Electronic Structure Method

↳ description of electrons in detail

Goal: solving the Schrödinger equation

$\boxed{\text{Ne Wiki}}$ it describes properties of molecules in quantum mechanical state, using non-relativistic wave equation

$\hat{H}\Psi = E\Psi$

↳ solution are generated by experiment or experimental data

↳ cannot be non-empirical models

(Introduction to Computational Chemistry, Frank Jensen)

The Adiabatic & Born-Oppenheimer Approximation:

Total Hamiltonian:

$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne} + \hat{V}_{NN}$

(kinetic energy of nuclei) (kinetic energy of electrons) (Coulomb repulsion between electrons) (Coulomb attraction between electrons and nuclei) (Coulomb repulsion between nuclei)

$\hat{H}_e = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee}$ → depends only on the nuclear positions $\vec{R}$ not on their momenta

(electronic Hamiltonian) (Born-Oppenheimer approximation) $\hat{H}_{BO} = -\frac{1}{2M_A}\left(\frac{\partial}{\partial \vec{R}_A}\right)^2$

Assumes: • both set of variables to the electronic Schrödinger equation is separable

$\{\vec{r}_i\}\{\vec{R}_A\}$ i : electron position, A : nuclear centroids

$\hat{H}_e(\{\vec{r}_i\};\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\};\{\vec{R}_A\}) = E_e(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$, $i=1,2,\ldots,n$

note: $\int \Psi_e^* \Psi_e \, d\tau = \langle \Psi_e | \Psi_e \rangle^* d\tau$

total wave function: $\Psi_{tot}(\{\vec{R}_A\})$

$\Psi_{tot}(\{\vec{r}_i\}) = \sum_{\nu=0}^{\infty} \Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

Inserting this in $\hat{H}\Psi = E\Psi$, we have:

$\sum_{\nu=1}^{\infty}(\hat{T}_N + \hat{H}_e)\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\}) = E_{tot}\sum_{\nu=1}^{\infty}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

$\sum_{\nu=1}^{\infty}\Psi_e(\{\vec{r}_i\})(\hat{T}_N + \hat{H}_e + E_{tot})\Psi_\nu(\{\vec{R}_A\}) = E_{tot}\sum_{\nu=1}^{\infty}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

$\sum_{\nu=1}^{\infty}(\Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) + \Psi_e(\{\vec{r}_i\})\hat{H}_e\Psi_\nu(\{\vec{R}_A\})) = E_{tot}\sum_{\nu=1}^{\infty}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

$\sum_{\nu=1}^{\infty}(\Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) + \Psi_e(\{\vec{r}_i\})\hat{H}_e\Psi_\nu(\{\vec{R}_A\})) = E_{tot}\sum_{\nu=1}^{\infty}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

$\sum_{\nu=1}^{\infty}\Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) + \sum_{\nu=1}^{\infty}\Psi_e(\{\vec{r}_i\})\hat{H}_e\Psi_\nu(\{\vec{R}_A\}) = E_{tot}\sum_{\nu=1}^{\infty}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

$\sum_{\nu=1}^{\infty}\Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) + \Psi_e(\{\vec{r}_i\})\hat{H}_e\sum_{\nu=1}^{\infty}\Psi_\nu(\{\vec{R}_A\}) = E_{tot}\sum_{\nu=1}^{\infty}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

$\sum_{\nu=1}^{\infty}\Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) + \Psi_e(\{\vec{r}_i\})\hat{H}_e\Psi_\nu(\{\vec{R}_A\}) = E_{tot}\sum_{\nu=1}^{\infty}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

$\Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) + \Psi_e(\{\vec{r}_i\})\hat{H}_e\Psi_\nu(\{\vec{R}_A\}) = E_{tot}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

$\Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) + \Psi_e(\{\vec{r}_i\})\hat{H}_e\Psi_\nu(\{\vec{R}_A\}) = E_{tot}\Psi_\nu(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

by second order vanishing chain

negligible for heavy nuclei, then the electronic contribution can be approximated to zero.

