

4. Atoms and diatomic molecules
energy levels & partition functions
distribution laws &
thermodynamic functions
nuclear spin statistics

QUANTUM MECHANICS OF N IDENTICAL PARTICLES

Identical particles (electrons, nuclei) are
INDISTINGUISHABLE

Quantum mechanics dictates that

- Identical particles which each have **HALF-INTEGER** spins must have **(INTEGER)** **ANTISYMMETRIC** wavefunctions. **(SYMMETRIC)**

This means that

$$P_{ij} \Psi(1, 2, 3, \dots) = \pm \Psi(1, 2, 3, \dots)$$

in which $+$ is taken if particles i and j have **INTEGER** ($0, 1, 2, \dots$) spins (**BOSONS**) and $-$ is taken if particles i and j have **HALF-INTEGER** ($\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$) spins (**FERMIONS**)

Ψ must include spin functions and need not be a product of single particle wavefunctions

"spin" = intrinsic angular momentum

SUMMARY OF SYMMETRY PROPERTIES OF MOLECULAR FUNCTIONS OF DIATOMICS

$$\Psi_{total} = \Psi_{elec, space} \times \Psi_{elec, spin} \times \Psi_{vib.} \times \Psi_{rot.} \times \Psi_{nucl. spin} \times \Psi_{transl.}$$

OPERATION
 I inversion of all space-fixed coords.
 $I \Psi_{total} = \pm \Psi_{total}$ total parity is + or -
 $I \Psi_{rot} = (-1)^J \Psi_{rot}$ rotational parity
 $I \Psi_{elec, space} = \pm \Psi_{elec, space}$ as in Σ^{\pm} electronic parity

i inversion of molecule-fixed electronic coords
 (same as inversion of space-fixed electronic coords)
 $i \Psi_{elec} = \begin{cases} \oplus \Psi_{elec} & \text{as in } \Sigma^+, \Sigma_g^+, \Sigma_u^+ \\ \ominus \Psi_{elec} & \text{as in } \Sigma^-, \Sigma_g^-, \Sigma_u^-, \Pi_g, \Pi_u \end{cases}$

$\infty \sigma_v$ reflection of molecule-fixed electronic coords
 $\infty \sigma_v \Psi_{elec, space} = \begin{cases} \oplus \Psi_{elec, space} & \text{as in } \Sigma^+ \text{ electronic parity} \\ \ominus \Psi_{elec, space} & \text{as in } \Sigma^- \end{cases}$
 same result as $I \Psi_{elec, space} = \begin{cases} \oplus \Psi_{elec, space} & \text{as in } \Sigma^+ \\ \ominus \Psi_{elec, space} & \text{as in } \Sigma^- \end{cases}$

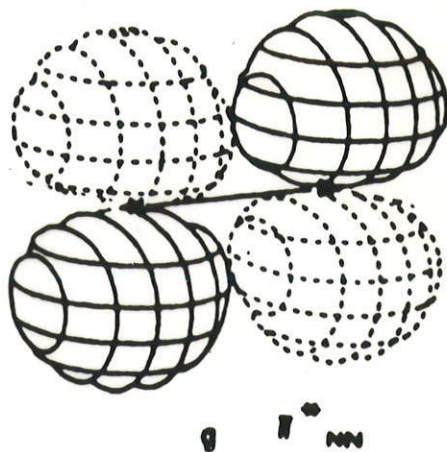
P_{AB} interchange of nuclei A + B which are indistinguishable
 $P_{AB} \Psi_{tot} = - \Psi_{tot}$ if (FERMIONS) $I = \text{half integer}$
 $P_{AB} \Psi_{tot} = + \Psi_{tot}$ if $I = 0, \text{integer}$ (BOSONS)
 $P_{AB} \Psi_{nucl, spin} = \begin{cases} \oplus \Psi_{nucl, spin} & \text{ORTHO states} \\ \ominus \Psi_{nucl, spin} & \text{PARA states} \end{cases}$
 $P_{AB} \Psi_{rot} = (-1)^J \Psi_{rot}$
 $P_{AB} \Psi_{elec} = \pm \Psi_{elec} = (\Sigma^{\pm})(g \text{ or } u) \Psi_{elec}$

P_{12} interchange of electrons 1 and 2
 $P_{12} \Psi_{elec, space} \Psi_{elec, spin} = - \Psi_{elec, space} \Psi_{elec, spin}$
 only antisym (electrons are fermions)
 $P_{12} \Psi_{elec, spin} = \begin{cases} \oplus \Psi_{elec, spin} & \text{ORTHO states} \\ \ominus \Psi_{elec, spin} & \text{PARA states} \end{cases}$
 as in helium

Electronic space function

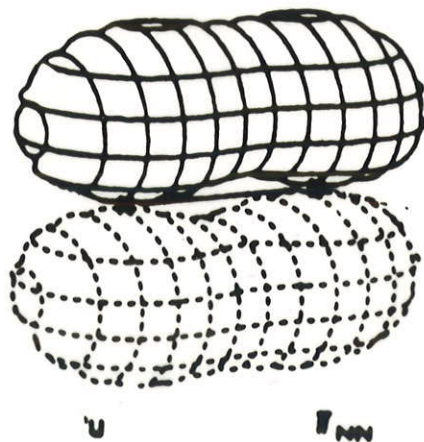
i = inversion of molecule-fixed electronic coordinates

π_g

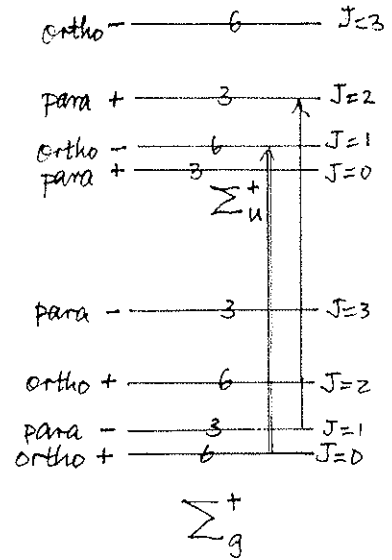
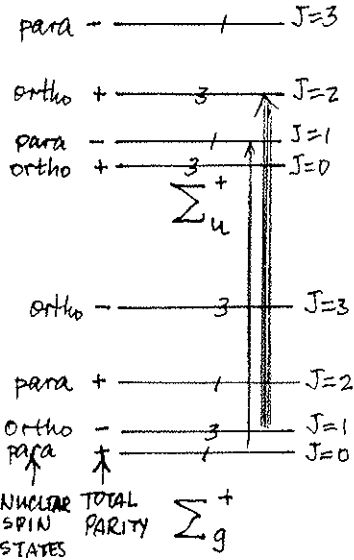
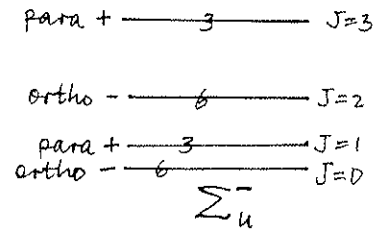
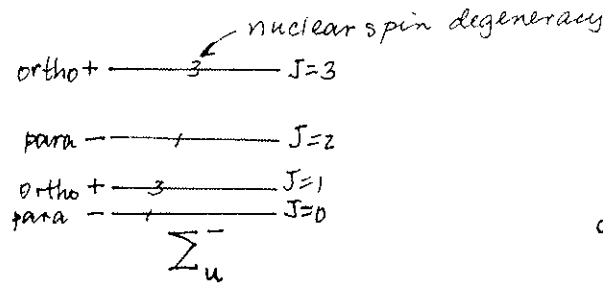


$$i \psi_{\pi_g} = + \psi_{\pi_g}$$

π_u



$$i \psi_{\pi_u} = - \psi_{\pi_u}$$



H_2 , for example
 $I = \frac{1}{2}$ FERMION

D_2 , for example
 $I = 1$ BOSON

Nuclear spin states:

