1 Schrödinger's Equation

Time dependent version

$$H\varphi = i\hbar \frac{\partial \varphi}{\partial t}$$

H: Hamiltonian.

If Hamiltonian is time independent, we have that

$$\begin{cases} H(r,t) = H(r) \\ \varphi(r,t) = \varphi(r)\, e^{-Et/\hbar} \\ H(r)\,\varphi(r) = E\varphi(r) \end{cases}$$

In principle we can find any solution by solving the eigenvalue problem for the time-independent equation.

2. N particles Hamiltonian

$H = T + V$

T: Kinetic energy

V: potential energy

$$V = \sum_{i=1}^{N} \sum_{j>i}^{N} V_{ij}$$

where V_{ij} is the Coulombic potential

$$V_{ij} = \frac{z_i z_j}{|r_i - r_j|}$$

and $$T = \sum_{i=1}^{N} T_i = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2$$

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

Again, problem is find ϵ such that

$$H\psi = \epsilon\psi$$

3) Born-Oppenheimer approximation.

Comes from the observation that

mass of electron << mass of nucleus (atoms)

therefore the motion of electrons can be thought as "slave" to motion of atoms

This leads to the following ansatz

$$H_{tot} \Psi_{tot}(R,r) = E_{tot} \Psi_{tot}(R,r)$$

$$H_{tot} = H_e + T_n$$

$$H_e = T_e + V_{ne} + V_{ee} + V_{nn}$$

$$\boxed{\Psi_{tot} = \Psi_n(R) \; \Psi_e(R,r)}$$

$$H_e \Psi_e(R,r) = E_e(R) \Psi_e(R,r)$$

$$(T_n + E_e(R)) \Psi_n(R) = E_{tot} \Psi_n(R)$$

Note $T_n \Psi_n(R)$ small $\Rightarrow \boxed{E_{tot} = E_e(R)}$

4. Language

1) The problem:

Determine $E_e(R)$: electronic structure calculation

$\varphi_e(R,r)$

R is given, and $E_e(R)$ is the minimum eigenvalue of $H_e \varphi_e(R,r) = E_e(R)\varphi_e(R,r)$

2) Chemistry: knowing the energy as a function of nuclear coordinates

3) Properties are knowing how energy changes upon adding a perturbation.

5 Hartree-Fock

The eigenvalue problem contains a differential operator over a $3N_e$ dimensional space.

Nanoparticles with metals : $\boxed{10^7 \text{ atoms} \times 3 \times 20 \ldots}$

What is known is that

1) He is symmetric $r_i \Leftrightarrow r_j$

2) All electrons cannot have all numbers equal

$$\boxed{\psi(R, \ldots r_i, \ldots r_j, \ldots) = -\psi(R, \ldots r_j, \ldots r_i, \ldots)}$$

Slater determinant

$$\Phi_{SD} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \ldots & \Phi_N(r_1) \\ \phi_1(r_2) & \Phi_2(r_2) & \ldots & \Phi_N(r_2) \\ \ldots & \ldots & \ldots & \ldots \\ \Phi_1(r_N) & \Phi_2(r_N) & \ldots & \Phi_N(r_N) \end{vmatrix}$$

$$\langle \Phi_i | \Phi_j \rangle = \delta_{ij} \qquad \boxed{\Phi_{SD}(r_i, r_j) = -\Phi_{SD}(r_j, r_i}$$

6 Hartree-Fock

Original problem: find smallest eigenvalue of $H_e \to E_e(R)$

H_e is self-adjoint, so

$$\boxed{\min_{\psi} \frac{\langle \psi | H_e | \psi \rangle}{\langle \psi | \psi \rangle}}$$

$\langle \cdot | \cdot \rangle$ scalar product in $\mathbb{C}(\mathbb{R}^{3N_e})$

Hartree-Fock

$$\boxed{\min_{\Phi_{SD}} \langle \Phi_{SD} H_e \Phi_{SD} \rangle}$$

It is an approximation, it would be exact if more SD are considered (asymptotically)

7) Hartree-Fock

The key is computig $\langle \Phi_{SD} | H_e | \Phi_{SD} \rangle = E$

and its derivatives w.r.t. the parameterization of Φ_i; $i = 1, 2 .. n_e$

$$E = \sum_{i}^{N} \langle \Phi_i | h_i | \Phi_i \rangle + \frac{1}{2} \sum_{ij}^{N} \langle \Phi_j | J_i | \Phi_j \rangle - \frac{1}{2} \sum_{ij}^{N} \langle \Phi_j | K_i | \Phi_j \rangle + V_{nn}$$

J_i & K_i are $\int$ operators so : $\boxed{6 \text{ dimensional} \int}$

The key is orthogonality

Optimality conditions with orthogonality constraints

=> generalized eigenvalue equations

Need to represent in a basis ... orbital basis

8) Density; Hohenberg-Kohn theorem

$$H_e = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{|R_A - r_i|} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{|r_i - r_j|} + \underbrace{\sum_{A=1}^{M}\sum_{B=A}^{M} \frac{Z_A Z_B}{|R_A - R_B|}}_{V_{NN}}$$