$\Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) = \sum_{A=1}^{N}\nabla_A^2\Psi_e(\{\vec{r}_i\})\Psi_\nu(\{\vec{R}_A\}) + \sum_{A=1}^{N}\nabla_A\Psi_e(\{\vec{r}_i\})\nabla_A\Psi_\nu(\{\vec{R}_A\}) + \Psi_e(\{\vec{r}_i\})\hat{T}_N\Psi_\nu(\{\vec{R}_A\}) = E_{tot}\Psi_\nu$

(single electron) (multiple electrons) (nuclear coordinates)

Adiabatic Approximation: signal transformation is restricted to one electronic surface. i.e. all coupling elements are neglected

$(\hat{T}_e + \hat{V}_{ee} + \langle\Psi_N|\hat{V}_{Ne}|\Psi_N\rangle + \langle\Psi_N|\hat{T}_N|\Psi_N\rangle)\Psi_e = E_{tot}\Psi_e$

$(\hat{T}_e + \hat{V}_{ee} + \langle\Psi_N|\hat{V}_{Ne}|\Psi_N\rangle)\Psi_e = E_{tot}\Psi_e$

$(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne})\Psi_e(\{\vec{r}_i\;\vec{R}_A\}) = E_{tot}\Psi_e(\{\vec{r}_i\;\vec{R}_A\})$

original Hamiltonian $\hat{H}(\{\vec{r}_i\;\vec{R}_A\})$

(BO) Born-Oppenheimer Approximation: $\hat{H}(\{\vec{R}\}) \to E_e(\{\vec{R}\})$

$(\hat{T}_e + \hat{V}_{ee} + \hat{V}_{Ne})\Psi_e(\{\vec{r}_i\;\vec{R}_A\}) = E_{tot}\Psi_e(\{\vec{r}_i\;\vec{R}_A\})$

(kinetic energy of the electrons) (potential energy)

relation leads to energy levels for molecular structure & structure (electronic, vibrational, quantum)

In BO picture, nuclei move on a potential energy surface (PES) due to a solution to the electronic S.E.

Into BO approximation, we only have to know E_e as a function of the nuclear coordinates $\vec{R}_A$

$\Psi_e(\{\vec{r}_i\;\vec{R}_A\}) = E_e(\{\vec{R}_A\})\Psi_e(\{\vec{r}_i\})$

solution: $\Psi_{tot} = \hat{T}_N + \hat{V}_{ee} + \hat{V}_{Ne} + \hat{V}_{NN}$

(SCF Convergence)

↳ Ans is a symmetric but the other matrix element will converge

• small size basis sets

• symmetric near equilibrium

SCF cycle is fully convergence:

① Extrapolation: extrapolate $F^{(n)}$ to generate a better $F^{\prime}$ then the new guessed density matrix logarithmically $F^{(n)}, F^{(n-1)}, F^{(n-2)}$ one and a the extrapolation

② Damping: alter this consequent to the F matrices

$F_n, F_{n-1}, F_{n-2} \to F_n, F_{n-1}$

$F_n = F_n$

$F_n = \alpha(F_n) + (1-\alpha)F_{n-1}$

(recommended: Typically even damping SCF procedure effective basis)

② Level Shifting: introduced in the diagonalizing of a matrix of the MO_i ε_i from the basis in the Fock matrix

Antisymmetry of the wavefunction achieved by taking the det.:

(Pauli principle: Fermions are fermions & quantum)

→ from Slaterminant (SD)

$\Psi_0 = \frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(1) & \phi_2(1) & \cdots & \phi_N(1)\\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2)\\ \vdots & \vdots & \ddots & \vdots\\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N)\end{vmatrix}\langle\phi_1|\phi_2\rangle = \delta_{ij}$

(orthonormality requirement)

$\phi_i(x)$ → orbital (Molecular orbital)

↳ single electron (no electron correlation)

sum of permutations over all "diagonal" of the determinant

$\hat{X} = A[\phi_1(1)\phi_2(2)\cdots\phi_N(N)] = A\Pi$

$A = \frac{1}{\sqrt{N!}}\sum_{i=1}^{N!}(-1)^{P_i} = \frac{1}{\sqrt{N!}}\left[1 - \sum_{i=1}^{N}P_i + \sum_{i=1}^{N}P_i P_j - \cdots\right]$

