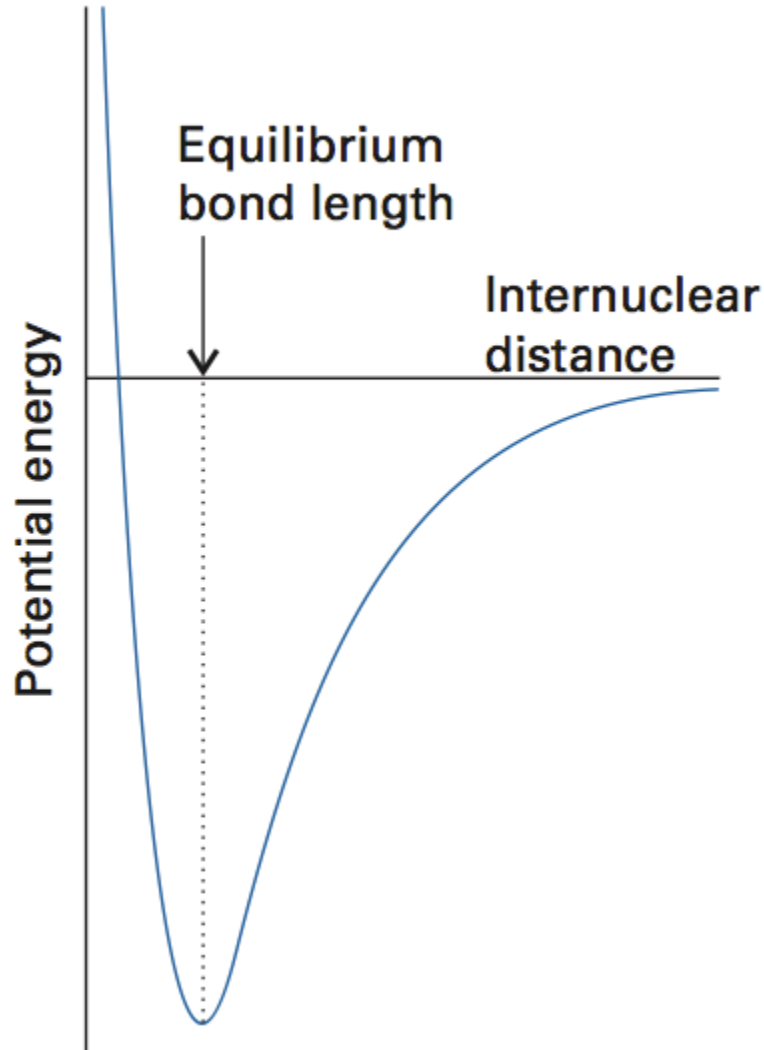
Separation of variables

$$\Psi(r,R) \approx \Psi_{el}(r,R)\Psi_{nucl}(R)$$

$$H = T_{tot} + V_{tot} = (T_N + T_e) + (V_{eN} + V_{NN})$$

$$H_{el}|\Psi_{el}(r;R)\rangle = E_{el}|\Psi_{el}(r;R)\rangle$$

$$H_{el} = (T_N + T_{el}) + (V_{eN} + V_{NN})$$

0

Constant

e$^-$

r_A

r_B

+

+

$r_{AB} = R$

H_A

H_B

Potential energy curves (PEC)

$$\Psi(r, R) \approx \Psi_{el}(r, R)\Psi_{nuclei}(R)$$

$$H\Psi(r, R) = E_{tot}\Psi(r, R)$$

$$H = H_{el} + H_{nuclei}$$

$$H_{el}\Psi_{el}(r; R) = E_{el}\Psi_{el}(r; R)$$

$$H_{nuclei}\Psi_{nuclei} = E_{nuclei}\Psi_{nuclei}$$

$$H_{nuclei} = T_N + V(R) + V_{NN}$$

Born-Oppenheimer approximation (3)

- SE for molecules is solved in two steps

- **Electron motion is much faster than nuclear (vibrations and rotations)**

  - Motion of the electrons around the nuclei at fixed position (electronic energy in which the nuclei are moved)

