



國立清華大學

化學工程學系

National Tsing Hua University  
Department of Chemical Engineering

# 2022 Summer School

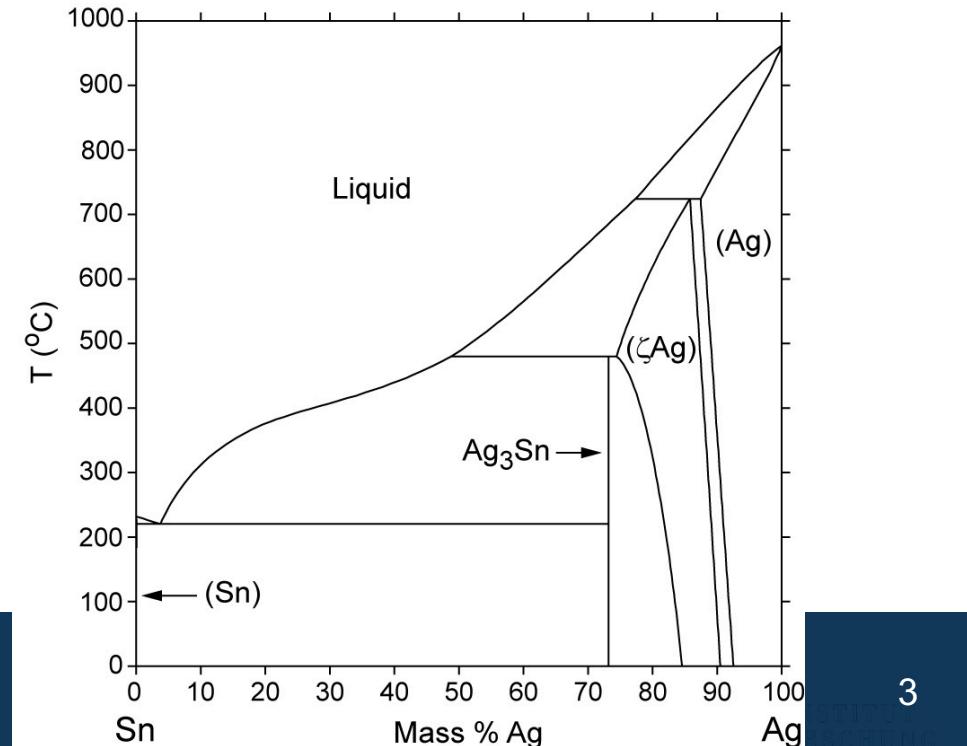
## Electronic Structure Calculations Using GFN2-xTB

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# Week 4. Thermodynamic properties

# What are thermodynamic properties?

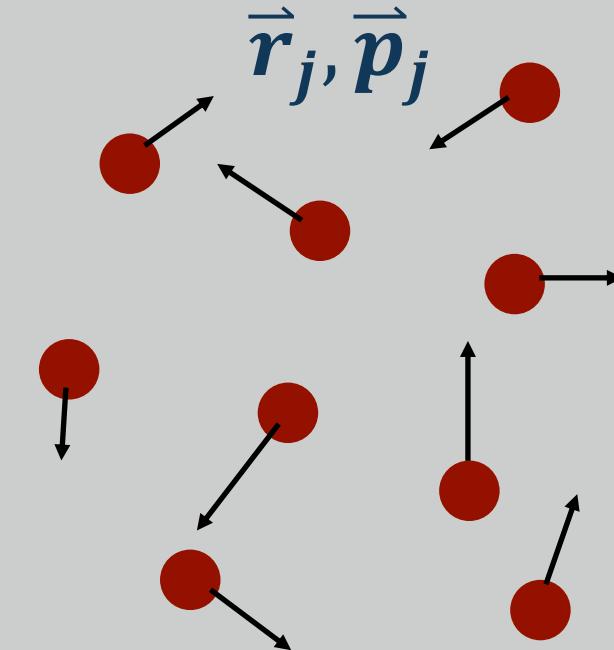
- Properties that specify the macroscopic states.
  - Intensive: temperature, pressure, density,...
  - Extensive: energy, free energy, volume, entropy,...
- Why is it important?
  - Define the macroscopic states
  - Spontaneous process
  - Stable phase



# Macroscopic vs microscopic description

$P, T, V, n_i$

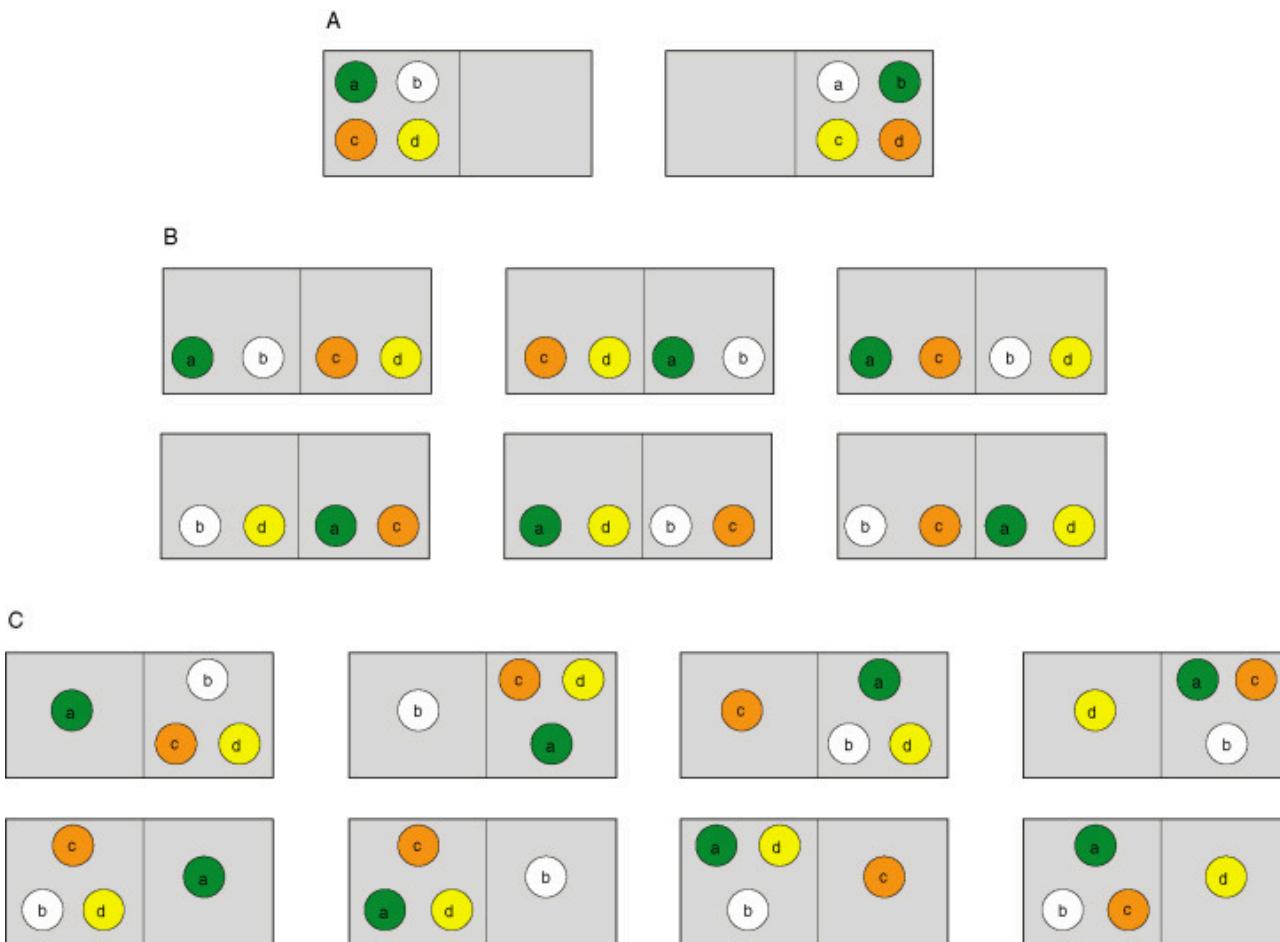
Macroscopic  
description



Microscopic  
description

- **A few vs  $6N$**  (phase space)
- Why only a few properties (variables) are necessary to determine a thermodynamic state?
- Is there a link between them?

