The Variational Principle

Problem

"Let's suppose we know all the functions such as $\mathbf{H}\varphi_i = E_i\varphi_i$*, with* $E_0 < E_1 < \ldots$ *and* $\langle\varphi_i|\varphi_j\rangle = \delta_{ij}$*. Show that, for any normalized* Ψ*, we have* $E = \langle\Psi|\mathbf{H}|\Psi\rangle \geq E_0$*"*

Solution

We expand Ψ in a clever basis

$$\Psi = \sum_{i=1}^{\infty} c_i\,\varphi_i \text{ with } \sum_{i=1}^{\infty} c_i^2 = 1$$

$$E = \langle\Psi|\mathbf{H}|\Psi\rangle = \left\langle \sum_i c_i\varphi_i \middle| \mathbf{H} \middle| \sum_j c_j\varphi_j \right\rangle = \sum_{ij} c_i c_j \langle\varphi_i|\mathbf{H}|\varphi_j\rangle$$

$$= \sum_{ij} c_i c_j E_j \langle\varphi_i|\varphi_j\rangle = \sum_{ij} c_i c_j E_j \delta_{ij} = \sum_i c_i^2 E_i \geq E_0 \sum_i c_i^2 = E_0$$

The Born-Oppenheimer Approximation

In the Schrödinger equation

$$\mathbf{H}\,\Phi(\boldsymbol{r},\boldsymbol{R}) = E\,\Phi(\boldsymbol{r},\boldsymbol{R})$$

The total Hamiltonian is

$$\boxed{\mathbf{H} = \mathbf{T}_n + \mathbf{T}_e + \mathbf{V}_{ne} + \mathbf{V}_{ee} + \mathbf{V}_{nn}}$$

What are all these terms?

- $\mathbf{T}_n$ is the kinetic energy of the nuclei
- $\mathbf{T}_e$ is the kinetic energy of the electrons
- $\mathbf{V}_{ne}$ is the Coulomb attraction between nuclei and electrons
- $\mathbf{V}_{ee}$ is the Coulomb repulsion between electrons
- $\mathbf{V}_{nn}$ is the Coulomb repulsion between nuclei

The Born-Oppenheimer Approximation (Take 2)

In atomic units ($m = e = \hbar = 1$)

$$\mathbf{T}_\mathrm{n} = -\sum_{A=1}^{N_\mathrm{nuc}} \frac{\nabla_A^2}{2M_A}$$

$$\mathbf{T}_\mathrm{e} = -\sum_{i=1}^{N} \frac{\nabla_i^2}{2}$$

$$\mathbf{V}_\mathrm{ne} = -\sum_{A=1}^{N_\mathrm{nuc}} \sum_{i=1}^{N} \frac{Z_A}{r_{iA}}$$

$$\mathbf{V}_\mathrm{ee} = \sum_{i<j}^{N} \frac{1}{r_{ij}}$$

$$\mathbf{V}_\mathrm{nn} = \sum_{A<B}^{N_\mathrm{nuc}} \frac{Z_A Z_B}{R_{AB}}$$

- ∇^2 is the Laplace operator (or Laplacian)
- M_A is the mass of nucleus A
- Z_A is the charge of nucleus A
- r_{iA} is the distance between electron i and nucleus A
- r_{ij} is the distance between electrons i and j
- R_{AB} is the distance between nuclei A and B

Electronic Hamiltonian

The electronic Hamiltonian is

$$\boxed{\mathbf{H}_\mathrm{e} = \mathbf{T}_\mathrm{e} + \mathbf{V}_\mathrm{ne} + \mathbf{V}_\mathrm{ee} + \mathbf{V}_\mathrm{nn}}$$

Because $M_A \gg 1$, the nuclear coordinates are "parameters": $\Phi(\boldsymbol{r}, \boldsymbol{R}) = \Xi(\boldsymbol{R})\Psi(\boldsymbol{r}, \{\boldsymbol{R}\})$

The Hartree-Fock energy

We know that

$$\mathbf{H}_e = \mathbf{T}_e + \mathbf{V}_{ne} + \mathbf{V}_{ee} + \mathbf{V}_{nn}$$

We define a few quantities:

- the one-electron Hamiltonian (or core Hamiltonian) = nice guy!