Nuclear spin states:

$$\text{ORTHO} \begin{cases} \alpha(A) \cdot \alpha(B) \\ \beta(A) \cdot \beta(B) \\ \frac{\alpha(A)\beta(B) + \beta(A)\alpha(B)}{\sqrt{2}} \end{cases}$$

$$\text{PARA} \begin{cases} \frac{\alpha(A)\beta(B) - \beta(A)\alpha(B)}{\sqrt{2}} \end{cases}$$

$$\text{ORTHO} \begin{cases} \alpha(A) \cdot \alpha(B) \\ \beta(A) \cdot \beta(B) \\ \gamma(A) \cdot \gamma(B) \\ \frac{1}{\sqrt{2}}(\alpha(A)\beta(B) + \beta(A)\alpha(B)) \\ \frac{1}{\sqrt{2}}(\alpha(A)\gamma(B) + \gamma(A)\alpha(B)) \\ \frac{1}{\sqrt{2}}(\beta(A)\gamma(B) + \gamma(A)\beta(B)) \end{cases}$$

In general:

$$\frac{\text{no. of ortho states}}{\text{no. of para states}} = \frac{(I+1)(2I+1)}{I(2I+1)}$$

$$\text{PARA} \begin{cases} \frac{1}{\sqrt{2}}(\alpha(A)\beta(B) - \beta(A)\alpha(B)) \\ \frac{1}{\sqrt{2}}(\alpha(A)\gamma(B) - \gamma(A)\alpha(B)) \\ \frac{1}{\sqrt{2}}(\beta(A)\gamma(B) - \gamma(A)\beta(B)) \end{cases}$$

$$P_{AB} \Psi_{\text{tot}} = \begin{cases} + \Psi_{\text{tot}} & (\text{bosons}) \\ - \Psi_{\text{tot}} & (\text{fermions}) \end{cases}$$

GIVEN THIS

$$= P_{AB} \Psi_{\text{elec}}^{\pm} \cdot P_{AB} \Psi_{\text{rot}}^J \cdot P_{AB} \Psi_{\text{nuclear spin}}$$

$$= (+)(g) \Psi_{\text{elec}}^{\pm} \cdot (-1)^J \Psi_{\text{rot}}^J \cdot (\pm) \Psi_{\text{nuclear spin}}$$

AND GIVEN THIS

ONLY ONE SET (ORTHO OR PARA) OF NUCLEAR SPIN STATES CAN GO WITH A PARTICULAR J LEVEL.

Example:

Consider the symmetry of functions describing the two electrons in He atom:

Electronic functions may be described as follows

$$\Psi_T(1,2) = \frac{1}{\sqrt{2}} (\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)) \left\{ \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) + \beta(1)\alpha(2)) \right\}$$

"triplet" states

space part
ANTISYMMETRIC
with respect to P_{12}

or
 $\alpha(1)\alpha(2)$
or
 $\beta(1)\beta(2)$

spin part
SYMMETRIC

$$\Psi_S(1,2) = \frac{1}{\sqrt{2}} (\phi_i(1)\phi_j(2) + \phi_j(1)\phi_i(2)) \frac{1}{\sqrt{2}} (\alpha(1)\beta(2) - \beta(1)\alpha(2))$$

"singlet" states

space
SYMMETRIC

spin
ANTISYMMETRIC

There are no restrictions on ϕ_i and ϕ_j except that IF $\phi_i = \phi_j$ then only $\Psi_S(1,2)$ is possible

Concept of a "SYSTEM QUANTUM STATE"

Example: Consider the quantum mechanical perfect gas, N particles having no internal structure, therefore only TRANSLATIONAL states have to be considered. If there is NO INTERACTION at all ("perfect gas") between particles, then

$$\Psi_{\text{system quantum state function}} = \frac{1}{\sqrt{N!}} \sum_P \psi_a(1) \cdot \psi_b(2) \cdot \psi_c(3) \dots \quad \text{for } N \text{ BOSONS}$$

$$\text{or } = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \psi_a(3) & \dots & \psi_a(N) \\ \psi_b(1) & \psi_b(2) & \psi_b(3) & \dots & \psi_b(N) \\ \psi_i(1) & \psi_i(2) & \psi_i(3) & \dots & \psi_i(N) \end{vmatrix} \quad \text{for } N \text{ FERMIONS}$$

3 BOSONS:

$$\Psi_{\text{symmetric}}(1,2,3) = \frac{1}{\sqrt{3!}} \left\{ \begin{aligned} &\psi_a(1)\psi_b(2)\psi_c(3) + \psi_a(1)\psi_b(3)\psi_c(2) + \psi_a(2)\psi_b(3)\psi_c(1) \\ &+ \psi_a(2)\psi_b(1)\psi_c(3) + \psi_a(3)\psi_b(1)\psi_c(2) + \psi_a(3)\psi_b(2)\psi_c(1) \end{aligned} \right\}$$

3 FERMIONS:

$$\Psi_{\text{anti-symmetric}}(1,2,3) = \frac{1}{\sqrt{3!}} \left\{ \begin{aligned} &\psi_a(1)\psi_b(2)\psi_c(3) - \psi_a(1)\psi_b(3)\psi_c(2) + \psi_a(2)\psi_b(3)\psi_c(1) \\ &- \psi_a(2)\psi_b(1)\psi_c(3) + \psi_a(3)\psi_b(1)\psi_c(2) - \psi_a(3)\psi_b(2)\psi_c(1) \end{aligned} \right\}$$

Note how the wavefunction does not change sign when P_{12} is applied to $\Psi_{\text{symmetric}}(1,2,3)$

Note how the wavefunction **CHANGES SIGN** when P_{12} is applied to $\Psi_{\text{anti-symmetric}}(1,2,3)$. (RECALL that a determinant changes sign when any two columns (or any two rows) are INTERCHANGED.)

ψ_a includes both space and spin parts

NOTE that in the wavefunctions $\Psi_{\text{symmetric}}(1,2,3)$ or $\Psi_{\text{anti-symmetric}}(1,2,3)$, we cannot say which particle is in state ψ_a , which is in ψ_b , which is in ψ_c , although the wavefunction does assert that the system is in a state in which the 3 single particle states (orbitals) ψ_a , ψ_b and ψ_c are occupied. Contrary to one's naive classical intuition, identical particles are **TRULY INDISTINGUISHABLE**.