# Ensemble theory



## Ensemble:

A collection of microstates that belong to the same macrostate (such as NVT, NVE, NPT,...).

## Postulation:

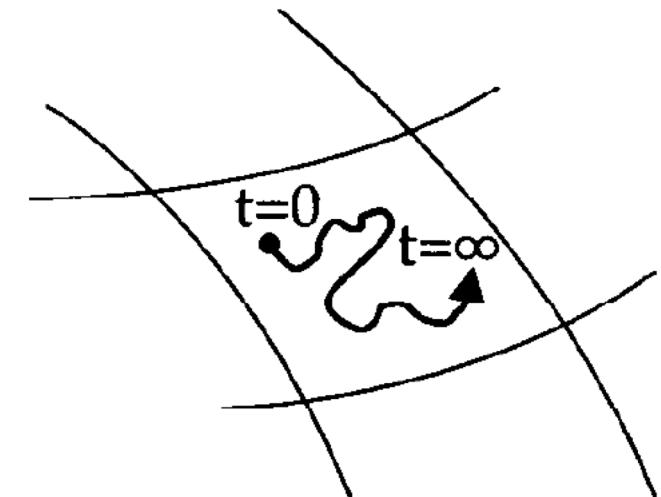
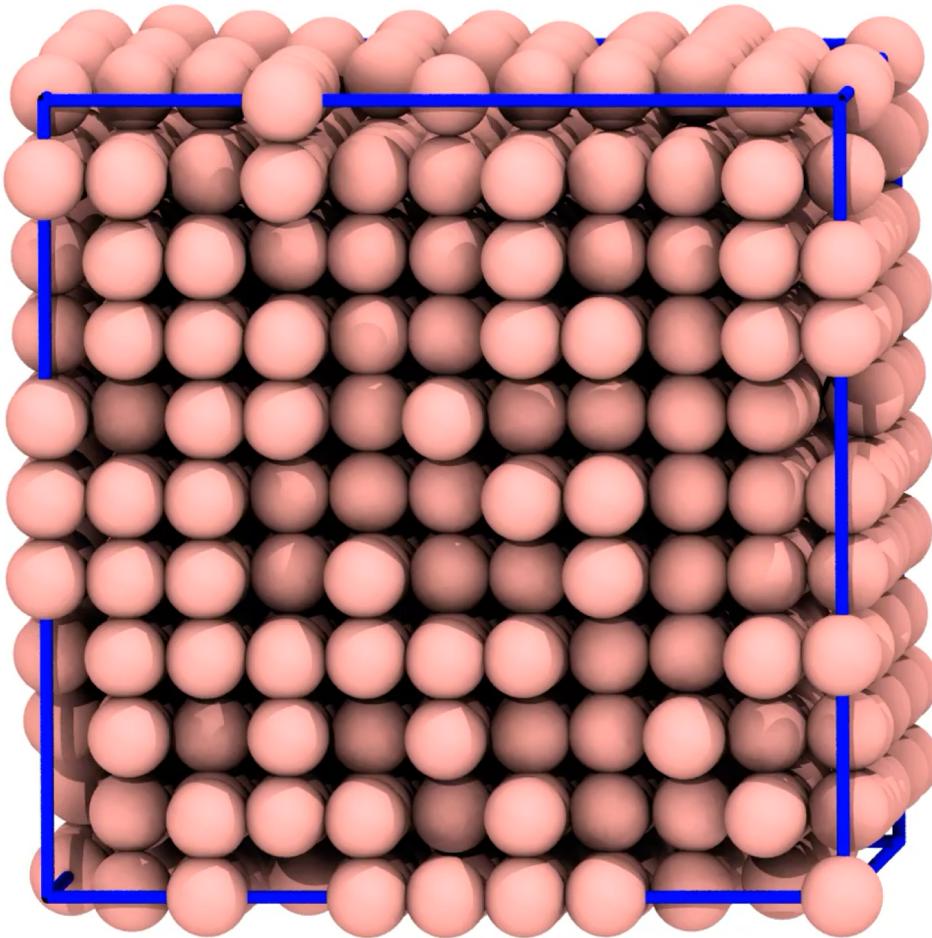
### 1. Ergodicity:

time average = ensemble average

### 2. Principle of equal a priori probabilities:

probability of all microstates are the same in NVE ensemble

# NVT MD simulations – Argon gas



phase space trajectory

# Canonical ensemble $NVT$

## Canonical ensemble:

A collection of microstates that belong to the macrostate specified by  $N$ ,  $V$  and  $T$ .

Partition function: 
$$Q(N, V, T) = \sum_j e^{-E_j(N, V)/k_B T}$$

the energy of the microstate  $j$

The Helmholtz free energy can be computed from  $Q(N, V, T)$ :

$$A = -k_B T \ln Q(N, V, T)$$

Using the relationship derived in classical thermodynamics, we could get all the thermodynamic variables.

# Other thermodynamic variables

Using  $A = -k_B T \ln Q(N, V, T)$  and  $dA = -SdT - pdV + \sum_{\alpha} \mu_{\alpha} dN_{\alpha}$

We get:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} = k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} + k_B \ln Q$$

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

$$\mu = -\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{\alpha \neq i}} = -k_B T \left(\frac{\partial \ln Q}{\partial N_i}\right)_{T,V,N_{\alpha \neq i}}$$

$$U = -k_B T \ln Q + T \left[ k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} + k_B \ln Q \right] = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}$$

$$U = A + TS$$

**BUT** how to compute Q?

# single-component ideal gas

The eigen-value problem of the whole system  $\hat{H}_{tot}\Psi_{tot} = E_{tot}\Psi_{tot}$

can be written as the sum of individual molecule:

$$\sum_i \hat{h}_i \Psi_{tot} = \sum_i \varepsilon_i \Psi_{tot}$$

there is no interaction term  $\hat{V}_{ij}$

Therefore, the NVT partition function of ideal gas with N molecules can be written as:

$$Q(N, V, T) = \sum_j e^{-E_j(N, V)/k_B T} = \frac{1}{N!} q^N$$

$$q = \sum_i e^{-\varepsilon_i/k_B T}$$

partition function of  
a single molecule

molecules are indistinguishable

**N-particle problem to 1-particle problem!**

# Quantum description of a molecule

We just simplify an N-particle problem to a one-particle problem, the problem left now is to evaluate  $q$ .

