

Molecular Hamiltonian. 分子的哈密顿量.

time-independent, non-relativistic. s.eq: $\hat{H}|\psi\rangle = E|\psi\rangle$.

\hat{H} : Hamiltonian operator

E : molecular total energy.

$|\psi\rangle$: molecular wavefunction.

→ don't care about the case when particles get close to the speed of light.

N : electrons $\vec{r}_i = (x_i, y_i, z_i)$. Vector. $i, j, k, l \dots$

M : nuclei $\vec{r}_A = (x_A, y_A, z_A)$. Vector. $A, B, C, D \dots$

↓

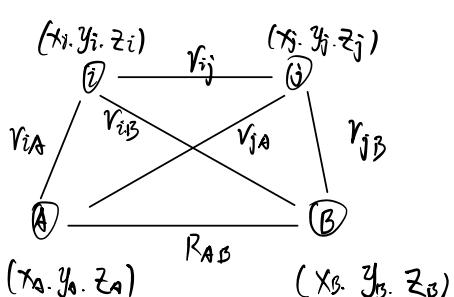
treat collections of protons and neutrons. $\vec{r}_{12} = (x_2 - x_1, y_2 - y_1, z_2 - z_1)$ Vector.

$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} = \Delta$. Laplacian operator.

as one point particle.

3-D Cartesian space.

many-electron system:



two electrons

two nuclei

复数: nuclei
单数: nucleus

$$\hat{H} = \hat{T} + \hat{V}$$

↑

\hat{T} kinetic energy of particles

$\hat{T} = \hat{T}_e + \hat{T}_n$ (电子 + 核子)

↑

\hat{V} potential energy of particle pairs

$\hat{V} = \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn}$
(电子-电子, 电子-核子, 核子-核子)

the total energy involves the attractions and repulsions between all of these pairs of charge particles.

$$\hat{H} = \underbrace{\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2}_{\text{electron + nuclei kinetic energy}} + \underbrace{\sum_{i=1}^N \sum_{j=i+1}^N k \frac{e^2}{r_{ij}}}_{\text{Coulomb's law}} - \underbrace{\sum_{i=1}^N \sum_{A=1}^M k \frac{z_i e^2}{r_{iA}}}_{\text{Coulomb's law}} + \underbrace{\sum_{A=1}^M \sum_{B=A+1}^M k \frac{z_A z_B e^2}{r_{AB}}}_{\text{Coulomb's law}}$$

$$\left. \begin{aligned} V_{12} &= k \frac{q_1 q_2}{r_{12}} \\ k &= \frac{1}{4\pi\epsilon_0} \end{aligned} \right\}$$

here. $N=2$, $M=2$, so there are total 6 interactions terms, $C^2 = 6$.

whether attractions (negative sign), or.
电荷异号

repulsion. (positive sign)
电荷同号.

Atomic Units 原子单位制. 简化数学形式.

m. kg. c. J ... : SI units are common in physical quantities like mass, distance.

SI units are inconvenient mathematically at molecular microscopic scale when we are talking about atoms, molecules, and any type of quantum mechanics calculation.

$$m_e = 9 \times 10^{-31} \text{ kg} \rightarrow m_e = 1.$$

$$\text{charge 电量 } e = 1.6 \times 10^{-19} \text{ C} \rightarrow e = 1$$

$$\text{angular momentum } \hbar = \frac{\hbar}{2\pi} = 1.1 \times 10^{-34} \text{ J.S} \rightarrow \hbar = 1.$$

$$\text{真空电容率 Vacuum permittivity: } 4\pi\epsilon_0 = 1.1 \times 10^{-10} \frac{\text{C}^2}{\text{J}\cdot\text{m}} \rightarrow 4\pi\epsilon_0 = 1.$$

真空介电常数

length $a = 5.3 \times 10^{-11} \text{ m.} \rightarrow a = 1. \text{ (Bohr radius).}$ (any distance would be in units of Bohr radius).

$$\Rightarrow \hat{T}_e = - \sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 = - \sum_i \frac{1}{2} \nabla_i^2$$

$$\hat{T}_N = - \sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2 = - \sum_A \frac{1}{2M_A} \nabla_A^2$$

$$\hat{V}_{NN} = \sum_{A=1}^M \sum_{B=A+1}^M \frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} = \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$$

$$\hat{V}_{Ne} = - \sum_{A=1}^M \sum_{i=1}^N \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} = - \sum_A \sum_i \frac{Z_A}{r_{iA}}$$

$$\hat{V}_{ee} = \sum_{i=1}^N \sum_{j \neq i}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} = \sum_{i < j} \frac{1}{r_{ij}}$$

$$\hat{H} = - \sum_i \frac{1}{2} \nabla_i^2 - \sum_A \frac{1}{2M_A} \nabla_A^2 - \sum_{iA} \frac{Z_A}{r_{iA}} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}$$

for the mass of nucleus, we usually use the mass of electron to express the mass of nucleus. for example. the hydrogen atom, which is the single proton is about 1836 Me. $M_A \rightarrow [Me]$. so $M_A \approx 1800 Me = 1800$.

for the charge of nucleus. it's in the unit of charge of the electron.