  - Nuclear WFs are searched by considering that the nuclei evolve under the PEC/PES associated to a particular electronic configuration (translation+rotation+vibration)
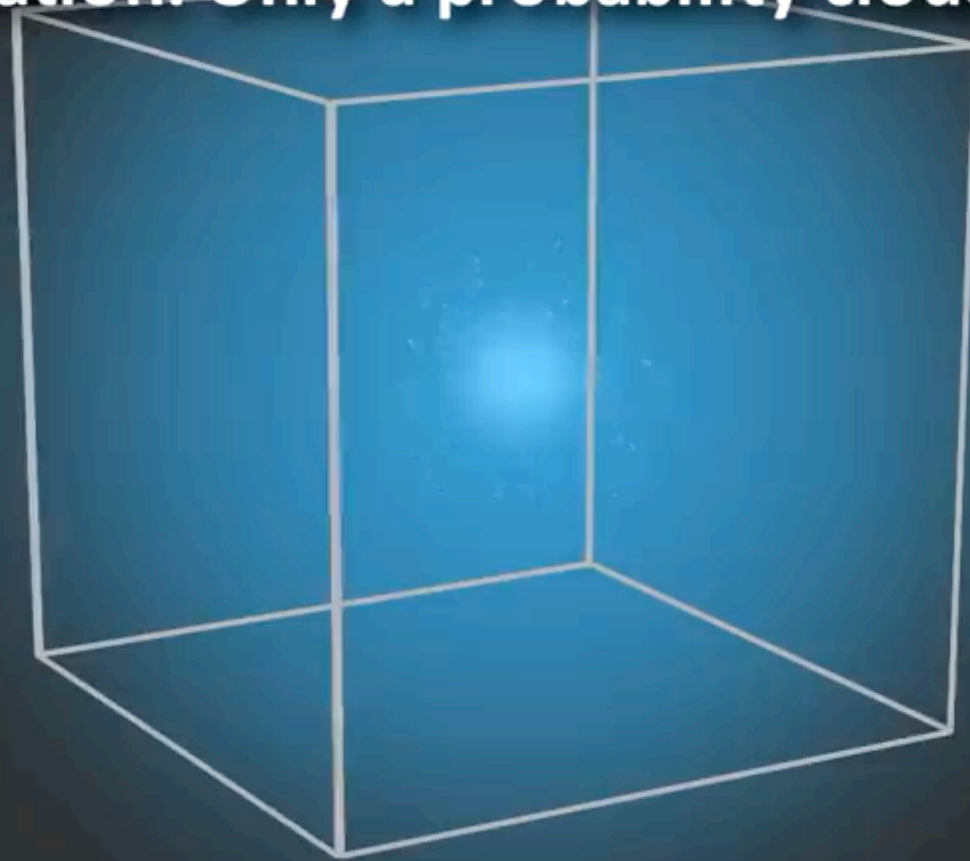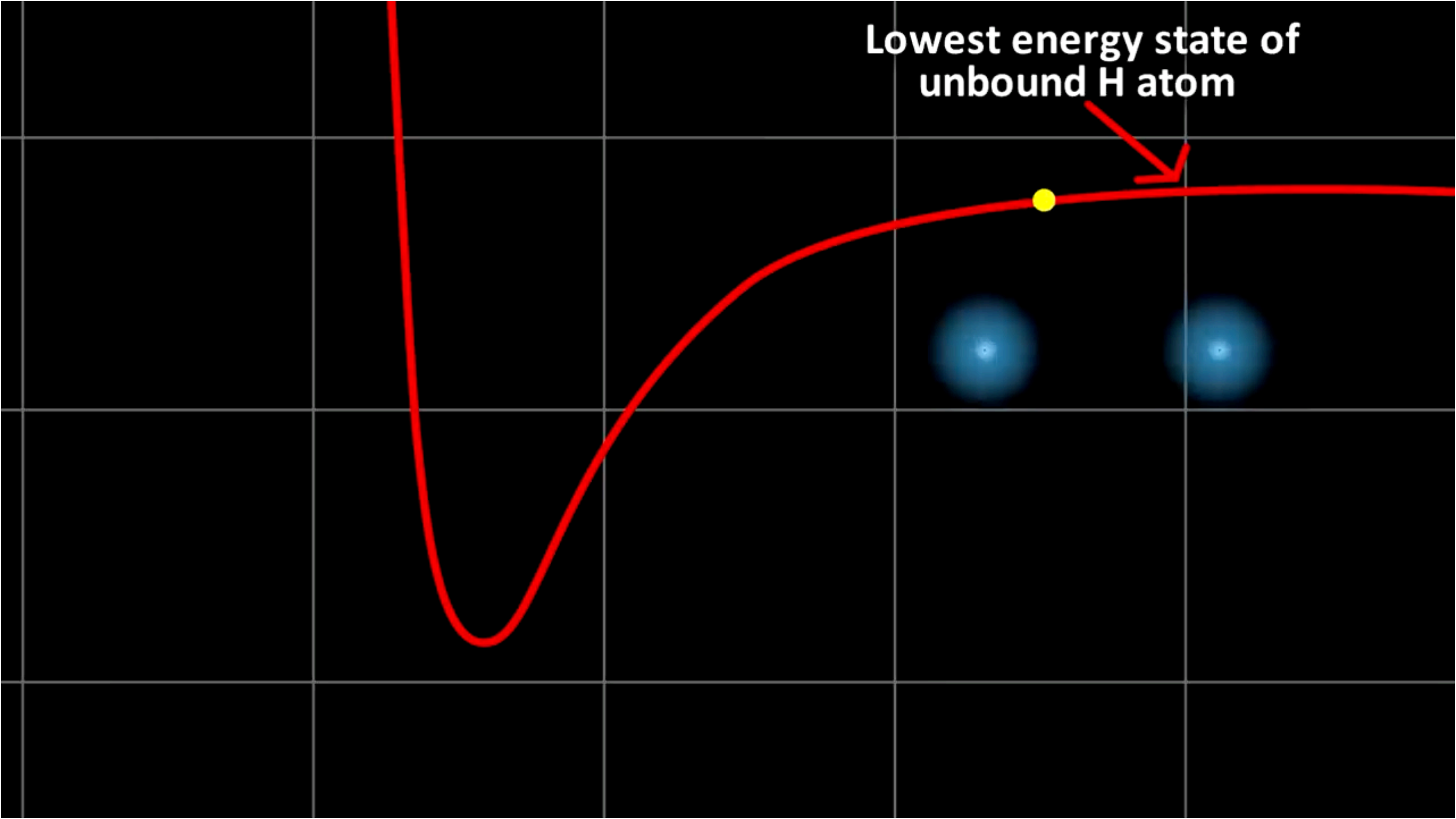
POTENTIAL ENERGY CURVES
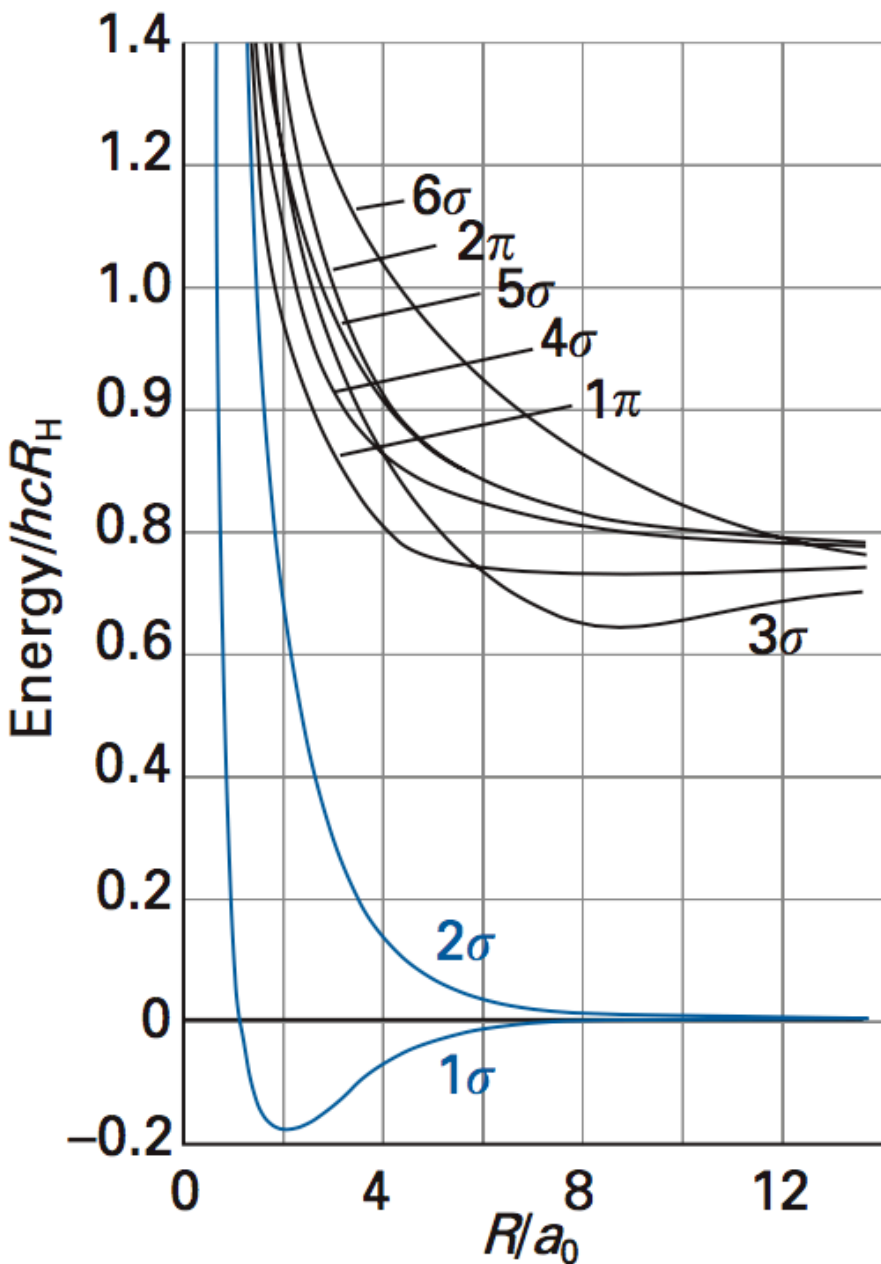
WAVE FUNCTIONS (MOLECULAR ORBITALS)

LARGER PROBABILITY

(a)

