

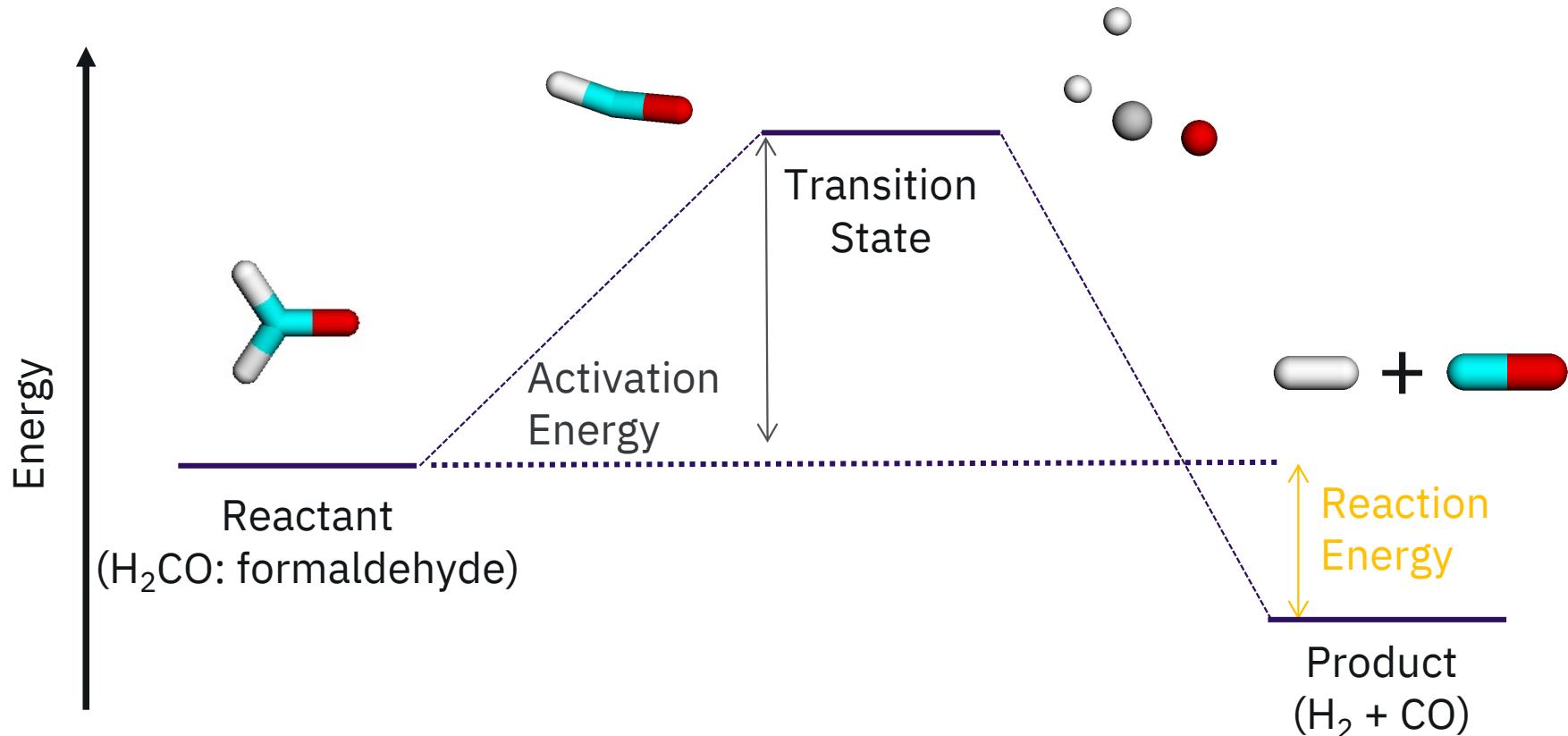
Outline (Methods of Quantum Chemistry Simulations)

- Introduction
- Schrödinger Equation and Born–Oppenheimer Approximation
- Quantum Chemistry Methods
 - Hartree–Fock Method
 - Basis Sets
 - Atomic Orbital Integrals
 - Semiempirical Methods
 - Correlation Methods
 - Perturbation Theory
 - Configuration Interaction
 - Coupled Cluster Methods
 - Density Functional Theory



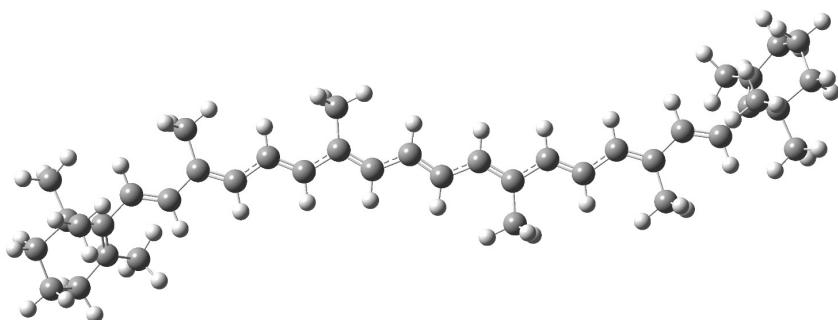
Introduction: What Can We Do with Quantum Chemistry Simulations?

Tackle Chemical Reaction

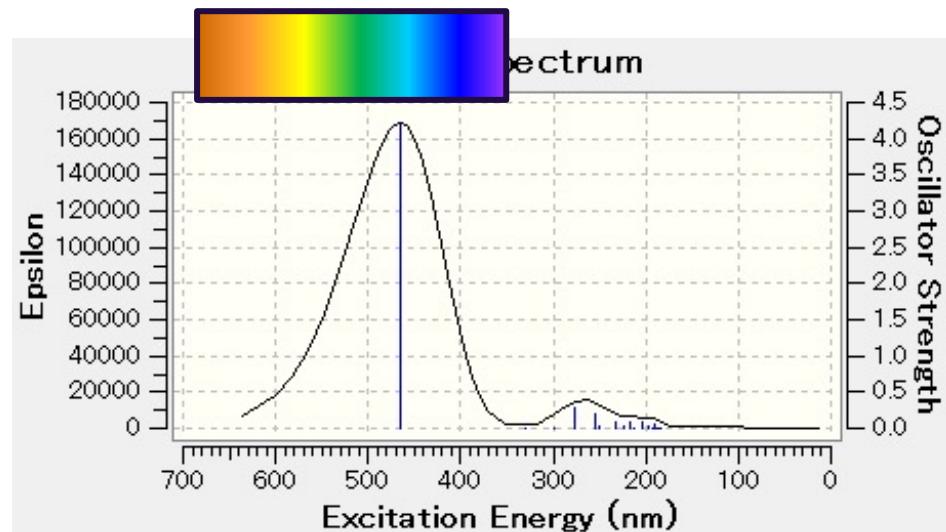


We can compute the activation energies and reaction energies
 We can predict the reaction pathway

Tackle Molecular Properties



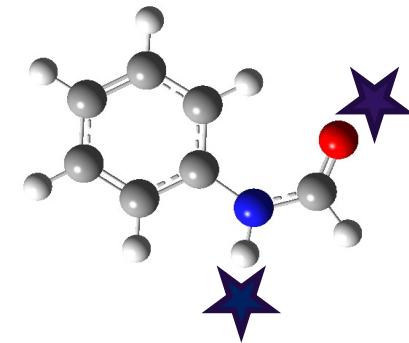
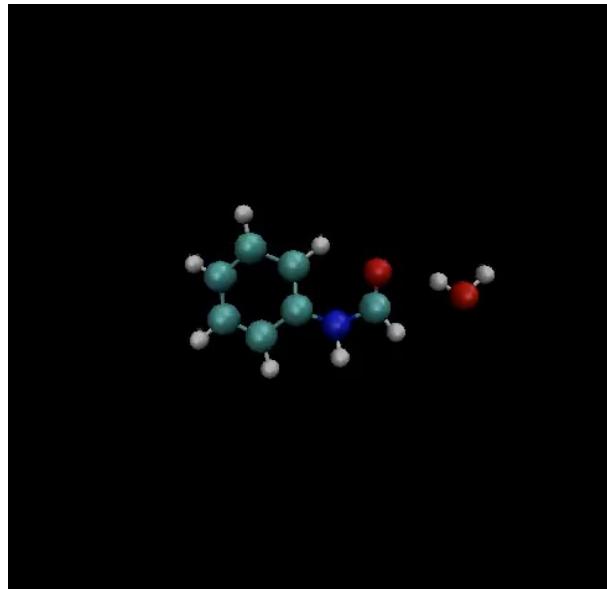
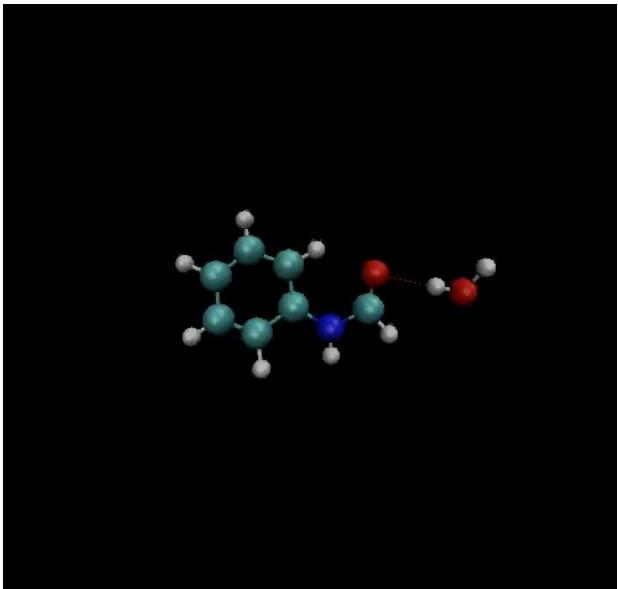
β -carotene molecule



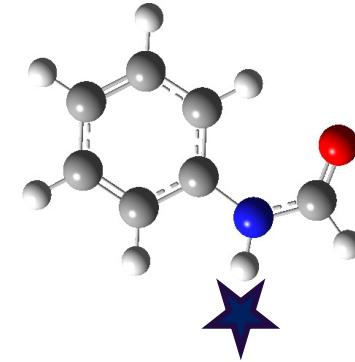
β -carotene absorbs light of specific wavelengths and others are reflected. Violet, blue, and green lights are absorbed, and yellow, orange, and red lights are reflected (thus, we see the orange color)

We can design a new pigment!