$Z_A \rightarrow [e]$, for hydrogen. $Z_H = 1$, for helium. $Z_{He} = 2$.

atomic units allow us to simplify all the terms quite a bit into a very simple form. and gives us the easier and manageable form of hamiltonian

Note : there is no any approximation so far.

Born - Oppenheimer Approximation. (BO).

actually: $\hat{H}|\psi\rangle = E|\psi\rangle \rightarrow$ can't solve exactly other than a hydrogen atom.
with a finite amount of computing resources in a finite amount of time. 算力不够.理论上可以解.但 $N \sim 10^{23}$

for N charged particles $\rightarrow C_n^2 = \frac{N(N-1)}{2}$ interacting pairs.

This is known for "many-body problem", which is unsolvable for $N > 2$.
that's why we can solve it for hydrogen atom, containing one electron, one nucleus. but we can't solve it exactly for any molecular system which has more than two charged particles

Here, in computational term or in computer science term, this is what we called:
"NP-complete" NP完全性問題.

\rightarrow the difficulty of solving such a problem scales as an exponential in the number of particles. $\rightarrow O(e^N)$

\rightarrow it's not twice as difficult to solve the problem if you go from 10 to 20 particles !!!

\rightarrow We hope it's polynomial. but it's exponential!

This is where we have to start approximations in order to be able to get a handle on the molecular hamiltonian and try to get out some approximate solutions which will eventually end up at Hartree-Fock theory

considering $M_A \gg m_e$. for hydrogen atom. its nucleus : $M_H = 1836 m_e$. and for heavy atoms, the mass of nucleus is much larger than the mass of electron. Hence : nuclei move very slow relative to electrons. \Rightarrow approximate $\{\vec{R}_A\}$ fixed $\Rightarrow \hat{T}_N = 0$.

Hence, we treat the nuclei as classical point particles. which means they don't have quantum behaviour. and we don't care about their wave functions.

so the \hat{H} :

$$\hat{H} = \underbrace{\sum_i -\frac{1}{2M_A} \nabla_A^2}_{0} + \underbrace{\sum_{A \neq B} \frac{z_A z_B}{R_{AB}}}_{\text{constant}} + \underbrace{\sum_i -\frac{1}{2} \nabla_i^2 - \sum_{iA} \frac{z_A}{r_{iA}} + \sum_{ij} \frac{1}{r_{ij}}}_{\text{still difficult.}}$$

we only focus on the electrons:

electronic hamiltonian acts on the electronic wave function, and gives us the electronic energy times over electronic wave functions:

$$\hat{H}_{\text{ele}} |\Psi_{\text{ele}}\rangle = E_{\text{ele}} |\Psi_{\text{ele}}\rangle$$

$$\text{Where: } \hat{H}_{\text{ele}} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_{iA} \frac{z_A}{r_{iA}} + \sum_{ij} \frac{1}{r_{ij}}$$

$$V_{\text{int}} = \sum_{A \neq B} \frac{z_A z_B}{R_{AB}} \cdot \text{constant. can be added or not. only effect } E. \text{ not } |\Psi\rangle.$$

Spin Orbitals.

"orbital" \rightarrow 1-electron wavefunction. we say orbital we generally mean a one electron wave function.

orbital is occupied: electron exists in orbital

orbital is virtual: unoccupied, no electron in the orbital.

spatial orbital: specifies x, y, z coordinates (no spin). $\vec{r} = (x, y, z)$

spin orbital: specifies x, y, z coordinates and spin, $\vec{x} = (\vec{r}, w) = (x, y, z, w)$.

here: spin variable: $w = |\alpha\rangle$ or $w = |\beta\rangle$
spin up spin down

$$\left. \begin{array}{l} \int dw \alpha^*(w) \alpha(w) = \int dw \beta^*(w) \beta(w) = 1 \Rightarrow \langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1 \\ \int dw \alpha^*(w) \beta(w) = \int dw \beta^*(w) \alpha(w) = 0 \Rightarrow \langle \alpha | \beta \rangle = \langle \beta | \alpha \rangle = 0 \end{array} \right\} \{|\alpha\rangle, |\beta\rangle\} \text{ orthonormal}$$

$$\text{spin orbital: } \chi(\vec{x}_i) = \phi(\vec{r}_i) \sigma(w_i) \quad \text{so: } \chi(\vec{x}_i) = \begin{cases} |\phi(\vec{r}_i)\alpha\rangle \\ |\phi(\vec{r}_i)\beta\rangle \end{cases}$$

\downarrow \downarrow \rightarrow spin function
 (kai) spatial orbital

$$\phi^*(\vec{r}_i) \phi(\vec{r}_i) \frac{d^3 \vec{r}_i}{\text{volume element } d^3 \vec{r}} = \text{probability of finding electron } i \text{ near point } r_i.$$

$$\int_{-\infty}^{\infty} d^3 \vec{r}_i \phi^*(\vec{r}_i) \phi(\vec{r}_i) = \langle \phi | \phi \rangle = 1 : \text{normalized.}$$

if $\{\phi_i\}$ are "complete" then any function of 3-D could be defined by: $f(\vec{r}) = \sum_i a_i \phi_i(\vec{r})$

the linear combination of a complete basis set can form any functions of that same number of variables

here, the coefficients $\{a_i\}$ come from

$$a_i = \langle \phi_i | f \rangle : \text{integral of } \phi^* \text{ with } f : \int d\vec{r} \phi^*(\vec{r}) f(\vec{r})$$

we will take whatever function we have multiply by the complex conjugate (复共轭) of our spatial function and integrate over all 3-D

Hartree products.

what's the wave functions of a set of electrons?