(b)
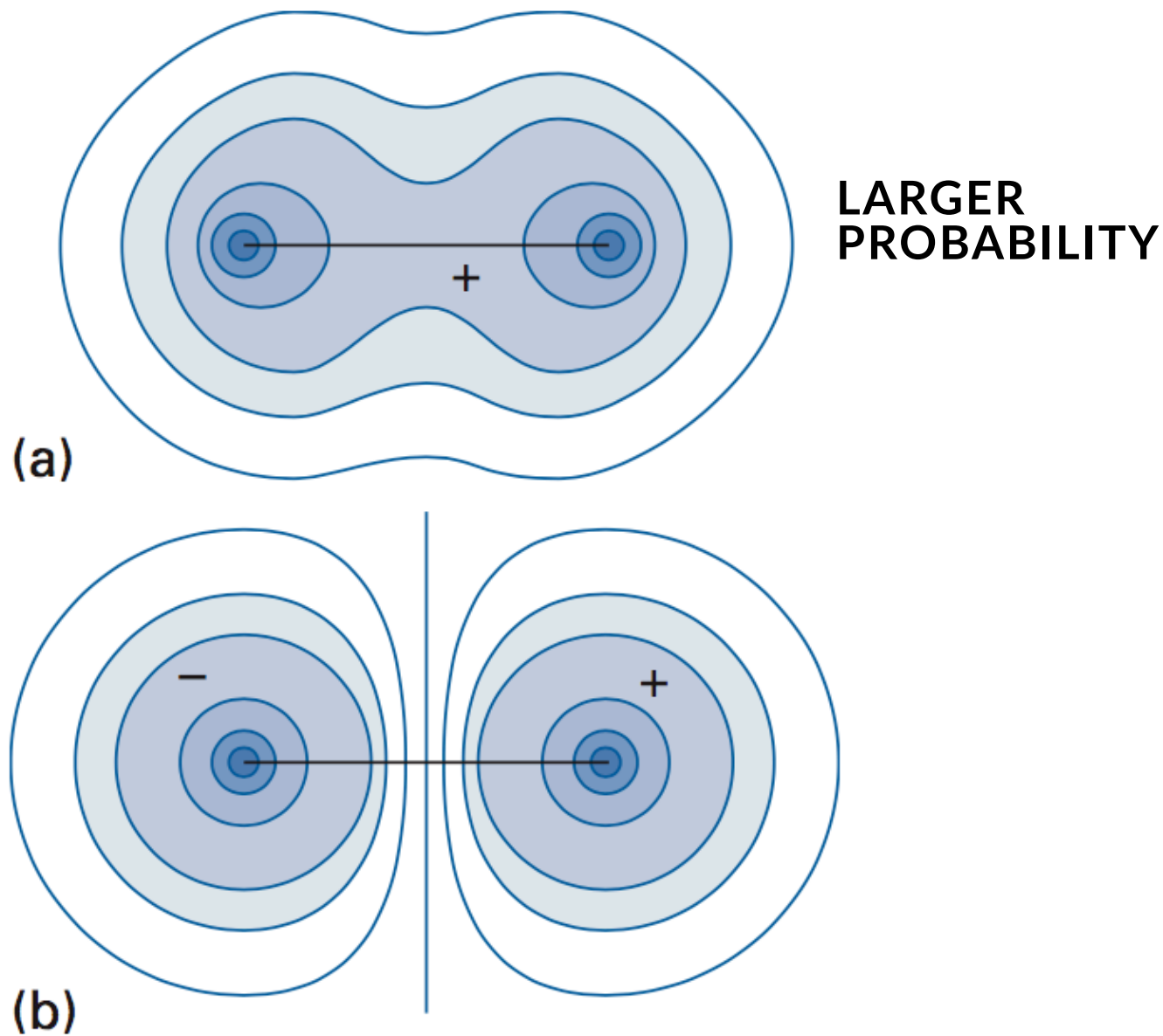
Note: central cluster of electrons exaggerated for illustration. Only a probability cloud exists

Lowest energy state of
unbound H atom

Term symbols for molecules

$$M_L = m_{l1} + m_{l2} + \cdots$$

SUM OF THE ANGULAR MOMENTUM OF THE ELECTRONS IN THE MOLECULAR ORBITALS

where $m_l = 0$ for a σ orbital, $m_l = \pm 1$ for a π orbital

$|M_L|$	Letter
0	Σ
1	Π
2	Δ
3	Φ

$$M_s = m_{s1} + m_{s2} + \cdots$$
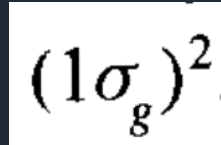
TOTAL SPIN ANGULAR MOMENTUM

For $S = 0$, $M_S = 0$;

for $S = 1/2$, $M_S = \pm 1/2$

for $S = 1$, $M_S = \pm 1, 0$

$$^{2S+1}|M_L|$$

Example: molecular hydrogen

ELECTRONIC
CONFIGURATION $(1\sigma_g)^2$

where $m_l = 0$ for a σ orbital, $m_l = \pm 1$ for a π orbital.

$|M_L|$	Letter
0	Σ
1	Π
2	Δ
3	Φ

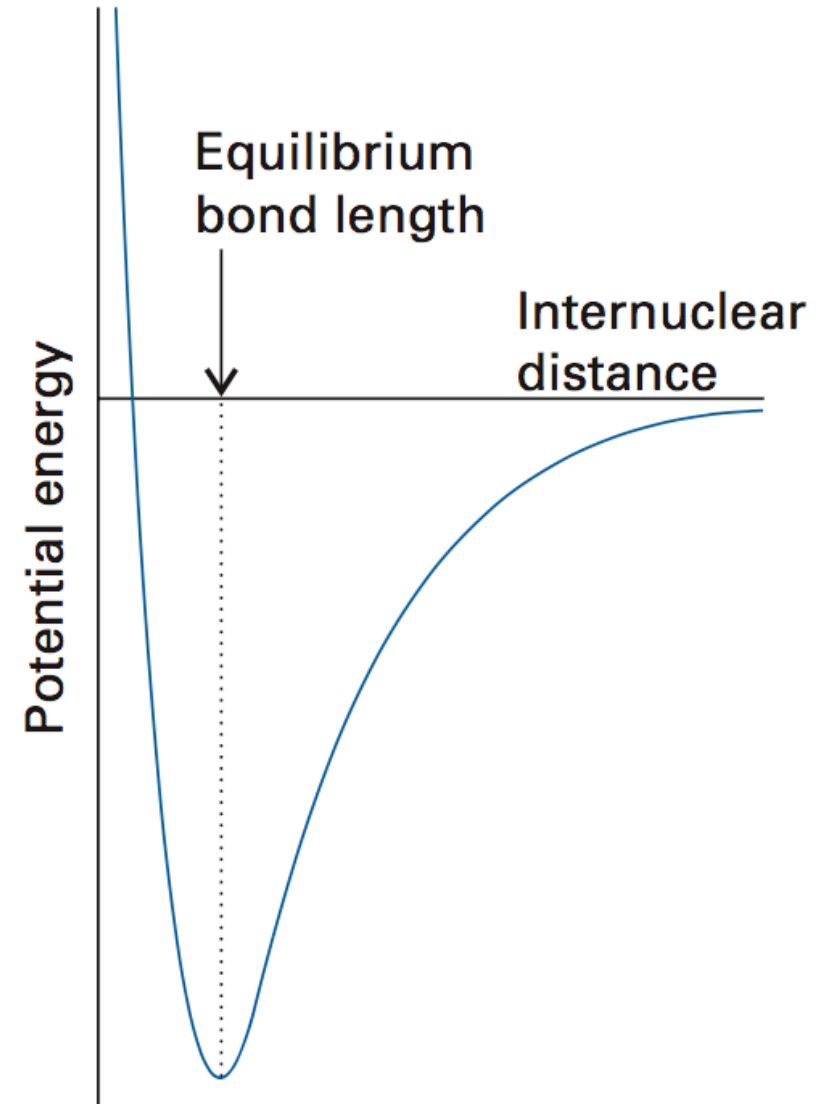$$M_s = m_{s1} + m_{s2} + \cdots$$

For $S = 0$, $M_S = 0$

$$^{2S+1}|M_L|$$

$^1\Sigma$ (a singlet sigma state)

