Chem231B: Assignment #5

March 3, 2020

Particles in a box via DFT

a) Write down the exact energies of the first three levels of the particle in a box of length 1, the sums of these energies for 1, 2, and 3 levels, plot the wavefunctions for each level, and plot the densities for 1, 2, and 3 same-spin fermions in the box.

Exact energies for one particle in a box

$$E_n = \frac{n^2 \pi^2}{2} \tag{1}$$

$$E_1 = \frac{\pi^2}{2} \tag{2}$$

$$E_2 = 2\pi^2 \tag{3}$$

$$E_3 = \frac{9\pi^2}{2} \tag{4}$$

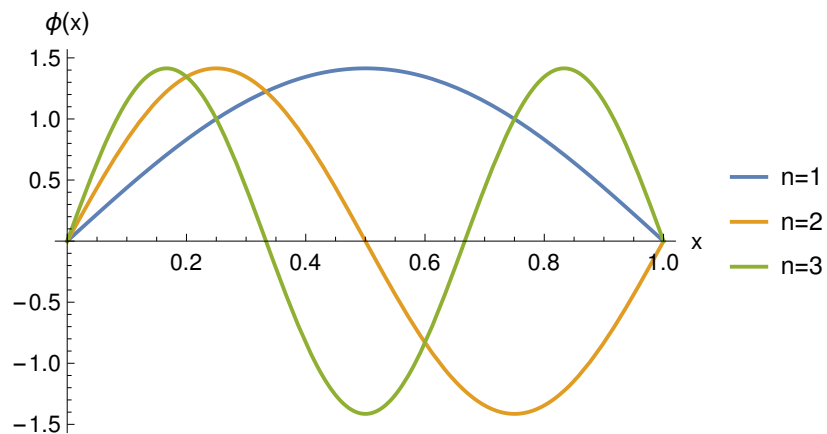$$\phi_i(x) = \sqrt{2} sin(\pi i x) \tag{5}$$

Figure 1: Particle in a box wavefunction for the three energy levels ($i = 1, 2, 3$).

The sums of the energies for 1, 2, and 3 levels are given

$$E_1 + E_2 = \frac{5\pi^2}{2} \tag{6}$$

$$E_1 + E_2 + E_3 = 7\pi^2 \tag{7}$$

The densities ($n_j(x)$) for 1, 2, and 3 same-spin fermions ($j = 1, 2, 3$) in the box are the sum of the $\phi_i(x)^2$

$$n_1(x) = \phi_1(x)^2 \tag{8}$$

$$n_2(x) = \phi_1(x)^2 + \phi_2(x)^2 \tag{9}$$

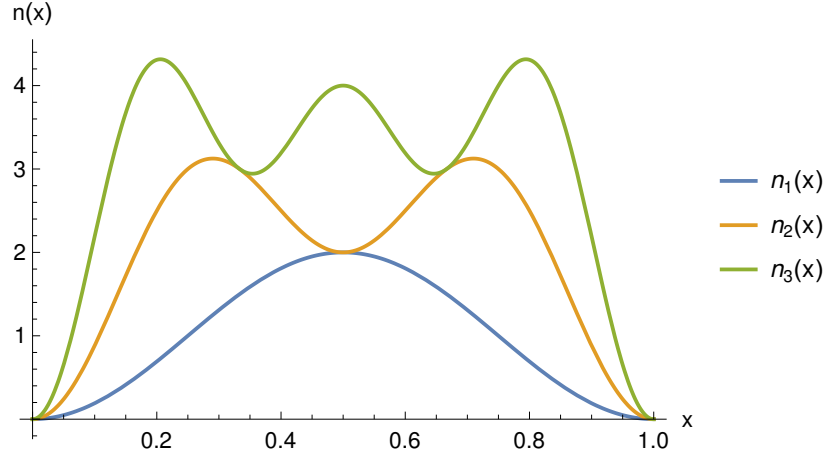$$n_3(x) = \phi_1(x)^2 + \phi_2(x)^2 + \phi_3(x)^2 \tag{10}$$

