Homework 2

1. [10 pt] The electron density for the hydrogen atom is $n(r) = \pi^{-1} \exp(-2r)$ in atomic units. Show that Kato's cusp condition is satisfied.

2. [15 pt] Take the electron density for the hydrogen atom. It corresponds to a single electron, so write it as a single orbital, and determine the single particle potential $v_s(r)$ corresponding to this orbital. (That is: perform the Kohn-Sham construction for this single particle density). Repeat for the normalized Gaussian density $n(r) = \pi^{-3/2} r_0^{-3} \exp(-(r/r_0)^2)$.

3. [20 pt] Showing that the electron density can be written as a sum of orthonormal orbitals is straightforward in 1D. Take a density $n(x) \geq 0$ on the finite domain $a \leq x \leq b$, and where the integral of the density over this range is an integer N. Let $s(x) := n(x)/N$, and $q(x) := \int_a^x dx' s(x')$. Define the set of orbitals

$$\phi_k(x) := \sqrt{s(x)} \exp(2\pi i k q(x))$$

where k is any integer. Show that

   a. $\langle \phi_k | \phi_{k'} \rangle = \delta_{kk'}$
   b. $n(x)$ can be written as the sum of *any* set of N distinct $|\phi_k(x)|^2$

4. [25 pt] Using the Thomas-Fermi kinetic energy density functional

$$T^{\text{TF}}[n] = \frac{3}{10}(3\pi^2)^{2/3} \int d^3r (n(r))^{5/3}$$

and the exchange energy density functional

$$E_x^{\text{TF}}[n] = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3} \int d^3r (n(r))^{4/3}$$

in the local density approximation, find the optimal electron density for the He atom singlet of the form $n(r) = 2\pi^{-1} r_0^{-3} \exp(-2r/r_0)$. How does your energy compare with your earlier estimate using Hartree-Fock? Comment on the errors.

5. [15 pt] When we derived the kinetic energy in the Thomas-Fermi approximation, we approximated the discrete sum as an integral; that is, we treated the *discrete* number of electrons N as if it was a *continuous* variable. However, if we were to consider an electron density that corresponded to a fractional number of electrons $N + \delta$, the kinetic energy would linearly interpolate between the N and $N + 1$ states. Write a short program that evaluates the *discrete* sum of the kinetic energies for non-interacting electrons for a given (integer) value of N, and then compare this with the continuous expression we found in class. If you plot both forms of the kinetic energy, what do you notice about the derivative?

6. [15 pt] We solved the self-consistent equation $x = f(x)$ with a linear mixing algorithm by starting from an initial guess x_0 and using the update formula $x_{n+1} = (1 - \alpha)x_n + \alpha f(x_n)$.

   a. Determine the optimal α value that leads to the fastest decrease in error. *Hint*: write $x_n = x^\star + \epsilon$, where $x^\star$ is the true solution $x^\star = f(x^\star)$. Estimate the error for x_{n+1} and find the α that minimizes it.

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b. Given your answer to (a), can you conceive of an *adaptive* algorithm that could lead to *even faster* convergence? Do you have any concerns about the applicability or limits of your algorithm?

c. Try out your ideas from (a) and (b) on an actual problem (using your favorite numerical programming language), and comment on what you see; e.g., solving $x = \cos(x)$, or a non-trivial problem of your choice.