

# Why quantum chemistry?

- The behavior of the particles is governed by the equation of motion, and its classical mechanical version is known as the Newton's law.
- The proper description of atoms, molecules, and electrons is given by the laws of quantum mechanics. For this reason, we need to consider the **Schrödinger equation**, which is a quantum-mechanical equation of motion.
- If the solutions of the Schrödinger equations are generated without reference to experimental data, the methods are usually called "ab initio" (latin: "from the beginning") or "first principle".

# The Schrödinger equation

- In chemistry or solid state physics, the fundamental interaction we are interested is the electrostatic interaction.
- Here we introduce three assumptions to the SE
  - i. time-independent
  - ii. non-relativistic
  - iii. Born-Oppenheimer approximation
- Under these approximations, the system of nuclei and electrons is described with a Hamiltonian below

$$\hat{H} = T_{\text{nuc}} + T_{\text{el}} + V_{\text{nuc-nuc}} + V_{\text{nuc-el}} + V_{\text{el-el}}$$

- These terms are written in the atomic unit as

$$T_{\text{nuc}} = \sum_{I=1}^L \frac{\nabla_I^2}{2M_I} \quad (\text{kinetic energy of nuclei})$$

$$T_{\text{el}} = \sum_{i=1}^N \frac{\nabla_i^2}{2} \quad (\text{kinetic energy of electrons})$$

$$V_{\text{nuc-nuc}} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|} \quad (\text{nuclei-nuclei repulsion})$$

$$V_{\text{nuc-el}} = - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \quad (\text{nuclei-electron attraction})$$

$$V_{\text{el-el}} = \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (\text{electron-electron repulsion})$$

- In this case, the Schrödinger equation becomes

$$\hat{H}_{\text{el}}(\{\mathbf{R}\})\Psi(\mathbf{r}, \{\mathbf{R}\}) = E_{\text{el}}(\{\mathbf{R}\})\Psi(\mathbf{r}, \{\mathbf{R}\})$$

- Here, one can make the direct functional relationship (or "mapping") between the nuclear coordinates  $\{\mathbf{R}\}$  and the electronic energy  $E_{\text{el}}$ .
- It is quite informative to visualize  $E_{\text{el}}(\{\mathbf{R}\})$  as the function of  $\{\mathbf{R}\}$ , which is often called **potential energy surface**.

# Dirac's bracket notation

- It is convenient to use the Dirac's "bra-ket notation" for wave functions and multi-dimensional integrals in electronic structure theory in order to simplify the notation.

The equivalences are defined as

$$\begin{aligned} |\Psi\rangle &\equiv \Psi, & \langle\Psi| &\equiv \Psi^* \\ \int d\mathbf{r} \Psi^* \Psi &= \langle\Psi|\Psi\rangle \\ \int d\mathbf{r} \Psi^* \hat{H} \Psi &= \langle\Psi|\hat{H}|\Psi\rangle \end{aligned}$$

- The ket  $|\Psi\rangle$  denotes a wave function while the bra  $\langle\Psi|$  denotes a complex conjugate wave function  $\Psi^*$ . The combined bracket denotes that the whole expression should be integrated over all coordinates.

# Hartree-Fock theory - Introduction

- Except for the simplest cases, there are no simple way to solve the SE in a closed analytical form so we have to solve it numerically.
- The SE is a second-order partial differential equation (PDE), so in principle it can be directly solve. However, this needs integration over a large number of dimensions ( $3 \times N_{\text{elec}}$ ), which is impossible.
- This difficulty can be solved by two approaches
  - i. Approximate the electron-electron interaction by the effective one-electron problem. This reduces the  $3N$  dim. integration to a sum of 3 dim. integrations.
  - ii. Expanding the wave function in some suitable basis set, as this will convert the PDE into a set of algebraic equations.
- The methodology based on above approaches is the **Hartree-Fock-Roothaan equation**, and is the basis of modern quantum chemistry calculations.

# Hartree product

- We are mainly interested in the electronic ground state energy  $E_0$ .
- There is an important quantum mechanical principle - the *Rayleigh-Ritz variational principle* - that provides a route to find approximate solutions for  $E_0$ .
- It states that the expectation value of  $\hat{H}$  of any  $\Psi$  is always higher than or equal to the exact  $E_0$ , i.e.

$$E_0 \leq \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

- So, the expectation value calculated by the wave function at your hand  $\Psi$  will always be an upper bound for the true ground state energy. By improving  $|\Psi\rangle$ , you will have a lower expectation value and that is closer to the true ground state energy.