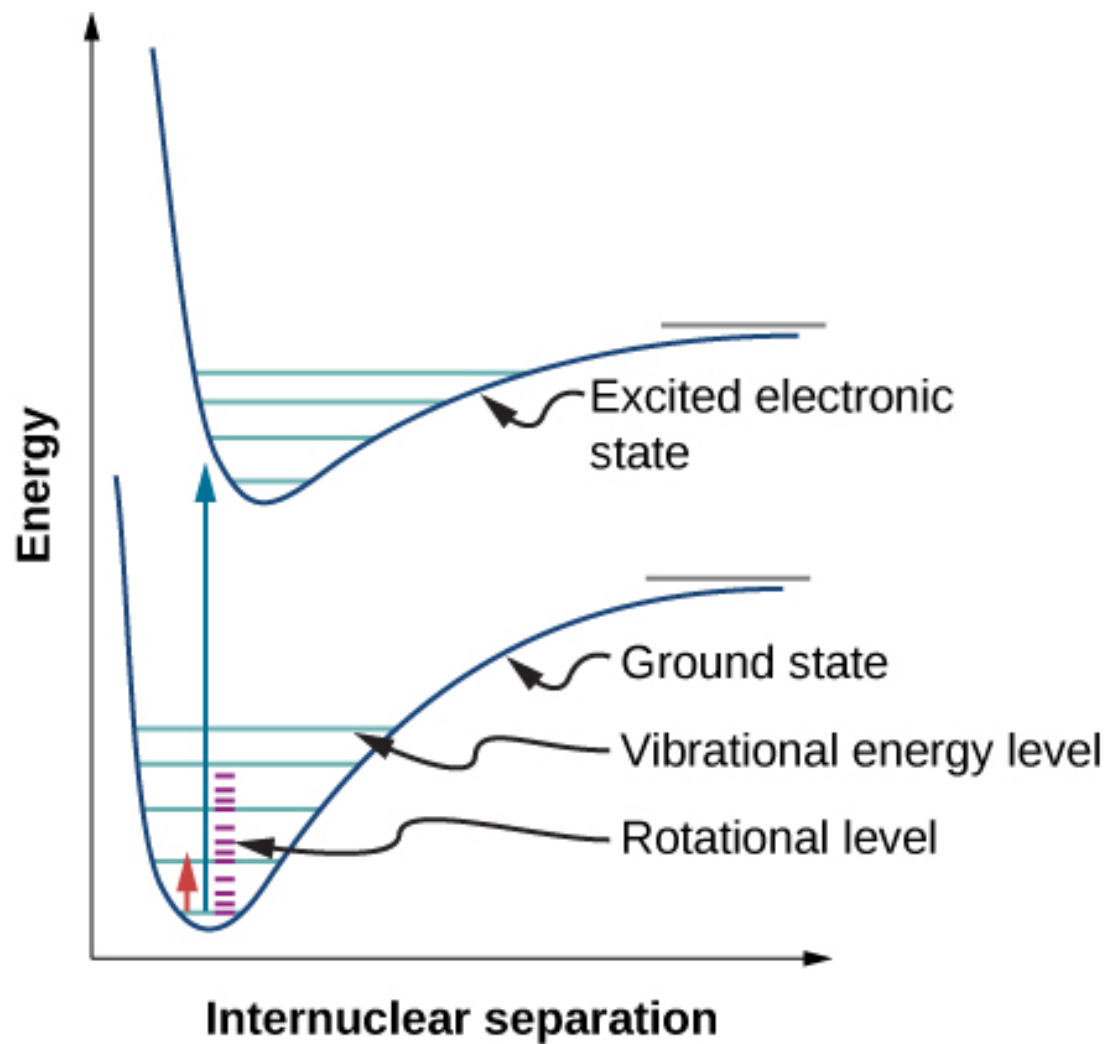| Molecule	Electron configuration	Term symbol
H_2^+	$(1\sigma_g)^1$	$^2\Sigma_g^+$
H_2	$(1\sigma_g)^2$	$^1\Sigma_g^+$
He_2^+	$(1\sigma_g)^2(1\sigma_u)^1$	$^2\Sigma_u^+$
Li_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2$	$^1\Sigma_g^+$
B_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^1(1\pi_u)^1$	$^3\Sigma_g^-$
C_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(1\pi_u)^2$	$^1\Sigma_g^+$
N_2^+	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(1\pi_u)^2(3\sigma_g)^1$	$^2\Sigma_g^+$
N_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^2(1\pi_u)^2(3\sigma_g)^2$	$^1\Sigma_g^+$
O_2^+	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^1$	$^2\Pi_g$
O_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^1(1\pi_g)^1$	$^3\Sigma_g^-$
F_2	$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(3\sigma_g)^2(1\pi_u)^2(1\pi_u)^2(1\pi_g)^2(1\pi_g)^2$	$^1\Sigma_g^+$