Tackle Molecular Dynamics



Neutral



Cation

How will the molecular orientation change after ionization of the molecule? We can investigate the dynamics which cannot be observed in experiment!

Quantum Chemistry Simulation

Quantum Chemistry Simulation (Calculation)
/ Electronic Structure Calculation:

Solve the distribution of electrons in molecules

Static properties of molecules

Also, can understand motions of molecules using quantum chemistry simulations

- Equilibrium geometries
- Barrier heights and reaction pathway of chemical reactions
- Spectra (absorption, NMR, CD, IR)
- Dipole moment, polarizability
- Thermodynamic properties

Schrödinger Equation and Born–Oppenheimer Approximation



Time-Dependent Schrödinger Equation

Time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \hat{H}(\mathbf{r}, t) \Psi(\mathbf{r}, t)$$

Hamiltonian

$$\hat{H}(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t)$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Kinetic term Potential term

- Describes the quantum system evolving in time
- Solve the propagation of the wavefunction
- Partial differential equation
- Note that we here do not consider relativistic effect or spins

Time-Independent Schrödinger Equation

$$\hat{H}(\mathbf{r}) \Psi_n(\mathbf{r}) = E_n \Psi_n(\mathbf{r}) \quad E_n \text{ Energy}$$

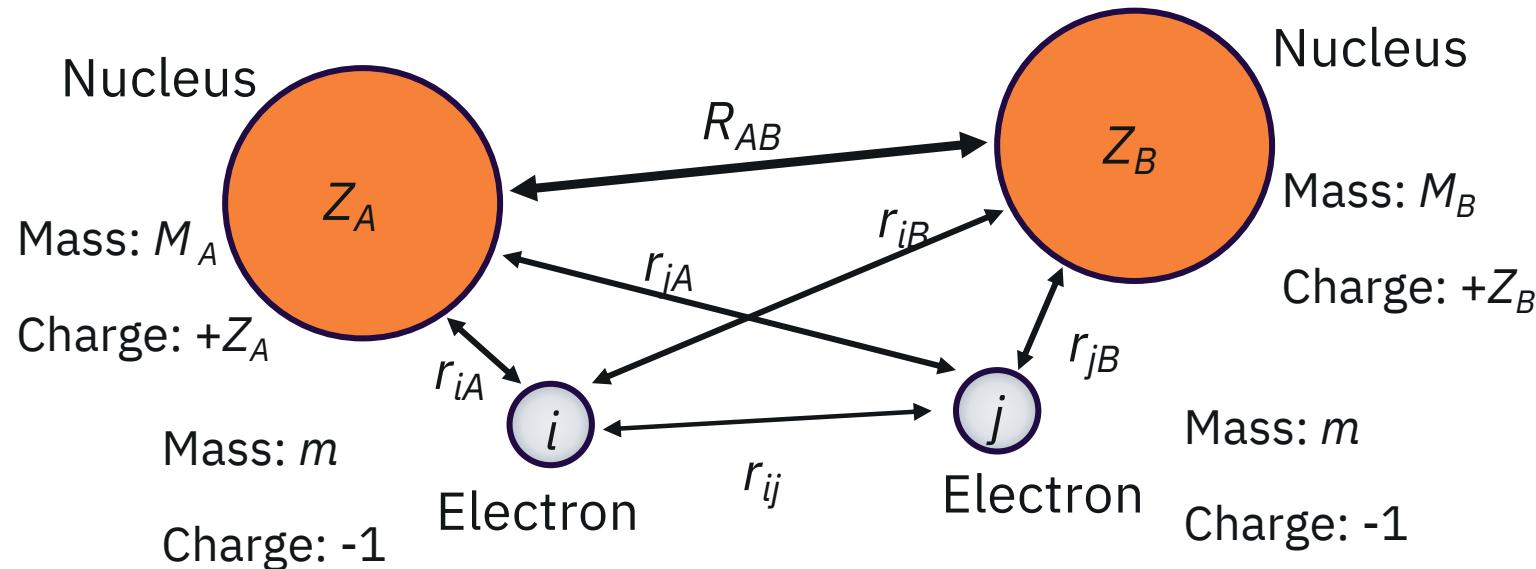
Hamiltonian

$$\hat{H}(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$$

Time independent

- Interested in the time-independent problem (quantities in equilibrium)
- This is the case for quantum chemistry methods (Hamiltonian is time-independent)
- Eigenvalue equation
- Eigenvalues will be the total energy, and eigenvectors are the wavefunctions

Molecular Hamiltonian



$$\hat{H}(\mathbf{r}, \mathbf{R}) = - \sum_A^{N_{nuc}} \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_i^{N_{ele}} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{A>B}^{N_{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i>j}^{N_{ele}} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Nuclear kinetic energy	Electronic kinetic energy	Nucleus- nucleus repulsion	Electron- nucleus attraction	Electron- electron repulsion
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Molecular Hamiltonian in atomic units

$$\hbar^2 = m = e = 4\pi\epsilon_0 = 1$$

$$\hat{H}(\mathbf{r}, \mathbf{R}) = - \sum_A^{N_{nuc}} \frac{\hbar^2}{2M_A} \nabla_A^2 - \sum_i^{N_{ele}} \frac{\hbar^2}{2m} \nabla_i^2 + \sum_{A>B}^{N_{nuc}} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i>j}^{N_{ele}} \frac{e^2}{4\pi\epsilon_0 r_{ij}}$$

Molecular Hamiltonian in atomic units

$$\hat{H}(\mathbf{r}, \mathbf{R}) = - \sum_A^{N_{nuc}} \frac{1}{2M_A} \nabla_A^2 - \sum_i^{N_{ele}} \frac{1}{2} \nabla_i^2 + \sum_{A>B}^{N_{nuc}} \frac{Z_A Z_B}{R_{AB}} - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N_{ele}} \frac{1}{r_{ij}}$$

Note that relativistic effect and spin-orbit coupling are not considered

Born–Oppenheimer Approximation

$$\hat{H}(\mathbf{r}, \mathbf{R}) = - \sum_A^{N_{nuc}} \frac{1}{2M_A} \nabla_A^2 - \sum_i^{N_{ele}} \frac{1}{2} \nabla_i^2 + \sum_{A>B}^{N_{nuc}} \frac{Z_A Z_B}{R_{AB}} - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A}{r_{iA}} + \sum_{i>j} \frac{1}{r_{ij}}$$

- Nuclear mass is very large compared to the mass of electrons
- Electronic motion is extremely fast compared to the nuclear motion
- The motion of the electrons can be decoupled with the motions of nuclei
- Freeze the nuclei

Electronic Hamiltonian

$$\hat{H}(\mathbf{r}, \mathbf{R}) = - \sum_A^N \frac{1}{2M_A} \nabla_A^2 - \sum_i^{N_{ele}} \frac{1}{2} \nabla_i^2 + \sum_{A>B}^{N_{nuc}} \frac{Z_A Z_B}{R_{AB}} - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N_{ele}} \frac{1}{r_{ij}}$$

Constant

- The kinetic energy of the nuclei can be removed
- The nuclei can be treated as classical point charges
- Nuclear coordinates are fixed

Electronic Hamiltonian $\hat{H}_{ele}(\mathbf{r}; \mathbf{R}) = - \sum_i^{N_{ele}} \frac{1}{2} \nabla_i^2 - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N_{ele}} \frac{1}{r_{ij}}$

Electronic Wavefunction

Introducing the spins

Wavefunction $\Psi = \Psi(x_1, y_1, z_1, \omega_1, x_2, y_2, z_2, \omega_2, \dots)$

x, y, z Spatial coordinates

ω Spin coordinates

$$|\Psi|^2 = \Psi^* \Psi$$

Conditional probability for finding electrons at the given coordinates

$$\Psi(x_2, y_2, z_2, \omega_2, x_1, y_1, z_1, \omega_1, \dots) = -\Psi(x_1, y_1, z_1, \omega_1, x_2, y_2, z_2, \omega_2, \dots)$$

The wavefunction is antisymmetric against the exchange of electrons

Electronic Schrödinger Equation

Electronic Schrödinger equation $\hat{H}_{ele}(\mathbf{r}; \mathbf{R}) \Psi_{ele}(\mathbf{r}; \mathbf{R}) = E_{ele}(\mathbf{R}) \Psi_{ele}(\mathbf{r}; \mathbf{R})$

$$\hat{H}_{ele}(\mathbf{r}; \mathbf{R}) = - \sum_i^{N_{ele}} \frac{1}{2} \nabla_i^2 - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A}{r_{iA}} + \sum_{i>j} \frac{1}{r_{ij}}$$

$$E_{total}(\mathbf{R}) = E_{ele}(\mathbf{R}) + \sum_{A>B}^{N_{nuc}} \frac{Z_A Z_B}{R_{AB}} = V(\mathbf{R})$$