If ψ_a , ψ_b and ψ_c are different, how many "system quantum states"?

BOLTZONS

$$3! = 6$$

$$\left\{ \begin{aligned} &\psi_a(1)\psi_b(2)\psi_c(3) \\ &\psi_a(1)\psi_b(3)\psi_c(2) \\ &2 \text{ etc.} \end{aligned} \right\}$$

BOSONS

1

shown

above

$$\Psi_{\text{symmetric}}(1,2,3)$$

FERMIONS

1

shown

above

$$\Psi_{\text{anti-symmetric}}(1,2,3)$$

If $\psi_a = \psi_b$ and ψ_c is different, how many "system quantum states"?

BOLTZONS

3

BOSONS

1

FERMIONS

0

If $\psi_a = \psi_b = \psi_c$, how many "system quantum states"?

BOLTZONS

1

BOSONS

1

FERMIONS

0

For the N particle quantum-mechanical perfect gas

$$E_{\substack{s_x \\ s_y \\ s_z}} = \frac{h^2}{8m} \left(\frac{s_x^2}{x^2} + \frac{s_y^2}{y^2} + \frac{s_z^2}{z^2} \right) \text{ for a single particle}$$

when the box is LARGE a small fractional interval of kinetic energy in the x direction say $\frac{dE_x}{E_x} \approx 10^{-5}$ corresponds to $\frac{ds_x}{s_x} \approx 500$

$\frac{ds_y}{s_y} \approx 500$, $\frac{ds_z}{s_z} \approx 500$ All these states $(500)^3$

of them, have energies which are in this small interval! The states are distinguishable that is, the set of 3 quantum numbers associated with each state is unique, but they can be grouped together as being approximately degenerate. We can group together all the g_s states in a narrow interval of energy. For N particles:

A distribution is characterized by the set of numbers N_1, N_2, N_3, \dots such that $\sum N_i = N$. N_i is in the large number of degenerate states g_{s_i} , etc.

Thus, we can still talk about a large number of system quantum states or configurations.

5. Statistical mechanics and chemical equilibrium

Consider a dissociation reaction:



molecule C

Constraints: total number of atoms of A $n_A = N_A + N_C$

Lagrange multiplier α^A

$$\sum_i N_i^C + \sum_j N_j^A = n_A$$

total number of atoms of B $n_B = N_B + bN_C$

α^B

$$b \sum_i N_i^C + \sum_k N_k^B = n_B$$

total energy

$$- \beta E = \sum_i N_i^C \epsilon_i^C + \sum_j N_j^A \epsilon_j^A + \sum_k N_k^B \epsilon_k^B$$

No. of configurations (CORRECTED BOLTZONS)

$$t = t^C \cdot t^A \cdot t^B$$

$$= \prod_i \frac{(g_i^C)^{N_i^C}}{N_i^C!} \prod_j \frac{(g_j^A)^{N_j^A}}{N_j^A!} \prod_k \frac{(g_k^B)^{N_k^B}}{N_k^B!}$$

$$\ln t = \sum_i N_i^C \left(\ln \frac{g_i^C}{N_i^C} + 1 \right) + \sum_j N_j^A \left(\ln \frac{g_j^A}{N_j^A} + 1 \right)$$

$$+ \sum_k N_k^B \left(\ln \frac{g_k^B}{N_k^B} + 1 \right)$$

Three sets of equations:

$$\frac{\partial(\ln t)}{\partial N_i^C} + (\alpha^A + b\alpha^B) - \beta E_i^C = 0 \quad i=1, \dots$$

$$\frac{\partial(\ln t)}{\partial N_j^A} + \alpha^A - \beta E_j^A = 0 \quad j=1, \dots$$

$$\frac{\partial(\ln t)}{\partial N_k^B} + \alpha^B - \beta E_k^B = 0 \quad k=1, \dots$$

$$\ln \frac{g_j^A}{N_j^A} + \alpha^A - \beta E_j^A = 0$$

$$\ln \frac{g_k^B}{N_k^B} + \alpha^B - \beta E_k^B = 0$$

$$\ln \frac{g_i^C}{N_i^C} + (\alpha^A + b\alpha^B) - \beta E_i^C = 0$$

get

$$N_j^A = g_j^A e^{\alpha^A} e^{-\beta E_j^A}$$

$$N_k^B = g_k^B e^{\alpha^B} e^{-\beta E_k^B}$$

$$N_i^C = g_i^C e^{\alpha^A} (e^{\alpha^B})^b e^{-\beta E_i^C}$$

$$N_A = \sum_j N_j^A = e^{\alpha_A} \underbrace{\sum_j g_j^A e^{-\beta E_j^A}}_{q_A}$$

recognize the
 q_A

$$N_B = \sum_k N_k^B = e^{\alpha_B} \underbrace{\sum_k g_k^B e^{-\beta E_k^B}}_{q_B}$$

q_B

$$N_C = \sum_i N_i^C = e^{\alpha_A} (e^{\alpha_B})^b \underbrace{\sum_i g_i^C e^{-\beta E_i^C}}_{q_C}$$

q_C

molecular
partition functions

Now form the ratio

$$\frac{N_A (N_B)^b}{N_C} = \frac{q_A (q_B)^b}{q_C}$$



The number of molecules can be converted into concentrations by simply dividing by the total volume.

Separability of translation and internal motion:

Any translational energy can occur with any internal energy,

$$\text{So } q \equiv \sum_i g_i e^{-\beta E_i}$$

we can write it as

$$q = \underbrace{\left(\sum_{\text{trans}} g_{\text{trans}} e^{-\beta E_{\text{trans}}} \right)}_{\left(\frac{2\pi m k T}{h^2} \right)^{3/2} V} \underbrace{\left(\sum_{\text{int}} g_{\text{int}} e^{-\beta E_{\text{int}}} \right)}_{q_{\text{int}}}$$

we derived
previously

q_{trans}

$$\begin{aligned}
 K &= \frac{\left(\frac{N_A}{V N_{\text{Add}}}\right) \left(\frac{N_B}{V N_{\text{Add}}}\right)^b}{\left(\frac{N_C}{V N_{\text{Add}}}\right)} = \frac{\left(\frac{g_{\text{transl}}^A}{V}\right) \left(\frac{g_{\text{transl}}^B}{V}\right)^b}{\left(\frac{g_{\text{transl}}^C}{V}\right)} \cdot \frac{\frac{g_{\text{int}}^A}{N_{\text{Add}}} \left(\frac{g_{\text{int}}^B}{N_{\text{Add}}}\right)^b}{\frac{g_{\text{int}}^C}{N_{\text{Add}}}} \\
 &= \frac{\left(\frac{2\pi m_A kT}{h^2}\right)^{3/2} \left(\frac{2\pi m_B kT}{h^2}\right)^{3/2 b}}{\left(\frac{2\pi m_C kT}{h^2}\right)^{3/2}} \cdot \dots \\
 &= \left(\frac{2\pi kT}{h^2}\right)^{3/2 b} \left(\frac{m_A m_B^b}{m_C}\right)^{3/2} \cdot \frac{g_{\text{int}}^A}{N_{\text{Add}}} \left(\frac{g_{\text{int}}^B}{N_{\text{Add}}}\right)^b \cdot \frac{1}{\frac{g_{\text{int}}^C}{N_{\text{Add}}}}
 \end{aligned}$$

NOTE that all energy levels must be expressed on the same scale, i.e., with the SAME ZERO for all g_i .