$$\Psi_{tot} = \Psi_{el}\Psi_{vib}\Psi_{rot}$$

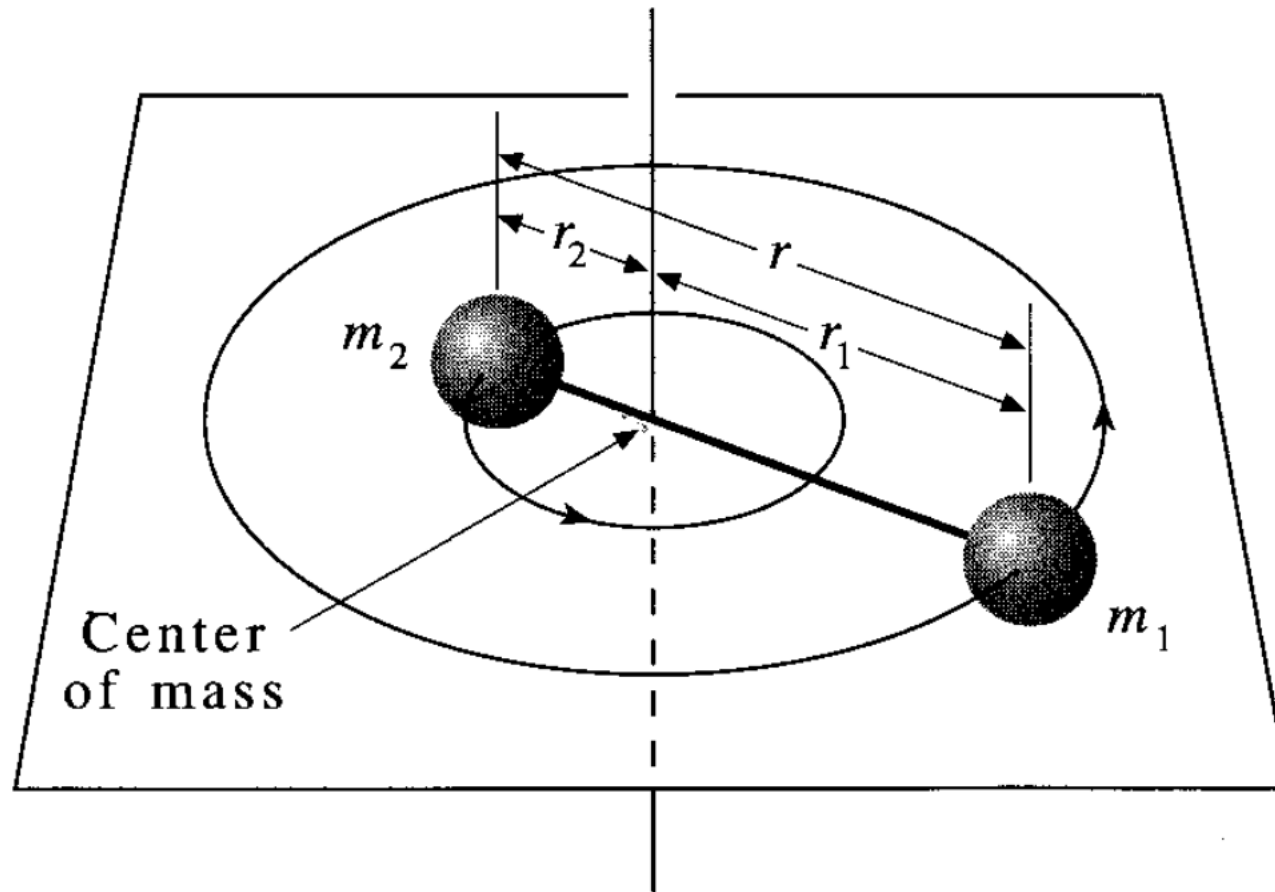$$E_{tot} = E_{el} + E_{vib} + E_{rot}$$
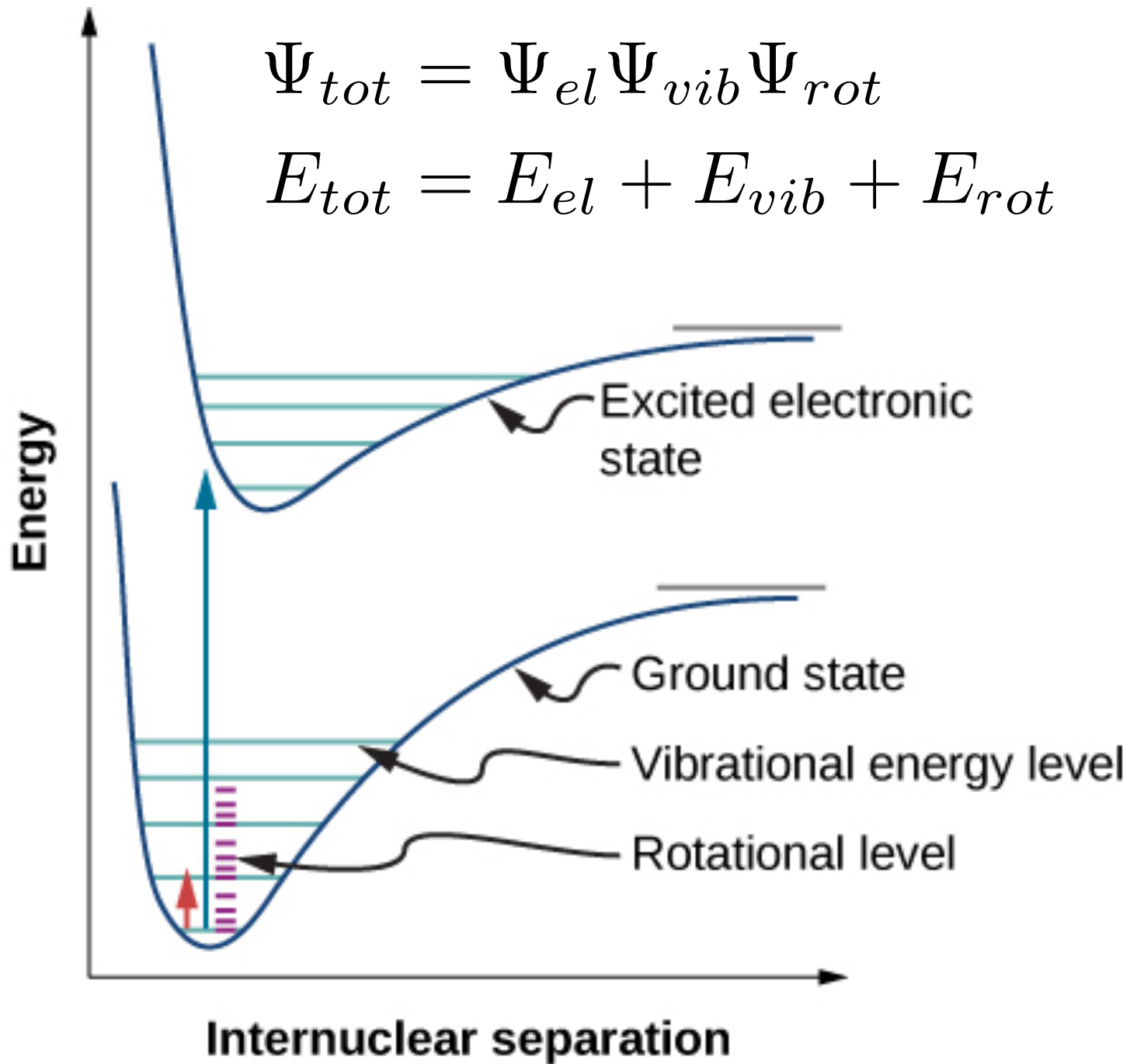
Molecular internal motion

Vibrations

m_1 m_2

Rotations

Energy

Excited electronic state

Ground state

Vibrational energy level

Rotational level

Internuclear separation

m_2 r_2 r r_1 m_1

Center of mass
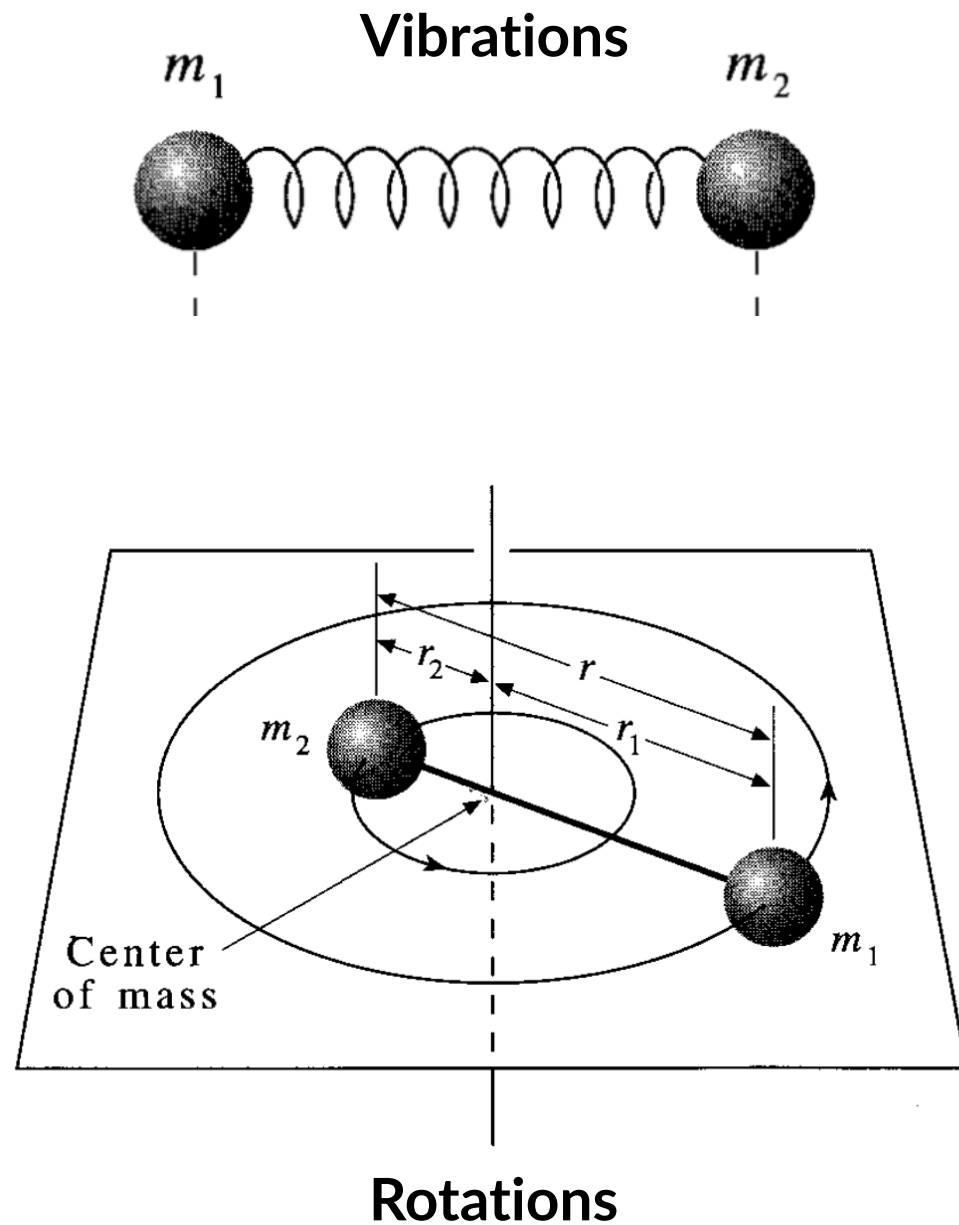
Rigid rotor approximation