Imagine: $\hat{V}_{ee} = 0$ (not correct).

then $\hat{H}_{elec} = \sum_{i=1}^N \hat{h}(i)$, where $\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{j=1}^N \frac{Z_j}{r_{ij}}$, for single electron.

$\chi(\vec{x}_i)$ becomes an eigenfunction of $\hat{h}(i)$: $\hat{h}(i)\chi(\vec{x}_i) = \epsilon_i \chi(\vec{x}_i)$, ϵ_i = orbital energy.

then: $\psi(\vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N) = \chi_1(\vec{x}_1)\chi_2(\vec{x}_2)\dots\chi_N(\vec{x}_N)$ Hartree product: a product of a bunch of spin orbitals in a system.

$\psi(\{\vec{x}_i\}) = \prod_{i=1}^N \chi_i(\vec{x}_i)$, $\chi_i = (x_i, y_i, z_i, w_i)$

which means: independent uncorrelated electrons.

$$|\psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N)|^2 d\vec{x}_1 d\vec{x}_2 \dots d\vec{x}_N \quad (\text{the magnitude of } \psi \text{ squared}) \\ = |\chi_1(\vec{x}_1)|^2 d\vec{x}_1 |\chi_2(\vec{x}_2)|^2 d\vec{x}_2 \dots |\chi_N(\vec{x}_N)|^2 d\vec{x}_N$$

above conclusions are based on independent ($V_{ee}=0$) and uncorrelated electrons

but: electrons are indistinguishable !!! we don't know which one is which. we don't know which orbital each electron is in



We will fix the problem using Slater determinants (SD).

Antisymmetry Principle. (for prove, see relativistic quantum mechanics, but for non-relativistic quantum mechanics, we treat this as a postulate)

No spin in \hat{H} .

$$\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_i, \vec{x}_j, \dots, \vec{x}_N) = -\Psi(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_j, \vec{x}_i, \dots, \vec{x}_N)$$

must be true for all $1 \leq \{i, j\} \leq N$.

not true for Hartree product: $\Psi(1, 2) = \psi_1(1) \psi_2(2)$.

$$\Psi(2, 1) = \psi_2(2) \psi_1(1) = \psi_1(1) \psi_2(2) = \Psi(1, 2) \neq -\Psi(1, 2).$$

Pauli exclusion principle:

We can't have two electrons with the same spin in the same orbital.

Instead, use anti-symmetric linear combination:

$\Psi(1, 2) = \frac{1}{\sqrt{2}} [\psi_1(1) \psi_2(2) - \psi_2(1) \psi_1(2)]$ equal probability of electron 1 in wave function 1 (orbital 1) and electron 2 in WF 2, (orbital 2), as the reverse, electron 1 in WF 2, and electron 2 in WF 1

$$\text{hence: } \Psi(2, 1) = \frac{1}{\sqrt{2}} [\psi_2(2) \psi_1(1) - \psi_1(2) \psi_2(1)] = -\Psi(1, 2).$$

for 3 electrons: $3! = 6$. permutation of 3 electrons in 3 orbitals.

$$\begin{aligned} \Psi(1, 2, 3) = & \frac{1}{\sqrt{6}} [\psi_1(1) \psi_2(2) \psi_3(3) - \psi_1(1) \psi_3(2) \psi_2(3) \\ & + \psi_2(1) \psi_3(2) \psi_1(3) - \psi_2(1) \psi_1(3) \psi_3(2) \\ & + \psi_3(1) \psi_2(2) \psi_1(3) - \psi_3(1) \psi_1(2) \psi_2(3)] \end{aligned}$$

If swap any two of electrons, and get the same wave function with a switch sign.

N electrons $\rightarrow N!$ terms \rightarrow normalization constant: $\frac{1}{\sqrt{N!}}$

Slater determinants.

if we formalize anti-symmetric wavefunctions

$$\Psi(1, 2, \dots, i, j, \dots, N) = -\Psi(1, 2, \dots, j, i, \dots, N)$$

for all $1 \leq \{i, j\} \leq N$.

$$\Psi(\vec{x}_1, \vec{x}_2) = \frac{1}{\sqrt{2}} \begin{vmatrix} X(\vec{x}_1) & X_2(\vec{x}_1) \\ X_1(\vec{x}_2) & X_2(\vec{x}_2) \end{vmatrix} \rightarrow \begin{cases} \text{rows: electrons } \vec{x}_1, \vec{x}_2, \vec{x}_3, \dots, \vec{x}_N \\ \text{columns: spin orbitals: } X \end{cases}$$

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} X_1(1) & X_2(1) & \dots & X_N(1) \\ X_1(2) & X_2(2) & \dots & X_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ X_1(N) & X_2(N) & \dots & X_N(N) \end{vmatrix} \begin{cases} N \text{ electrons.} \\ N \text{ spin orbitals.} \end{cases}$$

↑ 简写:
all the coordinates for electron 1, 2, 3 ...
 $\vec{x}_i = (x, y, z, w)$

Pauli exclusion principle:

we can't have two electrons with the same spin in the same orbital.

if 2 electrons in same orbital or 2 orbitals are the same $\rightarrow \Psi = 0$.