- Since  $V_{\text{nuc-el}}$  is an effective external potential for an electron, we write it

$$v_{\text{ext}}(\mathbf{r}) = - \sum_I \frac{Z_I}{|\mathbf{r} - \mathbf{R}_I|}$$

- And we define the one-electron Hamiltonian

$$\hat{h}(\mathbf{r}) = -\frac{\nabla^2}{2} + v_{\text{ext}}(\mathbf{r})$$

- Then one can form the one-electron SE as

$$\hat{h}(\mathbf{r})\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

- In this case, the  $N$ -electron wave function can be expressed by the product of  $\psi_i$  as

$$\Psi_{\text{HP}}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \cdots \psi_N(\mathbf{r}_N)$$

- This wave function is called **Hartree product**, and it is a first crude guess for the true  $N$ -electron wave function.
- Note that  $\psi_i$  is orthonormal thus  $\langle \psi_i(\mathbf{r}) | \psi_j(\mathbf{r}) \rangle = \delta_{ij}$ .



## Spatial and spin orbitals

- The one-electron wave function  $\psi_i(\mathbf{r})$  is called the *orbital*, and the Hartree product means that  $N$ -electron wave function is expressed by the product of orbitals.
- Up to now we assumed that the orbital depends only on  $\mathbf{r}$ , but an electron has the spin degree of freedom. We write this spin variable by  $\omega$ , and combine it with the spatial coordinate  $\mathbf{r}$  as  $\mathbf{x} = (\mathbf{r}, \omega)$ .

- Let the one-electron wave function in  $\mathbf{x}$  as  $\chi_i(\mathbf{x})$ .
- Assuming that  $\mathbf{r}$  and  $\omega$  are independent, we have  $\chi_i(\mathbf{x}) = \psi_i(\mathbf{r})\sigma_i(\omega)$ , where  $\psi$  and  $\sigma$  denote the spatial and spin parts.
- $\chi, \phi, \sigma$  are a spin orbital, spatial orbital, and spin function.
- Since an electron have no chance to take both  $\alpha$  and  $\beta$  spin simultaneously, following integration over the spin variable holds.

$$\int d\omega \alpha^*(\omega) \alpha(\omega) = 1$$

$$\int d\omega \beta^*(\omega) \beta(\omega) = 1$$

$$\int d\omega \alpha^*(\omega) \beta(\omega) = 0$$

$$\int d\omega \beta^*(\omega) \alpha(\omega) = 0$$

# Hartree equation

- Using the spin orbital  $\chi$  above, we determine the expectation value of the Hamiltonian

$$\hat{H} = \hat{h}(\mathbf{r}) + \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

with respect to the Hartree product. This becomes

$$\begin{aligned} \langle \Psi_{\text{HP}} | \hat{H} | \Psi_{\text{HP}} \rangle &= \sum_{i=1}^N \int d\mathbf{x} \chi_i^*(\mathbf{x}) \hat{h}(\mathbf{r}) \chi_i(\mathbf{x}) \\ &+ \frac{1}{2} \sum_{i=1}^N \int d\mathbf{x} d\mathbf{x}' \chi_i^*(\mathbf{x}) \chi_j^*(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \chi_i(\mathbf{x}) \chi_j(\mathbf{x}') \\ &+ V_{\text{nuc-nuc}} \end{aligned}$$

- Now we minimize this w.r.t.  $\chi_i(\mathbf{x})$  under the constraint that  $\chi_i^*(\mathbf{x})$  is normalized.
- This is a typical variational problem with the constraint taken into account via *Lagrange multipliers*, which gives

$$\frac{\delta}{\delta \chi_i^*} \left[ \langle \Psi_{\text{HP}} | \hat{H} | \Psi_{\text{HP}} \rangle - \sum_{i=1}^N \{ \epsilon_i (1 - \langle \chi_i | \chi_i \rangle) \} \right] = 0$$

- The  $\epsilon_i$  act as Lagrange multipliers ensuring the normalization of  $\chi_i(\mathbf{x})$ . This leads to the so-called **Hartree equation** as

$$\left[ \hat{h} + \sum_{j=1}^N \int d\mathbf{x}' \chi_j^*(\mathbf{x}') \chi_j(\mathbf{x}') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right] \chi_i(\mathbf{x}) = \epsilon_i \chi_i(\mathbf{x})$$

- This shows that an effective one-electron SE is solved for an electron embedded in the electrostatic field of all electrons (including itself).