$$E_{rot} = BJ(J+1)$$

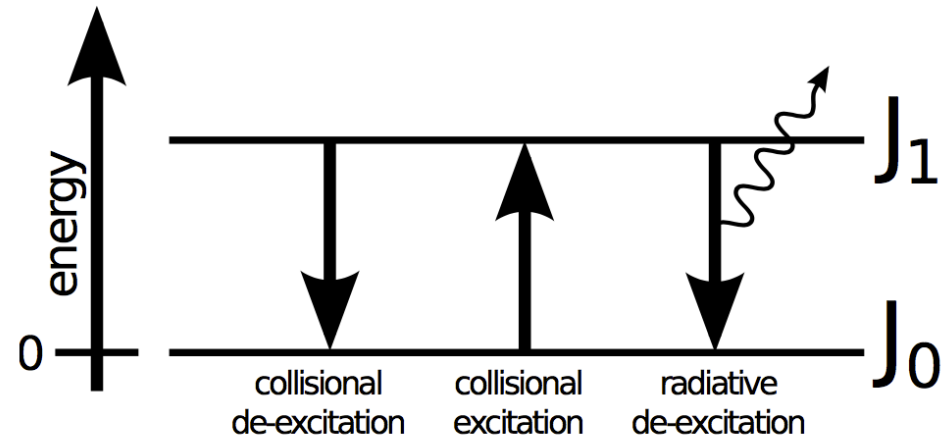# Energy spacing | Boltzmann distribution

$$B = \frac{\hbar^2}{2I}$$

cm² g s⁻¹

g cm²

$$\frac{N_J}{N} = \frac{2J+1}{q} e^{-hcBJ(J+1)/kT}$$
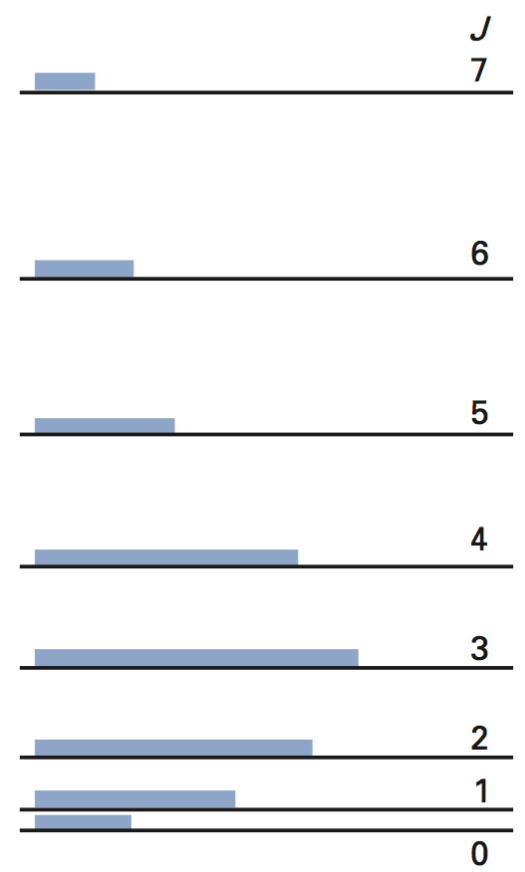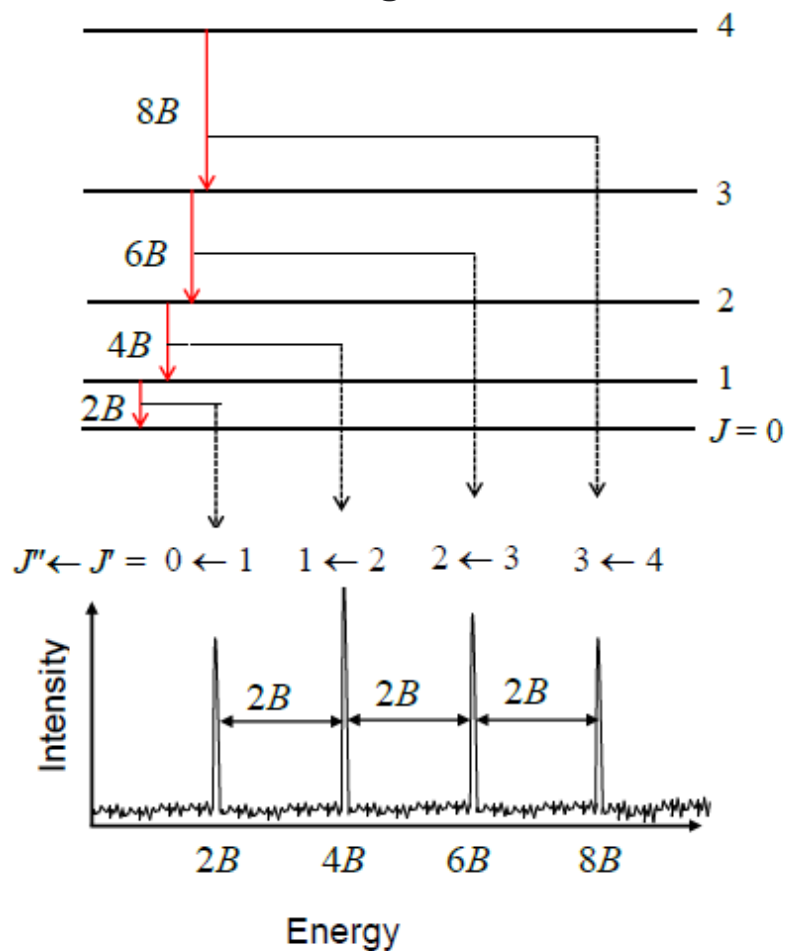
Inelastic collisions