$$\mathbf{O}_1 = \mathbf{T}_e + \mathbf{V}_{ne} = \sum_{i=1}^{N} h(i) \quad \text{where} \quad h(i) = -\frac{\nabla_i^2}{2} - \sum_{A=1}^{N_{nuc}} \frac{Z_A}{r_{iA}}$$

- the two-electron Hamiltonian (electron-electron repulsion) = nasty guy!

$$\mathbf{O}_2 = \mathbf{V}_{ee} = \sum_{i<j}^{N} g_{ij} \quad \text{where} \quad g_{ij} = \frac{1}{r_{ij}}$$

Therefore, we have

$$\boxed{\mathbf{H}_e = \sum_{i=1}^{N} h(i) + \sum_{i<j}^{N} g_{ij} + \mathbf{V}_{nn}}$$

The Hartree-Fock energy (Take 2)

- Nuclear repulsion: $\langle \Psi_{HF} | \mathbf{V}_{nn} | \Psi_{HF} \rangle = V_{nn} \langle \Psi_{HF} | \Psi_{HF} \rangle = V_{nn}$
- Core Hamiltonian:

$$\langle \Psi_{HF} | \mathbf{O}_1 | \Psi_{HF} \rangle = \sum_{i=1}^{N} \langle \chi_i(1) | h(1) | \chi_i(1) \rangle = \sum_{i=1}^{N} h_i$$

- Two-electron Hamiltonian:

$$\langle \Psi | \mathbf{O}_2 | \Psi \rangle = \sum_{i<j}^{N} \left[\langle \chi_i(1) \psi_j(2) | g_{12} | \chi_i(1) \chi_j(2) \rangle - \langle \chi_i(1) \chi_j(2) | g_{12} | \chi_j(1) \chi_i(2) \rangle \right]$$

$$= \sum_{i<j}^{N} (\mathcal{J}_{ij} - \mathcal{K}_{ij}) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} (\mathcal{J}_{ij} - \mathcal{K}_{ij}) \text{ because } \boxed{\mathcal{J}_{ii} = \mathcal{K}_{ii}}$$

$$\boxed{E_{HF} = \sum_{i=1}^{N} h_i + \sum_{i<j}^{N} (\mathcal{J}_{ij} - \mathcal{K}_{ij})}$$

Coulomb operator $\mathcal{J}_i(1) | \chi_j(2) \rangle = \langle \chi_i(2) | g_{12} | \chi_i(2) \rangle | \chi_j(1) \rangle$

Exchange operator $\mathcal{K}_i(1) | \chi_j(2) \rangle = \langle \chi_i(2) | g_{12} | \chi_j(1) \rangle | \chi_i(2) \rangle$

The Hartree-Fock energy (Take 3)

Problem: Normalization of the HF wave function

"Show that the HF wave function built with two spin orbitals χ_1 and χ_2 is normalized"

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Solution

$$\Psi_{\text{HF}} = \frac{1}{\sqrt{2}} \begin{vmatrix} \chi_1(1) & \chi_2(1) \\ \chi_1(2) & \chi_2(2) \end{vmatrix} = \frac{\chi_1(1)\chi_2(2) - \chi_1(2)\chi_2(1)}{\sqrt{2}}$$

$$\begin{aligned} \langle \Psi_{\text{HF}} | \Psi_{\text{HF}} \rangle &= \frac{1}{2} \langle \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2) | \chi_1(1)\chi_2(2) - \chi_2(1)\chi_1(2) \rangle \\ &= \frac{1}{2} \Big[\langle \chi_1(1)\chi_2(2) | \chi_1(1)\chi_2(2) \rangle - \langle \chi_1(1)\chi_2(2) | \chi_2(1)\chi_1(2) \rangle \\ &\quad - \langle \chi_2(1)\chi_1(2) | \chi_1(1)\chi_2(2) \rangle + \langle \chi_2(1)\chi_1(2) | \chi_2(1)\chi_1(2) \rangle \Big] \\ &= \frac{1}{2} \Big[1 - 0 - 0 + 1 \Big] = 1 \end{aligned}$$

Remember that $\langle \chi_1(1)\chi_2(2) | \chi_1(1)\chi_2(2) \rangle = \langle \chi_1(1) | \chi_1(1) \rangle \langle \chi_2(2) | \chi_2(2) \rangle$