Linear algebra: if any two rows or two columns are equal, the determinant is going to be 0.

$$\langle \Psi_A | \Psi_B \rangle = \begin{cases} 1 & \text{if all } \{x_i\} \text{ are same.} \\ 0 & \text{otherwise} \end{cases}$$

excited determinants.

N electrons. $\rightarrow N$ occupied orbitals

a set of basis functions: k basis functions

k basis functions. $\rightarrow 2k$ spin orbitals $\uparrow\downarrow \uparrow\downarrow$

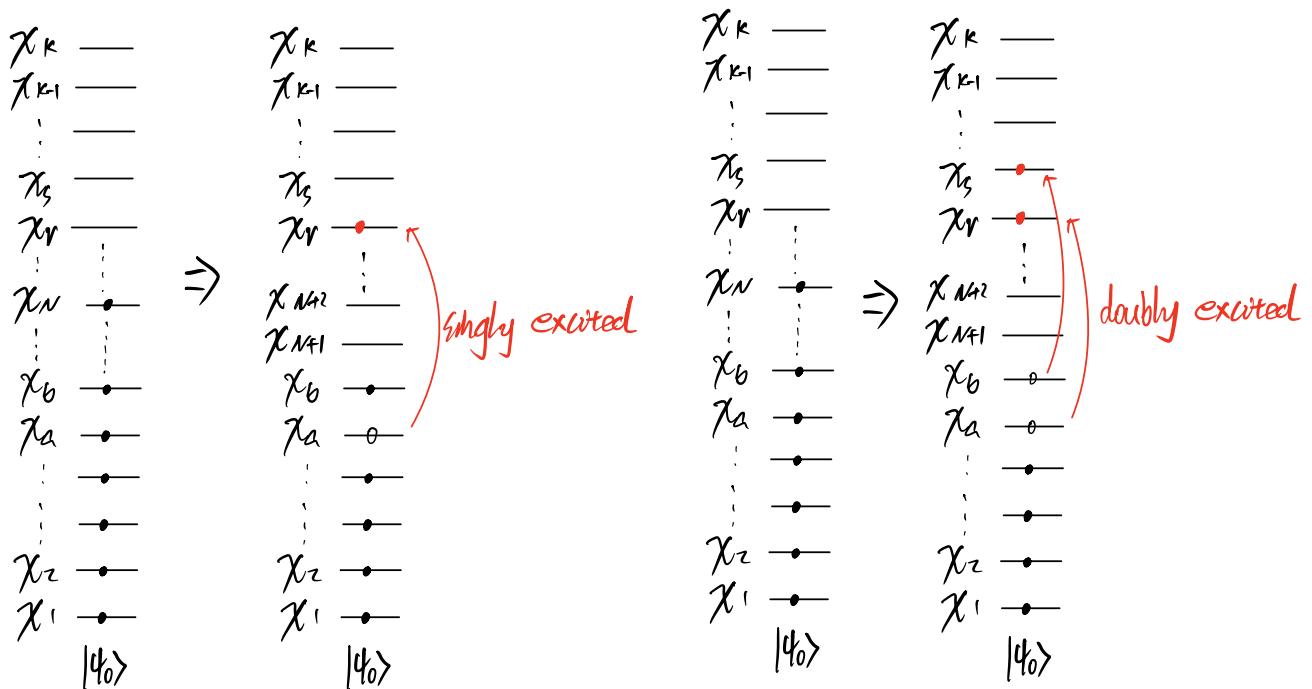
$2k-N$ virtual orbitals: unoccupied.

if these electrons aren't in the lowest possible energy level, which means they don't occupy from the ground state. there is: excited determinant.

Question: how many excited determinant?

if there are totally $2k$ spin orbitals, we have to choose which N of them are going to be occupied: $\binom{2k}{N} = \frac{(2k)!}{(2k-N)!N!}$

$|\Psi_0\rangle = |\chi_1 \chi_2 \dots \chi_a \chi_b \dots \chi_{N-1} \chi_N\rangle$ ground state, lowest energy



$|\Psi_0\rangle = |\chi_1 \chi_2 \dots \chi_a \chi_b \dots \chi_{N-1} \chi_N\rangle$ ground state, lowest energy

if we take one electron from spin orbital α (χ_a) to spin orbital ν (χ_ν)

$|\Psi_a^\nu\rangle = |\chi_1 \chi_2 \dots \chi_r \chi_b \dots \chi_{N-1} \chi_N\rangle$ singly excited.

if we take two electrons from χ_a and χ_b , to χ_ν and χ_s

$|\Psi_{a,b}^{\nu,s}\rangle = |\chi_1 \chi_2 \dots \chi_r \chi_s \dots \chi_{N-1} \chi_N\rangle$ doubly excited

how many singly excited SD? $C_{2k-N}^1 \cdot C_N^1 = (2k-N)N$

how many doubly excited SD? $C_{2k-N}^2 \cdot C_N^2 = \frac{(2k-N)!}{(2k-N-2)!2} \cdot \frac{N!}{(N-2)!2} = \frac{(2k-N)(2k-N-1)N(N-1)}{4}$

N -electron wavefunctions.

