

Lecture 17: Energy Expectation Value of Slater Determinants

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Energy Expectation Value

$$E[\Phi] = \langle \Phi | \hat{H} | \Phi \rangle = E_1[\Phi] + E_2[\Phi]$$

- One-electron energy functional:

$$E_1[\Phi] = \langle \Phi | \hat{T}_e + \hat{V}_{ne} + V_{nn} | \Phi \rangle$$

- \hat{T}_e and \hat{V}_{ne} are often combined to “core” or “bare nucleus” Hamiltonian

$$\hat{H}_{\text{core}} = \hat{T}_e + \hat{V}_{ne}$$

- Two-electron energy functional:

$$E_2[\Phi] = \langle \Phi | \hat{V}_{ee} | \Phi \rangle$$

One-Electron Energy Functional

$$E_1[\Phi] = \langle \Phi | \hat{H}_{\text{core}} | \Phi \rangle + V_{nn}$$

- Use $\Phi = \sqrt{N!} \hat{\mathcal{A}} \Phi_H$ to evaluate
- Projector property of $\hat{\mathcal{A}}$ implies $\hat{\mathcal{A}} = \hat{\mathcal{A}}^\dagger$, $\hat{\mathcal{A}}^2 = \hat{\mathcal{A}}$
- The N -electron Hamiltonian is invariant under electron permutations, so $[\hat{H}, \hat{\mathcal{A}}] = 0$. Also true for \hat{H}_{core} , \hat{V}_{ee} , etc.
- Expectation value of \hat{H}_{core} :

$$\begin{aligned} \langle \Phi | \hat{H}_{\text{core}} | \Phi \rangle &= N! \langle \Phi_H | \hat{\mathcal{A}}^\dagger \hat{H}_{\text{core}} \hat{\mathcal{A}} | \Phi_H \rangle = N! \langle \Phi_H | \hat{H}_{\text{core}} \hat{\mathcal{A}} | \Phi_H \rangle \\ &= \sum_{i=1}^N \langle \phi_N | \cdots \langle \phi_1 | \hat{h}(i) \left(\sum_{P \in S(N)} \text{sgn}(P) \hat{P} \right) | \phi_1 \rangle \cdots | \phi_N \rangle \\ &= \sum_{i=1}^N \langle \phi_i | \hat{h}_{\text{core}} | \phi_i \rangle \end{aligned}$$

Two-Electron Energy Functional

$$E_2[\Phi] = \langle \Phi | \hat{V}_{ee} | \Phi \rangle = \frac{1}{2} \sum_{ij=1}^N \langle ij || ij \rangle$$

- Two-electron repulsion integral (Dirac notation):

$$\langle ij || ij \rangle = \langle \phi_i | \langle \phi_j | \hat{V}_{ee} | \phi_i \rangle | \phi_j \rangle = \int dx_1 dx_2 \frac{\phi_i^*(x_1) \phi_j^*(x_2) \phi_i(x_1) \phi_j(x_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- Double bar integral: includes exchange terms

$$\langle ij || ij \rangle = \langle ij | ij \rangle - \langle ij | ji \rangle$$

- This leads to splitting $E_2[\Phi] = E_H[\Phi] + E_X[\Phi]$, where

$$E_H[\Phi] = \frac{1}{2} \sum_{ij=1}^N \langle ij | ij \rangle, \quad E_X[\Phi] = -\frac{1}{2} \sum_{ij=1}^N \langle ij | ji \rangle$$

Hartree Energy

$$E_H[\Phi] = \frac{1}{2} \sum_{ij=1}^N \langle ij | ij \rangle = \frac{1}{2} \int d^3 r_1 d^3 r_2 \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- Functional of the total electron density

$$\rho(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^N |\phi_i(\mathbf{r}, \sigma)|^2$$

- Electrostatic potential energy of electron charge distribution $-\rho(\mathbf{r})$
- Includes unphysical Coulomb self-repulsion

Exchange Energy

$$E_X[\Phi] = -\frac{1}{2} \sum_{ij=1}^N \langle ij | ij \rangle = -\frac{1}{2} \int dx_1 dx_2 \frac{|\gamma(x_1, x_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

- Functional of the one-electron density matrix

$$\gamma(x_1, x_2) = \sum_{i=1}^N \phi_i(x_1) \phi_i^*(x_2)$$

- Corrects Hartree energy for exchange effects by *lowering* Coulomb repulsion between same-spin electrons
- Removes Coulomb self-repulsion

Summary: Total Energy Expectation Value

$$\begin{aligned} E[\Phi] &= \langle \Phi | \hat{H} | \Phi \rangle = E_1[\Phi] + E_2[\Phi] \\ &= E_1[\Phi] + E_H[\Phi] + E_X[\Phi] \\ &= \sum_{i=1}^N \langle \phi_i | h_{\text{core}} | \phi_i \rangle + \frac{1}{2} \sum_{i,j=1}^N \langle ij || ij \rangle + V_{nn} \end{aligned}$$

- Electron interaction leads to two-electron energy describing pairwise “mean-field” interactions of electrons
- This is an *expectation value*, not an *eigenvalue*: Correlation energy is missing!
- Total valence energy of molecules: ~ 1 H per valence electron