Molecules are excited through collisions and $\Delta J = \pm 1$

Spontaneous emission:

$$A_{ul} \propto \nu^3 |\mu_d|^2 \qquad (2)$$

▶ the molecule must have a permanent dipole moment
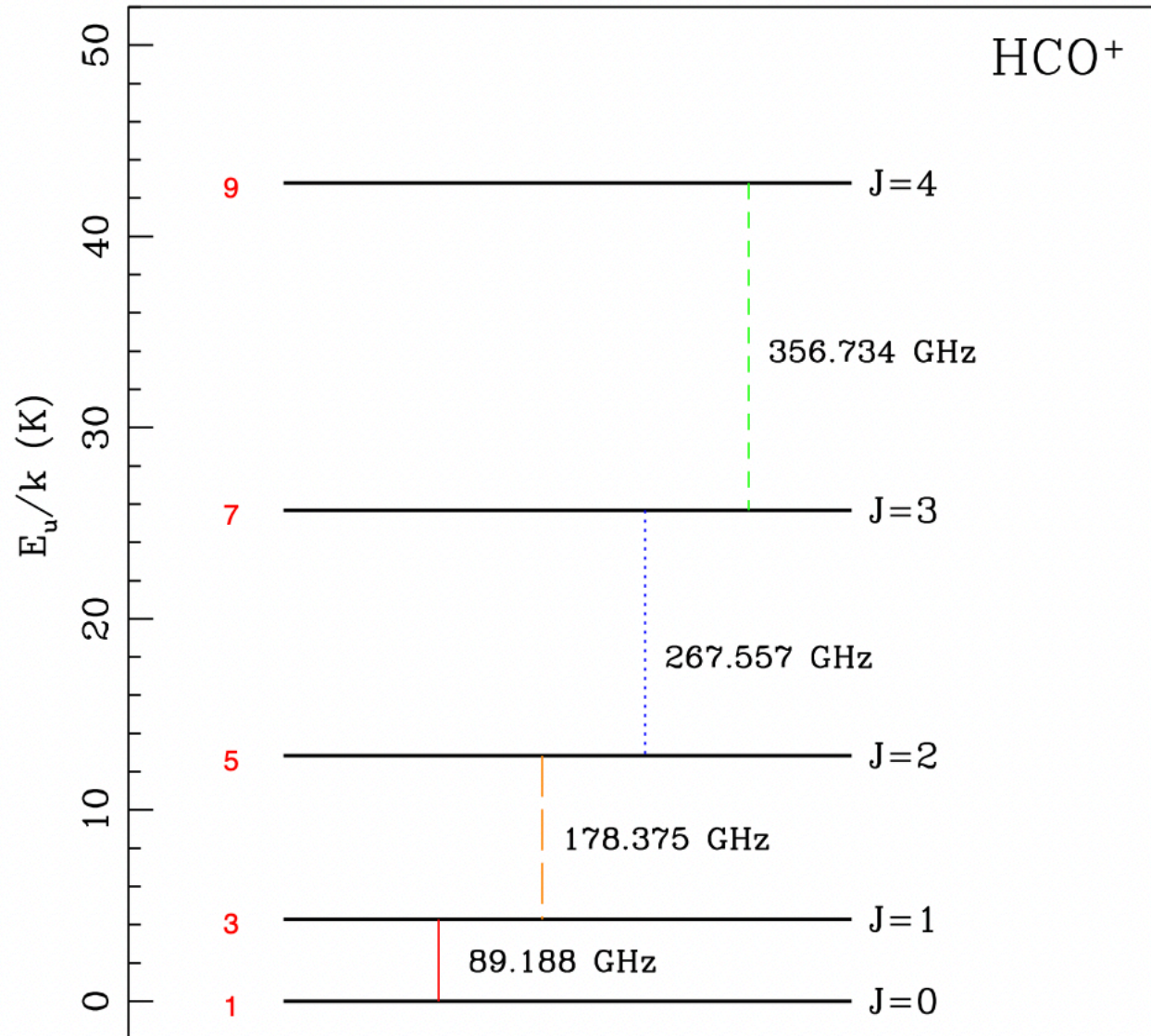
▶ a critical density required for significant excitation

Bulk of molecule transitions

$$n_{cr} \propto B^3 J^3 |\mu_d|^2 \qquad (4)$$

Larger dipole moment $(\mu_d) \rightarrow$ higher n_{cr} (density diagnostic)

- HCN $\rightarrow \mu_d = 2.98$ D
- $H_2O \rightarrow \mu_d = 1.85$ D
- CO $\rightarrow \mu_d = 0.11$ D

Rotational spectrum example

Shirley2015

Dipole moment integral

▸ the interaction of the electric component of the electromagnetic field with the electric dipole associated with the transition

▸ Selection rules
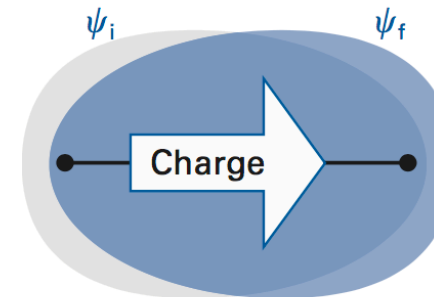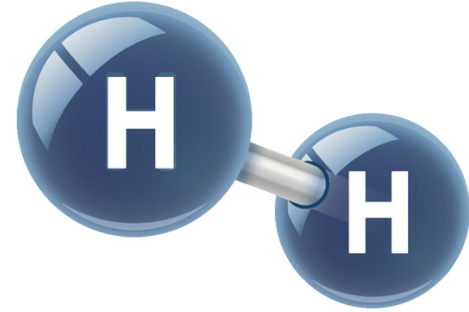
ψ_i ψ_f

Charge

Fig. 10.1 In order for a transition to be electric-dipole allowed, it must possess a degree of dipolar character. A purely spherically symmetrical (or some other non-dipolar) redistribution of charge cannot interact with the electric field vector of the electromagnetic field.

Most abundant molecule

H$_2$ symmetric homonuclear molecule:

► no dipole moment

► H$_2$ possesses a quadrupole (asymmetric distr. of charges)

► strict selection rules for transitions $\Delta J = \pm 2$

Let's calculate the minimum excitation temperature for H$_2$
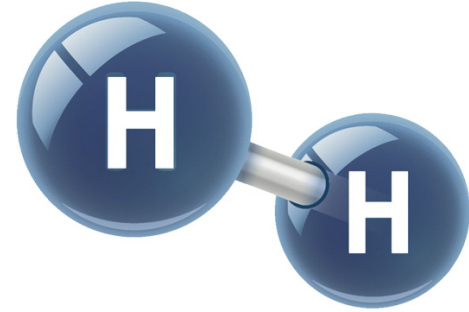$(J = 2 - 0)$

$$\hbar = 1.054 \times 10^{-27} \text{ erg s}$$
$$k_B = 1.38 \times 10^{-16} \text{ erg K}^{-1}$$
$$m_{\text{H}} = 1.67 \times 10^{-24} \text{ g}$$
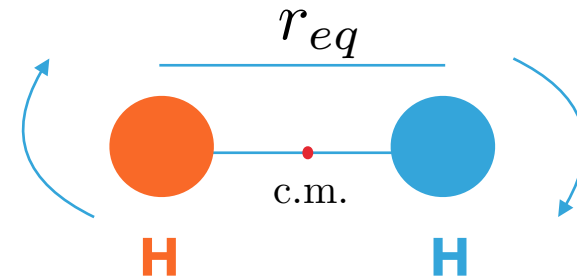$$r_e(\text{H}_2) = 0.75 \text{ Å}$$

A simple exercise

▸ The excitation rotational temperature for J = 2

$$\hbar = 1.054 \times 10^{-27} \,\text{erg}\,\text{s}$$

$$k_B = 1.38 \times 10^{-16} \,\text{erg}\,\text{K}^{-1}$$

$$r_{eq}(\text{H}_2) = 0.75\text{Å}$$

$$m_{\text{H}} = 1.67 \times 10^{-24}\text{g}$$

$$E_{rot} = BJ(J+1)$$

$$B = \frac{\hbar^2}{2I}$$

Question: Can we observe H$_2$ in dense regions (e.g. n~10^4 cm^{-3}, T ~ 10 K)?