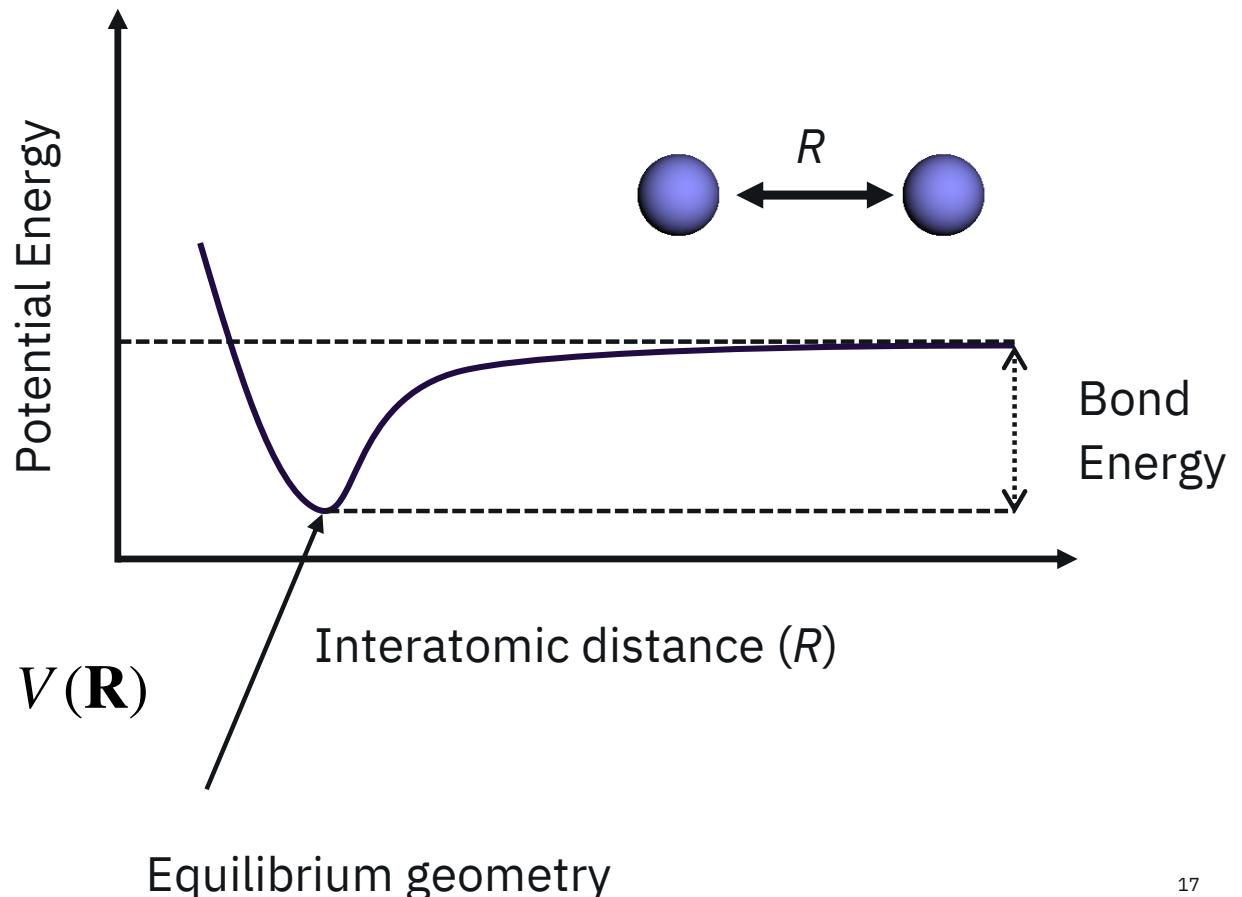
- The electronic energy can be calculated by solving the electronic Schrödinger equation
- The nucleus-nucleus repulsion term is just a shift in the energy
- The total energy is also called as a potential energy depending on the nuclear coordinates

Potential Energy Surface (PES)

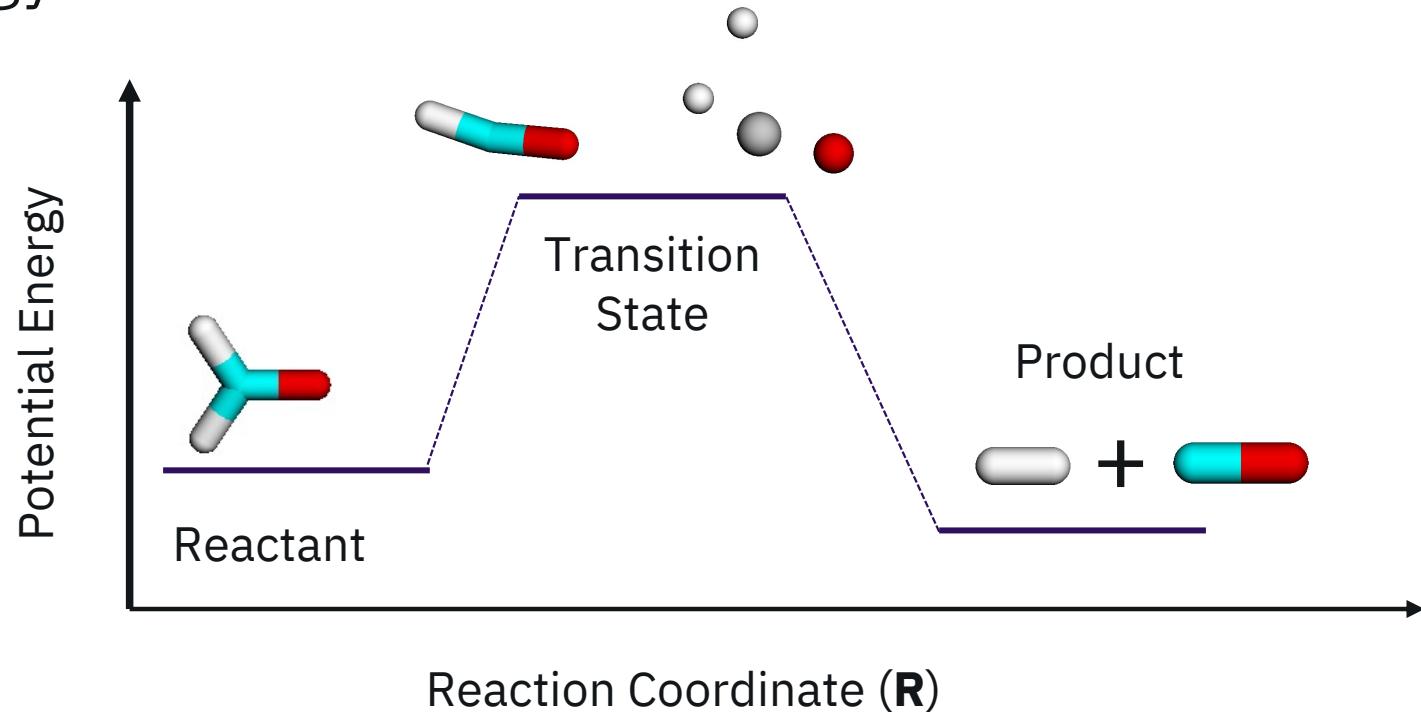
The potential energy depends on the nuclear coordinates

The surface constructed by varying the nuclear coordinates is the potential energy surface (PES)

$$E_{total}(\mathbf{R}) = E_{ele}(\mathbf{R}) + \sum_{A>B}^{N_{nuc}} \frac{Z_A Z_B}{R_{AB}} = V(\mathbf{R})$$



Potential Energy in Reaction



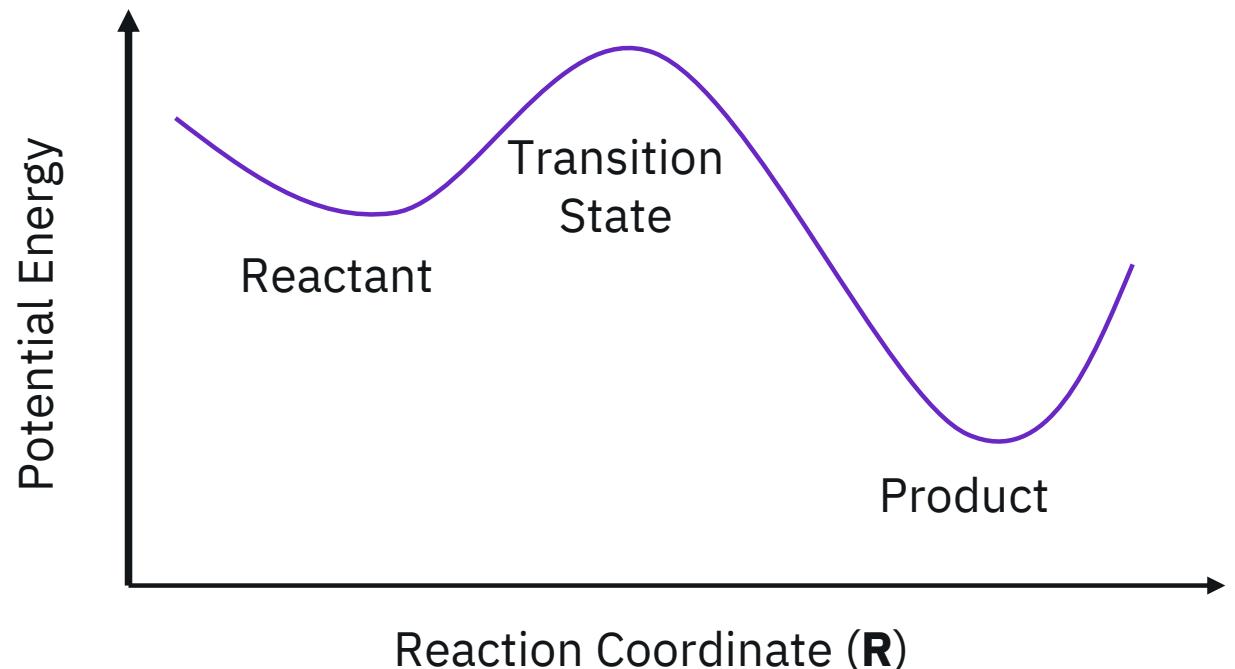
The diagram of the reaction we saw previously was the potential energy diagram along the reaction coordinate

Stationary points in PES

The three points are all at the stationary points in the PES $\frac{\partial V}{\partial \mathbf{R}_i} = 0$

The reactant and product structure are at the minimum of PES

Transition states are at the saddle point of PES



- Hessian Matrix $\frac{\partial^2 V}{\partial \mathbf{R}_i \partial \mathbf{R}_j}$
- Diagonalize the Hessian matrix
 - All eigenvalues are positive: minimum of PES
 - One eigenvalue is negative, and all other eigenvalues are positive: saddle point of PES