Translation is ok, all start from ZERO

Internal: different definition for each of A, B, C. Must put all on the same scale!

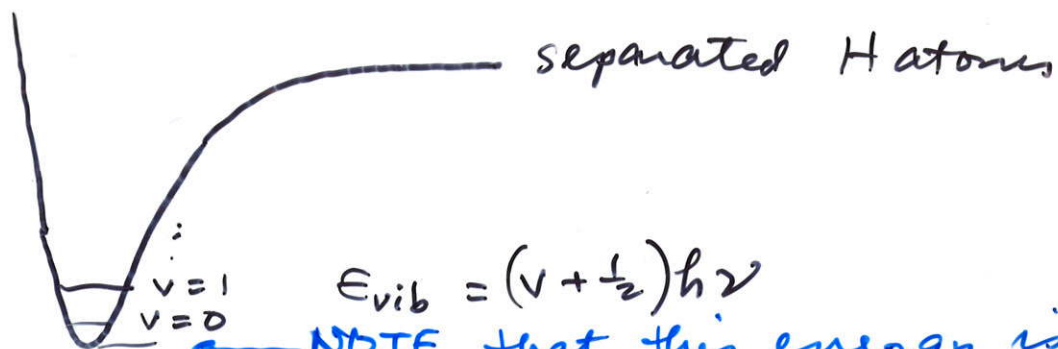
For example:
H atom

$$\begin{array}{l}
 \dots \dots \dots n=3 \\
 \text{---} \text{---} \text{---} n=2
 \end{array}$$

$$\text{---} \text{---} \text{---} n=1 \quad E_n = -\frac{Z^2 e^2}{n^2 2a_0}$$

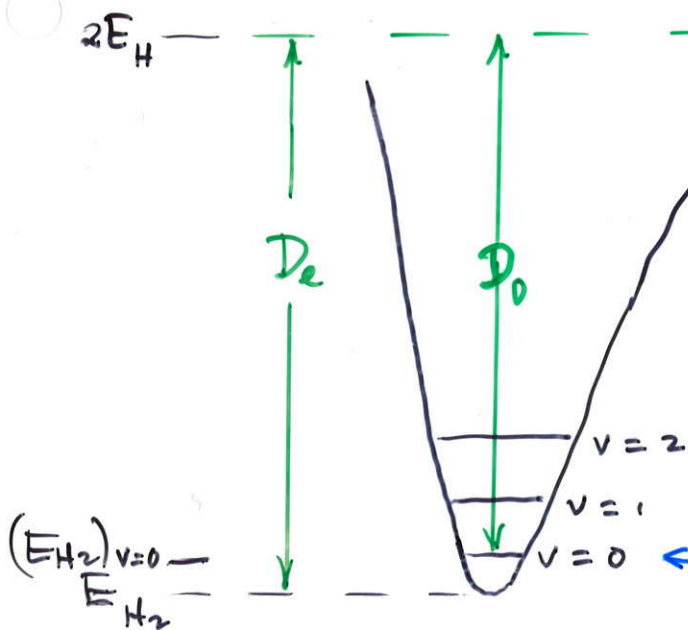
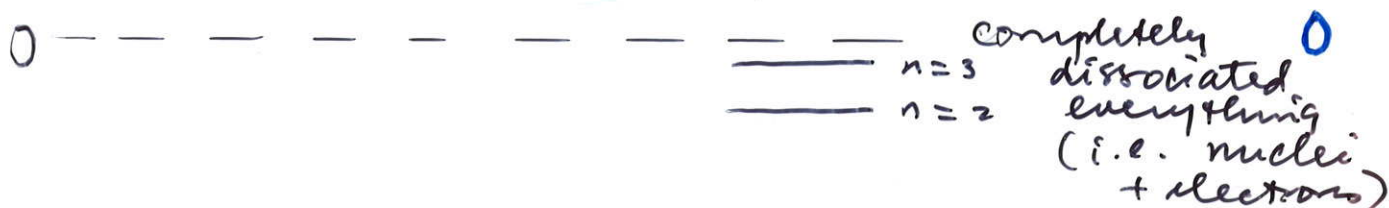
NOTE that this energy is based on the ZERO being the completely dissociated atom!

On the other hand : for H_2 molecule



$$E_{vib} = (v + \frac{1}{2}) h \nu$$

NOTE that this energy is based on the ZERO being at the bottom of the potential well.