Can represent any N -electron wavefunction as a linear combination of all determinants of a complete set of spin orbitals at every level.

$$|\Psi\rangle = C_0 |\Psi_0\rangle + \sum_{a,r} C_a^r |\Psi_a^r\rangle + \sum_{\substack{a,b \\ r,s}} C_{a,b}^{r,s} |\Psi_{a,b}^{r,s}\rangle + \dots \quad \text{linear combination of every possible SD.}$$

↑ ↑ ↑
 ground state singlets doubles.

$$\left\{ \begin{array}{l} C_0, C_a^r, C_{a,b}^{r,s} : \text{coefficients.} \\ |\Psi_a^r\rangle : \text{singly excited SD.} \\ |\Psi_{a,b}^{r,s}\rangle : \text{doubly excited SD.} \end{array} \right.$$

$$\left\{ \begin{array}{l} \sum_{a,r} : \sum_{a=1}^N \sum_{r=N+1}^{2k} \\ \sum_{\substack{a,b \\ r,s}} : \sum_{a=1}^N \sum_{b=a+1}^N \sum_{r=N+1}^{2k} \sum_{s=N+1}^{2k} \\ \sum_{\substack{a,b,c \\ r,s,t}} : \sum_{a=1}^N \sum_{b=a+1}^N \sum_{c=b+1}^N \sum_{r=N+1}^{2k} \sum_{s=N+1}^{2k} \sum_{t=s+1}^{2k} \end{array} \right.$$

$$|\Psi_0\rangle \rightarrow \text{HF}$$

$$|\Psi_0\rangle, \{|\Psi_a^r\rangle\} \rightarrow \text{CI}.$$

if we include the ground state and a bunch of doubly excited determinants \rightarrow CI-D
we get a method called configuration interaction doubles (CI-D).

$$|\Psi_0\rangle, \{|\Psi_a^r\rangle\}, \{|\Psi_{a,b}^{r,s}\rangle\} \rightarrow \text{CI SD} \quad \text{singlets, doubles.}$$

$$|\Psi_0\rangle, \{|\Psi_a^r\rangle\}, \{|\Psi_{a,b}^{r,s}\rangle\}, \{|\Psi_{a,b,c}^{r,s,t}\rangle\} \rightarrow \text{CI SDT} \quad \text{singlets, doubles, triples}$$

CLSDTQ

CLSDTQ5

CLSDTQ56

⋮

Full CI (Full configuration interaction).

Restricted and unrestricted determinants

Restricted determinants: α, β pairs must have same spatial orbital: $\downarrow \uparrow \quad 1s(\alpha) \ 1s(\beta)$

Unrestricted determinants: α, β pairs can have different spatial orbital: $\downarrow \uparrow \quad 1s(\alpha) \ 2s(\beta)$.

spin orbitals: has spatial part and a spin part (α or β)

restricted: (closed shell) for every pair of electrons where their spin are matched,
they are in the same spatial orbital

if you have even number of electrons that fully complete a shell, and anything
that would end in s_2, p_6, d_{10} , something where the shell is full — close shell.

unrestricted (open shell)

RHF: Restricted Hartree-Fock:

x_1	x_2	x_3	x_4	...	x_{n-1}	x_n
$1s(\alpha)$	$1s(\beta)$	$2s(\alpha)$	$2s(\beta)$			
\downarrow	\downarrow	\downarrow	\downarrow			
ψ_1	$\bar{\psi}_1$	ψ_2	$\bar{\psi}_2$...	$\psi_{\frac{n}{2}}$	$\bar{\psi}_{\frac{n}{2}}$

$$|\Psi_0\rangle = |x_1, x_2, \dots, x_N\rangle = |\psi_1, \bar{\psi}_1, \psi_2, \bar{\psi}_2, \dots, \psi_{\frac{n}{2}}, \bar{\psi}_{\frac{n}{2}}\rangle = |\uparrow \downarrow \uparrow \bar{\downarrow} \dots \uparrow \bar{\downarrow}\rangle$$

this type of $|\Psi_0\rangle$ indicating that you are using a restricted determinant

UHF: unrestricted Hartree-Fock

(other: ROHF: restricted open shell Hartree-Fock)

One-Electron Integrals in HF theory

wave functions: $|\psi_0\rangle = |\chi_1 \chi_2 \dots \chi_N\rangle$, a set of spin orbitals.