About the Molecular Dynamics Simulation

- Why not solving the time-dependent Schrödinger equation?
- The nuclear motion is classical, not quantum
- However, the nuclei are feeling the force from the electrons
- The quantum chemistry simulation is performed for calculating the force
- The force will depend on the coordinate of the nuclei (electron and nuclear motions are decoupled)
- The molecular dynamics simulation is the dynamics along the potential energy surface

Schrödinger Equation and Born–Oppenheimer Approximation

- Time-dependent Schrödinger equation
- Time-independent Schrödinger equation
- Born–Oppenheimer approximation
- Electronic Schrödinger equation
- Potential energy

Quantum Chemistry Methods

- Hartree–Fock Method
 - Basis Sets
 - Atomic Orbital Integrals
- Semiempirical Methods
- Correlation Methods
 - Perturbation Theory
 - Configuration Interaction
 - Coupled Cluster Methods
- Density Functional Theory

Hartree–Fock Method



Mean-field approximation

The Underlying Idea

$$\hat{H}_{ele}(\mathbf{r}; \mathbf{R}) = -\sum_i^{N_{ele}} \frac{1}{2} \nabla_i^2 - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A}{r_{iA}} + \sum_{i>j}^{N_{ele}} \frac{1}{r_{ij}}$$

Mean-field approximation

Independent particle model

$$\sum_{i>j}^{N_{ele}} \frac{1}{r_{ij}} \rightarrow \sum_i^{N_{ele}} v_i$$

$$-\sum_i^{N_{ele}} \frac{1}{2} \nabla_i^2 - \sum_A^{N_{nuc}} \sum_i^{N_{ele}} \frac{Z_A}{r_{iA}} + \sum_i^{N_{ele}} v_i = \sum_i^{N_{ele}} f_i$$

Each electrons feel the other electrons as an averaged field

All terms are expressed as one-electron terms

Wavefunction as product of orbitals

$$\Psi = \Psi(x_1, y_1, z_1, \omega_1, x_2, y_2, z_2, \omega_2, \dots) = \Psi(\mathbf{r}, \omega) = \Psi(\mathbf{x})$$

$\chi(\mathbf{x}_i)$ Spin orbitals

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

Fermions are antisymmetric against exchange

$$\cancel{\Psi(\mathbf{x}_2, \mathbf{x}_1)} = -\cancel{\Psi(\mathbf{x}_1, \mathbf{x}_2)}$$

$$\Psi(\mathbf{x}_2, \mathbf{x}_1) = -\Psi(\mathbf{x}_1, \mathbf{x}_2)$$

Wavefunction as Slater determinants

Two particles

$$\Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} (\chi_1(\mathbf{x}_1)\chi_2(\mathbf{x}_2) - \chi_1(\mathbf{x}_2)\chi_2(\mathbf{x}_1)) \quad \Psi(\mathbf{x}_1, \mathbf{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) \end{vmatrix}$$

N particles

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(\mathbf{x}_1) & \chi_2(\mathbf{x}_1) & \cdots & \chi_N(\mathbf{x}_1) \\ \chi_1(\mathbf{x}_2) & \chi_2(\mathbf{x}_2) & \cdots & \chi_N(\mathbf{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(\mathbf{x}_N) & \chi_2(\mathbf{x}_N) & \cdots & \chi_N(\mathbf{x}_N) \end{vmatrix}$$

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = |\chi(\mathbf{x}_1)\chi(\mathbf{x}_2)\cdots\chi(\mathbf{x}_N)\rangle$$

Variational Principle

$$\hat{H}_{ele}(\mathbf{x}; \mathbf{R}) \Psi_{ele}(\mathbf{x}; \mathbf{R}) = E_{ele}(\mathbf{R}) \Psi_{ele}(\mathbf{x}; \mathbf{R})$$

We can not solve the electronic Schrödinger equation analytically, we can employ the variational principle to solve it numerically

Ritz functional
 (functional to minimize) $\epsilon = \frac{\int \Psi_{ele}^* \hat{H}_{ele} \Psi_{ele} d\mathbf{r}}{\int \Psi_{ele}^* \Psi_{ele} d\mathbf{r}} = \frac{\langle \Psi_{ele} | \hat{H}_{ele} | \Psi_{ele} \rangle}{\langle \Psi_{ele} | \Psi_{ele} \rangle}$

Variational theorem: $\epsilon \geq E_{gs}$ (true ground state)

The variational theorem assures that the true ground state will be the lower bound

We can minimize the energy by varying the parameters (C_i) in the wavefunction (or optimize the Slater determinant) $\frac{\partial \epsilon}{\partial C_i} = 0$

Hartree–Fock Energy

$$E_{HF} = \sum_i^{N_{ele}} \langle i | \hat{h} | i \rangle + \sum_{i>j}^{N_{ele}} ([ii | jj] - [ij | ji]) \quad \hat{h}(i) = -\frac{1}{2} \nabla_i^2 - \sum_A \frac{Z_A}{r_{iA}}$$

One-electron integrals

$$\langle i | h | i \rangle = \int d\mathbf{x}_1 \chi_i^*(\mathbf{x}_1) \hat{h}(\mathbf{r}_1) \chi_i(\mathbf{x}_1)$$

Two-electron integrals

$$[ii | jj] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_i(\mathbf{x}_1) \frac{1}{r_{12}} \chi_j^*(\mathbf{x}_2) \chi_j(\mathbf{x}_2)$$

Coulomb integrals

$$[ij | ji] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_j^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2)$$

Two-electron integrals

Two-electron integrals

Coulomb integrals

$$[ii|jj] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_i(\mathbf{x}_1) \frac{1}{r_{12}} \chi_j^*(\mathbf{x}_2) \chi_j(\mathbf{x}_2)$$

Electrostatic potential of electrons

Exchange integrals

$$[ij|ji] = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j(\mathbf{x}_1) \frac{1}{r_{12}} \chi_j^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2)$$

Antisymmetry against exchange (from the Pauli principle)



Hartree–Fock Equation

$$\epsilon_i \chi_i(\mathbf{x}_1) = \hat{h}(\mathbf{x}_1) \chi_i(\mathbf{x}_1) + \sum_{j \neq i} \left(\int d\mathbf{x}_2 \frac{|\chi_j(\mathbf{x}_2)|^2}{r_{12}} \right) \chi_i(\mathbf{x}_1) - \sum_{j \neq i} \left(\int d\mathbf{x}_2 \frac{\chi_j^*(\mathbf{x}_2) \chi_i(\mathbf{x}_2)}{r_{12}} \right) \chi_j(\mathbf{x}_1)$$

↑
Energy
(Eigenvalue) of a
spin orbital

$$\hat{f}(\mathbf{x}_1) = \hat{h}(\mathbf{x}_1) + \sum_j \left(\hat{J}_j(\mathbf{x}_1) - \hat{K}_j(\mathbf{x}_1) \right) \quad \hat{K}_j(\mathbf{x}_1) \chi_i(\mathbf{x}_1)$$

$$\hat{f}(\mathbf{x}_1) \chi_i(\mathbf{x}_1) = \epsilon_i \chi_i(\mathbf{x}_1)$$

We arrive at an equation by minimizing the Hartree–Fock energy with respect to the orbitals

However, this is an integro-differential equation that is yet difficult to solve

Linear Combination of Atomic Orbitals

$$\chi_i = \sum_{\nu} C_{\nu i} \bar{\chi}_{\nu}$$

$\bar{\chi}_{\nu}$ atomic orbitals or basis sets

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \epsilon \sum_{\nu} S_{\nu} C_{\nu i}$$

$$\mathbf{FC} = \mathbf{SC}\epsilon$$

Overlap matrix

$$S_{\mu\nu} = \int d\mathbf{x}_1 \bar{\chi}_{\mu}^* (\mathbf{x}_1) \bar{\chi}_{\nu} (\mathbf{x}_1)$$

Fock matrix

$$F_{\mu\nu} = \int d\mathbf{x}_1 \bar{\chi}_{\mu}^* (\mathbf{x}_1) \hat{f} (\mathbf{x}_1) \bar{\chi}_{\nu} (\mathbf{x}_1)$$

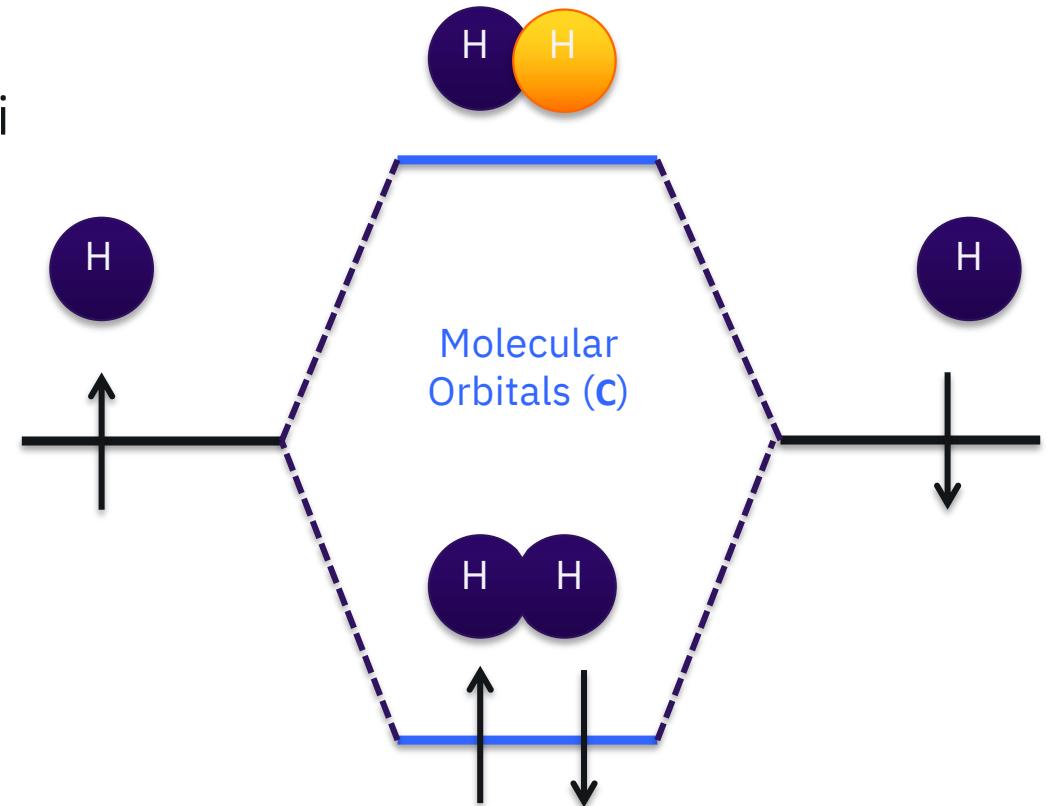
The molecular orbitals are described as linear combination of atomic orbitals

The introduction of the atomic orbitals (basis set) convert the problem into a pseudo-eigenvalue problem (eigenvectors are the molecular orbitals (coefficients), and the eigenvalues are the molecular orbital energies), which we can solve!