$$(E_{H_2})_{v=0} + D_0 = 2E_H$$

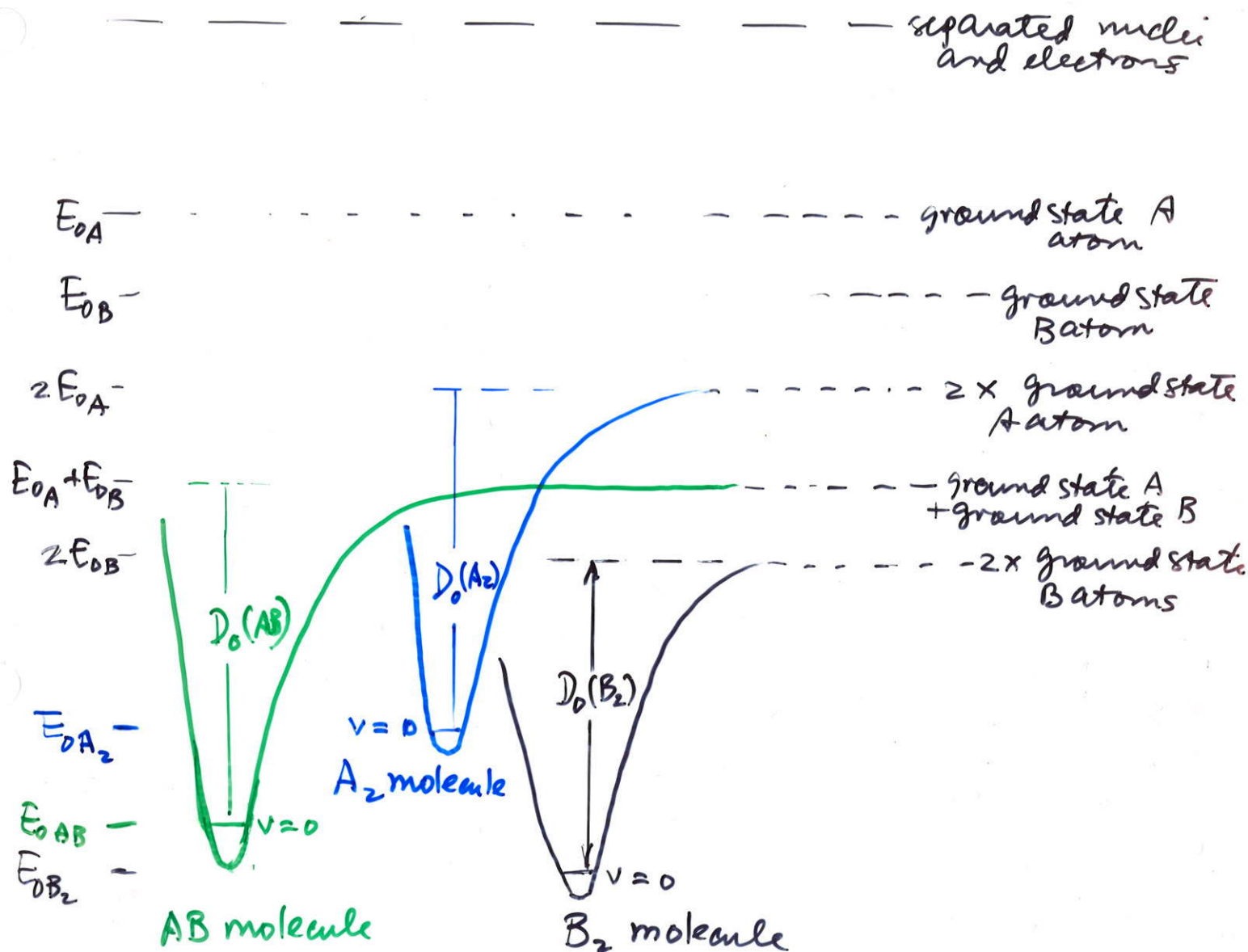
for the reaction



$$\left[-2 \frac{Z^2 e^2}{n^2 2a_0} - |D_e| + (v + \frac{1}{2}) h \nu \right]$$

$$\text{or } -2 \frac{Z^2 e^2}{n^2 2a_0} - |D_0| + v h \nu$$

For the reaction



Arbitrary zero of energy

$$\Delta E_D \equiv 2E_{0AB} - E_{0A_2} - E_{0B_2}$$

$$A_2 = 2A$$

$$-D_0(A_2) = E_{0A_2} - 2E_{0A}$$

$$B_2 = 2B$$

$$-D_0(B_2) = E_{0B_2} - 2E_{0B}$$

$$AB = A + B$$

$$-D_0(AB) = E_{0AB} - E_{0A} - E_{0B}$$

$$\Delta E_D = - \{ 2D_0(AB) - D_0(A_2) - D_0(B_2) \}$$

$$q^{AB} = \sum_k g_k^{AB} e^{-\epsilon_k^{AB}/kT}$$

ϵ_k^{AB} measured relative to the arbitrary zero of energy

$$q^{A_2} = \sum_j g_j^{A_2} e^{-\epsilon_j^{A_2}/kT}$$

$\epsilon_j^{A_2}$... also

$$q^{B_2} = \sum_i g_i^{B_2} e^{-\epsilon_i^{B_2}/kT}$$

$\epsilon_i^{B_2}$... also

$$q^{AB} = \left[\sum_k g_k^{AB} e^{-\epsilon_k^{AB}/kT} \right] e^{-E_{OAB}/kT}$$

$$\epsilon_k^{AB} = \epsilon_k^{AB} + E_{OAB}$$

$$q^{A_2} = \left[\sum_j g_j^{A_2} e^{-\epsilon_j^{A_2}/kT} \right] e^{-E_{OA_2}/kT}$$

$$\epsilon_j^{A_2} = \epsilon_j^{A_2} + E_{OA_2}$$

$$q^{B_2} = \left[\sum_i g_i^{B_2} e^{-\epsilon_i^{B_2}/kT} \right] e^{-E_{OB_2}/kT}$$

$$\epsilon_i^{B_2} = \epsilon_i^{B_2} + E_{OB_2}$$

$$K \propto \frac{(q^{AB})^2}{q^{A_2} q^{B_2}} = \frac{(q^{AB})^2}{q^{A_2} q^{B_2}} e^{-[2E_{OAB} - E_{OA_2} - E_{OB_2}]/kT}$$

$$= \frac{(q^{AB})^2}{q^{A_2} q^{B_2}} e^{+[2D_0^{(AB)} - D_0^{(A_2)} - D_0^{(B_2)}]/kT}$$

K_N
in terms
of molecules
per liter

$$= \left(\frac{2\pi kT}{h^2} \right)^{\frac{3}{2}(\rho-r)} \left\{ \frac{q_{\text{products}}}{q_{\text{reactants}}} \right\} e$$

$(D_{\text{products}} - D_{\text{reactants}})/kT$

same form as K except with masses
same form as K except with q

The molecular partition function
(internal degrees of freedom only)

$$\epsilon_{int} = \epsilon_{elec} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{elec\ spin} + \epsilon_{nuclear\ spin}$$

(in presence of fields)

$$q_{int} = q_{elec} \cdot q_{rot} \cdot q_{vib} \cdot q_{nuclear\ spin}$$

↑
This includes the degeneracy due to electron spin states

IF there are no external fields, spin-orbit states are DEGENERATE and nuclear spin states are DEGENERATE

$$q_{int} = q_{elec} \cdot q_{rot} \cdot q_{vib} \cdot q_{nuc\ spin}$$

Note that THIS NEGLECTS any interactions between them:

no vibronic effects

no vibrational-rotational coupling

ATOMS

$$q_{elec} = \sum_i g_i e^{-\epsilon_i/kT}$$

For atoms, ϵ_i are usually very far apart (many electron volts) so that at ordinary temperatures only the LOWEST excited state, if at all, needs to be considered.

$$\text{atoms: } q_{elec} = \underbrace{g_{ground}} + g_{1st\ excited} e^{-\epsilon_1/kT}$$

↑
This is the degeneracy of the spin-orbit multiplet

For example: 3D_3 3D_2 3D_1 $2S+1$
 L
 J
 means $L=2$ $S=1$ term
symbol

$J = |L+S|, \dots, |L-S|$ net electronic angular momentum
 Each J state is $(2J+1)$ degenerate since
 $M_J = -J, -J+1, \dots, +J$ which states remain
 degenerate until an external magnetic
 field is applied.

The total number of states in the
 multiplet is $(2L+1)(2S+1) = \sum_{|L-S|}^{|L+S|} (2J+1)$

Example: O atom

3P_2	0	$\frac{(2S+1)}{(5)}$	Conversion factor: kT at 300K is $\approx 208 \text{ cm}^{-1}$
3P_1	158.5 cm^{-1}	(3)	
3P_0	226.5 cm^{-1}	(1)	
1D_2	$15,867.7 \text{ cm}^{-1}$	(5)	

For O atom the (internal) molecular partition
 function is

$$q_{\text{int}} = 5 + 3e^{-\frac{158.5}{kT}} + 1e^{-\frac{226.5}{kT}} + 5e^{-\frac{15867.7}{kT}} + \dots$$

$$= 5 + 3(0.467) + 1(.34) + \underbrace{\text{very small}}_{5(7 \times 10^{-34})}$$

$$= 6.74 \text{ at } 300 \text{ K}$$

$$\approx 5 + 3 + 1 \text{ at high temperatures} + 5e^{-\frac{15867.7}{kT}}$$

or

$$\begin{matrix} (3)(3) \\ \uparrow \quad \uparrow \\ 2L+1 \quad 2S+1 \end{matrix}$$