# Hartree potential

- Using the electron density

$$\rho(\mathbf{r}) = \sum_{i=1}^N \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r})$$

the *Hartree potential*  $\hat{v}_H$  can be defined as

$$\hat{v}_H(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

which corresponds to the electrostatic potential of all electrons. With  $\hat{v}_H$ , the Hartree equation can be written as

$$\left[ \hat{h} + \hat{v}_H \right] \chi_i(\mathbf{x}) = \epsilon_i \chi_i(\mathbf{x})$$

## Self-consistent field

- The Hartree equation have the form of one-electron SE. However, the solutions  $\chi_i(\mathbf{x})$  enter the effective one-particle Hamiltonian via  $\hat{v}_H$ .
- This dilemma can be resolved in an iterative fashion: One starts with some initial guess for the wave functions which enter the effective one particle Hamiltonian. The Hartree equations are then solved and a new set of solutions are determined.
- This cycle is repeated so often until the iterations no longer modify the solutions, i.e. self-consistency is reached. Such method is known as **self-consistent field (SCF)** method.

## Hartree-Fock method

- The Hartree product obeys the Pauli' exclusion principle only to some extent.
- In the Hartree product wave function, each electronic state is occupied by one electron. However, it does not take into account the anti-symmetry character of the wave function, which is also required by the Pauli principle.
- This requires that the sign of wave function should change when two electrons are exchanged; this is anti-symmetric character of the electronic wave function.



# Slater determinant

- The anti-symmetric problem can be fixed by replacing the product of the one-electron wave function by the determinant of them. This is called a **Slater determinant**, and it has the form of

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \cdots & \chi_1(\mathbf{x}_N) \\ \vdots & \ddots & \vdots \\ \chi_N(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

- For example in two-electron case,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) \quad (\text{Hartree product})$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_1(\mathbf{x}_1) \quad (\text{Slater determinant})$$

- Then the expectation value of the Hamiltonian with the Slater determinant is

$$\begin{aligned}
\langle \Psi | H | \Psi \rangle = & \sum_{i=1}^N \int d\mathbf{r} \psi_i^*(\mathbf{r}) \hat{h} \psi_i(\mathbf{r}) \\
& + \frac{1}{2} \sum_{i,j=1}^N \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}') \\
& - \frac{1}{2} \sum_{i,j=1}^N \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \delta_{\omega_i, \omega_j} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}') \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}) \\
& + V_{\text{nuc-nuc}}
\end{aligned}$$

where Kronecker delta  $\delta_{\omega_i, \omega_j}$  is coming from the integration in the spin variable.

- Just like the Hartree equation, we minimize the expectation value with respect to  $\psi^*$  under the constraint of normalization. This gives the **Hartree-Fock equation** as

$$\left[ \hat{h} + \hat{v}_H(\mathbf{r}) \right] \psi_i(\mathbf{r}) - \sum_{j \neq i} \int d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_j^*(\mathbf{r}') \psi_i(\mathbf{r}') \psi_j(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

- The last term of the left-hand side corresponds to the *exchange interaction* of electrons, as it exchanges  $\psi_i$  into  $\psi_j$  when it applies to  $\phi_i$ . This term arises by replacing the Hartree product into the determinant, and has purely quantum-mechanical character (no classical-mechanics interpretation)
- $\delta_{\omega_i, \omega_j}$  in this term means that the exchange interaction is only present among the electrons of same spin.
- By using the *Fock operator*  $\hat{f}$ , the HF equation becomes

$$\hat{f}(\mathbf{x})\chi(\mathbf{x}) = \epsilon_i \chi(\mathbf{x})$$

# Hartree-Fock-Roothaan equation

- The HF equation is a very complicated integro-differential equation, so we expand  $\chi_i$  with a suitable basis set  $\tilde{\chi}_i$  as

$$\chi_i(\mathbf{x}) = \sum_{\mu=1}^K C_{\mu i} \tilde{\chi}_{\mu}(\mathbf{x})$$

- Where  $C_{\mu i}$  is the expansion coefficient. Lets' introduce the overlap and Fock integrals

$$S_{\mu\nu} = \int d\mathbf{x} \tilde{\chi}_{\mu}(\mathbf{x}) \tilde{\chi}_{\nu}(\mathbf{x}), \quad F_{\mu\nu} = \int d\mathbf{x} \tilde{\chi}_{\mu}(\mathbf{x}) \hat{f}(\mathbf{x}) \tilde{\chi}_{\nu}(\mathbf{x})$$

- Then the HF equation becomes the **Hartree-Fock-Roothaan** equation

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \quad \text{or} \quad \mathbf{FC} = \mathbf{SC}\epsilon$$

- This is a general eigenvalue problem, and easily solved.
- As  $\mathbf{F}$  depends on  $\mathbf{C}$ , it should be solved by the SCF manner.