Matrix F includes C! (We need to solve this iteratively)

Self-consistent field procedure

1. Input 3D coordinates of atomic nuclei and atomic orbitals
2. Initial guess of the molecular orbitals
3. Construct the Fock matrix
4. Diagonalize the Fock matrix (we get a new C)
5. If converged, goto 6, if not, go to 3
6. Molecular orbitals (C) and the Hartree–Fock energy is obtained



Hartree–Fock Method

- We use a single Slater determinant as the wavefunction
- The variational principle will be used to calculate the minimized energy
 - The parameters in the wavefunction (get the suitable Slater determinant)
- This introduces the mean-field approximation (each electrons feel the other electrons as an averaged field)
- Linear combination of atomic orbitals
- Self-consistent field procedure

Basis Sets and Atomic Orbital Integrals



Basis Sets

Functions for representing the atomic orbitals to describe the electronic wavefunction
(to construct the molecular orbitals)

1. Gaussian basis set (STO-3G, 6-31G*, cc-pVDZ)
2. Plane wave basis set
3. Real-space basis set (finite element, wavelets....)

Quantum chemistry calculations for isolated molecules mostly use Gaussian basis sets

Accuracy vs computational cost

Gaussian basis sets

Spatial orbitals $\psi(\mathbf{r}) = \sum_i^{N_{AO}} c_i \phi_i(\mathbf{r})$ Center of the Gaussian function (X_i, Y_i, Z_i)

$$\phi_i(\mathbf{r}) = N_i(x - X_i)^{l_x}(y - Y_i)^{l_y}(z - Z_i)^{l_z} \exp(-\alpha_i(\mathbf{r} - \mathbf{R}_i)^2)$$

Contracted basis $\phi_i(\mathbf{r}) = N_i \sum_{j=1}^{N_d} d_{ij} (x - X_i)^{l_x} (y - Y_i)^{l_y} (z - Z_i)^{l_z} \exp(-\alpha_{ij}(\mathbf{r} - \mathbf{R}_i)^2)$

- Minimal basis sets (minimum number required to represent all electrons on atom): STO-nG
- Split-valence basis sets (represent valence orbitals by more than one function): Pople basis sets (6-31G*, 6-311+G**) *: polarization functions (higher angular momentum), +: diffused functions (diffused functions (small alpha) for molecules such as anions)
- Correlation consistent basis sets (systematic basis for converging correlation methods): cc-pVnZ (n=D, T, Q, 5) (2, 3, 4, 5 functions for each AO)

Gaussian basis sets 2

Contracted $\phi_i(\mathbf{r}) = N_i(x - X_i)^{l_x}(y - Y_i)^{l_y}(z - Z_i)^{l_z} \sum_{j=1}^{N_d} d_{ij} \exp\left(-\alpha_{ij}(\mathbf{r} - \mathbf{R}_i)^2\right)$

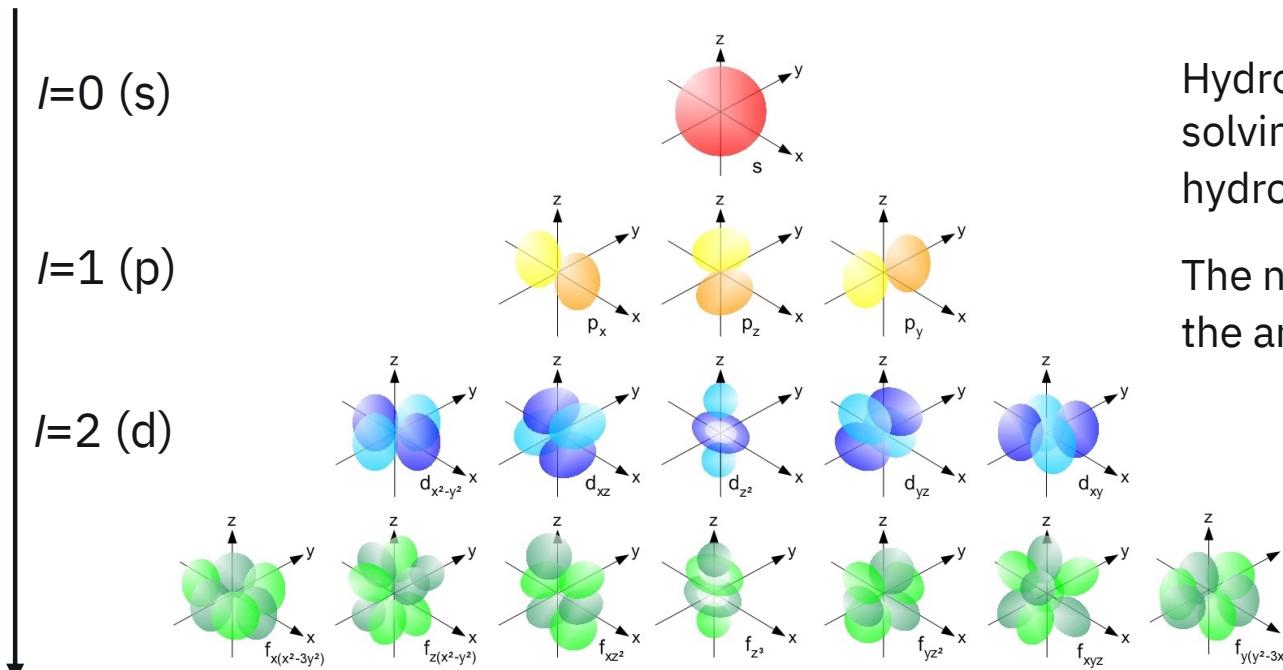
- Minimal basis sets (minimum number required to represent all electrons on atom)
 - STO-nG (n contracted basis to construct an atomic orbital)
- Split-valence basis sets (represent valence orbitals by more than one function)
 - Pople basis sets (6-31G*, 6-311+G**)
 - First “6” is describing the number of contracted basis for a core atomic orbital
 - The next numbers “31” shows that two basis are used (if there are two numbers) to describe the valence atomic orbital, and “311” shows that three basis are used.
 - The two basis are described by 3 and 1 contracted basis, respectively

Angular Momentum

l_x, l_y, l_z

$$\phi_i(\mathbf{r}) = N_i(x - X_i)^{l_x}(y - Y_i)^{l_y}(z - Z_i)^{l_z} \exp(-\alpha_i(\mathbf{r} - \mathbf{R}_i)^2)$$

From Wikipedia



Hydrogen (atomic) orbitals you get by solving the Schrödinger equation of hydrogen atom

The number of nodal planes increase as the angular momentum becomes higher

Atomic orbitals of higher quantum numbers are required to describe the molecular orbitals accurately

Gaussian Product Theorem

$$\exp(-\alpha_1(x - x_1)^2) \exp(-\alpha_2(x - x_2)^2) = \boxed{\exp(-\mu X_{12}^2)} \boxed{\exp\left((-p(x - x_p)^2)\right)}$$

prefactor

A new Gaussian

$$x_p = \frac{\alpha_1 x_1 + \alpha_2 x_2}{p}$$

$$X_{12} = x_1 - x_2$$

$$p = \alpha_1 + \alpha_2$$

$$\mu = \frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2}$$

A product of two Gaussians is a Gaussian (a 1-D example)

Recursion Relation

$$\phi_i(\mathbf{r}) = N_i(x - X_i)^{l_x}(y - Y_i)^{l_y}(z - Z_i)^{l_z} \exp(-\alpha_i(x - X_i)^2) \exp(-\alpha_i(y - Y_i)^2) \exp(-\alpha_i(z - Z_i)^2)$$

x,y,z are separable

$$G_l = (x - X)^l \exp(-\alpha(x - X)^2)$$

Recursion

$$G_{l+1} = (x - X)G_l$$

Gradient

$$\frac{\partial G_l}{\partial X} = -\frac{\partial G_l}{\partial x} = 2\alpha G_{l+1} - lG_{l-1}$$

Gradients and Gaussians with high angular momentum can be treated easily with the recursion relation

Integrals in Atomic Orbitals

$$\phi_\mu(\mathbf{r}) = N_\mu (x - X_\mu)^{l_x} (y - Y_\mu)^{l_y} (z - Z_\mu)^{l_z} \exp\left(-\alpha_\mu (\mathbf{r} - \mathbf{R}_\mu)^2\right)$$

$$h_{\mu\nu} = \int d\mathbf{r} \phi_\mu^*(\mathbf{r}) \left(-\frac{\nabla^2}{2} - \sum_A \frac{Z_A}{r_{iA}} \right) \phi_\nu(\mathbf{r})$$

$$g_{\mu\nu\lambda\sigma} = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi_\mu^*(\mathbf{r}_1) \phi_\nu(\mathbf{r}_1) \phi_\lambda^*(\mathbf{r}_2) \phi_\sigma(\mathbf{r}_2)}{\mathbf{r}_{12}}$$