**RECALL:** Under **Born-Oppenheimer approximation**:

$$\Psi(\mathbf{r}, \mathbf{R}) = \varphi_e(\mathbf{r}; \mathbf{R}) \varphi_N(\mathbf{R}) \quad \hat{H}_{el}\varphi_e(\mathbf{r}; \mathbf{R}) = E_{el}\varphi_e(\mathbf{r}; \mathbf{R})$$

$$E_{DFT,xTB,\dots} = E_{el} + V_{NN} = E_{el} + \frac{1}{4\pi\epsilon_0} \sum \frac{Q_i Q_j}{|\mathbf{R}_i - \mathbf{R}_j|}$$

kinetic energy  
of electron

e-N  
attraction

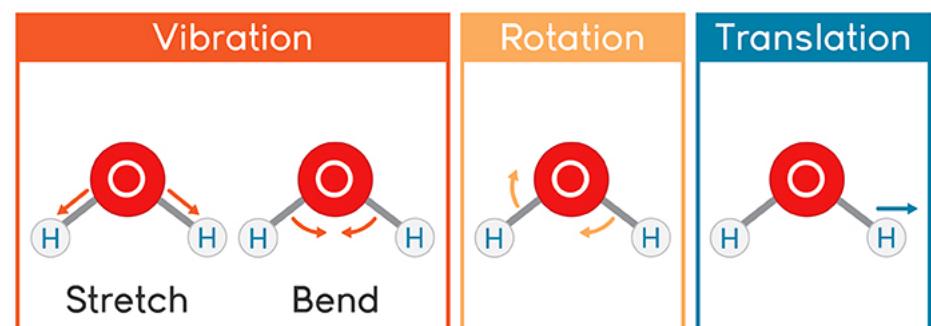
$$\hat{H}_{el} = \hat{T}_{el} + \hat{V}_{ee} + \hat{V}_{eN}$$

e-e repulsion

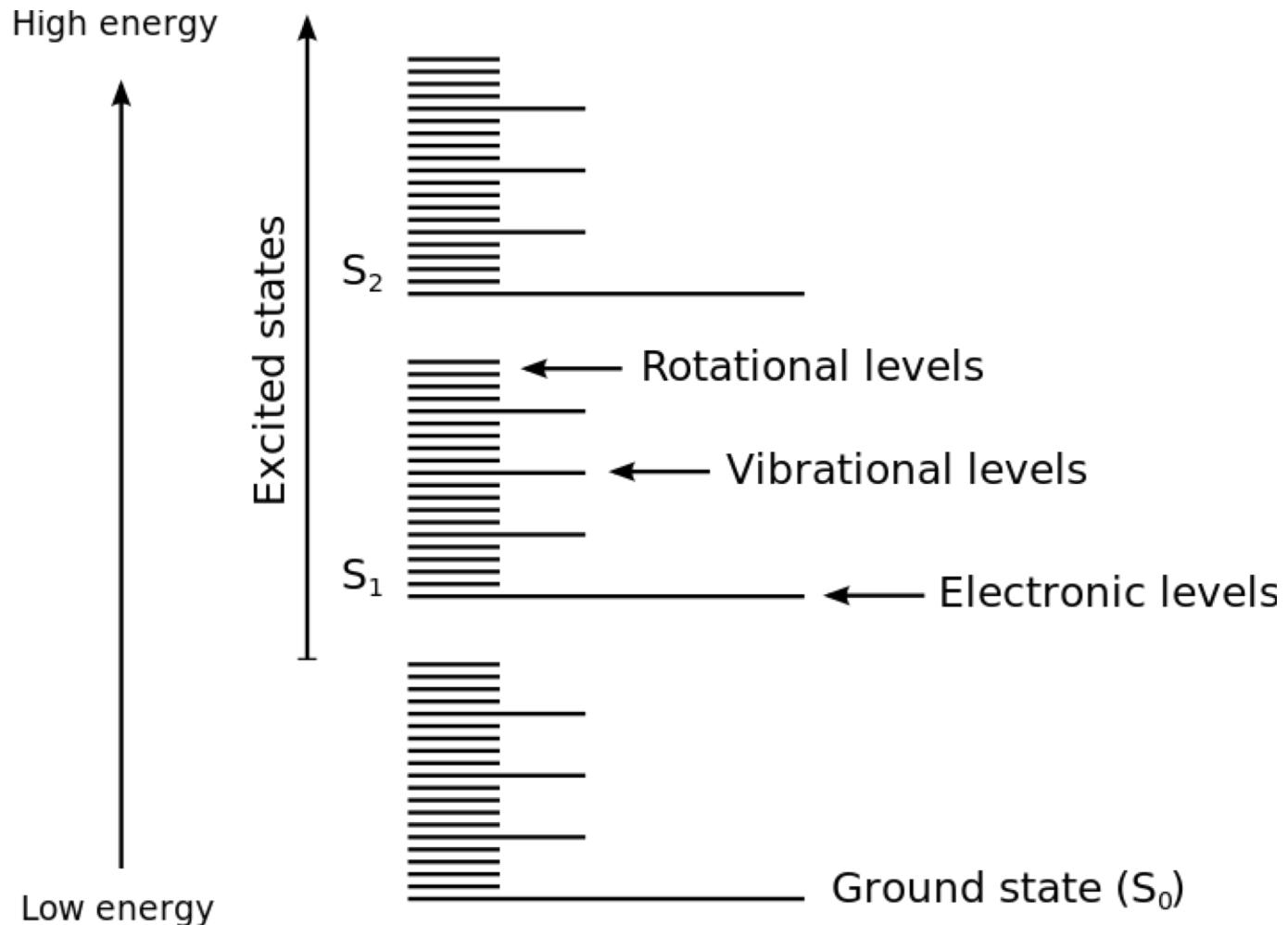
This is the total energy  
we get in xtb.out