Figure 2: Densities for 1, 2, and 3 fermions same-spin are plotted.

b) Solve the Euler-Lagrange equation with the TF approximation to the kinetic energy to find the relation between N and μ. Solve for the mininimizing density, and plot it on your density plots. Comment on the errors made by this approximate density, and how the error behaves as N grows. Calculate the integral of $n^2(x)$ for $N = 1, 2, 3$, both exactly and approximately and comment as N grows.

$$L[n, \mu] = T^{\mathrm{TF}}[n] - \mu \int dx \, n(x) \tag{11}$$

$$\frac{\delta L}{\delta n} = \frac{\delta T^{\mathrm{TF}}[n]}{\delta n} - \mu = 0 \tag{12}$$

$$\frac{\delta T^{\mathrm{TF}}[n]}{\delta n} = \frac{\pi^2 n(x)^2}{2} = \mu \tag{13}$$

$$\mu = \frac{\pi^2 N^2}{2} \tag{14}$$

Since the multiplier μ has been determined in terms of N, the approximate minimizing density is given

$$n(x) = N. \tag{15}$$

The integral of $n^2(x)$ for $N = 1, 2, 3$ for the approximate TF density becomes worse with increasing N and the $n^2(x)$ integral is N^2 while the exact density yields the correct number of electrons at $N = 1, 2, 3$.
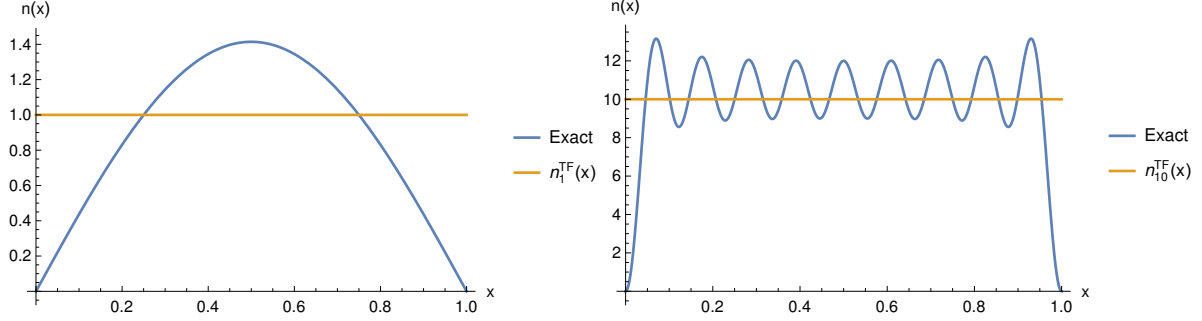
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Figure 3: Thomas-Fermi minimizing density and exact density given for 1 and 10 particles.

With increasing N, the TF density looks closer to describing exact density.

c) Make a table of the exact and approximate kinetic energies for each N and report the percentage error. Comment on the absolute error and percent error as N grows.

Table 1: Comparison between exact and approximate Thomas–Fermi kinetic energies with respect to increasing N particles.

N	T^{exact}	$T^{\text{TF}}[n_{\text{approx}}]$	Error (%)
1	4.935	1.645	-66.667
2	24.674	13.160	-46.667
3	69.0872	44.413	-35.714
4	148.044	105.276	-28.889
5	271.414	205.617	-24.242
6	449.067	355.306	-20.879
7	690.872	564.212	-18.333
8	1006.7	842.206	-16.340
9	1406.42	1199.16	-14.737
10	1899.9	1644.93	-13.420
11	2497.01	2189.41	-12.319
12	3207.62	2842.45	-11.385
13	4041.6	3613.92	-10.582
14	5008.82	4513.7	-9.885
15	6119.15	5551.65	-9.274
100	1.6697×10^6	1.6449×10^6	-1.4826

Approximate TF kinetic energy improves with increasing N. The TF consistently underestimate the kinetic energies.

d) Now calculate the TF kinetic energy on the exact densities and add the results to the table, including errors and comment as N grows. What do you conclude is the main source of error in the self-consistent TF calculation?