Two-electron Integrals

$$\phi_\mu(\mathbf{r}) = N_\mu(x - X_\mu)^0(y - Y_\mu)^0(z - Z_\mu)^0 \exp\left(-\alpha_\mu(\mathbf{r} - \mathbf{R}_\mu)^2\right)$$

$$\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi_\mu^*(\mathbf{r}_1)\phi_\nu(\mathbf{r}_1)\phi_\lambda^*(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2)}{\mathbf{r}_{12}} = \frac{2\pi^{5/2}K_1K_2}{pq(p+q)^{1/2}}F_0(\alpha R_{pq}^2)$$

$$K_1 = \exp\left(-\frac{\alpha_\mu\alpha_\nu}{\alpha_\mu + \alpha_\nu}(R_\mu - R_\nu)^2\right) \quad K_2 = \exp\left(-\frac{\alpha_\lambda\alpha_\sigma}{\alpha_\lambda + \alpha_\sigma}(R_\lambda - R_\sigma)^2\right)$$

$$p = \alpha_\mu + \alpha_\nu, \quad q = \alpha_\lambda + \alpha_\sigma, \quad R_{pq} = R_p - R_q \quad R_p = \frac{\alpha_\mu R_\mu + \alpha_\nu R_\nu}{\alpha_\mu + \alpha_\nu}, \quad R_q = \frac{\alpha_\lambda R_\lambda + \alpha_\sigma R_\sigma}{\alpha_\lambda + \alpha_\sigma}, \quad \alpha = \frac{pq}{p+q}$$

Use the recursion relations to get values with $\phi_\mu(\mathbf{r}) = N_\mu(x - X_\mu)^{l_x}(y - Y_\mu)^{l_y}(z - Z_\mu)^{l_z} \exp\left(-\alpha_\mu(\mathbf{r} - \mathbf{R}_\mu)^2\right)$

Incomplete gamma function

$$F_m(T) = \int_0^1 t^{2m} \exp(-Tt^2) dt$$

Basis sets and atomic orbitals

- Basis sets
 - Gaussian basis sets
 - Gaussian product theorem & recursion relations
 - Atomic orbital integrals
 - Two-electron integrals as an example

ab initio Molecular Orbital Methods

- *ab initio* Molecular Orbital Methods
 - Hartree–Fock Method
 - Perturbation Theory
 - Configuration Interaction
 - Coupled Cluster Methods
- Semiempirical Methods
- Density Functional Theory

Semi-empirical Methods



Concept of Semiempirical Methods

- Treat only the valence electrons
- Use minimal basis sets
- Zero differential overlap approximation
 - Approximate the integrals!

$$v_{\mu\nu} = \int d\mathbf{r} \phi_\mu^*(\mathbf{r}) \left(- \sum_A \frac{Z_A}{r_{iA}} \right) \phi_\nu(\mathbf{r}) \quad g_{\mu\nu\lambda\sigma} = \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi_\mu^*(\mathbf{r}_1) \phi_\nu(\mathbf{r}_1) \phi_\lambda^*(\mathbf{r}_2) \phi_\sigma(\mathbf{r}_2)}{\mathbf{r}_{12}}$$

$$v_{\mu_B \nu_C} = 0 \quad (A \neq B, A \neq C, B \neq C)$$

$$g_{\mu_A \nu_B \lambda_C \sigma_D} = 0 \quad (A \neq B \text{ or } C \neq D)$$

Semiempirical Methods

- Zero-differential overlap
 - Neglect of Diatomic Differential Overlap (NDDO)
 - Intermediate Neglect of Differential Overlap (INDO): Only $g_{\mu_A \mu_A \nu_B \nu_B}$ $g_{\mu_A \mu_A \lambda_A \sigma_A}$
 - Complete Neglect of Differential Overlap (CNDO): Only $g_{\mu_A \mu_A \nu_A \nu_A}$ $g_{\mu_A \mu_A \nu_B \nu_B}$
- Parameterization
 - Modified INDO (MINDO): Parameterize based on bonding atoms (diatomic)
 - Modified NDDO (MNDO): Atomic parameterization (AM1, PM3)
- Can tackle larger molecules than *ab initio* methods
- Lack some parameters for new molecular systems
- Performance (accuracy) is less reliable compared to *ab initio* methods, but they are improving (PM7 (dispersion correction))

Correlation Methods



Electron Correlation

HF: 99% of the total energy (N^{2-3})

However, there are many cases, where Hartree–Fock methods do not provide enough accuracy

How can we improve Hartree–Fock?

Correlation energy $E_{correlation} = E_{exact} - E_{HF}$

Electron Correlation Methods

- Configuration interaction
- Coupled cluster
- Perturbation theory

Second Quantization

Spin orbitals (molecular orbitals) χ_p

Each determinant (Fock state) is represented by an occupation number vector

Fock state: $|\mathbf{k}\rangle = |k_1, k_2, \dots, k_M\rangle$

$k_p = 0$	χ_p unoccupied
$k_p = 1$	χ_p occupied

Creation operator $\hat{a}_p^\dagger |\chi_q(\mathbf{x}_q)\cdots\chi_N(\mathbf{x}_N)\rangle = |\chi_p(\mathbf{x}_p)\chi_q(\mathbf{x}_q)\cdots\chi_N(\mathbf{x}_N)\rangle$

Annihilation operator $\hat{a}_p |\chi_p(\mathbf{x}_p)\chi_q(\mathbf{x}_q)\cdots\chi_N(\mathbf{x}_N)\rangle = |\chi_q(\mathbf{x}_q)\cdots\chi_N(\mathbf{x}_N)\rangle$

Quantize the field (where the electron is) using the spin-orbitals,
rather than describing the spatial distribution

Second Quantized Hamiltonian

Slater determinants of N electrons can be created from the vacuum

$$\hat{a}_N^\dagger \cdots \hat{a}_s^\dagger \hat{a}_q^\dagger \hat{a}_p^\dagger |\Psi_{vacuum}\rangle = |\chi_p(\mathbf{x}_p) \chi_q(\mathbf{x}_q) \chi_s(\mathbf{x}_s) \cdots \chi_N(\mathbf{x}_N)\rangle$$

Second quantized Hamiltonian

$$\hat{H} = \sum_{pq} h_{pq} \hat{a}_p^\dagger \hat{a}_q + \sum_{pqrs} g_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s$$

$$h_{pq} = \int d\mathbf{x} \chi_p^*(\mathbf{x}) \left(-\frac{\nabla^2}{2} - \sum_A \frac{Z_A}{r_{iA}} \right) \chi_q(\mathbf{x})$$

$$g_{pqrs} = \int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\chi_p^*(\mathbf{x}_1) \chi_q^*(\mathbf{x}_2) \chi_r(\mathbf{x}_2) \chi_s(\mathbf{x}_1)}{\mathbf{r}_{12}} = \langle pq | rs \rangle$$

How is the Second Quantized Hamiltonian Constructed?

One-body term

$$\mathbf{h}_{pq}^{\text{MO}} = \mathbf{C}_{\mu p}^* \mathbf{h}_{\mu\nu}^{\text{AO}} \mathbf{C}_{\nu q}$$

Coefficient matrix C, is optimized by the Hartree-Fock method.

Two-body term

$$\langle \mu\nu | \lambda s \rangle = \sum \mathbf{C}_{\sigma s} \langle \mu\nu | \lambda\sigma \rangle$$

The second-quantized (molecular orbital) Hamiltonian is constructed by transforming the atomic orbital Hamiltonian (integrals) using C

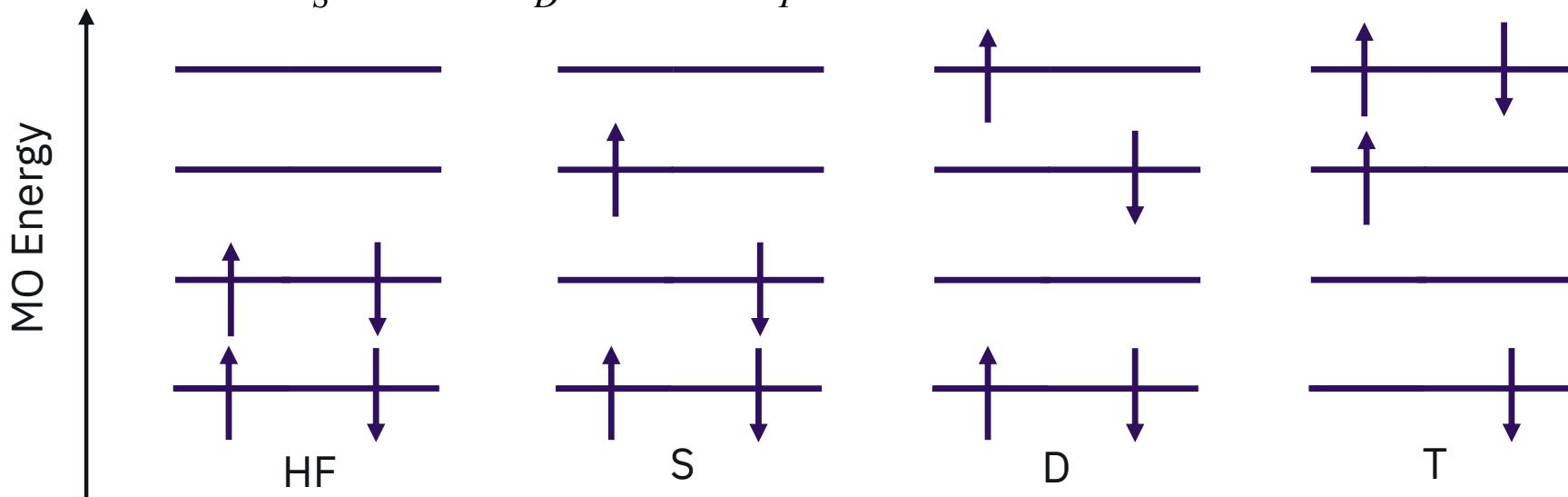
$$\langle \mu\nu | rs \rangle = \sum_{\lambda} \mathbf{C}_{\lambda r} \langle \mu\nu | \lambda s \rangle$$

$$\langle \mu q | rs \rangle = \sum_{\nu} \mathbf{C}_{\nu q} \langle \mu\nu | rs \rangle$$

$$\langle pq | rs \rangle = \sum_{\mu} \mathbf{C}_{\mu p} \langle \mu q | rs \rangle$$