(orthogonality operator)

P_i = all possible permutations of 2 electrons

P_j = all possible permutation of 3 electrons

NOTE:

the commutation of A & $\hat{H}$: $AH = HA$

$AA = (A)A$

Consider the Hamiltonian operator:

$\hat{H}_N = \hat{T}_N + \hat{V}_{ne} + \hat{V}_{ee} = \left[\sum_{i=1}^{N}h_i + \sum_{i>j}^{N}\frac{1}{r_{ij}}\right] + V_{NN}$

(kinetic energy of electrons) (potential energy of electrons) (electron-electron repulsion)

$T_i = -\frac{1}{2}\nabla_i^2$

$V_{ne} = -\sum_{A=1}^{M}\frac{Z_A}{|r_i - R_A|}$

$V_{ee} = \sum_{i>j}^{N}\frac{1}{|r_i - r_j|}$

$V_{NN} = \sum_{A>B}^{M}\frac{Z_A Z_B}{|R_A - R_B|}$

(nuclear-nuclear repulsion)

Exchange & the Slater determinant:

$\langle\Phi|H|\Phi\rangle = \langle A\Pi|H|A\Pi\rangle$

$= \langle\Pi|H|A^\dagger A\Pi\rangle$

$= \sqrt{N!}\langle\Pi|H|\frac{1}{\sqrt{N!}}\sum_P(-1)^P P\Pi\rangle$

$= \sum_P(-1)^P\langle\Pi|\frac{1}{2}\sum_i\nabla_i^2 + \sum_i v_{ne}(i) + \sum_{i>j}\frac{1}{r_{ij}}|P\Pi\rangle$

$= \sum_P(-1)^P\langle\Pi|\sum_i h_i|P\Pi\rangle + \sum_P(-1)^P\langle\Pi|\sum_{i>j}\frac{1}{r_{ij}}|P\Pi\rangle + \sum_P(-1)^P\langle\Pi|V_{NN}|P\Pi\rangle$

$\langle\Phi|\hat{H}_{NN}|\Phi\rangle = V_{NN}$

Take consider each term:

(A) $\sum_P(-1)^P\langle\Pi|\sum_i h_i|P\Pi\rangle = \langle\Pi|\sum_i h_i|\Pi\rangle - \sum_{i>j}\Pi_{ij}\Pi_{ij} + \sum_{i>j}\Pi_{ij}\Pi_{ij} - \ldots\rangle$

$= \sum_i\langle\Pi|h_i|\Pi\rangle - \sum_{i>j}\langle\Pi|h_i|\Pi_{ij}\rangle\Pi_{ij}\rangle + \sum_{i>j}\langle\Pi|h_i|\Pi_{ij}\Pi_{ij}\rangle - \ldots$

$= \sum_{i>j}\langle\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)|h_1|\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)\rangle - \sum_{i>j}\langle\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)|h_1|\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)\rangle$

$\sum_{i>j}h_i$ ZERO

since the energy of 2 different MO are orthogonal.

For consistently $S = 1/2$:

$= \langle\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)|h_1|\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)\rangle$

$= \langle\phi_i(1)\phi_j(2)|h_1|\phi_i(1)\phi_j(2)\rangle - \langle\phi_i(1)\phi_j(2)|h_1|\phi_j(1)\phi_i(2)\rangle$

$= \langle\phi_i(1)\phi_j(2)|h_1|\phi_i(1)\phi_j(2)\rangle - \langle\phi_i(1)\phi_j(2)|h_1|\phi_i(2)\phi_j(1)\rangle$

$= \langle\phi_i(1)|h_1|\phi_i(1)\rangle = h_i$

(B) $\sum_P(-1)^P\langle\Pi|\sum_{i>j}\frac{1}{r_{ij}}|P\Pi\rangle = \langle\Pi|\sum_{i>j}\frac{1}{r_{ij}}|\Pi\rangle - \sum_{i>j}\Pi_{ij}\Pi_{ij} - \ldots\rangle$

$= \langle\Pi|\sum_{i>j}\frac{1}{r_{ij}}|\Pi\rangle - \langle\Pi|\sum_{i>j}\frac{1}{r_{ij}}\Pi_{ij}\Pi_{ij}\rangle$