We still need to evaluate nuclear kinetic energy  $\hat{T}_N$

$$\hat{T}_N = \hat{H}_{translation} + \hat{H}_{rotation} + \hat{H}_{vibration}$$

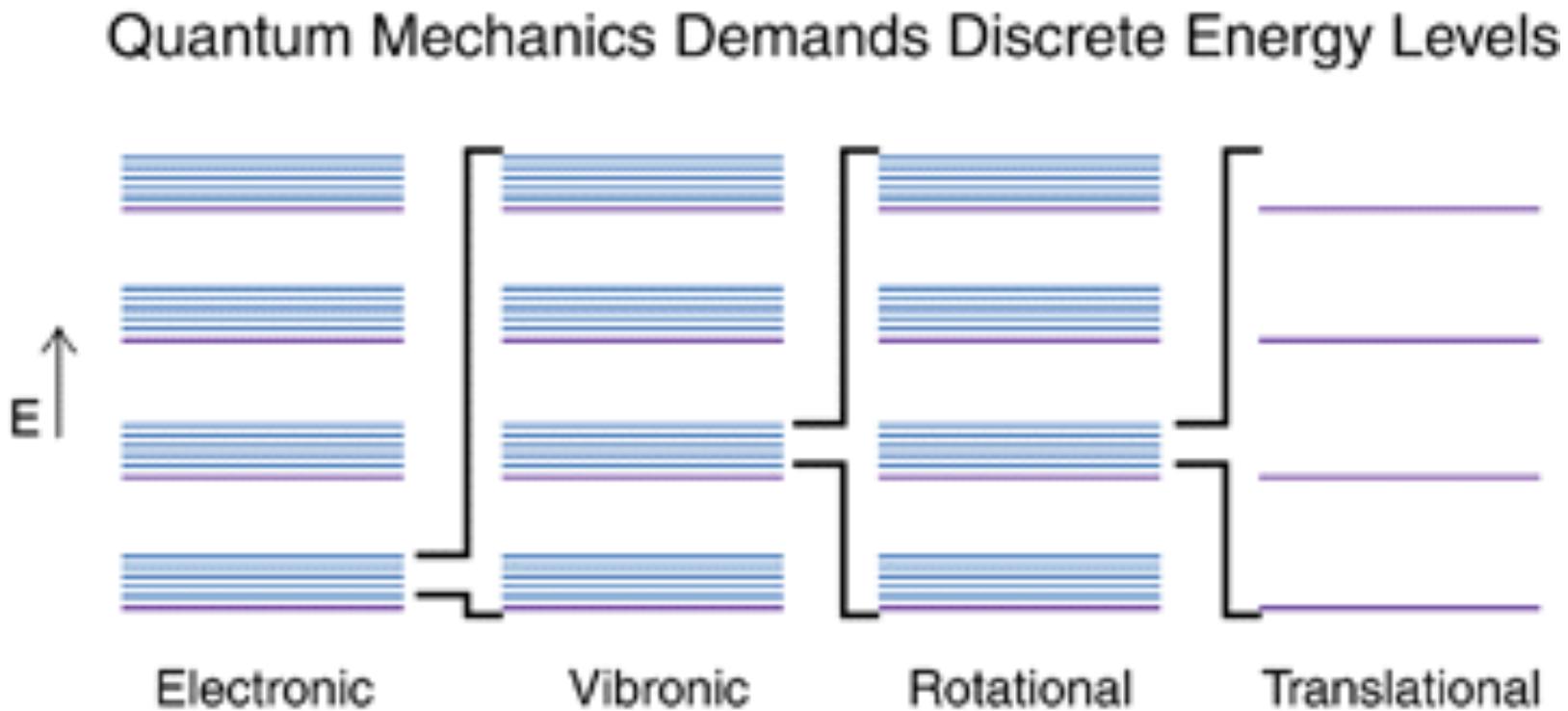


# Energy scale

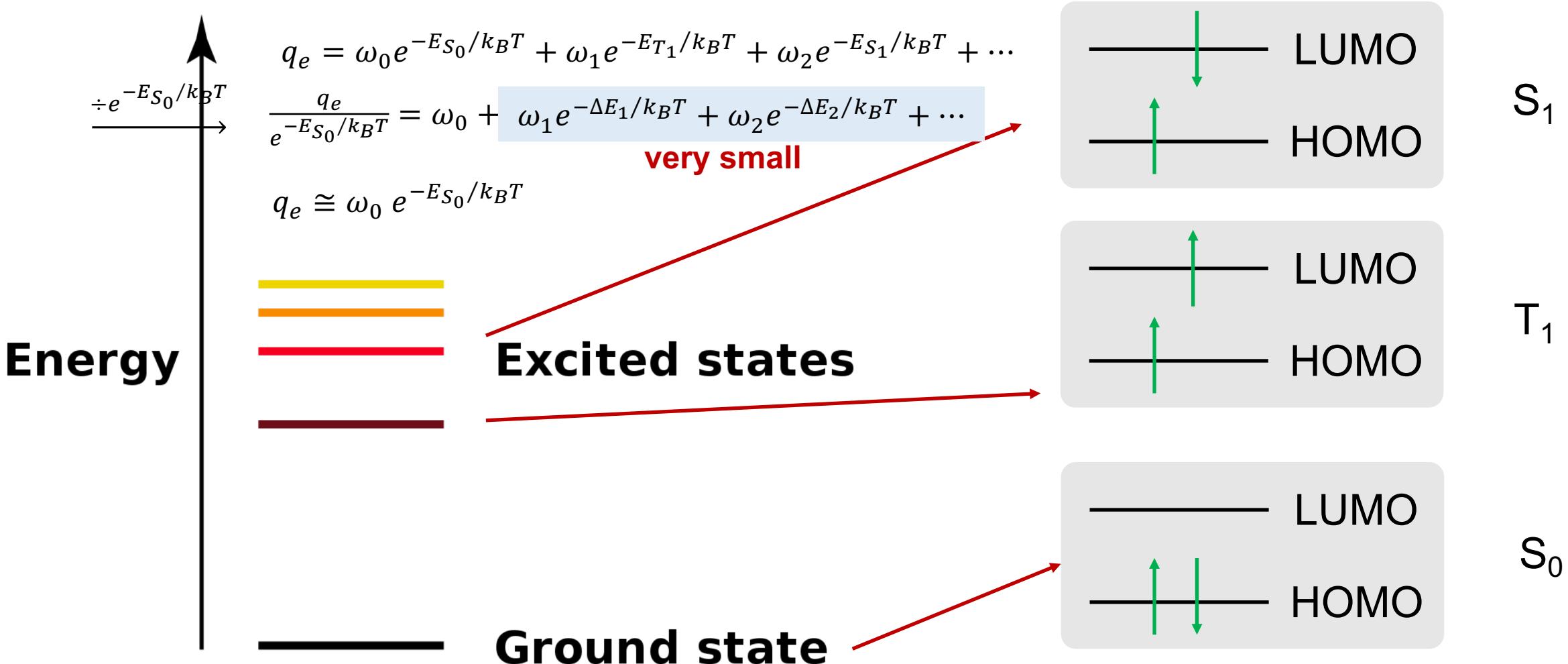


- Electronic ( $E_{S_0}, E_{S_1}, E_{S_2}, \dots$ )
  - UV-vis range
  - $\sim 1$  eV
- Vibrational ( $E_{\nu_0}, E_{\nu_1}, E_{\nu_2}, \dots$ )
  - IR range
  - $10^{-3} \sim 1$  eV
- Rotational ( $E_{J_0}, E_{J_1}, E_{J_2}, \dots$ )
  - Microwave to radiowave
  - $< 10^{-4}$  eV