$E = \langle \psi_0 | H | \psi_0 \rangle$ energy = expectation value of the hamiltonian operator.

two types of operators in \hat{H} :

$\hat{O}_1 \rightarrow 1\text{-electron operator}:$ $\begin{cases} \hat{T}_e \text{ (kinetic energy operator)} \\ \hat{V}_{ne} \text{ (potential energy operator for nuclear electron attraction)} \end{cases}$

$\hat{O}_2 \rightarrow 2\text{-electron operator: } \hat{V}_{ee} \text{ (electron-electron repulsion)}$

break the hamiltonian into two sums: $\hat{H} = \sum_i^N \hat{O}_1^{(ii)} + \sum_{i < j} \hat{O}_2^{(ij)}$ (one electron operator + two electron ~)

for one electron operator

$$E = \langle \psi_0 | \hat{O}_1 | \psi_0 \rangle = \langle \psi_0 | \sum_{i=1}^N \hat{h}_i | \psi_0 \rangle = \sum_{i=1}^N \langle \psi_0 | \hat{h}_i | \psi_0 \rangle = \sum_{i=1}^N \langle \psi_0 | \hat{O}_1^{(ii)} | \psi_0 \rangle$$

$$\text{hence: } E = \sum_i^N \langle \psi_0 | \hat{O}_1^{(ii)} | \psi_0 \rangle + \sum_{i < j} \langle \psi_0 | \hat{O}_2^{(ij)} | \psi_0 \rangle \quad (\hat{h}_i: \text{单电子 } h)$$

for 2-electron system:

$$|\psi_0\rangle = |\chi_1 \chi_2\rangle = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \begin{matrix} \text{column: spin orbital} \\ \text{row: electron} \end{matrix} = \frac{1}{\sqrt{2}} [\chi_1(1) \chi_2(2) - \chi_1(2) \chi_2(1)]$$

$$\begin{aligned} \langle \psi_0 | \hat{O}_1^{(11)} | \psi_0 \rangle &= \underbrace{\int dx_1 dx_2 \left[\frac{1}{\sqrt{2}} (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1)) \right]^* \hat{O}_1^{(11)}}_{\psi_0^*} \underbrace{\hat{O}_1^{(11)} \left[\frac{1}{\sqrt{2}} (\chi_1(x_1) \chi_2(x_2) - \chi_1(x_2) \chi_2(x_1)) \right]}_{\psi_0} \\ &= \frac{1}{2} \left[\int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \hat{O}_1^{(11)} \chi_1(x_1) \chi_2(x_2) - \int dx_1 dx_2 \chi_1^*(x_1) \chi_2^*(x_2) \hat{O}_1^{(11)} \chi_2(x_1) \chi_1(x_2) \right. \\ &\quad \left. - \int dx_1 dx_2 \chi_2^*(x_1) \chi_1^*(x_2) \hat{O}_1^{(11)} \chi_1(x_1) \chi_2(x_2) + \int dx_1 dx_2 \chi_2^*(x_1) \chi_1^*(x_2) \hat{O}_1^{(11)} \chi_2(x_1) \chi_1(x_2) \right] \end{aligned}$$

factor out all $f(x_2)$. $\hat{O}_1^{(0)} = f(x)$

$$\begin{aligned}
 &= \frac{1}{2} \left[\int dx_2 \underbrace{\chi_2^*(x_2) \chi_2(x_2)}_{\text{2个电子分开, 对 } \hat{O}_1^{(0)} \text{ 不变.}} \int dx_1 \chi_1^*(x_1) \hat{O}_1^{(0)} \chi_1(x_1) - \frac{1}{2} \int dx_1 \underbrace{\chi_1^*(x_1) \chi_1(x_1)}_{=0} \int dx_2 \chi_2^*(x_2) \hat{O}_1^{(0)} \chi_2(x_2) \right. \\
 &\quad \left. - \frac{1}{2} \int dx_2 \underbrace{\chi_2^*(x_2) \chi_2(x_2)}_{=0} \int dx_1 \chi_1^*(x_1) \hat{O}_1^{(0)} \chi_1(x_1) + \frac{1}{2} \int dx_2 \underbrace{\chi_1^*(x_2) \chi_1(x_2)}_{=1} \int dx_1 \chi_1^*(x_1) \hat{O}_1^{(0)} \chi_2(x_1) \right] \\
 &= \frac{1}{2} [\langle \chi_1(x_1) | \hat{O}_1^{(0)} | \chi_1(x_1) \rangle + \langle \chi_2(x_1) | \hat{O}_1^{(0)} | \chi_2(x_1) \rangle] = \frac{1}{2} [\langle 1 | \hat{O}_1^{(0)} | 1 \rangle + \langle 2 | \hat{O}_1^{(0)} | 2 \rangle]
 \end{aligned}$$

for 1st electron and 2nd electron, it's the same result.

