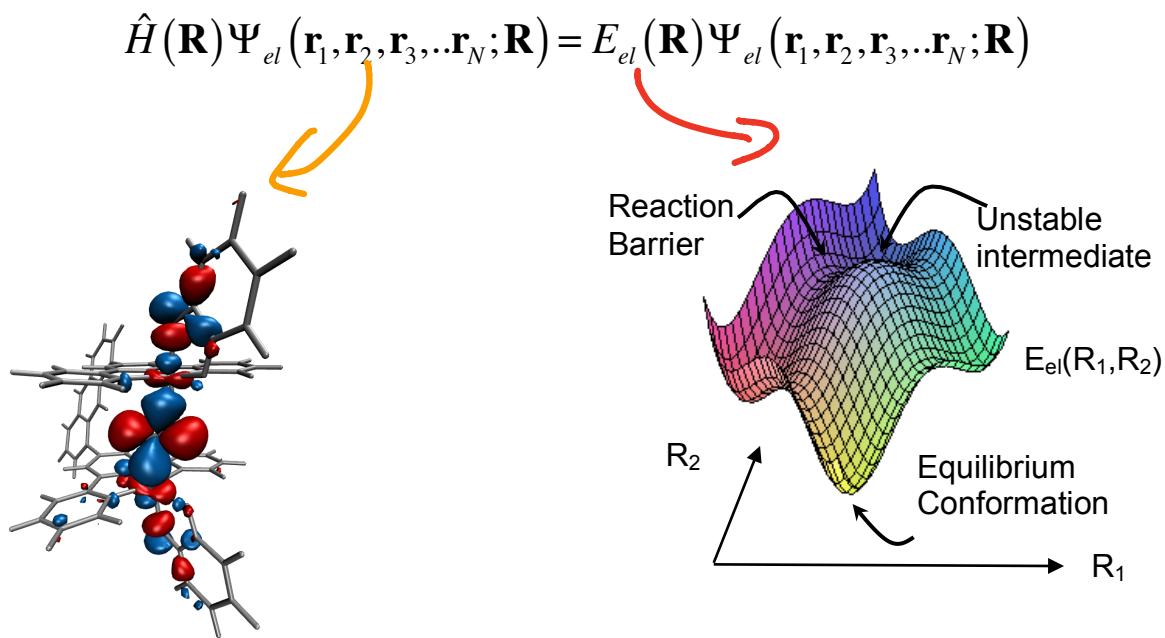


Suggested Reading: Szabo&Ostlund 1&2; Parr&Yang 1&2; McWeeny 1,2&3

Ber n Oppenheimer

$$\hat{H}_e(\mathbf{R}) \equiv -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{I=1}^L \frac{Z_I}{|\hat{\mathbf{r}}_i - \mathbf{R}_I|} + \sum_{i < j} \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} \equiv \hat{h} + \hat{v}$$

one e^- operators two e^- operators



Brute Force Solution

Complete Basis of Orbitals

$$\{\psi_i(\mathbf{r})\} \quad \langle \psi_i | \psi_j \rangle = \delta_{ij} \quad \sum_i |\psi_i\rangle \langle \psi_i| = 1$$

orthonormal complete

$$\Psi_{el}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) = \sum_{ijk\dots} C_{ijk\dots} \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \psi_k(\mathbf{r}_3) \dots \psi_l(\mathbf{r}_N)$$

Hand Full CI

$$\bar{\Psi}_{el}(x_1, x_2, x_3, \dots, x_N) = \sum_{ijk\dots}^{\infty} C_{ijk\dots} | \psi_i(x_1) \psi_j(x_2) \dots \psi_l(x_N) |$$

Spin Orbitals

$$\psi_i(\mathbf{r})\alpha(\sigma) \equiv \psi_i(\mathbf{r}, \sigma) \equiv \psi_i(x)$$

spin orbital

$$\psi_i(\mathbf{r})\beta(\sigma) \equiv \psi_{\bar{i}}(\mathbf{r}, \sigma) \equiv \psi_{\bar{i}}(x)$$

$x \equiv \vec{r}, \sigma$

Antisymmetry

$$\Psi_i(1) \Psi_j(2) \xrightarrow{\text{exchange}} \Psi_j(2) \Psi_i(1) \quad \underline{\text{different!}}$$

Slater Determinant:

$$\Phi(1, 2, 3, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_3}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_3}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(3) & \psi_{k_2}(3) & \psi_{k_3}(3) & \cdots & \psi_{k_N}(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_3}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix}$$

$$\equiv |\Psi_{k_1} \Psi_{k_2} \Psi_{k_3} \cdots \Psi_{k_N}|$$

$$\Phi(2, 1, 3, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_3}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_3}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(3) & \psi_{k_2}(3) & \psi_{k_3}(3) & \cdots & \psi_{k_N}(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_3}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix}$$

↙ ↘

$$\frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_{k_1}(1) & \psi_{k_2}(1) & \psi_{k_3}(1) & \cdots & \psi_{k_N}(1) \\ \psi_{k_1}(2) & \psi_{k_2}(2) & \psi_{k_3}(2) & \cdots & \psi_{k_N}(2) \\ \psi_{k_1}(3) & \psi_{k_2}(3) & \psi_{k_3}(3) & \cdots & \psi_{k_N}(3) \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \psi_{k_1}(N) & \psi_{k_2}(N) & \psi_{k_3}(N) & \cdots & \psi_{k_N}(N) \end{vmatrix} = -\Phi(1, 2, 3, \dots, N)$$

