Homework 3

1. [15 pt] Consider the exchange-correlation double-counting term that appears in total energy, $E_{\mathrm{xc}}[n] - \int d^3r\; v_{\mathrm{xc}}[n](r)n(r)$.

   a. Using the exchange LDA, compute the double-counting term for the hydrogen electron density $n(r) = \pi^{-1}\exp(-2r)$.

   b. The single atom code `TinyDFT` does not have a double-counting term in its total energy expression. Why not?

2. [15 pt] In class, we discussed the perimeter functional in polar coordinates for $r(\theta) \geq 0$,

$$P[r] := \int_0^{2\pi} d\theta \sqrt{(r(\theta))^2 + (r'(\theta))^2},$$

   and in class, derived a local approximation

$$P^{\mathrm{local}}[r] := \int_0^{2\pi} d\theta\; r(\theta)$$

   and a gradient expansion approximation

$$P^{\mathrm{GEA}}[r] := \int_0^{2\pi} d\theta \left\{ r(\theta) + \frac{1}{2}\frac{(r'(\theta))^2}{r(\theta)} \right\}.$$

   We saw that for the function $r(\theta) = 1 + \epsilon\cos(n\theta)$ that the gradient expansion was poorly behaved as $r'(\theta)$ got large. Note that integrand in $P[r]$ should never be larger than $r(\theta) + |r'(\theta)|$; and while $P^{\mathrm{local}}[r]$ satisfies this, $P^{\mathrm{GEA}}[r]$ does not. Implement a "GGA" approximation to the perimeter functional that enforces this maximum, and test it out on the same range of ϵ and n values from class, and discuss how well this new approximation performs.

3. [20 pt] In 3D, the normalized $1s$ H wavefunction is $\psi(r) = \pi^{-1/2}\exp(-r)$. A normalized Gaussian is $\phi_\alpha(r) = \left(\frac{2\alpha}{\pi}\right)^{3/4}\exp(-\alpha r^2)$. Let's consider Gaussian approximations of the $1s$ orbital.

   a. Find the optimal value of α that minimizes the squared error in approximating the $1s$ orbital. (Note: you will want to find this value numerically). Make a plot of the two functions to compare.

   b. With a Gaussian basis, the matrix elements for the H hamiltonian are:

$$\langle\alpha|\alpha'\rangle = \frac{2\sqrt{2}(\alpha\alpha')^{3/4}}{(\alpha+\alpha')^{3/2}}$$

$$\langle\alpha|\hat{T}|\alpha'\rangle = \frac{6\sqrt{2}(\alpha\alpha')^{7/4}}{(\alpha+\alpha')^{5/2}}$$

$$\langle\alpha| -\frac{1}{r}|\alpha'\rangle = -\frac{4\sqrt{2}(\alpha\alpha')^{3/4}}{\sqrt{\pi}(\alpha+\alpha')}$$

   Using your favorite language for solving numerical problems, select a set of α's (covering a range of your selection) and find the ground state energy. How large does your basis set need to be to get a good approximation of the true value?

4. [10 pt] Use `TinyDFT` to compute the Kohn-Sham orbitals for Al, Al^{+}, and Al^{3+}. Discuss the changes you see in the levels of these orbitals.

5. [40 pt] Modify `TinyDFT` to include correlation using the simplified correlation energy fit by Chachiyo (doi:10.1063/1.4958669) and Karasiev (doi:10.1063/1.4964758). Compute the energies and Kohn-Sham energy levels for He, Be, and Ne, and comment on the changes.

6. [10 pt bonus] Perform a convergence study of the total energy with respect to the number of gaussians for H, He, and Ne in `TinyDFT`. Fit the curve to extrapolate to the energy with a complete basis set, and estimate the error from the default setting of 80 gaussians.