J_{ij} Coulomb integral

K_{ij} Exchange integral

$= \sum_{i>j}^{N}\sum_{j=1}^{N}(J_{ij} - K_{ij})$

consider the H: $i=1, j=2$:

$\langle\Pi|\Pi_{12}|\Pi\rangle = \langle\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)|\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)\rangle$

$= \langle\phi_1(1)\phi_2(2)|\phi_1(1)\phi_2(2)\rangle - \langle\phi_1(1)\phi_2(2)|\phi_2(1)\phi_1(2)\rangle$

$= \langle\phi_1(1)\phi_2(2)|\phi_1(1)\phi_2(2)\rangle - \langle\phi_1(1)\phi_2(2)|\phi_1(2)\phi_2(1)\rangle$

↳ 2 quantum system for 2 energy

Antisymmetry Accounted by $\phi_1^2(1) \leq \phi_1^2(1)$

the exchange energy from Φ_0:

$\langle\Pi|\Pi_{12}|\Pi\rangle = \langle\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)|\phi_1(1)\phi_2(2) - \phi_2(1)\phi_1(2)\rangle$

$= \langle\phi_1(1)\phi_2(2)|\phi_1(1)\phi_2(2)\rangle - \langle\phi_1(1)\phi_2(2)|\phi_2(1)\phi_1(2)\rangle - \langle\phi_2(1)\phi_1(2)|\phi_1(1)\phi_2(2)\rangle + \langle\phi_2(1)\phi_1(2)|\phi_2(1)\phi_1(2)\rangle$

$= \langle\phi_1(1)\phi_2(2)|\phi_1(1)\phi_2(2)\rangle - \langle\phi_1(1)\phi_2(2)|\phi_2(1)\phi_1(2)\rangle$

$= \langle\phi_i(1)|\phi_j(1)\rangle|\phi_j(2)|\phi_i(2)\rangle$

Thus the energy may also be written in a more symmetrical form:

$E = \sum_{i=1}^{N}h_i + \sum_{i>j}^{N}\sum_{j=1}^{N}(J_{ij} - K_{ij}) + V_{NN}$

$= \sum_{i=1}^{N}h_i + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}(J_{ij} - K_{ij}) + V_{NN}$

(2 normal set equations)

$E = \sum_i^N\langle\phi_i|h_i|\phi_i\rangle + \frac{1}{2}\sum_{i=1}^{N}\langle\phi_i|J|\phi_i\rangle - \langle\phi_i|K|\phi_i\rangle + V_{NN}$

note: self-interaction J_{ii} is exactly cancelled by the exchange element K_{ii}

Hartree-Fock Equations (Article Hartree, Wiki = Slater)

Hartree-Fock Energy

↳ variational principle

↳ Coulomb principle

Many Electron Wave Functions & Operators

Slater

① energy electron operator (e.g. distribution)

② Slater determinant & linear combination of Slater determinants.

The electronic problem:

no exact, but the approximate solutions of the non-relativistic time-independent Schrödinger equation.

$\hat{H}|\Phi\rangle = E|\Phi\rangle$

(Hamiltonian: $\hat{H}$ = sum of single & pairwise contributions) (energy) (N)

Electron i & nucleus A separated by distance $r_{iA} = |\vec{r}_i - \vec{R}_A|$

Electron i & j separated by distance $r_{ij} = |\vec{r}_i - \vec{r}_j|$

Electron i & j separated by distance $r_{ij} = |\vec{r}_i - \vec{r}_j|$

Nuclei A & B separated by distance $R_{AB} = |\vec{R}_A - \vec{R}_B|$

$i = 1, 2, \ldots$ electron index

$A = 1, 2, \ldots$ charge

$\vec{r}_i = (x_i, y_i, z_i)$ electron coordinate

$\vec{R}_A = (X_A, Y_A, Z_A)$ nucleus coordinate

In atomic units:

Hamiltonian for H atoms & H molecule:

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

(kinetic energy) (nuclear attraction) (electron repulsion) (nuclear repulsion)

How has unit energy?

