Phys 5870: Modern Computational Methods in Solids
Homework 5

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Exercise 1:

Calculate numerically the overlap between two gaussian orbitals:

$$\langle p|q\rangle = \int d^3r \chi_p(r)\chi_q(r), \tag{1}$$

where the wavefunctions correspond to those used for the helium atom in the lecture notes.

For simplicity, just take one par with $p = 1$,$q = 2$. Plot the functions and choose an appropriate integration window. Plot the absolute numerical error as a function of the integration step, in a log scale:

$$E = |I(h) - \langle p|q\rangle| \tag{2}$$

Notice that this is a three dimensional integral.

Try this integral using both cartesian and polar coordinates: what remarks can you make about the performance of both approaches?

Exercise 2:

Same as the previous exercise, but for the K-S exchange interaction:

$$X_{pq} = \int d^3r \left(2\sum_{rs} C_r C_s \chi_r^*(r)\chi_s(r)\right)^{1/3} \chi_p^*(r)\chi_q(r) \tag{3}$$

Calculate this again just for $p = 1$ and $q = 2$. For simplicity take all the coefficients $C_q = 1/2$.

Notice that a proper calculation should assume tha the orbitals χ_p are normalized, which is not the case here. To verify this, calculate the total number of particles:

$$N = \int d^3 r n(r) = 2 \sum_{rs} C_r C_s \int d^3 r \chi_r^*(r) \chi_s(r) \tag{4}$$

and show that it is not equal to 1.

What is the proper normalization factor for each χ_p?

Notice that the basis functions are not orthonormal, so a choice of $C_q = 1.2$ won't reproduce the correct normalization. In more detail, if the basis functions are orthonormal:

$$\langle p|q \rangle = \delta_{pq} \Rightarrow \langle \phi|\phi \rangle = \sum_p C_p^2 = 1 \tag{5}$$

However, in our case we have

$$\langle p|q \rangle = S_{pq} \Rightarrow \langle \phi|\phi \rangle = \sum_{pq} C_p C_q S_{pq} \tag{6}$$

If we take all the $C_q = C$ the same, then we obtain

$$\langle \phi|\phi \rangle = C^2 \sum_{pq} S_{pq} \tag{7}$$

We want this to be equal to 1, therefore we obtain the value of C that will give us the right normalization as

$$C = \frac{1}{\sqrt{\sum_{pq} S_{pq}}} \tag{8}$$

Exercise 3:

Using finite differences, pick the proper interval and solve the Poisson equation for the density introduced above:

$$\frac{d^2}{dr^2} U(r) = -4\pi n(r).$$

Notice that r is the radial coordinate. Use the proper normalization for the density.