Configuration Interaction Method

$$\begin{aligned}\Psi_{\text{CI}} &= C_0 \Psi_{\text{HF}} + \sum_{ia} C_{ia} \hat{a}_a^\dagger \hat{a}_i \Psi_{\text{HF}} + \sum_{ijab} C_{ijab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \Psi_{\text{HF}} + \sum_{ijkabc} C_{ijkabc} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_k \hat{a}_j \hat{a}_i \Psi_{\text{HF}} + \dots \\ &= C_0 \Psi_{\text{HF}} + \sum_S C_S \Psi_S + \sum_D C_D \Psi_D + \sum_T C_T \Psi_T \dots\end{aligned}$$



Describe the wavefunction by linear combination of Slater determinants
Determine “C”. It is exact without truncation (Full-CI)

CI as an Eigenvalue Problem

$$\Psi_{\text{CI}} = C_0 \Psi_{\text{HF}} + \sum_{ia} C_{ia} \hat{a}_a^\dagger \hat{a}_i \Psi_{\text{HF}} + \sum_{ijab} C_{ijab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i \Psi_{\text{HF}} + \sum_{ijkabc} C_{ijkabc} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_c^\dagger \hat{a}_k \hat{a}_j \hat{a}_i \Psi_{\text{HF}} + \dots$$

Use the variational theorem

$$E_{\text{CI}} = \frac{\langle \Psi_{\text{CI}} | \hat{H} | \Psi_{\text{CI}} \rangle}{\langle \Psi_{\text{CI}} | \Psi_{\text{CI}} \rangle} \quad \frac{\partial E_{\text{CI}}}{\partial C_i} = 0$$

$$\mathbf{H}\mathbf{C} = E_{\text{CI}}\mathbf{C}$$

Eigenvalue problem

Note that the number of elements in the matrix scale exponentially against the system size without truncation. We do not explicitly diagonalize the full matrix.

The CI Matrix

$$\mathbf{H}_{ij} = \langle \Psi_i | \hat{H} | \Psi_j \rangle$$



Brillouin's theorem

$$\langle \Psi_S | \hat{H} | \Psi_{HF} \rangle = 0$$

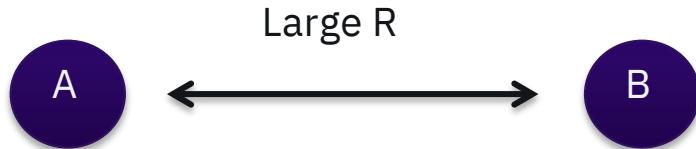
Slater–Condon rules

$$\langle \Psi_N | \hat{H} | \Psi_{M>N+2} \rangle = 0$$

$$\langle \Psi_N | \hat{H} | \Psi_{M<N-2} \rangle = 0$$

	$ \Psi_{HF}\rangle$	$ \Psi_S\rangle$	$ \Psi_D\rangle$	$ \Psi_T\rangle$	$ \Psi_Q\rangle$
$\langle \Psi_{HF} $		0		0	0
$\langle \Psi_S $	0				0
$\langle \Psi_D $					
$\langle \Psi_T $	0				
$\langle \Psi_Q $	0	0			

Size inconsistency for Truncated CISD



$$E_{\text{CI}}(AB) = E_{\text{CI}}(A) + E_{\text{CI}}(B) ?$$

$$E_{\text{FullCI}}(AB) = E_{\text{FullCI}}(A) + E_{\text{FullCI}}(B)$$

$$E_{\text{CISD}}(AB) > E_{\text{CISD}}(A) + E_{\text{CISD}}(B)$$

$$\Psi_{\text{HF}}(A) \times \Psi_{\text{HF}}(B) = \Psi_{\text{HF}}(A + B)$$

$$\vdots$$

$$\Psi_{\text{HF}}(A) \times \Psi_{\text{D}}(B) = \Psi_{\text{D}}(A + B)$$

$$\Psi_{\text{D}}(A) \times \Psi_{\text{HF}}(B) = \Psi_{\text{D}}(A + B)$$

$$\Psi_{\text{S}}(A) \times \Psi_{\text{D}}(B) = \boxed{\Psi_{\text{T}}(A + B)}$$

$$\Psi_{\text{D}}(A) \times \Psi_{\text{S}}(B) = \boxed{\Psi_{\text{T}}(A + B)}$$

$$\Psi_{\text{D}}(A) \times \Psi_{\text{D}}(B) = \boxed{\Psi_{\text{Q}}(A + B)}$$

CISD does not satisfy size-consistency

Coupled Cluster Method

Coupled cluster ansatz $|\Psi\rangle = \exp(\hat{T})|\Psi_{HF}\rangle$

Cluster Operator $\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots$ $\hat{\tau}_k$ General excitation operator

$$\hat{T}_1 = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i = \sum_S t_S \hat{\tau}_S \quad \hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i = \frac{1}{4} \sum_D t_D \hat{\tau}_D$$

Coupled cluster wavefunction

$$|\Psi\rangle = \left(1 + T_1 + T_2 + \dots + \frac{1}{2}(T_1 + T_2 + \dots)^2 + \dots \right) |\Psi_{HF}\rangle$$

$$= \underbrace{\left(1 + T_1 + T_2 + \frac{1}{2}T_1^2 + T_1 T_2 + \frac{1}{2}T_2^2 + \dots \right)}_{\text{Connected excitations (CI)}} \underbrace{|\Psi_{HF}\rangle}_{\text{Disconnected excitations}}$$

Coupled Cluster Energy and Amplitude Equation

Put the CC wavefunction in the Schrödinger equation

Multiply $\exp(-T)$ from the left-hand side
Project to all Slater determinants

Energy expression

Amplitude equation
(orbitals are orthogonal)

$$\hat{H}\Psi_{\text{CC}} = E_{\text{CC}}\Psi_{\text{CC}}$$

$$\hat{H}\exp(\hat{T})|\Psi_{\text{HF}}\rangle = E_{\text{CC}}\exp(\hat{T})|\Psi_{\text{HF}}\rangle$$

$$E_{\text{CC}} = \langle\Psi_{\text{HF}}|\exp(-\hat{T})\hat{H}\exp(\hat{T})|\Psi_{\text{HF}}\rangle$$

$$R_{\text{CC}} = \langle\Psi_{\text{HF}}|\hat{t}_k^\dagger\exp(-\hat{T})\hat{H}\exp(\hat{T})|\Psi_{\text{HF}}\rangle = 0$$

- We solve the nonlinear equation (the amplitude equation)
- Size consistent! The higher excitation terms of the disconnected terms
- Coupled-cluster method is not variational
- CCSD(T) (perturbative triples) is the gold standard method

Unitary Coupled Cluster

Coupled cluster ansatz

$$|\Psi\rangle = \exp(\hat{T} - \hat{T}^\dagger) |\Psi_{HF}\rangle$$

Cluster Operator

$$\hat{T}_1 = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i = \sum_S t_S \hat{\tau}_S \quad \hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i = \frac{1}{4} \sum_D t_D \hat{\tau}_D$$

$$E(\hat{\tau}_k) \equiv \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

The ansatz is unitary

$$\exp(\hat{T} - \hat{T}^\dagger)$$

Unitary coupled cluster is variational

However...

$$\text{CCSD} \quad \exp(-\hat{T})\hat{H}\exp(\hat{T}) = \hat{H} + [\hat{H}, \hat{T}] + \frac{1}{2}[[\hat{H}, \hat{T}], \hat{T}] + \frac{1}{6}[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}] + \frac{1}{24}[[[[\hat{H}, \hat{T}], \hat{T}], \hat{T}], \hat{T}]$$

Terminates at finite order

Unitary CCSD $[\hat{H}, [\hat{T}, \hat{T}^\dagger]]$ There is no termination point

Therefore, UCCSD needs to be truncated in a finite order to be implemented on a classical computer. It will lose its advantage...

Rayleigh–Schrödinger Perturbation Theory

Partition the Hamiltonian

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)}$$

The solution to the inexact operator is known

$$\hat{H}^{(0)} \Psi_n^{(0)} = E_n^{(0)} \Psi_n^{(0)}$$

The perturbed energy and wavefunction are expressed as power series

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots$$

$$\Psi_n = \Psi_n^{(0)} + \lambda \Psi_n^{(1)} + \lambda^2 \Psi_n^{(2)} + \dots$$

Schrodinger Equation

$$\begin{aligned} & \left(\hat{H}^{(0)} + \lambda \hat{H}^{(1)} \right) \left(|\Psi_n^{(0)}\rangle + \lambda |\Psi_n^{(1)}\rangle + \lambda^2 |\Psi_n^{(2)}\rangle + \dots \right) \\ &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \dots \right) \left(|\Psi_n^{(0)}\rangle + \lambda |\Psi_n^{(1)}\rangle + \lambda^2 |\Psi_n^{(2)}\rangle + \dots \right) \end{aligned}$$

Perturbation is small

We want to map an inexact operator to an exact operator using perturbation theory with increasing order of accuracy

Energy and Wavefunction

Comparing coefficients of each power of lambda:

k -th order Schrödinger equation

$$H^{(0)} |\Psi_n^{(k)}\rangle + H^{(1)} |\Psi_n^{(k-1)}\rangle = \sum_{i=0}^k E_n^{(i)} |\Psi_n^{(k-i)}\rangle$$

$$\langle \Psi_0^{(0)} | H^{(0)} | \Psi_n^{(k)}\rangle + \langle \Psi_0^{(0)} | H^{(1)} | \Psi_n^{(k-1)}\rangle = \sum_{i=0}^k \langle \Psi_0^{(0)} | E_n^{(i)} | \Psi_n^{(k-i)}\rangle$$

k -th order energy correction

$$\langle \Psi_0^{(0)} | H^{(1)} | \Psi_n^{(k-1)}\rangle = E_n^{(k)}$$

First-order Perturbed wavefunction

k -th order Perturbed wavefunction

$$|\Psi_n^{(k)}\rangle = \sum_j C_j^{(k)} |\Psi_j^{(0)}\rangle \quad |\Psi_n^{(1)}\rangle = \sum_{j \neq n} \frac{\langle \Psi_j^{(0)} | \hat{H}^{(1)} | \Psi_n^{(0)}\rangle}{E_n^{(0)} - E_j^{(0)}} |\Psi_j^{(0)}\rangle$$

