

Homework 0 – Background Review

Problems from Quantum Chemistry by Donald McQuarrie, 2nd Edition

Example 9-4

EXAMPLE 9-4

The wave function $\Psi_2(1, 2)$ given by Equation 9.39 is not normalized as it stands. Determine the normalization constant of $\Psi_2(1, 2)$ given that the “1s” parts are normalized.

$$\Psi_2(1, 2) = \psi(1, 2) - \psi(2, 1) = 1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1) \quad (9.39)$$

and problem 9-26

9-26. Show that the two-electron determinantal wave function in Problem 9-25 factors into a spatial part and a spin part.

$$J_{11} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \psi^*(\mathbf{r}_1)\psi(\mathbf{r}_1) \frac{1}{r_{12}} \psi^*(\mathbf{r}_2)\psi(\mathbf{r}_2) \quad (9.25)$$

or 9-31

9-31. Consider the determinantal atomic wave function

$$\Psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_{211}\alpha(1) & \psi_{21-1}\beta(1) \\ \psi_{211}\alpha(2) & \psi_{21-1}\beta(2) \end{vmatrix}$$

where $\psi_{21\pm 1}$ is a hydrogen-like wave function. Show that $\Psi(1, 2)$ is an eigenfunction of

$$\hat{L}_{z,\text{total}} = \hat{L}_{z1} + \hat{L}_{z2}$$

and

$$\hat{S}_{z,\text{total}} = \hat{S}_{z1} + \hat{S}_{z2}$$

What are the eigenvalues?

Chapter 12 worksheet/test:

Answer the following questions – potentially by reading through Chapter 12.1

- 1) Define a closed-shell system and how the HF equations can be simplified when solving the eigensystem of a closed-shell system.
- 2) Explain why the exchange integral for the same two electrons, K_{ii} , is equal to the coulomb integral of the same two electrons, J_{ii} . (See problem 12-2)

3) How does equation 12.2, for molecules, differ from equation 9.67, for atoms?

$$\hat{F}(\mathbf{r}_1) \left[\sum_{v=1}^K c_v \phi_v(\mathbf{r}_1) \right] = \epsilon \sum_{v=1}^K c_v \phi_v(\mathbf{r}_1) \quad (9.67)$$

$$E = \langle \Psi^*(1, 2, \dots, 2N) | \hat{H} | \Psi(1, 2, \dots, 2N) \rangle \quad (12.2)$$

$$E = 2 \sum_{j=1}^N I_j + \sum_{i=1}^N \sum_{j=1}^N (2J_{ij} - K_{ij}) \quad (12.3)$$

$$I_j = \int d\mathbf{r}_j \psi_j^*(\mathbf{r}_j) \left(-\frac{1}{2} \nabla_j^2 - \sum_A^M \frac{Z_A}{r_{jA}} \right) \psi_j(\mathbf{r}_j) \quad (12.4)$$

$$J_{ij} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_1) \psi_j(\mathbf{r}_2) \quad (12.5)$$

$$K_{ij} = \iint d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(\mathbf{r}_1) \psi_j^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_2) \psi_j(\mathbf{r}_1) \quad (12.6)$$

- 4) What is the Fock operator? Please give the equation, defining each term, and a general description of how it should be used.
- 5) Explain why the energy of a molecular system is NOT the sum of the eigenvalues from the Fock operator.
- 6) Explain why a self-consistent method or field is needed to solve multielectron systems.
- 7) What is the Hartree-Fock limit and why does it not find the true molecular wavefunctions?
- 8) Given a basis set of 25 orbitals, about how many integrals would you need to evaluate using Slater determinants?

“The advantage of using Gaussian functions is that the product of two Gaussian functions centered at two different positions can be written as a single Gaussian function centered at one position. The problem is that Slater orbitals and Gaussian function have very different behavior for small values of r (and for large values of r as well).”