In SI units

$\hbar = 1$ $\frac{4\pi\varepsilon_0}{e^2} = 1$

$m = m_e$ $\frac{e^2}{4\pi\varepsilon_0} = 1$

$\frac{\hbar^2}{m_e e^2} = a_0$ $\frac{\hbar^2}{m_e e^2} = 1a_0^2$

$\frac{\hbar^2}{m_e e^2} = \frac{\hbar^2}{m_e a_0^2} = 1E_h$

(Coulomb energy) (Bohr radius) (Hartree)

$-\frac{1}{2}\nabla^2 = -\frac{1}{2}\frac{\partial^2}{\partial r^2} = 1E_h$

$-\frac{1}{2}\nabla^2 = -\frac{1}{2}\frac{\partial^2}{\partial r^2} = 1E_h$

(Coulomb operator) $-\frac{1}{2}\nabla^2 = -\frac{1}{2}\frac{\partial^2}{\partial r^2} = 1E_h$

(Hamiltonian operator) $-\frac{1}{2}\nabla^2 = -\frac{1}{2}\frac{\partial^2}{\partial r^2} = 1E_h$

e.g. ground state of the hydrogen atom

$E = -1E_h = -13.6\,\text{eV}$ (atomic unit of energy)

Quantity E_h is defined in atomic units $\hbar$ by

$E_h = \hbar^2$

Born-Oppenheimer Approximation

Hartree-Fock

↳ variational principle

↳ Coulomb principle

Slater Determinants

Hartree-Fock Equations

Hartree-Fock Approximation

Hartree-Fock Equations

Hartree-Fock Approximation

Hartree-Fock Equations

Hartree-Fock Approximation

Condensed Matter Physics: ← modern formulation include liquids such as liquid He

(Bible:) Ashcroft & Mermin

interacting quantum many-body system

Solid State Physics:

What is a solid?

↳ rigidity (resist shear deformation)

CM "theory of everything"

$$H = \sum_i \frac{P_i^2}{2M} + \sum_i \frac{p_i}{2m_D} + \underbrace{\frac{(Z_k)^2}{2}\sum_{i\neq} \frac{1}{|\vec{R}_i - \vec{R}_j|}}_{V_{nn}} - \underbrace{\frac{e^2}{2}\sum \frac{1}{|\vec{r}_1 - \vec{r}_2|}}_{V_{ee}} - \underbrace{Ze^2 \sum \frac{1}{|R_i - r_i|}}_{V_{ne}}$$

lattice of nuclei

$N = 10^{23}$ # of atoms in cm^3 of a solid → system becomes qualitatively different, that's what C.M. is all about

$N = 1$ hydrogen

$N = 2$ He

⋮

$N = 2 \sim 100$ Atomic physics

$N = 100 - 10^5$ Molecules (chemistry)

size of the Hilbert space for $N = 10^{23}$ particles

— spin $\frac{1}{2}$ $\uparrow, \downarrow$ (2 states per particle)

$2^N = 2^{10^{23}} \sim 10^{10^{23}}$

Earth: # of atoms 3.8×10^{50}

Sun: 1.2×10^{57}

Universe: 1.3×10^{78}

Born-Oppenheimer Approximation:

↳ $\frac{m_e}{M} = 10^{-5}$ Separate "core" & "free electrons"

$$H = \sum \frac{P_i^2}{2M} + \sum_{j=free} \frac{P^2}{2m} + \sum_{i,j} V_{ij}(|\vec{R}_i - \vec{R}_j|) + \frac{e}{2}\sum_{\vec{R}_j \neq m} \frac{1}{|\vec{r}_2 - \vec{r}_1|} + \sum_{A,i=free} V_{Ai}(|\vec{r}_i - \vec{R}_A|)$$

"Screened Coulomb"