# Basis set

- Quantum chemical methods usually describe the electrons by a localized basis set.
- Historically, two localized basis set is commonly known
  - i. Slater type functions:  $\exp(-\alpha r_{iI})$
  - ii. Gaussian type functions:  $\exp(-\alpha r_{iI}^2)$ .
- $\alpha$  is the exponent of the function and  $r_{iI}$  is the distance between the electron  $i$  and the nucleus  $I$ .
- The Gaussian type function is more often used because they allow the analytic evaluation of the matrix elements necessary to perform an electronic structure calculation.
- In GAUSSIAN, only the Gaussian type function is used.

# Electron correlation

- The Hartree-Fock method generates solutions to the Schrodinger equation where the real electron-electron interaction is replaced by an average interaction.
- In a sufficiently large basis set, the HF wave function accounts for ~99% of the total energy.
- The remaining 1% is often very important for describing chemical phenomena such as chemical bond formation or breaking.
- The difference in energy between the HF and the lowest possible energy in the given basis set is called the **electron correlation energy**.
- As the HF solution usually gives ~99% of the correct answer, electron correlation methods normally use the HF wave function as a starting point for improvements.

# Density Functional Theory

- A *function* is a prescription for producing a number from a set of *variables*.
- A *functional* is a prescription for producing a number from a *function*, which in turn depends on variables.
- A wave function and the electron density are thus *functions*, while the energy depending on a wave function or an electron density is a *functional*.
- We will denote a function depending on a set of variables  $\mathbf{x}$  with  $f(\mathbf{x})$ , while a functional depending on a function  $f$  is denoted as  $F[f]$ .

# Orbital-free DFT

- The electronic energy functional of electron density  $\rho$  can be divided into three parts
  - kinetic energy functional  $T[\rho]$
  - the nuclei-electron attraction energy functional  $E_{ne}[\rho]$
  - the electron-electron repulsion energy functional  $E_{ee}[\rho]$ .
- With reference to the Hartree-Fock theory,  $E_{ee}[\rho]$  may be divided into Coulomb and exchange parts,  $J[\rho]$  and  $K[\rho]$ .
- Among these energy functionals,  $E_{ne}[\rho]$  and  $J[\rho]$  can be interpreted by the classical electrodynamics,

$$E_{ne}[\rho] = - \sum_i^{N_{nuc}} \int \frac{Z_a(R_a)\rho(\mathbf{r})}{|\mathbf{R}_a - \mathbf{r}|} d\mathbf{r} \quad J[\rho] = \frac{1}{2} \int \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$



- Here, the factor of 1/2 in  $J[\rho]$  allows the integration to be done over all space for both  $\mathbf{r}$  and  $\mathbf{r}'$  variables. Unlike these energy components, exchange part  $K[\rho]$  can only be interpreted by the quantum mechanics.
- Early attempts of deducing functionals for the kinetic and exchange energies considered a uniform electrons gas where it may be shown that  $T[\rho]$  and  $K[\rho]$  are given by Thomas, Fermi, and Dirac as

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(\mathbf{r}) d\mathbf{r} \quad K_D[\rho] = -C_X \int \rho^{4/3}(\mathbf{r}) d\mathbf{r} \quad C_F = \frac{3}{10} (3\pi^2)^{2/3}, \quad C_X = \frac{3}{4} \left( \frac{3}{\pi} \right)^{1/3}$$

- Since  $T[\rho]$  and  $K[\rho]$  functionals are depending directly on the electron density, these methods are called *orbital-free DFT*, as opposed to the Kohn-Sham theory discussed in the next section.
- Unfortunately, the accuracy of the orbital-free DFT is too low to be of general use.

# Kohn-Sham theory

- The main drawback in the orbital-free DFT is the poor representation of the kinetic energy.
- The idea in the Kohn-Sham formalism is to split the kinetic energy functional into two parts, one which can be calculated exactly, and a small correction term.
- Assume for the moment a Hamiltonian operator of the form with  $0 \leq \lambda \leq 1$ .

$$H_\lambda = \mathbf{T} + \mathbf{V}_{ext}(\lambda) + \lambda \mathbf{V}_{ee}$$

- The external potential operator  $\mathbf{V}_{ext}$  is equal to  $\mathbf{V}_{ee}$  for  $\lambda = 1$ , but for intermediate  $\lambda$  value it is assumed that  $\mathbf{V}_{ext}(\lambda)$  is adjusted such that the same density is obtained for  $\lambda = 1$  (the real system), for  $\lambda = 0$ .