Table 2: Comparison between exact kinetic energy and Thomas–Fermi kinetic energy on exact density.

N	T^{exact}	$T^{\text{TF}}[n_{\text{exact}}]$	Error (%)
1	4.9348	4.11234	-16.667
2	24.674	21.7954	-11.667
3	69.0872	62.9187	-8.929
4	148.044	137.352	-7.222
5	271.414	254.965	-6.061
6	449.067	425.627	-5.220
7	690.872	659.207	-4.583
8	1006.7	965.576	-4.085
9	1406.42	1354.6	-3.684
10	1899.9	1836.16	-3.355
11	2497.01	2420.11	-3.080
12	3207.62	3116.33	-2.846
13	4041.6	3934.68	-2.646
14	5008.82	4885.04	-2.471
15	6119.15	5977.28	-2.319
100	1.6697×10^6	1.6635×10^6	-0.370

Errors are even smaller with the exact density. One main source of the error arise from a poor density.

e) Remake your table to report eigenvalues, by calculating the difference between having N and $N-1$ particles in the box, and calculate errors for both self-consistent TF and TF on exact densities.

Table 3: Kinetic energy difference computed between N and $N-1$ state ($\epsilon_{N-1,N}$).

$\epsilon_{N-1,N}$	T^{exact}	$T^{\text{scf,TF}}$	Error (%)	$T^{\text{TF}}[n_{\text{exact}}]$	Error (%)
$\epsilon_{1,2}$	19.739	11.5145	-41.667	17.683	-10.417
$\epsilon_{2,3}$	44.413	31.2537	-29.630	41.123	-7.407
$\epsilon_{3,4}$	78.957	60.8626	-22.917	74.433	-5.730
$\epsilon_{4,5}$	123.370	100.341	-18.667	117.613	-4.667
$\epsilon_{5,6}$	177.653	149.689	-15.741	170.662	-3.935
$\epsilon_{6,7}$	241.805	208.907	-13.605	233.581	-3.401
$\epsilon_{7,8}$	315.827	277.994	-11.979	306.369	-2.995
$\epsilon_{8,9}$	399.719	356.951	-10.700	389.027	-2.675
$\epsilon_{9,10}$	493.480	445.777	-9.667	481.554	-2.417
$\epsilon_{10,11}$	597.111	544.473	-8.815	583.952	-2.204
$\epsilon_{11,12}$	710.612	653.039	-8.102	696.218	-2.025
$\epsilon_{12,13}$	833.982	771.474	-7.495	818.355	-1.874
$\epsilon_{13,14}$	967.221	899.779	-6.973	950.361	-1.743
$\epsilon_{14,15}$	1110.330	1037.95	-6.519	1092.240	-1.630
$\epsilon_{99,100}$	49348.	48856.2	-0.997	49225.1	-0.249

f) Deduce formulas for E_N for the exact and two approximate sets of numbers, and then add $N = 100$ to your table. What aspect of the formulas show that TF becomes relatively exact as N gets large? (Hint: In every case, the formulas are cubic polynomials in N with no constant term (why?) whose coefficients could be found by fitting to 3 values of N.)

$$E_N^{\text{exact}} = \frac{\pi^2 N^3}{6} + \frac{\pi^2 N^2}{4} + \frac{\pi^2 N}{12} \tag{16}$$

$$E_N^{\text{TF}} = \frac{\pi^2 N^3}{6} + \frac{\pi^2 N^2}{4} + \frac{\pi^2 N}{12} \tag{17}$$

$$E_N^{\text{scf,TF}} = \frac{\pi^2 N^3}{6} \tag{18}$$

Harmonic oscillators in DFT

a) For the harmonic oscillator $v(x) = x^2/2$, write the formula for the TF density in terms of μ.