For example at 3000 K
 $kT = 2080 \text{ cm}^{-1}$
 $5 + 3(.427) + 1(.897)$
 $+ 5(.00049) = 8.68$

DIATOMIC MOLECULES

ROTATION and NUCLEAR SPIN

Consider the rigid rotor

$$E_{rot} = \underbrace{B_e}_{\substack{\uparrow \\ \text{rotational} \\ \text{constant}}} J \underbrace{(J+1)}_{\substack{\uparrow \\ \text{rotational quantum} \\ \text{number}}}$$

$$B_e = \frac{\hbar^2}{2I} = \frac{\hbar^2}{2\mu R_e^2}$$

\uparrow moment of inertia \uparrow reduced mass $R_e = \text{equil. bond distance}$

$$\begin{array}{l}
 6B_e \text{ --- } J=2 \\
 2B_e \text{ --- } J=1 \\
 E=0 \text{ --- } J=0
 \end{array}$$

For each J value,
 $M_J = 0, \pm 1, \pm 2, \dots, \pm J$
 $\underbrace{\hspace{10em}}$
 $2J+1$ values

degenerate as long as no external magnetic fields

For homonuclear diatomics, we also have to consider the indistinguishability of the two nuclei, that is,

P_{AB} interchanges two nuclei A and B which are indistinguishable

If nuclei are FERMIONS

$$P_{AB} \Psi_{total} = - \Psi_{total}$$

if BOSONS

$$P_{AB} \Psi_{total} = + \Psi_{total}$$

$\Psi_{elec} \Psi_{rot} \Psi_{nuc\ spin}$ are affected

$$P_{AB} \Psi_{elec} = \pm \Psi_{elec} \text{ according to } (\sum^{\pm})(g_{nu})$$

$$P_{AB} \Psi_{\text{rot}} = (-1)^J \Psi_{\text{rot}}$$

$$P_{AB} \Psi_{\text{nuclear spin}} = + \Psi_{\text{nuclear spin}} \text{ or } - \Psi_{\text{nuclear spin}}$$

(ORTHO nuclear spin states) (if PARA)

Consider H_2

H nuclei have spin $I = 1/2$ FERMIONS
nuclear spin states are

$$\text{ORTHO} \left\{ \begin{array}{l} \alpha(A) \cdot \alpha(B) \\ \beta(A) \cdot \beta(B) \\ [\alpha(A) \cdot \beta(B) + \beta(A) \cdot \alpha(B)] / \sqrt{2} \end{array} \right.$$

$$\text{PARA} \left\{ [\alpha(A) \cdot \beta(B) - \beta(A) \cdot \alpha(B)] / \sqrt{2} \right.$$

In general,

$$\frac{\text{number of ortho states}}{\text{number of para states}} = \frac{(I+1)(2I+1)}{I(2I+1)}$$

Electronic ground state of H_2 molecule is Σ_g^+ , that is,

$$P_{AB} \Psi_{\text{elec}}(\Sigma_g^+) = (+) \Psi_{\text{elec}}(\Sigma_g^+)$$

$$P_{AB} \Psi_{\text{total}} = - \Psi_{\text{total}}$$

↑
H are FERMIONS

This means that if
J = even ORTHO states are not allowed, only PARA
J = odd PARA states are not allowed, only ORTHO

PARA ————— J = 2

ORTHO ————— J = 1

PARA ————— J = 0

H_2 molecule Σ_g^+ electronic ground state

If A and B nuclei are different isotopes or different atoms, then no interchange is possible because the nuclei are **DISTINGUISHABLE** and ALL of the $(2I_A+1)(2I_B+1)$ nuclear spin states can go with EVERY J rotational level!

(Why $2I+1$ spin states for each nucleus?
Spin angular momentum,

$$M_I = -I, -I+1, \dots, +I \text{ are possible values}$$

These are degenerate until the system is placed in a magnetic field (NMR spectrometer, for example)

Back to H_2 molecules in electronic ground state,

$$g_{\text{rot}} \cdot g_{\text{nuc spin}} = \sum_{J=0}^{\text{all EVEN } J} (2J+1) e^{-B_e J(J+1)/kT} \cdot \underbrace{I(2I+1)}_{\text{PARA states}}$$

$$+ \sum_{J=1}^{\text{all ODD } J} (2J+1) e^{-B_e J(J+1)/kT} \cdot \underbrace{(I+1)(2I+1)}_{\text{ORTHO states}}$$

If different atoms

$$g_{\text{rot}} \cdot g_{\text{nuc spin}} = (2I_A+1)(2I_B+1) \sum_{J=0}^{\text{all } J} (2J+1) e^{-B_e J(J+1)/kT}$$

D₂ molecules in the electronic ground state,

$$g_{\text{rot}} \cdot g_{\text{spin}} = \sum_{J=0}^{\text{all EVEN } J} (2J+1) e^{-B_e J(J+1)/kT} \cdot \underbrace{(I+1)(2I+1)}_{\substack{6 \\ \text{ORTHO STATES}}} \\ + \sum_{J=1}^{\text{all ODD } J} (2J+1) e^{-B_e J(J+1)/kT} \cdot \underbrace{I(2I+1)}_{\substack{3 \\ \text{PARA STATES}}}$$

$\left(\frac{\text{ORTHO}}{\text{PARA}} \right) = ?$ at equilibrium at any temperature
 (i.e. in contact with ortho-para conversion catalyst)

$$N_i = \frac{N}{g} g_i e^{-\beta \epsilon_i}$$

$$\frac{N_J}{N} = \frac{1}{g} (2J+1) e^{-B_e J(J+1)/kT} \begin{matrix} \text{ORTHO} \\ (I+1)(2I+1) \text{ or} \\ \text{PARA} \\ I(2I+1) \end{matrix}$$

$$= \frac{(I+1)(2I+1)}{I(2I+1)} \frac{\sum_{J=1}^{\text{ODD } J} (2J+1) e^{-B_e J(J+1)/kT}}{\sum_{J=0}^{\text{EVEN } J} (2J+1) e^{-B_e J(J+1)/kT}} \text{ for FERMIONS}$$

$$= \frac{(I+1)(2I+1)}{I(2I+1)} \frac{\sum_{J=0}^{\text{EVEN } J} (2J+1) e^{-B_e J(J+1)/kT}}{\sum_{J=1}^{\text{ODD } J} (2J+1) e^{-B_e J(J+1)/kT}} \text{ for BOSONS}$$

High temperature limit: (at equilibrium)
 Sum over ODD J \approx sum over EVEN J

$$\left(\frac{\text{ORTHO}}{\text{PARA}} \right) \approx \frac{(I+1)(2I+1)}{I(2I+1)}$$

Low temperature limit: (at equilibrium)
 all **PARA** at $J=0$ for H₂ at 0K
 all **ORTHO** at $J=0$ for D₂

Molecular partition function at the high temperature limit:

