Hartree-Fock: Coulomb Interaction in Density Matrix Representation with Exchange Correction

Density Matrix Representation

In Hartree-Fock theory, the one-particle density matrix is:

$$\rho(\boldsymbol{r}, \boldsymbol{r}') = \sum_{i=1}^{N} \varphi_i(\boldsymbol{r}) \varphi_i^*(\boldsymbol{r}')$$

where the electron density is: $n(\boldsymbol{r}) = \rho(\boldsymbol{r}, \boldsymbol{r})$

Electron-Electron Interaction Energy

Coulomb (Hartree) Term

The classical Coulomb energy **includes self-interaction**:

$$J = \frac{1}{2} \int \int \frac{n(\boldsymbol{r}) n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}'$$

Exchange Term

The exchange energy in density matrix form:

$$K = \frac{1}{2} \int \int \frac{|\rho(\boldsymbol{r}, \boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}'$$

Exchange Hole Function

The **exchange hole** describes the density depletion around an electron:

$$\rho_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}') = -\frac{|\rho(\boldsymbol{r}, \boldsymbol{r}')|^2}{n(\boldsymbol{r})}$$

Physical Interpretation

- Creates a "hole" of depleted probability around each electron
- Prevents same-spin electrons from occupying the same position
- **Exactly cancels self-interaction**

Self-Interaction Corrected Form

The total electron-electron energy can be written as:

$$E_{\mathrm{ee}} = \frac{1}{2} \int \int \frac{n(\boldsymbol{r}) [n(\boldsymbol{r}') + \rho_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}')]}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}'$$

Or equivalently:

$$E_{\mathrm{ee}} = J - K = \frac{1}{2} \int \int \frac{n(\boldsymbol{r}) n(\boldsymbol{r}') - |\rho(\boldsymbol{r}, \boldsymbol{r}')|^2}{|\boldsymbol{r} - \boldsymbol{r}'|} \, \mathrm{d}\boldsymbol{r} \, \mathrm{d}\boldsymbol{r}'$$

Key Properties

✓ Exchange hole integrates to exactly −1 electron

✓ Self-interaction cancels exactly in Hartree-Fock

✓ Each electron interacts with (N-1) others, not itself

Expanded Form

For specific orbitals φ_i, the density matrix can be expanded:

$$\rho(\boldsymbol{r}, \boldsymbol{r}') = \sum_{i=1}^{N} \varphi_i(\boldsymbol{r}) \varphi_i^*(\boldsymbol{r}')$$

Coulomb integral:

$$J_{ij} = \int \int \frac{\varphi_i^*(\boldsymbol{r}_1) \varphi_i(\boldsymbol{r}_1) \varphi_j^*(\boldsymbol{r}_2) \varphi_j(\boldsymbol{r}_2)}{r_{12}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2$$

Exchange integral:

$$K_{ij} = \int \int \frac{\varphi_i^*(\boldsymbol{r}_1) \varphi_j(\boldsymbol{r}_1) \varphi_j^*(\boldsymbol{r}_2) \varphi_i(\boldsymbol{r}_2)}{r_{12}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2$$

Total energy:

$$E_{\mathrm{ee}} = \frac{1}{2} \sum_{i,j}^{N} \left(J_{ij} - K_{ij} \right)$$

Proof of Self-Interaction Cancellation

When $i = j$:

$$\begin{aligned} J_{ii} &= \int \int \frac{|\varphi_i(\boldsymbol{r}_1)|^2 \ |\varphi_i(\boldsymbol{r}_2)|^2}{r_{12}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \\ K_{ii} &= \int \int \frac{\varphi_i^*(\boldsymbol{r}_1) \varphi_i(\boldsymbol{r}_1) \varphi_i^*(\boldsymbol{r}_2) \varphi_i(\boldsymbol{r}_2)}{r_{12}} \, \mathrm{d}\boldsymbol{r}_1 \, \mathrm{d}\boldsymbol{r}_2 \\ &= J_{ii} \end{aligned}$$

Therefore: $J_{ii} - K_{ii} = 0$ ✓

Conclusion: In Hartree-Fock theory, the exchange term exactly cancels the self-interaction error in the Coulomb term, ensuring that each electron only interacts with other electrons.