$$L[n, \mu] = T^{\text{TF}}[n] + \int dx\, v(x)n(x) - \mu \int dx\, n(x) \tag{19}$$

$$\frac{\delta L}{\delta n} = \frac{\delta T^{\text{TF}}[n]}{\delta n} v(x) - \mu = 0 \tag{20}$$

$$n^{\text{TF}}(x) = \frac{\sqrt{2(\mu - \frac{1}{2}x^2)}}{\pi} \tag{21}$$

b) By doing the integral between the turning points, find a formula for N as a function of μ.

$\mu = N$

c) Get formulas for T_N and E_N.

$$T_N = 2\frac{\pi^2}{6} \int_0^{\sqrt{2N}} dx \left(\frac{\sqrt{2(N - \frac{1}{2}x^2)}}{\pi} \right)^3$$

$$= \frac{N^2}{4}$$

$$V_N = \frac{N^2}{4}$$

$$E_N = \frac{N^2}{2}$$

d) By subtracting $N - 1$ from N, deduce a formula for the N-th energy level. What is its error?

$E_N^{\text{TF}} - E_{N-1}^{\text{TF}} = N - 1/2$ which is exact

e) For $N = 1, 2, 3$, plot both the exact and the approximate densities of the harmonic well. Why would the phrase "getting the right answer for the wrong reason" come to mind?
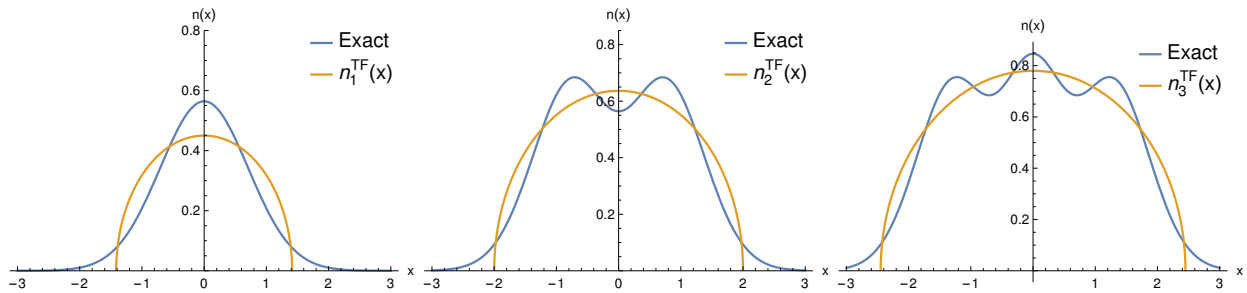

Figure 4: Exact and the approximate densities of the harmonic well for 1, 2, and 3 particles (from left to right).

f) Calculate the integral of $n^2(x)$ for $N = 1, 2, 3$ both exactly and approximately and comment on trends of errors with N.

Both the exact and TF densities yield the same integral of $n^2(x)$ for $N = 1, 2, 3$ which correspond to the number of electrons.

Morse oscillators in DFT

a) For the Morse potential given for the diatomics problem,

$$E_N^{TF} = -NV_0(1 - y + y^2/3)$$

where $y = N/\alpha$. Deduce a formula for individual eigenvalues.

$$E_N^{TF} - E_{N-1}^{TF} = -\frac{V_0(N^2 - 3N\alpha + 3\alpha^2)}{3\alpha^2} \tag{22}$$

b) For your parameters for H_2 modelled as a Morse potential. List the exact and approximate vibrational energy levels. Comment on where the largest errors are.

c) What happens for D_2? Does the TF result do better or worse than in H_2? Does it depend on which eigenvalues you look at? Why does it get better or worse?