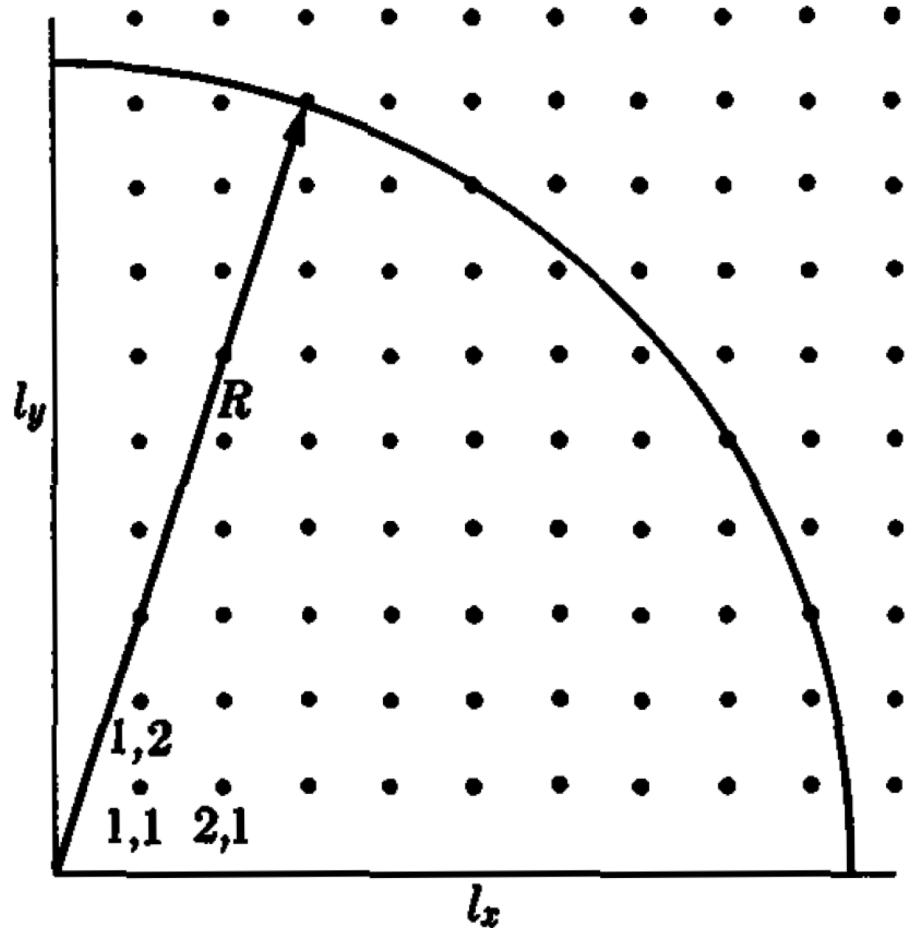
# Energy scale



# Electronic: electronic structure method



# Translation: 3D particle in a box

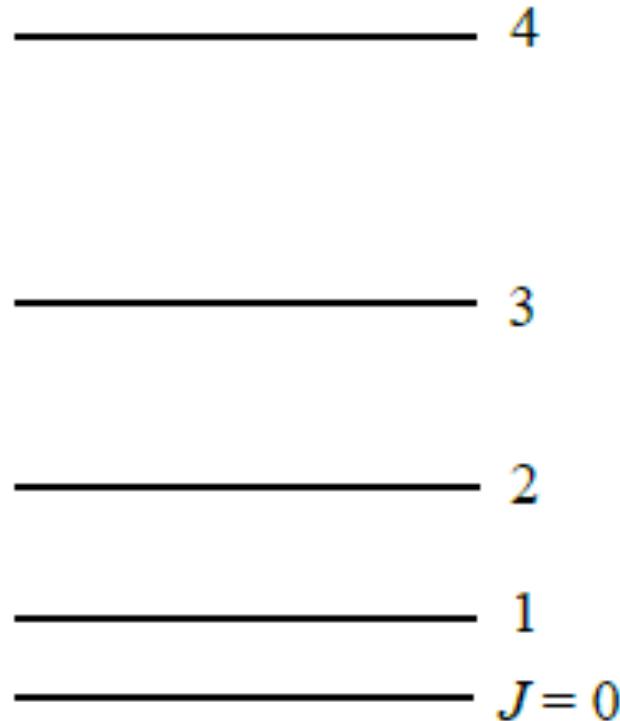


$$E_{n_x, n_y, n_z} = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

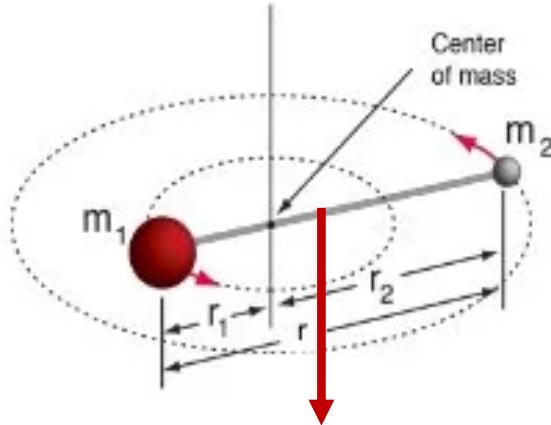
for cubic  $= \frac{\hbar^2}{8mV^{2/3}} (n_x^2 + n_y^2 + n_z^2)$

What is order of magnitude of the energy level difference for H<sub>2</sub>O molecule in a 1 cm<sup>3</sup> container?

# Rotation: rigid rotors



Bond length does not change in rigid rotor



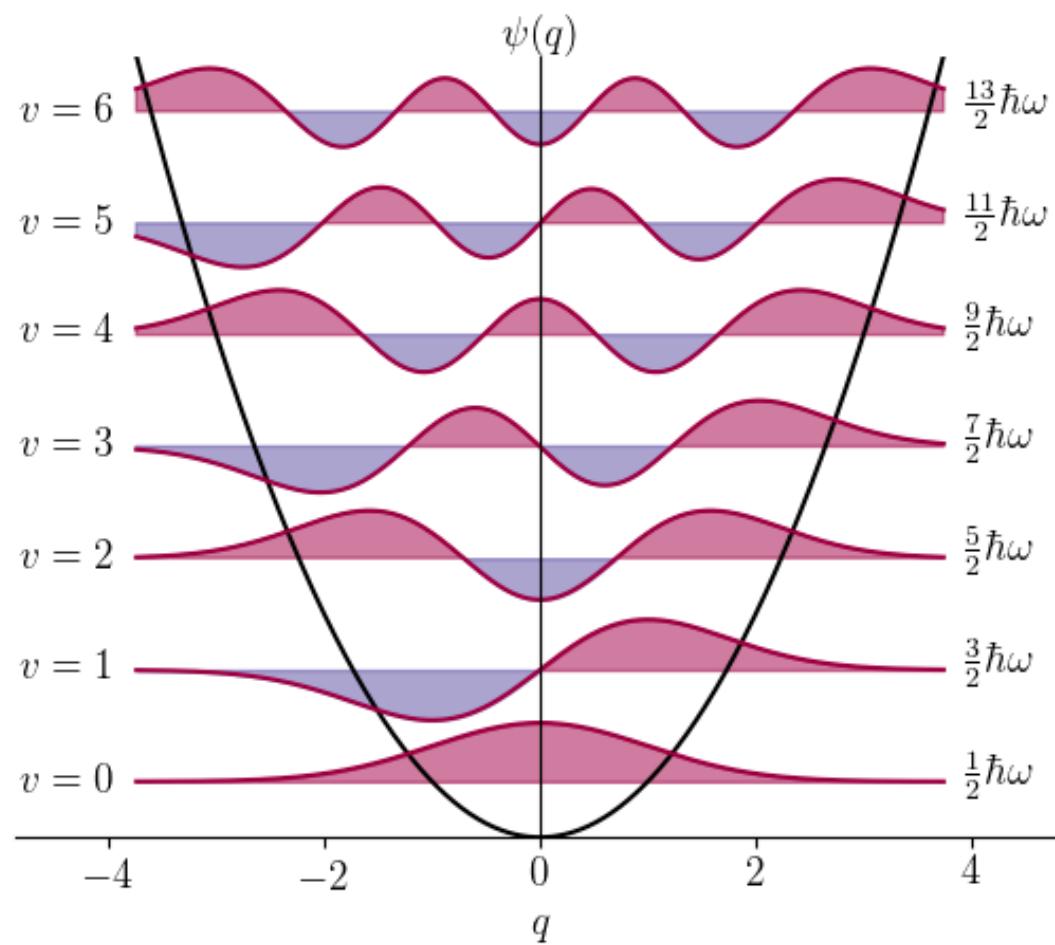
For special case ( $I_A = I_B = I_C$ )

$$E_{A,J} = J(J + 1) \frac{h^2}{8\pi^2 I_A}$$

$$\Omega_{A,J} = (2J + 1)^2$$

What is order of magnitude of the energy level difference for  $N_2$ ?