$$\text{1st electron: } \langle \psi_0 | \hat{O}_1^{(0)} | \psi_0 \rangle = \frac{1}{2} [\langle \chi_1(x_1) | \hat{O}_1^{(0)} | \chi_1(x_1) \rangle + \langle \chi_2(x_1) | \hat{O}_1^{(0)} | \chi_2(x_1) \rangle]$$

$$\text{2nd electron: } \langle \psi_0 | \hat{O}_1^{(2)} | \psi_0 \rangle = \frac{1}{2} [\langle \chi_1(x_2) | \hat{O}_1^{(2)} | \chi_1(x_2) \rangle + \langle \chi_2(x_2) | \hat{O}_1^{(2)} | \chi_2(x_2) \rangle]$$

if there are 2 electrons:

$$\begin{aligned}
 E &= \sum_{i=1}^2 \langle \psi_0 | \hat{O}_1^{(i)} | \psi_0 \rangle = \langle \psi_0 | \hat{O}_1^{(1)} | \psi_0 \rangle + \langle \psi_0 | \hat{O}_1^{(2)} | \psi_0 \rangle \\
 &= \frac{1}{2} \left[\langle \chi_1(x_1) | \hat{O}_1^{(0)} | \chi_1(x_1) \rangle + \langle \chi_2(x_1) | \hat{O}_1^{(0)} | \chi_2(x_1) \rangle + \langle \chi_1(x_2) | \hat{O}_1^{(2)} | \chi_1(x_2) \rangle + \langle \chi_2(x_2) | \hat{O}_1^{(2)} | \chi_2(x_2) \rangle \right] \\
 &= \frac{1}{2} [\langle 1 | \hat{h}_1 | 1 \rangle + \langle 2 | \hat{h}_1 | 2 \rangle + \langle 1 | \hat{h}_2 | 1 \rangle + \langle 2 | \hat{h}_2 | 2 \rangle], \quad \hat{O}_1^{(i)} = \hat{h}_1^{(i)}, \quad \hat{O}_1^{(2)} = \hat{h}_1^{(2)}
 \end{aligned}$$

add over all the electrons.

此处指单电子 \hat{h}_i . (1st or 2nd)

$$E = \sum_{i=1}^2 \langle i | \hat{h}_i | i \rangle$$

$$\text{if there are } N \text{ electrons: } E = \sum_{i=1}^N \langle i | \hat{h}_i | i \rangle$$

core hamiltonian for that particular electron. $\hat{O}_i = \sum_{i=1}^N \hat{h}_i^i$, $\hat{h}_i^i = -\frac{1}{2} \nabla_i^2 - \sum_{A=1}^M \frac{z_A}{r_{iA}}$ (core hamiltonian)

two electron integral.

$$\hat{O}_2 = \hat{V}_{ee} = \sum_{i=1}^N \sum_{j=i+1}^N \frac{1}{r_{ij}} = \sum_{ij} \frac{1}{r_{ij}} \quad \text{electron-electron repulsion.}$$

$$\begin{aligned} \langle \Psi_0 | \frac{1}{r_{ij}} | \Psi_0 \rangle &= \frac{1}{2} \left[\int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^*(\mathbf{x}_1) \chi_2^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) - \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^*(\mathbf{x}_1) \chi_1^*(\mathbf{x}_2) \frac{1}{r_{11}} \chi_1(\mathbf{x}_1) \chi_1(\mathbf{x}_2) \right. \\ &\quad \left. - \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^*(\mathbf{x}_1) \chi_2^*(\mathbf{x}_2) \frac{1}{r_{22}} \chi_2(\mathbf{x}_1) \chi_1(\mathbf{x}_2) + \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_2^*(\mathbf{x}_1) \chi_1^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_2(\mathbf{x}_1) \chi_1(\mathbf{x}_2) \right] \\ &= \frac{1}{2} \left[\int d\mathbf{x}_1 d\mathbf{x}_2 \chi_1^*(\mathbf{x}_1) \chi_2^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_1(\mathbf{x}_1) \chi_2(\mathbf{x}_2) + \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_2^*(\mathbf{x}_1) \chi_1^*(\mathbf{x}_2) \frac{1}{r_{12}} \chi_2(\mathbf{x}_1) \chi_1(\mathbf{x}_2) \right] \\ &= \frac{1}{2} \left[\underbrace{\int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\chi_1^*(\mathbf{x}_1) \chi_1(\mathbf{x}_1)}{r_{11}} \frac{\chi_2^*(\mathbf{x}_2) \chi_2(\mathbf{x}_2)}{r_{12}}}_{\text{1st ele}} + \underbrace{\int d\mathbf{x}_1 d\mathbf{x}_2 \frac{\chi_2^*(\mathbf{x}_1) \chi_2(\mathbf{x}_1)}{r_{22}} \frac{\chi_1^*(\mathbf{x}_2) \chi_1(\mathbf{x}_2)}{r_{12}}}_{\text{2nd ele}} \right] \end{aligned}$$

$$E_2 = \sum_{i=1}^N \sum_{j=i+1}^N \left(\langle ij | ij \rangle - \langle ij | ji \rangle \right) = \sum_{ij} V(i,j)$$

(electron 1 in orbital i , electron 2 in orbital j)

\downarrow : physicist's notation: $\langle ij | kl \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(1) \chi_j^*(2) \frac{1}{r_{12}} \chi_k(1) \chi_l(2)$

chemist's notation: $\langle ik | jl \rangle = \int d\mathbf{x}_1 d\mathbf{x}_2 \chi_i^*(1) \chi_k(1) \frac{1}{r_{12}} \chi_j^*(2) \chi_l(2)$

Hartree-Fock approximation. (mean field approximation.)