At very high T , $y = B_e/kT \ll 1$ and can replace the sum by an integral

$$\begin{aligned}
 \text{H}_2: \quad q_{\text{rot}} q_{\text{vib}} &= \sum_{J=0}^{\text{EVEN } J} (2J+1) e^{-J(J+1)y} \cdot 1 \\
 &+ \sum_{J=0}^{\text{ODD } J} (2J+1) e^{-J(J+1)y} \cdot 3 \\
 &\approx 1 \cdot \int_{\text{even}} (2J+1) e^{-J(J+1)y} dJ + 3 \cdot \int_{\text{odd}} (2J+1) e^{-J(J+1)y} dJ \\
 &\approx 1 \cdot \frac{1}{2} \int_0^{\infty} (2J+1) e^{-J(J+1)y} dJ + 3 \cdot \frac{1}{2} \int_0^{\infty} (2J+1) e^{-J(J+1)y} dJ \\
 &\approx 2 \cdot \int_0^{\infty} (2J+1) e^{-J(J+1)y} dJ \\
 &\quad \text{of the form } \int_0^{\infty} e^{-au} du = \frac{1}{a} \\
 &\approx \frac{2}{y} \quad \text{or} \quad \frac{2}{(B_e/kT)}
 \end{aligned}$$

D_2 :

$$\begin{aligned}
 q_{\text{rot}} q_{\text{vib}} &\approx 6 \int_{\text{even}} \dots + 3 \int_{\text{odd}} \dots \\
 &\approx \frac{9}{2y}
 \end{aligned}$$

HD :

$$\begin{aligned}
 q_{\text{rot}} q_{\text{vib}} &= [2(\frac{1}{2}+1)] [2(1)+1] \cdot \int_0^{\infty} \dots \\
 &= \frac{6}{y}
 \end{aligned}$$

High temperature limit is

$$q_{\text{rot}} q_{\text{spin}} \approx \frac{1}{\sigma} \underbrace{(2I_A + 1)(2I_B + 1)}_6 \quad \text{for HD}$$

$$\approx \frac{1}{2\sigma} \underbrace{(2I_A + 1)(2I_B + 1)}_4 \quad \text{for H}_2$$

$$\approx \frac{1}{2\sigma} \underbrace{(2I_A + 1)(2I_B + 1)}_4 \quad \text{for D}_2$$

$$\approx \frac{1}{\sigma} (2I_A + 1)(2I_B + 1)$$

$\sigma \equiv$ symmetry number $\quad \gamma \equiv \frac{Be/kT}{\sigma} = \frac{h^2}{2IkT}$

= 1 for heteronuclear diatomic

= 2 for homonuclear "

The use of symmetry number applies only at the high temperature limit.

VIBRATION:

if harmonic oscillator,

$$E_v = (v + \frac{1}{2}) h\nu$$

or taking $v=0$ as local zero of energy,

$$E_v = v h\nu$$

$$q_{\text{vib}} = \sum_{v=0}^{\infty} e^{-v h\nu / kT}$$

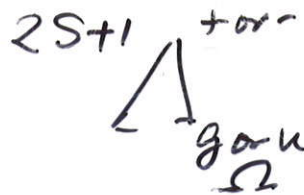
$$\text{let } u \equiv \frac{h\nu}{kT}$$

$$= \sum_{v=0}^{\infty} e^{-vu}$$

This is an infinite series with a known sum = $\frac{1}{1-e^{-u}}$

ELECTRONIC :

Term symbol



$$\Lambda = 0, 1, 2, 3$$

$$\Sigma \quad \Pi \quad \Delta \quad \Phi$$

orbital angular momentum component along internuclear axis is

$$\Omega = \Lambda + S, \dots, |\Lambda - S|$$

$\pm \Lambda h$ doubly degenerate except when $\Lambda = 0$ or for Σ electronic states

$$\text{degeneracy} = (2S+1) \binom{1}{2}$$

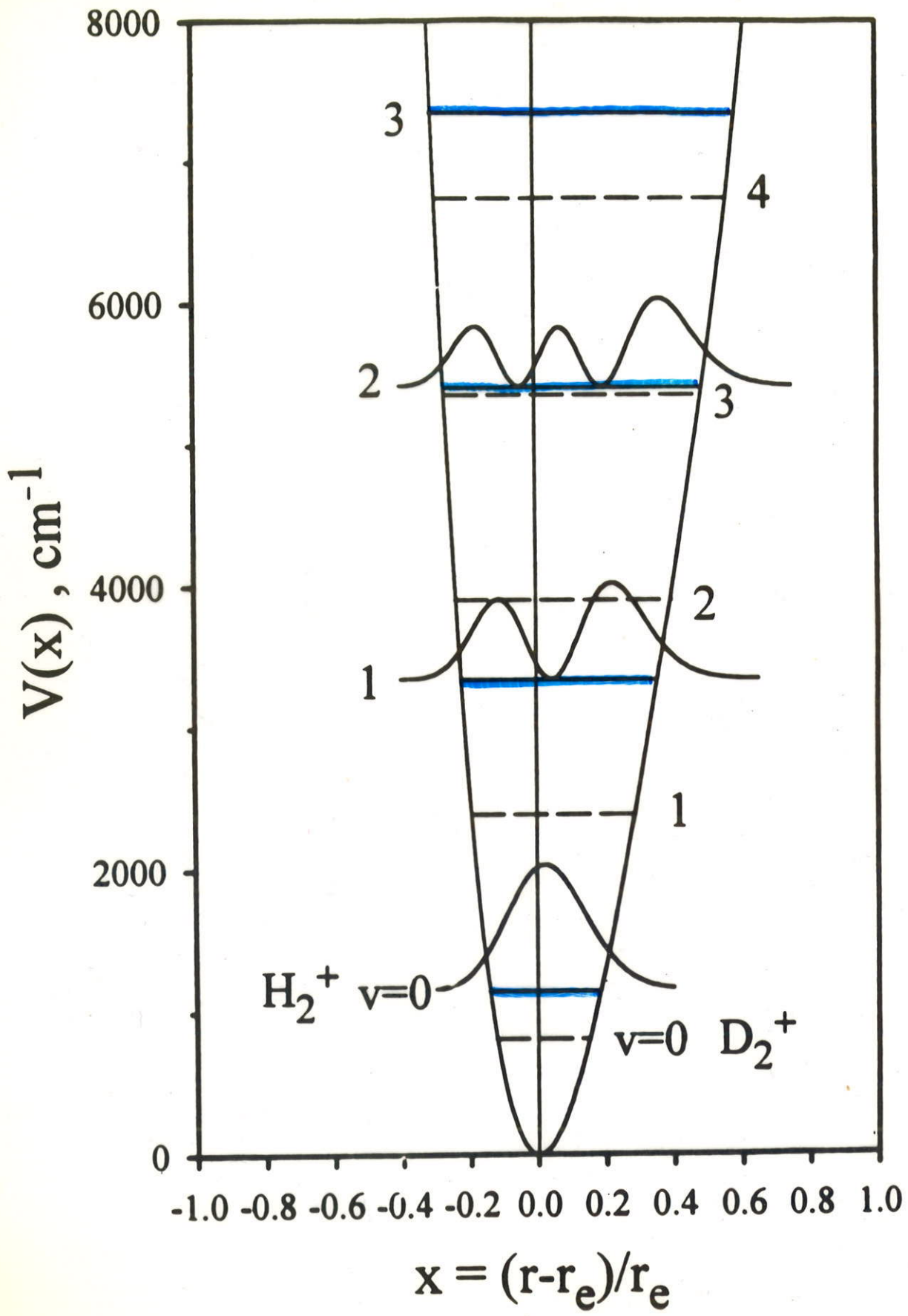
Effects of isotopic mass on partition function:

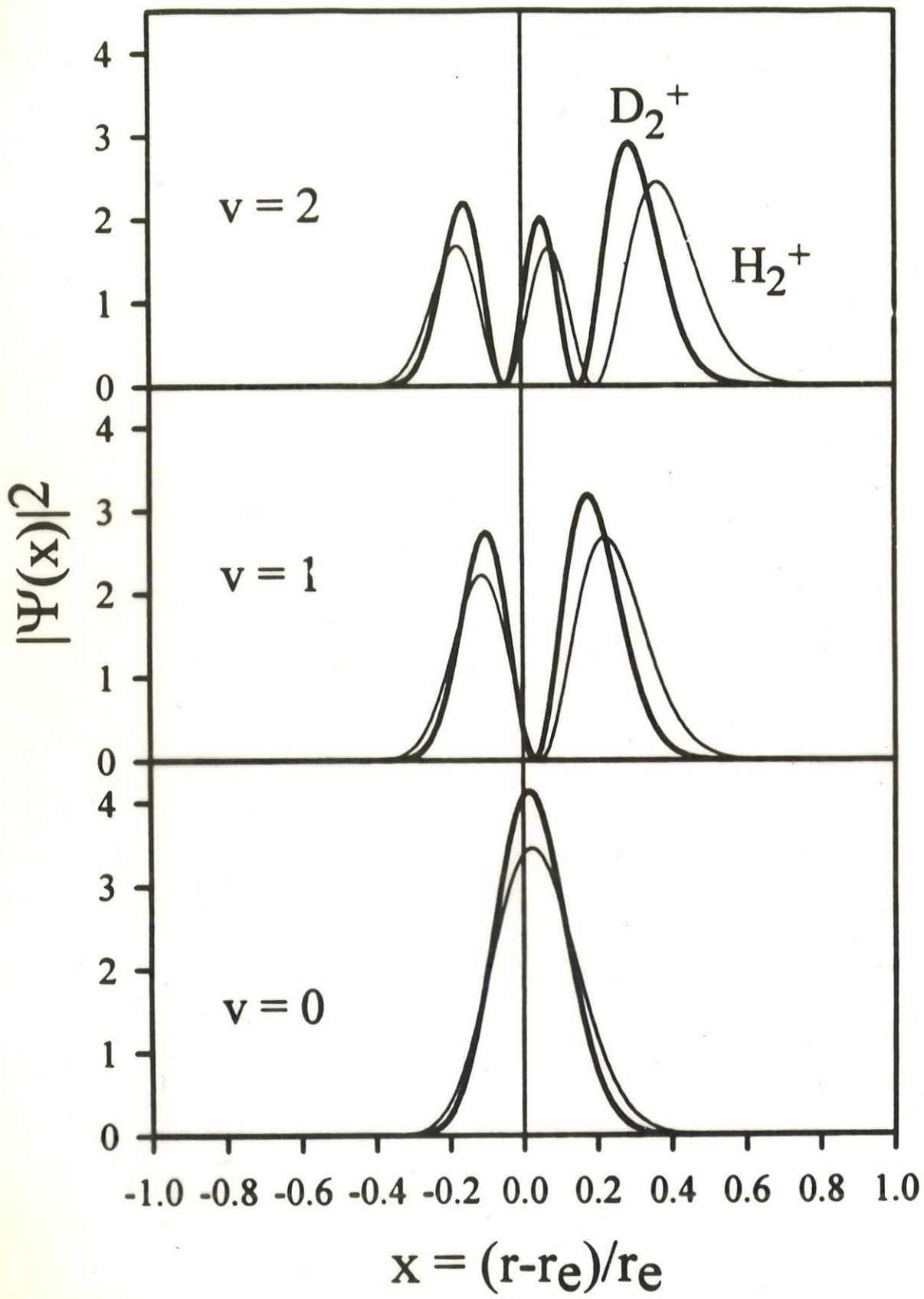
1) Translation : explicit dependence on mass in $\left(\frac{2\pi m k T}{h^2}\right)^{3/2}$

2) Vibration: $\nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$

$$\nu_e \propto \mu^{-1/2}$$

Heavier isotopic species sit lower in the potential well, has larger D_0 and also has smaller spacings in the vibrational ladder.





2)

Example :

H ₂	4395.24 cm ⁻¹
HD	3817.09
D ₂	3118.46
HT	3608.3
T ₂	2553.8

3) Rotation $\epsilon_J = B_e J(J+1)$

$$B_e = \frac{h^2}{2I} = \frac{h^2}{2\mu R_e^2}$$

$$B_e \propto \frac{1}{\mu}$$

different spacings between rotational levels for different isotopomers.

As a consequence, the equilibrium constant depends on isotopic masses especially in dissociation reactions:

$$AB = A + B$$

$$K = \left(\frac{2\pi kT}{h^2}\right)^{3/2} \left(\frac{m_A m_B}{m_{AB}}\right)^{3/2} \frac{q_A q_B}{q_{AB}} e^{+\Delta D_0/kT}$$

$$q^{AB} = \frac{kT}{B_e} \frac{1}{1 - e^{-h\nu/kT}}$$

or if using ΔD_e form

$$q^{AB} = \frac{kT}{B_e} \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}, \text{ and } K = \dots \dots e^{+\Delta D_e/kT}$$



mass-dependence of the equilibrium constants:
(continued) *Use D_e form since D_e is same*

$$\frac{K'}{K} = \frac{\left(\frac{m'_A m'_B}{m'_{AB}}\right)^{1/2} (1 - e^{-h\nu'/kT})}{\left(\frac{m_A m_B}{m_{AB}}\right)^{1/2} (1 - e^{-h\nu/kT})} \frac{e^{-h\nu/2kT}}{e^{-h\nu'/2kT}}$$

This $\frac{(u')^{1/2}}{(u)^{1/2}}$ But $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$

or $\frac{\nu}{\nu'}$

$$\frac{K'}{K} = \frac{u}{u'} e^{-(u-u')/2} \frac{1 - e^{-u'}}{1 - e^{-u}} \quad \text{where } u \equiv \frac{h\nu}{kT}$$

The limiting form at low T is $\left\{ \begin{array}{l} e^{-u} = 1 - u + \frac{u^2}{2} - \dots \\ 1 - e^{-u} \approx u + \dots \end{array} \right.$

$$\frac{K'}{K} \sim 1 + \frac{1}{2} (u' - u)$$

negative for heavier lighter

$$\frac{K'}{K} < 1$$

Diatomic molecule with the LIGHTER ISOTOPE dissociates more than the HEAVIER ONE.