# Vibration: harmonic oscillators



Zero Point Energy (ZPE)

$$E_{\omega_j,n} = \hbar\omega_j \left( n + \frac{1}{2} \right)$$

What is order of magnitude of the energy level difference for C-H bond stretching ( $2800\text{cm}^{-1}$ )?

# Normal mode analysis

The vibrational motion of a N-atom molecule is **complicated!**

## Normal mode:

- all N atoms move *in phase* and *sinusoidally*.
- Normal modes  $\vec{Q}_i$  are orthogonal to each other  $\vec{Q}_j$ .
- There are  $3N-6$  (nonlinear),  $3N-5$  (linear) normal modes.

$$\vec{Q}_i \cdot \vec{Q}_j = \delta_{ij}$$

# Hessian matrix

In classical harmonic oscillator:

$$V = \frac{1}{2} k x^2$$

$$k = \frac{\partial^2 V}{\partial x^2}$$

*diagonalization*

$$\mathbf{H} = \begin{bmatrix} \frac{\partial^2 E_{xTB}}{\partial x_1^2} & \frac{\partial^2 E_{xTB}}{\partial x_1 \partial x_2} & \dots & \frac{\partial^2 E_{xTB}}{\partial x_1 \partial x_{3N}} \\ \frac{\partial^2 E_{xTB}}{\partial x_2 \partial x_1} & \frac{\partial^2 E_{xTB}}{\partial x_2^2} & \dots & \frac{\partial^2 E_{xTB}}{\partial x_2 \partial x_{3N}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E_{xTB}}{\partial x_{3N} \partial x_1} & \frac{\partial^2 E_{xTB}}{\partial x_{3N} \partial x_2} & \dots & \frac{\partial^2 E_{xTB}}{\partial x_{3N}^2} \end{bmatrix}_{3N \times 3N}$$

$$0 \quad 0$$

$k_1, k_2, k_3, k_4, k_5, k_6, k_7, k_8 \dots k_{3N}$

translation rotation vibration

3 3 3N-6

# Individual contributions

	Partition function	Entropy	Energy	Heat capacity
electronic	$q_e \cong \omega_0$ $\omega_0$ : spin multiplicity *The ground state energy is set to zero	$R \ln q_e$	0	0
translation	$q_t = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P}$	$R \left( \ln q_t + \frac{5}{2} \right)$	$\frac{3}{2} RT$	$\frac{3}{2} R$
rotation (linear)	$q_r = \frac{1}{\sigma_r} \left( \frac{T}{\Theta_r} \right); \Theta_r = \frac{h^2}{8\pi^2 I k_B}$ I: moment of inertia	$R(\ln q_r + 1)$	$RT$	$R$
rotation (nonlinear)	$q_r = \frac{\pi^{1/2}}{\sigma_r} \left( \frac{T^{3/2}}{(\Theta_{r,x}\Theta_{r,y}\Theta_{r,z})^{1/2}} \right)$	$R \left( \ln q_r + \frac{3}{2} \right)$	$\frac{3}{2} RT$	$\frac{3}{2} R$
vibration	$q_v = \prod_K \frac{e^{-\Theta_{v,K}/2T}}{1 - e^{-\Theta_{v,K}/T}}$ ; $\Theta_{v,K} = \frac{h\nu_K}{k_B}$ $\nu_K$ : frequency of mode K	$R \sum_K \left[ \frac{\Theta_{v,K}/T}{e^{\Theta_{v,K}/T} - 1} - \ln(1 - e^{-\Theta_{v,K}/T}) \right]$	$R \sum_K \Theta_{v,K} \times \left( \frac{1}{2} + \frac{1}{e^{\Theta_{v,K}/T} - 1} \right)$	$R \sum_K e^{\Theta_{v,K}/T} \times \left( \frac{\Theta_{v,K}/T}{e^{-\Theta_{v,K}/T} - 1} \right)^2$

# Hands-on: electronic structure and molecular properties

## Learning Goal

- Learn how to perform frequency computations for H<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub>.
- Calculate the thermodynamic properties of H<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub> at 1 atm and 298K.
- Calculate the Gibbs free energy changes of 3/2H<sub>2</sub> + 1/2N<sub>2</sub> → NH<sub>3</sub> at 1 atm and 298.15 K.

# Frequency computations for H<sub>2</sub>, N<sub>2</sub> and NH<sub>3</sub>

# Inputs and output of this exercise

The outputs of this exercise were uploaded on Github repository

- W4/freq

# Step-by-step operation

- There will be no detailed step-by-step operational tutorial this week. Only the general steps will be given.
- Frequency computations with unoptimized geometry

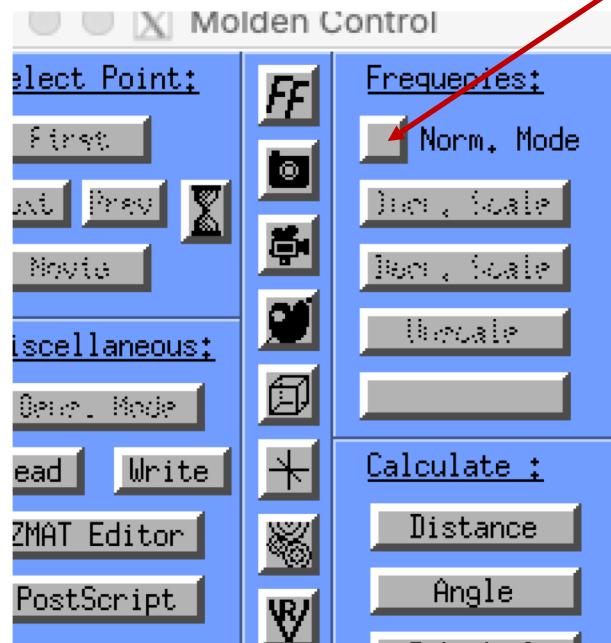
Perform frequency computations for  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{NH}_3$  molecules without xTB optimization (use the structure from Avogadro with FF optimization). You would need to put "--hess" in the command line of the xTB bash script.

- Frequency computations with optimized geometry

Perform frequency computations for  $\text{H}_2$ ,  $\text{N}_2$  and  $\text{NH}_3$  molecule. But in this time, optimize each molecule using xTB first before the frequency computation.

