Week 5 – Homework Assignment 1

Exchange interaction

Problem 1. Slater determinants. Consider a Slater determinant built from two single-electron spin orbits $[\phi_a(x)$ and $\phi_b(x)]$, where x denotes the position *r* and spin *s* of an electron. Write down the anti-symmetric wave function (Slater determinant) for two electrons (x_1 and x_2).

Question 1.1 What happens to the wavefunction if you try to put two electrons in the same quantum state, i.e. $\phi_a(x)=\phi_b(x)$?

a) The resulting wavefunction is zero, two electrons in the same states is not allowed X

b) The wavefunction is the product of the two individual wavefunctions

c) The wavefunction is equal to $\phi_a(x)$

Problem 2. The exchange hole. Now we will write the spin orbitals as a product of an spatial orbital and a spin function: $\phi(r)g_i(s)$. The spin function can only take two forms: $g_u(s)$ and $g_d(s)$ for up and down spin respectively. The two spin functions are orthonormal:

$$\sum_s g_i(s)g_j(s) = \delta_{ij}$$

Consider the following two two-electron wave functions constructed from two orbitals and with electrons of the same spin:

i) $\psi_1(x_1,x_2)=\varphi_\alpha(r_1)g_u(s_1)\varphi_\beta(r_2)g_u(s_2)$ (a simple product of two one-electron wave functions), and

ii) $\psi_2(x_1,x_2) = \begin{vmatrix} \varphi_\alpha(r_1)g_u(s_1) & \varphi_\beta(r_1)g_u(s_1) \\ \varphi_\alpha(r_2)g_u(s_2) & \varphi_\beta(r_2)g_u(s_2) \end{vmatrix}$ (a properly anti-symmetric Slater determinant).

Question 2.1. Are wavefunctions ψ_1 and ψ_2 allowed for electrons?

a) None of them are allowed

b) ψ_1 is not allowed but ψ_2 is X

c) Both are allowed

Write an expression for the probability density of finding one electron at position r_1 and the other at position r_2 for both wave functions. Hints: Remember the definition of probability function from week 1 and note that you need to sum over the spin variables (we are not interested in what spin the electrons have, just where they are).

Question 2.2. Which statement is true regarding the probability density functions?

a) For ψ_1 the probability is simply the product of probabilities corresponding to the individual orbitals

b) For ψ_2 the probability is simply the product of probabilities corresponding to the individual orbitals X

Compare the two results and analyze the effect of anti-symmetrization on the correlations between the two electrons?

Question 2.3 What is the probability of finding both electrons at the same location for the anti-symmetric ψ_2 wavefunction?

a) Zero X

b) The product of the probabilities of the individual orbitals

This shows that when the electrons have the same spin they are aware of each other due to the antisymmetric nature of the wavefunction and they avoid each other. The two electrons cannot be at the same spot at the same time even if the individual orbitals are non zero at the location. This is called *exchange correlation* or the *exchange hole*; since the electrons avoid each other their energy is lower (less repulsion) and this is the origin of Hund's rule.