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 Schrodinger equations are generated without reference to experimental data, the methods are usually called "ab initio" (latin: "from the beginning") or "first principle".

Schrodinger equation

- SE is

Hatree-product

Hartree-Fock method

- The Hartree product obeys the Pauli' exclusion principle only to some extent; in the Hatree 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.

- Mathemtatically, this requres that the sign of Ψ changes when two electrons are exchanged.

Slater determinant

- The requirement is overcome by using a detarminant. This is called a **Slater determinant**.

- The Slater determinant is constructed from the single-particle wave functions by

$$\Psi(\mathbf{r_1}, \mathbf{r_2} \cdots \mathbf{r_N}) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r_1}) & \cdots & \psi_1(\mathbf{r_N}) \\ \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r_1}) & \cdots & \psi_N(\mathbf{r_N}) \end{vmatrix}$$

- Then the expectation value of the total energy becomes

$$\langle \Psi | H | \Psi \rangle = \sum_{i=1}^{N} \int d^3 r \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + v_{ext}(\mathbf{r}) \right) \psi_i(\mathbf{r})$$

$$+ \frac{1}{2} \sum_{i,j=1}^{N} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}')$$

$$- \frac{1}{2} \sum_{i,j=1}^{N} \int d^3 r d^3 r' \frac{e^2}{|r - r'|} \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}') \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r})$$

$$+ V_{nuc-nuc}$$

- The last term $V_{nuc-nuc}$ is the nuclar-nuclear repulsion term, and the second last term is called **exchange repulsion term**.

- If we minimize the above expression with respect to the ψ_i^* under the constraint of normalization.

- Lagrange constrained minimization

- Finally, we have **Hartree-Fock equation**.

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\mathbf{r}) + v_H(\mathbf{r})\right]\psi_i(\mathbf{r})$$

$$-\sum\int \frac{e^2}{|r-r'|}\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

- Explain terms.

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 (from Atkins)

- 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 diffreaction, and microwave spectroscopy.

- Calculation of derivatives of the potential energy with respect to nuclar 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 chnge in energy as each nuclear coordiate is varied.

Energy derivatives

- For a diatomic molecule, the molecular potential energy E depends only on the internuclar 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 cpmplicated 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 nuclar 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 paritition funciton (for mode i) and overall one is

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

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