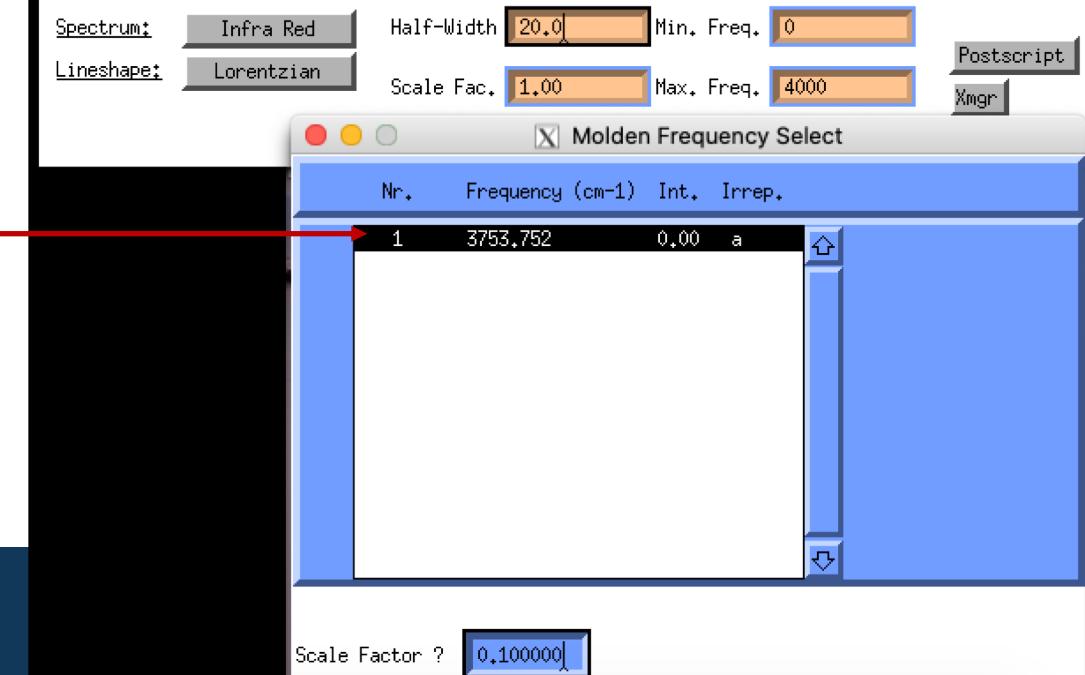
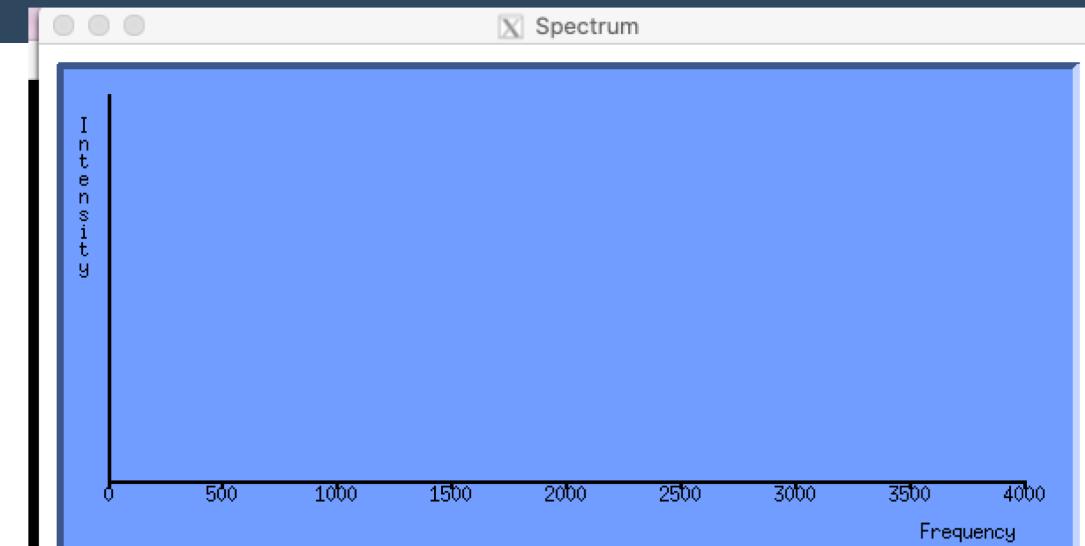
# Visualizing the vibrational modes

molden g98.out

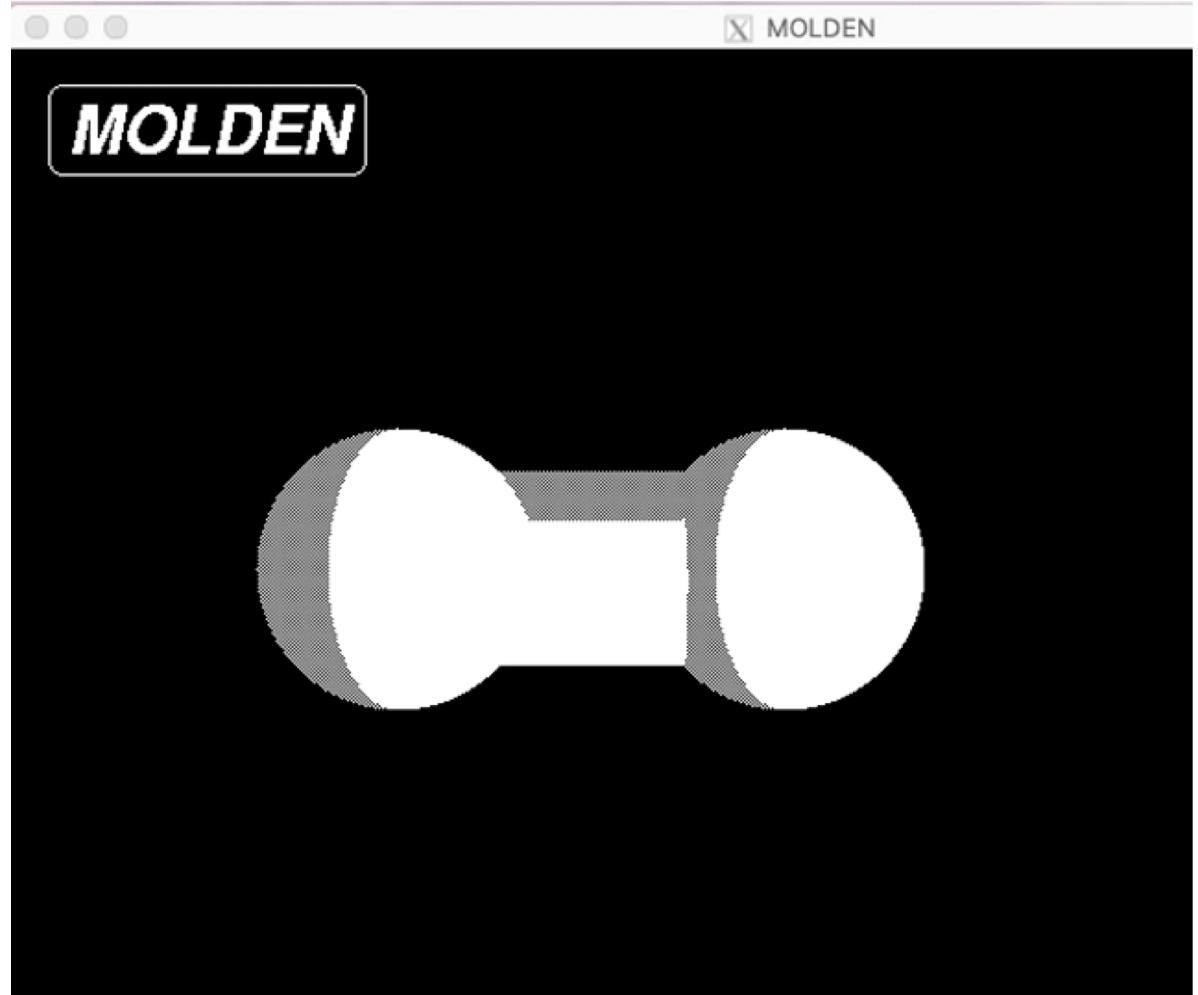
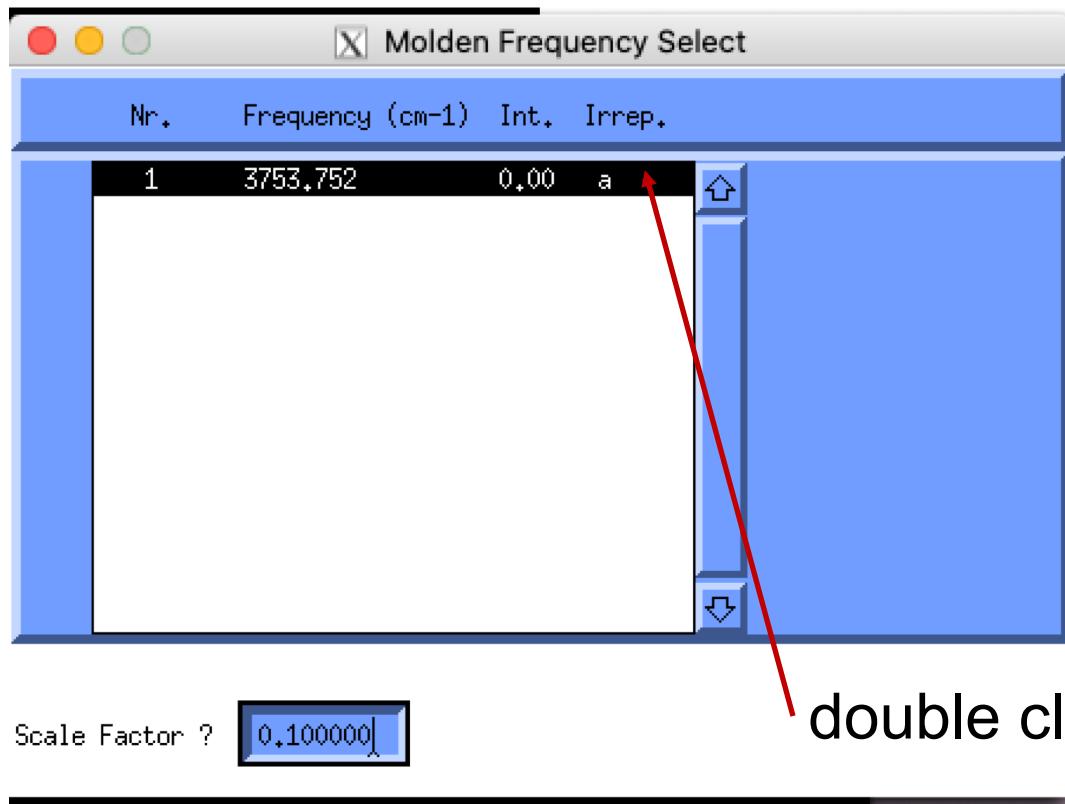