so the molecular \hat{H} :

$$\hat{H} = \underbrace{\sum_A -\frac{1}{2M_A} \nabla_A^2}_{0} + \underbrace{\sum_{A \neq B} \frac{z_A z_B}{r_{AB}}}_{\text{constant}} + \underbrace{\sum_i -\frac{1}{2} \nabla_i^2 - \sum_{iA} \frac{z_A}{r_{iA}} + \sum_{ij} \frac{1}{r_{ij}}}_{\text{still difficult.}}$$

we only focus on the electrons:

electronic hamiltonian acts on the electronic wave function, and gives us the electronic energy times over electronic wave functions:

$$\hat{H}_{\text{ele}} |\Psi_{\text{ele}}\rangle = E_{\text{ele}} |\Psi_{\text{ele}}\rangle .$$

where: $\hat{H}_{\text{ele}} = -\sum_i \frac{1}{2} \nabla_i^2 - \sum_{iA} \frac{z_A}{r_{iA}} + \sum_{ij} \frac{1}{r_{ij}}$ \Rightarrow electron hamiltonian. (N electrons)

\hat{O}_i : one-electron operator, separable

for each electron: kinetic energy + all the nuclear attraction terms. depending on one electron at a time.

$-\sum_i \frac{1}{2} \nabla_i^2$: kinetic energy operator second partial derivative
of each spatial dimension (x,y,z) for electron 1,2,3,...

\hat{O}_i : two-electron operator, depending on the coordinates of 2 electrons, depending on two electrons at a time. non-separable. not exactly solvable. \rightarrow many-body problem
in order to solve it \rightarrow approximate!

Hartree-Fock approximation. = mean field approximation.

What to do? split our one electron total energy operator (Fock operator)

average over "mean field" of other electrons.

$$\hat{f}(i) = \hat{h}(i) + \hat{V}^{\text{HF}}(i)$$

↑ mean field operator for electron i
 Fock operator core hamiltonian for electron i = kinetic energy + attraction to all the nuclei

here, the \hat{V}^{HF} mean field operator is going to be the solution to $\sum_{i=1}^N \sum_{j=1}^N \frac{1}{r_{ij}}$

The Fock operator acts on a particular spin orbital $\chi_i(x_i)$ (eigenvalue problem)

$$f(i) \chi_i(x_i) = \epsilon_i \chi_i(x_i) \quad \left\{ \begin{array}{l} \chi_i: \text{spin orbital} \\ \epsilon_i: \text{orbital energy} \end{array} \right. \quad \downarrow \quad \text{pseudo eigenvalue problem}$$

$V_i^{\text{HF}} \rightarrow i$ feels effects of all the other electrons: $\{1, 2, \dots, i-1, i+1, \dots, N\}$

averaged over all positions \vec{r}_i

electron i interacts with $N-1$ electrons. (not itself).

the mean field operator depends on what all of the other spin orbitals are, so we can't solve $f(i)\chi_{il}(x_i) = \epsilon_i \chi_{il}(x_i)$ on its own, because you have to simultaneously solve this for all the electrons and every time you solve it for one electron, its orbital changes and then all the other orbitals change too.

Hartree-Fock energy

$\psi_i(w)$: spin function.

$$E = \frac{\sum_{i=1}^N \langle i | \hat{h}_i | i \rangle}{\downarrow} + \frac{\sum_{i=1}^N \sum_{j=i+1}^N \langle ii | jj \rangle - S \sigma_i \sigma_j \langle ij | ji \rangle}{\downarrow}$$

$$w = \begin{cases} \alpha & (\text{spin up}) \\ \beta & (\text{spin down}) \end{cases}$$

each electron has kinetic energy
+ nuclear attraction
each pair of electrons has coulomb + exchange interaction

$$h_i = \langle i | \hat{h}_i | i \rangle.$$

$J_{ij} = \langle ij | ij \rangle$: coulomb interaction between all pairs.

$k_{ij} = S \sigma_i \sigma_j \langle ij | ji \rangle$: exchange interaction between all same-spin pairs.

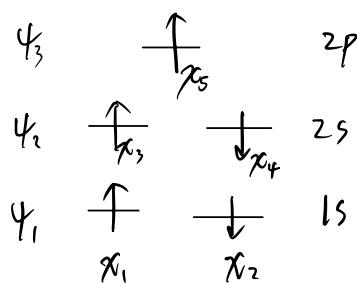
$$E = \sum_i h_i + \sum_{ij} J_{ij} - k_{ij}$$

e.g.: B: 共 5↑ e⁻. spatial orbital: $\psi_1: 1s$, $\psi_2: 2s$, $\psi_3: 2p$

spin orbital: $x_1(1s(1)\alpha(1))$, $x_2(1s(2)\beta(2))$

$x_3(2s(3)\alpha(3))$, $x_4(2s(4)\beta(4))$

$x_5(2p(5)\alpha(5))$.



$$E_{\text{RHF}} = \frac{2h_1 + 2h_2 + h_3}{\text{one-electron energy}}$$

$$\left. \begin{aligned} &+ J_{11} + 4J_{12} - 2k_{12} \\ &+ 2J_{13} - k_{13} + J_{23} \\ &+ 2J_{23} - k_{23} \end{aligned} \right\} \text{two-electron energy}$$