The perturbed wavefunction is a linear combination of basis of unperturbed wavefunction

Møller-Plesset Perturbation Theory

Partition the Hamiltonian $\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$

$$\hat{H}_0 = \sum_{i=1}^N \hat{f}(i) \quad \hat{H}^{(1)} = \sum_{i>j} \frac{1}{\mathbf{r}_{ij}} - \sum_{ij} \left(\hat{J}_j(i) - \hat{K}_j(i) \right)$$

“Fluctuation potential”: The difference between the “real” two-electron term and mean-field approximation

Fock operator $\hat{f}(i) = \hat{h}(i) + \sum_j \left(\hat{J}_j(i) - \hat{K}_j(i) \right)$

We want to map an inexact operator to an exact operator using perturbation theory

In Møller-Plesset perturbation theory, the sum of Fock operators is mapped to the correct Hamiltonian

Zero-th and first order energies

$$\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)}$$

Orbital energies

“Ground state” $|\Psi_0^{(0)}\rangle = |\Psi_{\text{HF}}\rangle$ $E_0^{(0)} = \langle\Psi_{\text{HF}}|\hat{H}^{(0)}|\Psi_{\text{HF}}\rangle = \sum \epsilon_i$

First-order energy correction $E_0^{(1)} = \langle\Psi_{\text{HF}}|\hat{H}^{(1)}|\Psi_{\text{HF}}\rangle = \sum_{i>j}^{N_{ele}} ([ii|jj] - [ij|ji]) = E_{\text{HF}} - E_0^{(0)}$

$$E_0^{(0)} + E_0^{(1)} = E_{\text{HF}}$$

The first-order correction to the energy is regaining the Hartree–Fock energy

MP2 (Second-order Perturbation)

First-order wavefunction

$$|\Psi_n^{(1)}\rangle = \sum_{j \neq n} \frac{\langle \Psi_j^{(0)} | \hat{H}^{(1)} | \Psi_n^{(0)} \rangle}{E_n^{(0)} - E_j^{(0)}} |\Psi_j^{(0)}\rangle$$

Second-order energy correction

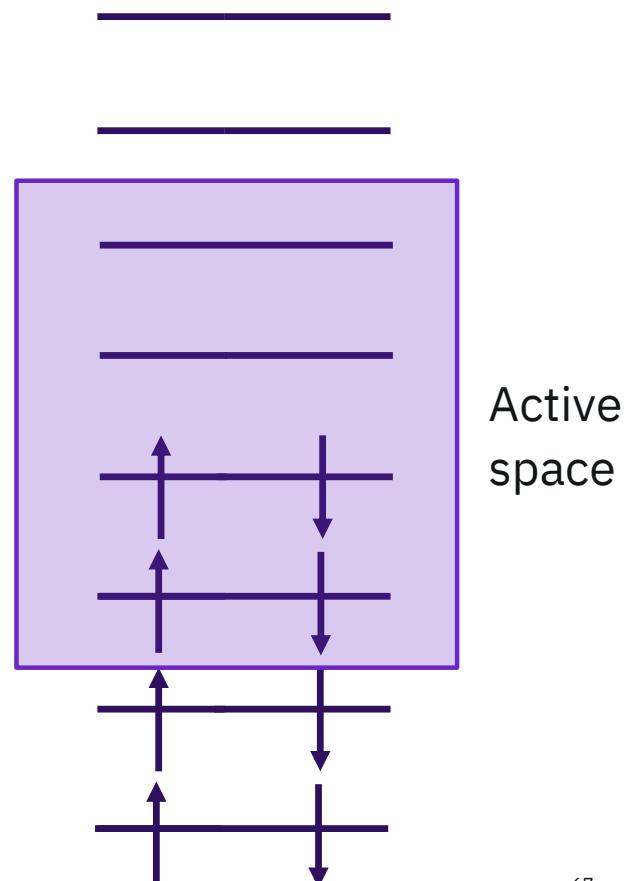
$$\begin{aligned} E_0^{(2)} &= \langle \Psi_{\text{HF}} | H^{(1)} | \Psi_0^{(1)} \rangle = \sum_{j \neq n} \frac{\langle \Psi_j^{(0)} | \hat{H}^{(1)} | \Psi_n^{(0)} \rangle \langle \Psi_n^{(0)} | \hat{H}^{(1)} | \Psi_j^{(0)} \rangle}{E_n^{(0)} - E_j^{(0)}} \\ &= \sum_D \frac{\langle \Psi_D | \hat{H}^{(1)} | \Psi_{\text{HF}} \rangle \langle \Psi_{\text{HF}} | \hat{H}^{(1)} | \Psi_D \rangle}{E_0^{(0)} - E_D^{(0)}} = \sum_{i>j}^{N_{\text{occ}}} \sum_{a>b}^{N_{\text{vir}}} \frac{|[ia|jb] - [ib|ja]|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \end{aligned}$$

MP2 does not require SCF procedure

Increasing the order of perturbation does not always result to better results

Active Space CI & SCF

- Rather than truncating the excitation, truncating the space to perform CI (Full CI) is sometimes a better strategy. We can treat the electrons and orbitals important for the problem more accurately than the others
- The important orbitals can be reoptimized: Multiconfigurational SCF (or Complete Active Space SCF if Full CI is used)
- Perturbation, CI, and CC can be carried out using MCSCF wavefunction as a reference (multireference)



Scaling of Correlation Methods

HF: 99% of the total energy (N^{2-3})

MP2: 80% of the last 1 (N^{4-5})

CISD: 90% of the last 1% (N^6)

CCSD: 95% of the last 1% (N^6)

CCSD(T): >99% of the last 1% (N^7)

We can achieve systematic improvement using correlation methods

The computational resource for Full CI grows exponentially

Correlation Methods

- Electron Correlation
- Second quantization
- Configuration interaction
 - Brillouin theorem
 - Slater–Condon rules
 - Size consistency
- Coupled-cluster methods
- Perturbation theory (MP2)
- Active space

Density Functional Theory



Density Functional Theory (DFT): Hohenberg–Kohn Theorem

- The first theorem: The electron density ($\rho(x, y, z)$) uniquely determines the external potential (charges and position of the nucleus)
 - Properties of a many-electron system in the ground state is determined by the electron density
- The second theorem: The electron density minimizes the energy functional $E[\rho]$
 - We can start from a trial electron density and optimize it to get the minimum energy (variational theorem)

DFT: The Energy Functional

$$E[\rho] = T[\rho] + V_{eN}[\rho] + J[\rho] + E_{xc}[\rho]$$

Electron-nucleus attraction

$$V_{eN}[\rho] = \sum_A Z_A \int d\mathbf{r}_1 \frac{\rho(\mathbf{r}_1)}{r_{1A}}$$

Coulomb interaction

$$J[\rho] = \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}$$

Kinetic energy

$$T[\rho] \quad \text{Not trivial}$$

Exchange-correlation energy

$$E_{xc}[\rho] \quad \text{Not trivial}$$

Kinetic energy and exchange-correlation functional (Kohn & Sham)

The density corresponds to a wavefunction described as a Slater determinant

The kinetic energy as seen in HF

$$\rho(\mathbf{r}) = \sum_i^{N_{ele}} |\chi(\mathbf{x})|^2$$

$$T_S[\rho] = \sum_{i=1}^{N_{ele}} \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle$$

$$E_{KS}[\rho] = T_S[\rho] + V_{eN}[\rho] + J[\rho] + E_{xc}[\rho]$$

$$E_{xc}[\rho] = T[\rho] - T_S[\rho] + E_x[\rho] + E_{corr}[\rho]$$

Kohn and Sham proposed to use a fictitious model (noninteracting electrons)

It is assuming that the density in this model is the same as the as the interacting electron system

Kohn-Sham Equation

Kohn-Sham equation
 (Obtained by minimizing
 the energy functional by
 varying the orbitals)

$$\left[-\frac{1}{2} \nabla^2 + V_{eff}(\mathbf{r}) \right] \chi_i(\mathbf{x}) = \epsilon_i \chi_i(\mathbf{x})$$

Effective potential

$$V_{eff}(\mathbf{r}) = - \sum_A \frac{Z_A}{r_{1A}} + \int d\mathbf{r}_2 \frac{\rho(\mathbf{r}_2)}{r_{12}} + V_{xc}(\mathbf{r})$$

Exchange-
 correlation potential

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}}{\partial \rho(\mathbf{r})}$$

Kohn-Sham equation allows us to perform SCF calculation for DFT

We can treat correlation with the same or smaller cost compared to HF

Exchange-correlation Functionals

Heaven of Chemical Accuracy (1 kcal/mol)

Double Hybrids (Virtual MO)

Hybrid (Occupied MO)

MetaGGA $\nabla^2 \rho$

GGA $\nabla \rho$

LDA ρ

The Hartree World

The “exact” functional is unknown
We can improve the performance perturbatively

The accuracy (and complexity) of the approximation increases up the ladder!

Hybrid GGA: Modify GGA with HF exchange (B3LYP)

MetaGGA: Modify GGA with $\nabla^2 \rho$ and kinetic energy density

Generalized Gradient Approximation (GGA): Modify LDA with the gradient of density $\nabla \rho$

Local Density Approximation (LDA) :Functional depending only on the electron density ρ (uniform electron gas model)

Outline

- Introduction
- Schrödinger Equation and Born–Oppenheimer Approximation
- Quantum Chemistry Methods
 - Hartree–Fock Method
 - Basis Sets
 - Atomic Orbital Integrals
 - Semiempirical Methods
 - Correlation Methods
 - Perturbation Theory
 - Configuration Interaction
 - Coupled Cluster Methods
 - Density Functional Theory

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