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

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

- These terms are written in the atomic unit as

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\begin{align*}
T_{\rm nuc} &= \sum_{I=1}^L\frac{\nabla_I^2}{2M_I} &\text{(kinetic energy of nuclei)} \\
T_{\rm el}  &= \sum_{i=1}^N\frac{\nabla_i^2}{2} &\text{(kinetic energy of electrons)} \\
V_{\rm nuc-nuc} &= \frac{1}{2}\sum_{I \ne J}\frac{Z_I Z_J}{|{\bf R}_I - {\bf R}_J|} &\text{(nuclei-nuclei repulsion)} \\
V_{\rm nuc-el} &= -\sum_{i,I}\frac{Z_I}{|{\bf r}_i - {\bf R}_I|} &\text{(nuclei-electron attraction)} \\
V_{\rm el-el} &= \frac{1}{2}\sum_{i \ne j}\frac{1}{|{\bf r}_i - {\bf r}_j|} &\text{(electron-electron repulsion)}
\end{align*}
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- In this case, the Schrödinger equation becomes

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\hat{H}_{\rm el}(\left\{ {\bf R} \right\}) \Psi({\bf r}, \left\{ {\bf R} \right\}) = E_{\rm el}(\left\{ {\bf R} \right\}) \Psi({\bf r}, \left\{ {\bf R} \right\})
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- Here, one can make the direct functional relationship (or "mapping") between the nuclear coordinates $\{\mathbf{R}\}$ and the electronic energy $E_{\rm el}$.

- It is quite informative to visualize $E_{\rm el}(\{\mathbf{R}\})$ as the function of $\{\mathbf{R}\}$, which is often called **potential energy surface**.

Dirac's braket 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

$$|\Psi\rangle \equiv \Psi, \quad \langle\Psi| \equiv \Psi^*$$

$$\int d\mathbf{r}\,\Psi^*\Psi = \langle\Psi|\Psi\rangle$$

$$\int d\mathbf{r}\,\Psi^*\hat{H}\Psi = \langle\Psi|\hat{H}|\Psi\rangle$$

- The ket $|\Psi\rangle$ denotes a wave function while the bra $\langle\Psi|$ denotes a complex conjugate wave function Ψ^*. The combined braket 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 Ψ 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 Ψ 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 $V_{\mathrm{nuc-el}}$ is an effective external potential for an electron, we write it

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

- And we define the one-electron Hamiltonian

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

- 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 ψ_i as

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

- This wave function is called **Hartree product**, and it is a first crude guess for the true N-electron wave function.

- Note that ψ_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 ω, 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 ω are independent, we have $\chi_i(\mathbf{x}) = \psi_i(\mathbf{r})\sigma_i(\omega)$, where ψ and σ denote the spatial and spin parts.

- χ, ϕ, σ are a spin orbital, spatial orbital, and spin function.

- Since an electron have no chance to take both α and β 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 χ 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

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

- 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

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

- The ϵ_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 charactor 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

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

- For example in two-electron case,

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

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

$$\langle \Psi | H | \Psi \rangle = \sum_{i=1}^{N} \int d\mathbf{r} \, \psi_i^*(\mathbf{r}) \hat{h} \psi_i(\mathbf{r})$$

$$+ \frac{1}{2} \sum_{i,j=1}^{N} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}')$$

$$- \frac{1}{2} \sum_{i,j=1}^{N} \int d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \delta_{\omega_i, \omega_j} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}') \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r})$$

$$+ V_{\mathrm{nuc-nuc}}$$

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 ψ^* 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 ψ_i into ψ_j when it applies to ϕ_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 χ_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: $\exp(-\alpha r_{iI}^2)$.
- α 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 ρ 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,

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

- Here, the factor of 1/2 in $J[\rho]$ allows the integration to be done over all space fo 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

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

- 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 λ 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 forced f_i exerted on a nucleus by electrons and other nuclei must vanish:

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

- 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 wa 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

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

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