Example: Sodium (Na) metal

$Z = 11$

Na ⇒ $\underbrace{(1s^2 2s^2 2p^6)}_{\text{Neon}(Z=10)} 3s$

Want to solve Schrodinger Eq:

$$H\Psi(\vec{R}, \vec{r}) = E\Psi(\vec{R}, \vec{r})$$

where: $\vec{R} = \{\vec{R}_i\}$, $\vec{r} = \{\vec{r}_i\}$

$$\Psi(\vec{R}, \vec{r}) = \sum_i \boxed{\phi_n(R)} \Psi_n(\vec{r}, \vec{R})$$

ionic wavefunctions / coefficients of expansion

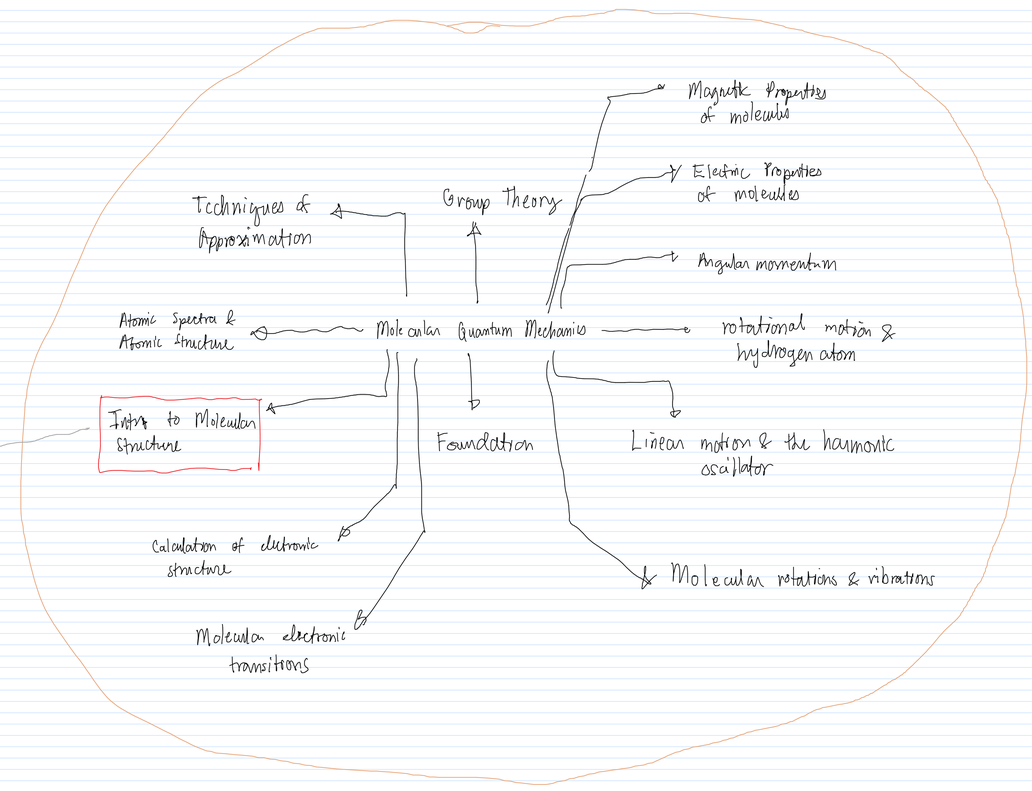
How do we solve for this wavefunctions $\phi_n(R)$?

$$(T_i + V_{ii})\Psi + \sum \phi_n \underbrace{\boxed{(T_e + V_{ei} + V_{ee})\Psi_n}}_{E_{in}\Psi_n} = E\Psi$$

Quantum Transport (Q.T.)
- Heat Transport
- Electron Transport
- Spin transport

→ Boltzmann Q.T.

→ NEGF (Non-equilibrium Green's Function)



Introduction to Molecular Structure

- 8.1 Born-Oppenheimer Approximation
- 8.2 Molecule Orbital theory
- 8.3 Molecule Orbital Theory of Polyatomic Molecules
- 8.4 Band Theory of Solids

An application: hydrogen molecule-ion (H_2^+)

1 electron only

Hamiltonian for this species:

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi r_A \varepsilon_0} - \frac{e^2}{4\pi r_B \varepsilon_0} + \boxed{\frac{e^2}{4\pi\varepsilon_0 R}}$$

constant under B.O. approx.