✓

Option 1: Approximate the Wave Function

Hope: Hidden structure in Ψ_{ee}
Structure in \hat{H}

One Electron Integrals

$$h_{ij} \equiv \langle \psi_i | \hat{h} | \psi_j \rangle = \int \psi_i^*(x) \hat{h} \psi_j(x) dx = \int \psi_i^*(x) \left(-\frac{1}{2} \nabla^2 + v(\mathbf{r}) \right) \psi_j(x) dx$$

$$\hat{h} \leftrightarrow \underline{\underline{h}}$$

Two Electron Integrals

$$\langle ij | kl \rangle \equiv \langle \psi_i \psi_j | \frac{1}{r_{12}} | \psi_k \psi_l \rangle = \int \int \frac{\psi_i^*(x_1) \psi_j^*(x_2) \psi_k(x_1) \psi_l(x_2)}{r_{12}} dx_1 dx_2$$

$$\langle ij || kl \rangle \equiv \langle ij | kl \rangle - \langle ij | lk \rangle$$

↗
Antisymmetry

① Maximal Coincidence.

If two determinants are identical:

$$\langle \phi_i \phi_j \phi_k \dots | \hat{h} | \phi_i \phi_j \phi_k \dots \rangle = \sum_m h_{mm} \quad \langle \phi_i \phi_j \phi_k \dots | \hat{V} | \phi_i \phi_j \phi_k \dots \rangle = \frac{1}{2} \sum_{mn} \langle mn | mn \rangle$$

If two determinants differ by one spin orbital:

$$\langle \dots \phi_i \phi_j \phi_k \dots | \hat{h} | \dots \phi_i \phi_j \phi_k \dots \rangle = h_{jl} \quad \langle \phi_i \phi_j \phi_k \dots | \hat{V} | \phi_i \phi_j \phi_k \dots \rangle = \sum_m \langle jm | lm \rangle$$

If two determinants differ by two spin orbitals:

$$\langle \dots \phi_i \phi_j \phi_k \dots | \hat{h} | \dots \phi_i \phi_j \phi_k \dots \rangle = 0 \quad \langle \phi_i \phi_j \phi_k \dots | \hat{V} | \phi_i \phi_j \phi_k \dots \rangle = \langle jk | lm \rangle$$

If two determinants differ by three or more spin orbitals:

$$\langle \dots \phi_i \phi_j \phi_k \dots | \hat{h} | \dots \phi_i \phi_j \phi_k \dots \rangle = 0 \quad \langle \phi_i \phi_j \phi_k \dots | \hat{V} | \phi_i \phi_j \phi_k \dots \rangle = 0$$

Slater-London Rules

Thor*

$$|\phi_i \phi_j \phi_k \phi_l| \xrightarrow{\text{Ket}} |\sigma_i \sigma_j \sigma_i^* \sigma_j^*|$$

11 σ

Option 2: Densities and Density Matrices

Often don't need all of Ψ

Electron Density

$$\rho(x) \equiv \int \Phi^*(x, x_2, x_3, \dots, x_N) \Phi(x, x_2, x_3, \dots, x_N) dx_2 dx_3 \dots dx_N$$

Classical!: Easy to represent (3D)

$$1PDM \quad \gamma(x, x') \equiv \int \underline{\Phi}^*(x, x_2, x_3, \dots, x_N) \underline{\Phi}(x', x_2, x_3, \dots, x_N) dx_2 dx_3 \dots dx_N$$

$$\rho(x) = \gamma(x, x)$$

$$E[\rho] ? \quad E[\delta] ?$$

Exercise: Densities and Wave Functions

Task: Use the Slater-Condon Rules to work out an expression for $\gamma(x, x')$ for a Slater Determinant.

$$\underline{\Phi} = |\psi_1 \psi_2 \psi_3 \dots \psi_N|$$

$$\gamma(x, x') \rightarrow \hat{\gamma} = |x \rangle \langle x'|$$

$$\delta(x, x') = \langle |\psi_1 \psi_2 \psi_3 \dots \psi_N| | \hat{\delta} | |\psi_1 \psi_2 \psi_3 \dots \psi_N| \rangle$$

$$\Rightarrow \delta(x, x') = \sum_i^n \langle \psi_i | x \rangle \langle x' | \psi_i \rangle = \underbrace{\sum_i^n \psi_i^*(x) \psi_i(x')}$$

Basis Set Expansion

Expand orbitals in a complete basis

$$\psi_i(x) \equiv \sum_{\mu=1}^N c_{\mu i} \chi_{\mu}(x)$$

$$\Rightarrow \delta(x, x') = \sum_i \Psi_i^*(x) \Psi_i(x') = \sum_i \sum_{\mu\nu} c_{\mu i}^* \chi_{\mu}(x) c_{\nu i} \chi_{\nu}(x')$$

$$\Rightarrow = \sum_{\mu\nu} \chi_{\mu}(x) \chi_{\nu}(x') \sum_i c_{\mu i}^* c_{\nu i}$$

$$\equiv P_{\mu\nu}$$

Task: Use the basis expansion to work out expressions for h_{ij} and $\langle ij|kl \rangle$ in terms of integrals involving the basis functions ($h_{\mu\nu}$ and $\langle \mu\nu|\lambda\sigma \rangle$).

$$h_{ij} = \langle \phi_i | \hat{h} | \phi_j \rangle = \sum_{\mu\nu} c_{\mu i}^* \langle \chi_{\mu} | \hat{h} | \chi_{\nu} \rangle c_{\nu j}$$

$$\langle ij | kl \rangle = \sum_{\mu\nu\lambda\sigma} c_{\mu i}^* c_{\nu j}^* c_{\lambda k} c_{\sigma l} \langle \chi_{\mu} \chi_{\nu} | \hat{h} | \chi_{\lambda} \chi_{\sigma} \rangle$$