Click Norm. Mode

Summary of  
normal modes



# Visualizing the vibrational modes



# NM analysis results in xtb.out

First five is zero out.  
H<sub>2</sub> is linear (3N-5)

One vibrational mode

```
|-----|  
|          Frequency Printout          |  
|-----|  
vibrational frequencies (cm⁻¹)  
eigval : 0.00    0.00    0.00    0.00    0.00 3753.75  
reduced masses (amu)  
 1: 1.01  2: 1.01  3: 1.01  4: 1.01  5: 1.01  6: 1.01  
IR intensities (km·mol⁻¹)  
 1: 0.00  2: 0.00  3: 0.00  4: 0.00  5: 0.00  6: 0.00  
Raman intensities (amu)  
 1: 0.00  2: 0.00  3: 0.00  4: 0.00  5: 0.00  6: 0.00  
output can be read by thermo (or use thermo option).  
writing <g98.out> molden fake output.  
recommended (thermochemical) frequency scaling factor: 1.0
```

# Thermodynamics results in xtb.out

```
|           Thermodynamic Functions           |
|-----|
Molecule has the following symmetry elements: (i) (Cinf) (C2) 2*(sigma)
It seems to be the Dinfh point group ----->
din symmetry found (for desy threshold:  0.10E+00) used in thermo

.....
:           SETUP           :
:-----:
: # frequencies           1   -----> # of vib. modes
: # imaginary freq.       0   -----> # of vib. Modes with
: linear?                 true -----> imaginary frequency (why?)
: only rotor calc.        false
: symmetry                din
: rotational number        2   -----> # of rotational motion
: scaling factor           1.0000000
: rotor cutoff              50.0000000 cm-1
: imag. cutoff             -20.0000000 cm-1
:-----:
```

Identify the point group to be  $D_\infty$

# of vib. modes

# of vib. Modes with imaginary frequency (why?)

# of rotational motion

# Thermodynamics results in xtb.out

temperature used for computing Q

this is actually energy not enthalpy...

temp. (K)	partition function	enthalpy cal/mol	heat capacity cal/K/mol	entropy J/K/mol
298.15	VIB 1.00	0.000	0.000	0.000
	ROT 1.87	592.502	1.987	3.230
	INT 1.87	592.502	1.987	3.230
	TR 0.277E+25	1481.254	4.968	28.068
	TOT	2073.7556	6.9554	31.2976 130.9493
T/K	H(0)-H(T)+PV	H(T)/Eh	T*S/Eh	G(T)/Eh
298.15	0.330474E-02	0.118564E-01	0.148705E-01	-0.301410E-02
-----				
::: THERMODYNAMIC :::				
::: total free energy -0.985700278015 Eh :::				
::: total energy -0.982686174876 Eh :::				
::: zero point energy 0.008551677957 Eh :::				
::: G(RRH0) w/o ZPVE -0.011565781096 Eh :::				
::: G(RRH0) contrib. -0.003014103139 Eh :::				
::: :::: :::: :::: :::				

$$E_{DFT,xTB,\dots} = E_{el} + V_{NN}$$

$$E_{ZPE} = \sum_j \frac{1}{2} \hbar \omega_j$$

enthalpy

cumulative manner

correction for Gibbs energy

# Question set:

- Please compare the results from optimized and unoptimized structures, describe your observation.
- Visualize the vibrational modes of the three molecules and rationalize the results you obtain from xTB.
- Calculate the  $\Delta G$  of  $3/2\text{H}_2 + 1/2\text{N}_2 \rightarrow \text{NH}_3$  at 1 atm and 298.15K.
- Compare the calculated  $\Delta G$  with the exp. value. How different they are? What may be the reason of the discrepancy? Please rationalize your answer.

# Readings

- Statistical thermodynamics
  - Terrell L. Hill, An Introduction to Statistical Thermodynamics, Dover Publications, 1986
  - Donald A. McQuarrie, Statistical Mechanics, 1st ed., University Science Books, 2000
- Normal mode analysis
  - Chemistry LibreTexts, Normal Modes
  - <https://gaussian.com/vib>