S.E. separable & solvable when expressed in "ellipsoidal coordinates" (μ, ν, ϕ)

azimuthal angle around the internuclear axis

where:

$$\mu = \frac{r_A + r_B}{R}, \quad \nu = \frac{r_A - r_B}{R}$$

Solutions are called: molecular orbitals

resembles atomic orbitals but spread over both nuclei

S.E. for H_2^+ is complicated, we must resort for another approximation, using the exact solutions for H_2^+ as a guide.

From the approximation (Born-Oppenheimer)

Linear combinations of atomic orbitals:

the partial justification for simulating molecular orbitals as an LCAO, can be expressed by examining the Hamiltonian (8.9)

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi r_A \varepsilon_0} - \frac{e^2}{4\pi r_B \varepsilon_0} + \frac{e^2}{4\pi\varepsilon_0 R}$$

When e^- is close to nucleus A, $r_A \ll r_B$, & H is approx:

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi r_A \varepsilon_0} + \frac{e^2}{4\pi\varepsilon_0 R}$$

Note: this H is similar to hydrogen atom.

$\therefore$ close to atomic A, the wavefunctions of the electron resemble a hydrogen atomic orbital. Same is true close to B.

captured by the 2 linear combinations

So we write the molecular orbitals as:

$$\psi = \sum_r c_r \boxed{\phi_r}$$

atomic orbitals constitute the basis set for the calculation

Optimum value of the coefficients are found by applying the variation principle:

$$\sum_r c_r \{H_{rs} - E S_{rs}\} = 0 \quad \text{(Secular equation)}$$

H_{rs} = matrix element of the Hamiltonian

S_{rs} = matrix element of the overlap matrix elements

Has solution if secular determinant vanishes:

$$|H - ES| = 0$$

e.g. 2 basis of atomic orbitals (one for atom A & one for atom B)

$S_{AA} = S_{BB} = 1$

$S_{AB} = S_{BA} = S$ (overlap integral)

$H_{AA} = H_{BB} = \alpha$ (Coulomb integral)

$H_{AB} = H_{BA} = \beta$ (Resonance integral)

$$\left| \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} - E \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \right| = 0$$

$$\left| \begin{pmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{pmatrix} \right| = 0$$

$$(\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$\alpha - E = \pm(\beta - ES)$$

$$(\pm ES - E) = \pm\beta - \alpha$$

$$E = \frac{\pm\beta - \alpha}{(\pm S - 1)} = \frac{\alpha \pm \beta}{(1 \pm S)}$$

$$\therefore E = \frac{\alpha \pm \beta}{1 \pm S}$$

Note: (from Q.C. notes)

$$= \underbrace{\langle \Pi | \sum_{i=1}^{N} \sum_{j>i}^{N} g_{ij} | \Pi \rangle}_{J_{ij}} - \underbrace{\langle \Pi | \sum_{i=1}^{N} \sum_{j>i}^{N} g_{ij} | \sum_{j'i'} P_{j'i'} \Pi \rangle}_{K_{ij}}$$

Coulomb integral

Exchange Integral

coulom integral

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi r_A \varepsilon_0} + \frac{e^2}{4\pi\varepsilon_0 R}$$

$$\alpha = \langle \phi_A | H | \phi_A \rangle = \langle A | H | A \rangle$$

$$\alpha = \langle A | \frac{\hbar^2}{2m_e}\nabla^2 | A \rangle - \frac{e^2}{4\pi\varepsilon_0}\langle A | \frac{1}{r_B} | A \rangle + \boxed{\frac{e^2}{4\pi\varepsilon_0 R}} \langle A | A \rangle$$

Coulomb interaction bet. electron density ϕ^2 & nucleus B.

$$\alpha = \boxed{E_{1s}} - \boxed{j_0 \langle A | \frac{1}{r_B} | A \rangle} + \frac{j_0}{R}$$

$j_0 = \frac{e^2}{4\pi\varepsilon_0 R}$

j_0

obtain because ϕ_A is an eigenfunction of the atomic hamiltonian

$$j' = j_0 \langle A | \frac{1}{r_B} | A \rangle = j_0 \int \frac{\phi_A^2}{r_B} d\tau$$

We have:

$$\alpha = E_{1s} - j' + j_0/R$$