Note that

$$V(r) = \sum_{A=1}^{M} \frac{Z_A}{|R_A - r|} = V_{ext}(r; R)$$

$$H_e = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N} V_{ext}(r_i, R) + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{|r_i - r_j|} + V_{nn}(R)$$

$\boxed{\text{Density}}$

$$\rho(r) = \int_{r_2, r_3 .. r_{n-1}} |\psi(r, r_2, r_3, .. r_n)|^2 \, dr$$

Antisymmetry: does not matter which coordinate

9) Hohenberg -Kohn

$$V_{ext}^1 \to H^1 \qquad H^1\psi^1 = E^1\psi^1$$

$$V_{ext}^2 \to H^2 \qquad H^2\psi^2 = E^2\psi^2$$

→ minimal

Assume $\rho^1 = \rho^2$

$$\langle \psi^2 | H^1 | \psi^2 \rangle > E^1$$

$$\langle \psi^2 | H^2 | \psi^2 \rangle + \langle \psi^2 | \hat{v}^1 - \hat{v}^2 | \psi^2 \rangle > E^1$$

$$E^2 + N\int \rho(r)\,(\bar{v}^1 - \bar{v}^2) > E^1$$

$$E^1 + N\int \rho(r)\,(\bar{v}^2 - \bar{v}^1) > E^2$$

$$\Rightarrow \boxed{\text{Contradiction}}$$

10) Density representation of energy

$$\begin{tikzcd} V^{1} \arrow[r] \arrow[d, "\text{injective}"] & E^{e}_{V^{1}} \\ \rho_{V'} \arrow[ur, dashed] & \end{tikzcd}$$

$$\Rightarrow \boxed{E^{e} = E^{e}(\rho)} = E^{e}(\rho, R)$$

There exists a functional of density alone that defines energy

If the functional is known, then there is also a variational principle

$$\boxed{E^{e}(R) = \min_{\int \rho(r)\,dr = N} E^{e}(\rho, R)}$$

But... which functional?

11) Density functional approaches to compute $E_e(R)$

All based on Hartree-Fock ansatz

$$E_{DFT}[\rho] = T[\rho] + J[\rho] + K[\rho] + E_{ne}[\rho] + V_{nn}(R)$$

$$E_{ne}[\rho] = -\sum_a \int \frac{Z_a \rho(r)}{|R_a - r|} \, dr$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(r)\, \rho(r')}{|r - r'|} \, dr \, dr'$$

$$V_{nn}(R) = \frac{1}{2} \sum_{\substack{a,b \\ a \neq b}} \frac{Z_a Z_b}{|R_A - R_B|}$$

The key is in $T[\rho]$ & $K[\rho]$

12) $T[\rho]$ & $K[\rho]$ by orbital free approaches

Are computed by forcing the expressions to match the computation in different regimes

1) Thomas Fermi

$$T_{TF}[\rho] = C_F \int \rho^{5/3}(r)\,dr \qquad C_F = \frac{3}{10}(3\pi^2)^{2/3}$$

$$K_D[\rho] = -C_x \int \rho^{4/3}(r)\,dr \qquad C_x = \frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}$$

Kinetic energy tends to be the problem

2) More evolved functionals: → $\boxed{\text{very realistic results for bulk}}$

$$T[\rho] = T_{TF}[\rho] + T_{vW}[\rho] + \sum_{\alpha} d_\alpha T_x^\alpha[\rho]$$

$$T_{vW}[\rho] = \frac{1}{8}\int \frac{|\nabla \rho(r)|^2}{\rho(r)}\,dr$$

$$T_x^\alpha[\rho] = \iint \rho^\alpha(r)\, w^\alpha(r-r')\, \rho^\alpha(r')\,dr\,dr'$$

$\boxed{\text{Good models for numerical analysis}}$

(3) Kohn-Sham

$$T[\rho_{exact}] = \sum_{i=1}^{\infty} \langle \Phi_i^{NO} | -\frac{1}{2} \nabla^2 | \Phi_i^{NO} \rangle$$

"Natural orbitals"

$$\rho_{exact} = \sum_{i=1}^{\infty} n_i |\Phi_i^{NO}|^2$$

$$N = \sum_{i=1}^{\infty} n_i$$

Ansatz

$$\rho(r) = \sum_{i=1}^{N} |\Phi_i(r)|^2$$

$$T_s[\rho(r)] = \sum_{i=1}^{N} \langle \phi_i | -\frac{1}{2} \nabla^2 | \Phi_i \rangle$$

with constraints $\langle \Phi_i | \Phi_j \rangle = \delta_{i,j}$

Optimality conditions $\Rightarrow$ pseudo-eigenvalue problem again