1 Angstrom = 10^{-8} cm
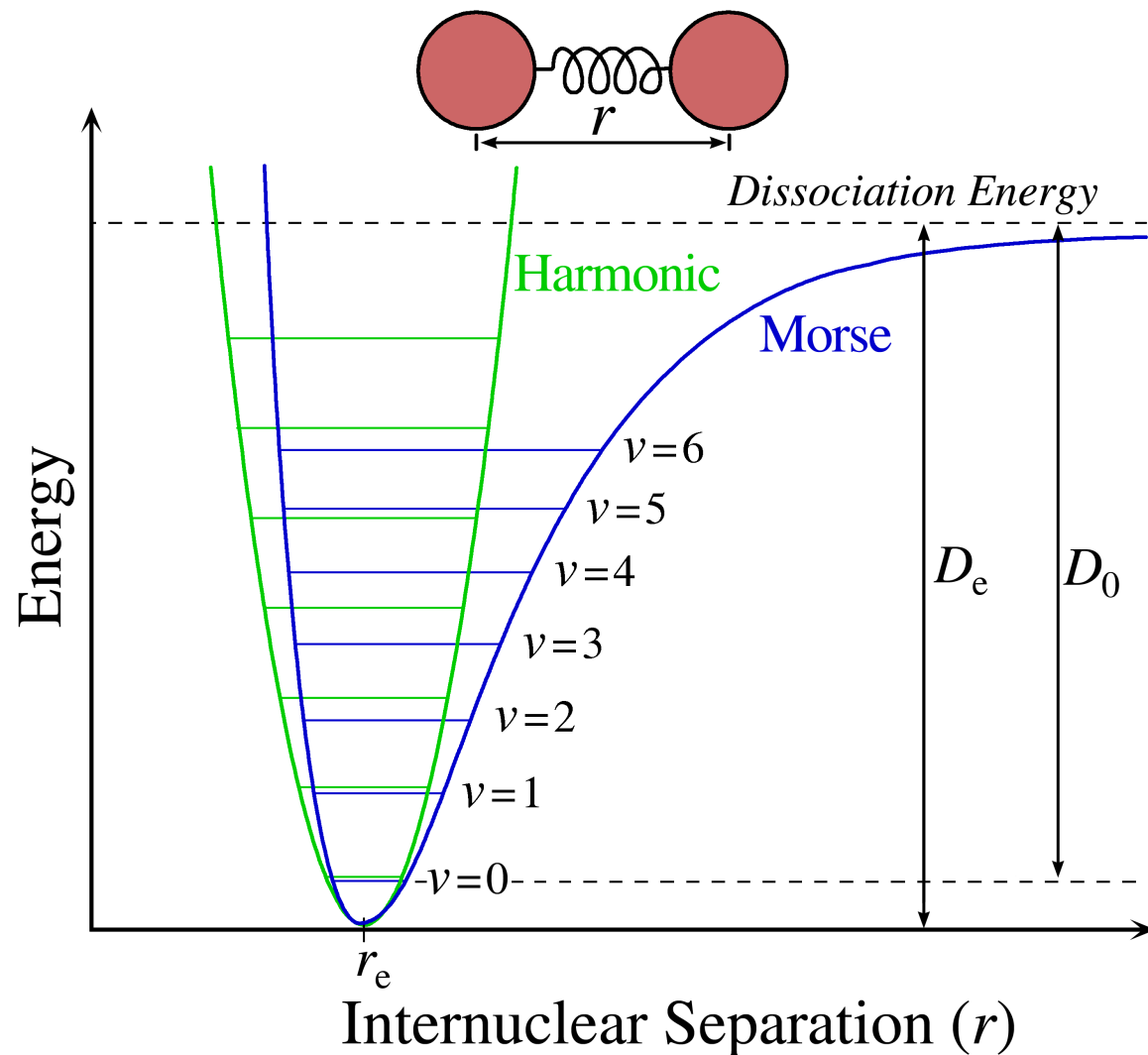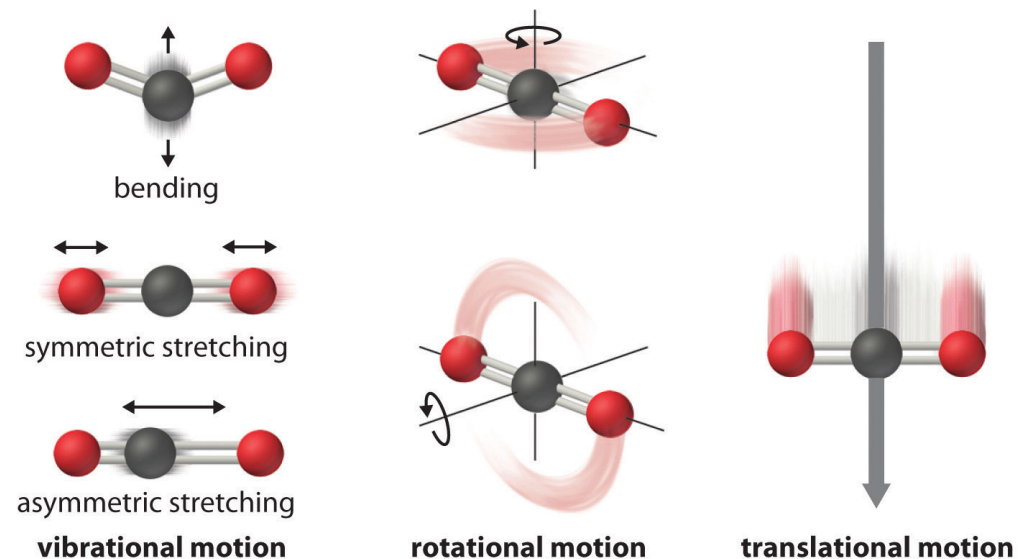
A simple exercise

$$514 \text{ K!!! } (28 \ \mu m)$$

▶ difficult to observe in dense regions (even if most abundant molecule)

▶ in shocked regions, where T becomes high enough

▶ or in the vicinity of hot stars

Probe for molecular hydrogen

▶ $x_{CO}/x_{H_2} \sim 10^{-4}$

▶ higher Einstein A-values

	CO	H_2
Symmetry	asymmetric	symmetric
Dipole moment	0.112 Debye	none
Binding energy	11.09 eV	4.48 eV
Isotope variants	^{13}CO, $C^{17}O$, $C^{18}O$	none
Rotational constant	2.77 K	87.5 K
First transition	2.6 mm (5.5 K)	28.2 μm (514 K)

Vibrational energies

bending

symmetric stretching

asymmetric stretching

vibrational motion

rotational motion

translational motion

$$E_v = (v + 1/2)h\nu$$

$$v = 0, 1, 2...$$

r

Dissociation Energy

Harmonic

Morse

$v=6$

$v=5$

$v=4$

$v=3$

$v=2$

$v=1$

$v=0$

D_e D_0

Energy

r_e

Internuclear Separation (r)

Observations

- Molecules introduce complexity compared to atoms

- Molecular energy is quantized

- BO approximation approx. allows us to solve for the internal structure of molecules

- Electronic + Rotational + Vibrational energies

- Remind: transitions between different states allow us to observe atoms and molecules in the ISM

Transitions	Energy (eV)	Temperature (K)	λ
Electronic	4 eV	40,000 K	visible and UV
Vibrational	0.1 eV	1,000 K	NIR/MIR ($\sim$2-20μm)
Rotational	< 0.01 eV	< 100 K	mm/submm