- For the  $\lambda = 0$  case, the electrons are non-interacting, and the exact solution to the Schrodinger equation is given as a Slater determinant.
- The exact kinetic energy functional is

$$T_{KS} = \sum_i^{N_{el}} \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_i \rangle$$

- The  $\lambda = 1$  corresponds to interacting electrons, and Eq.X is therefore only an approximation to the real kinetic energy.
- The key to Kohn-Sham theory is to calculate the kinetic energy under the assumption of non-interacting electrons.
- The remaining kinetic energy is absorbed into an exchange-correlation term, and a general DFT energy expression can be written as

$$E_{DFT}[\rho] = T_{KS}[\rho] + E_{ne}[\rho] + J[\rho] + E_{XC}[\rho]$$

# Gradient methods and molecular property

- Once the electronic energy is obtained by solving the electronic Schrodinger equation, a number of molecular properties, perhaps the most important being the equilibrium molecular geometry, can be determined.
- The calculation of molecular or crystal structures is a variable supplement to experimental data in areas of structural chemistry such as X-ray crystallography, electron diffraction, and microwave spectroscopy.
- Calculation of derivatives of the potential energy with respect to nuclear coordinates is crucial to the efficient determination of equilibrium structures.
- The derivatives can be computed numerically by calculating the potential energy at many geometries and determining the change in energy as each nuclear coordinate is varied.

# Energy derivatives

- For a diatomic molecule, the molecular potential energy  $E$  depends only on the internuclear distance  $R$ ; therefore, to find the potential minimum (or in general the energy stationary point) we need to locate a zero in  $dE/dR$ .
- The search is more complicated for polyatomic molecules because the potential energy is a function of many nuclear coordinates,  $q_i$ .
- At the equilibrium geometry, each of the forces  $f_i$  exerted on a nucleus by electrons and other nuclei must vanish:

$$f_i = -\frac{\partial E}{\partial q_i} = 0 \text{ (for all } i\text{)}$$

- Therefore, in principle, the equilibrium geometry can be found by computing all the forces at a given molecular geometry and seeing if they vanish.

# Hessian

- A zero gradient characterizes a stationary point on the surface, but does not tell whether it is minima, maxima, or saddle points.
- To distinguish the types of stationary points, it is necessary to consider the second derivatives of the energy with respect to the nuclear coordinates.
- The quantities  $\partial^2 E / \partial q_i \partial q_j$  comprise the **Hessian or Hesse matrix**.
- A maximum (minimum) of a multi-dimensional potential energy surface is characterized by the eigenvalues of the Hessian all being positive (negative).
- A transition state (a first-order saddle point) correspond to one negative eigenvalue and all the rest positive.

## Transition state

- The transition state (TS) is a point on the PES connecting the two energy minima.
- A clear example of this is that the bond dissociation or formation process (Fig.X).
- The minimum at right corresponds to the state that has the O-H bond in this example, while the left minimum corresponds to the state with N-H bond.
- There is a saddle point between them, and the activation energy ( $E_a$ ) can be measured by the energy difference between minima and the saddle point.

## Activation energy

- When we have the  $E_a$ , we can calculate the rate constant of the chemical reaction by Arrhenius equation as

$$k = A \exp \left( -\frac{E_a}{RT} \right)$$

where  $A$  is the pre-exponential factor and  $R$  is the gas constant.

- $A$  is less dependent to molecular species, but  $E_a$  is highly dependent.
- Therefore obtaining the transition state structure is critically important topic in the chemical reaction.



# Thermodynamics

- The important thermodynamics quantities such as enthalpy, entropy, Gibbs free energy has contributions from translational, electronic, rotational, and vibrational motions of molecules.
- To calculate them, the partition function  $q(V, T)$  is needed.
- From  $q(V, T)$  to these quantities, the entropy  $S$ , internal energy  $E$ , and heat capacity  $C_V$  is obtained as

$$S = R + R \ln q + RT \left( \frac{\partial \ln q}{\partial T} \right)_V$$

$$E = RT^2 \left( \frac{\partial \ln q}{\partial T} \right)_V$$

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{N,V}$$

# Partition functions

- The translation partition function is

$$q_{\text{trans}} = \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

- For the non-linear polyatomic molecule, the rotational partition function is

$$q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma_{\text{rot}}} \left[ \frac{T^{3/2}}{\Theta_{\text{rot,x}}^{1/2} \Theta_{\text{rot,y}}^{1/2} \Theta_{\text{rot,z}}^{1/2}} \right]$$

- The vibrational partition function (for mode  $i$ ) and overall one is

$$q_{\text{vib},i} = \frac{\exp(-\Theta_i/2T)}{1 - \exp(-\Theta_i/T)}$$
$$q_{\text{vib}} = \prod_i \frac{\exp(-\Theta_i/2T)}{1 - \exp(-\Theta_i/T)}$$