

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

$$E_n = \frac{n^2\pi^2}{2} \quad (1)$$

$$E_1 = \frac{\pi^2}{2} \quad (2)$$

$$E_2 = 2\pi^2 \quad (3)$$

$$E_3 = \frac{9\pi^2}{2} \quad (4)$$

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

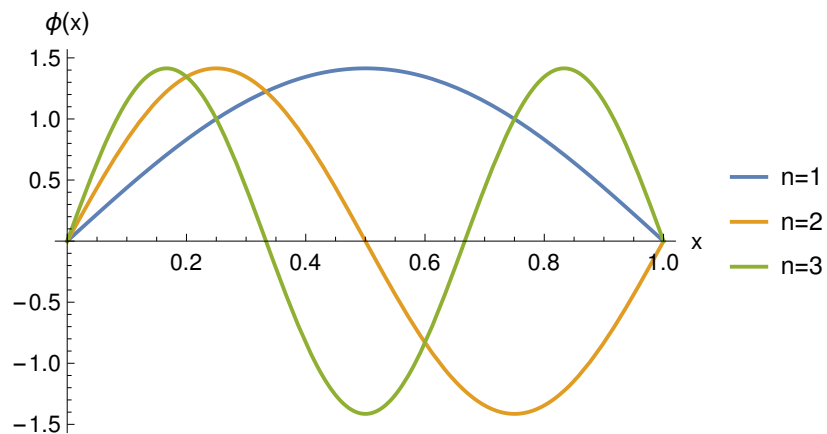


Figure 1: Particle in a box wavefunction for the three energy levels ($i = 1, 2, 3$).

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

$$E_1 + E_2 = \frac{5\pi^2}{2} \quad (6)$$

$$E_1 + E_2 + E_3 = 7\pi^2 \quad (7)$$

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 $\phi_i(x)^2$

$$n_1(x) = \phi_1(x)^2 \quad (8)$$

$$n_2(x) = \phi_1(x)^2 + \phi_2(x)^2 \quad (9)$$

$$n_3(x) = \phi_1(x)^2 + \phi_2(x)^2 + \phi_3(x)^2 \quad (10)$$

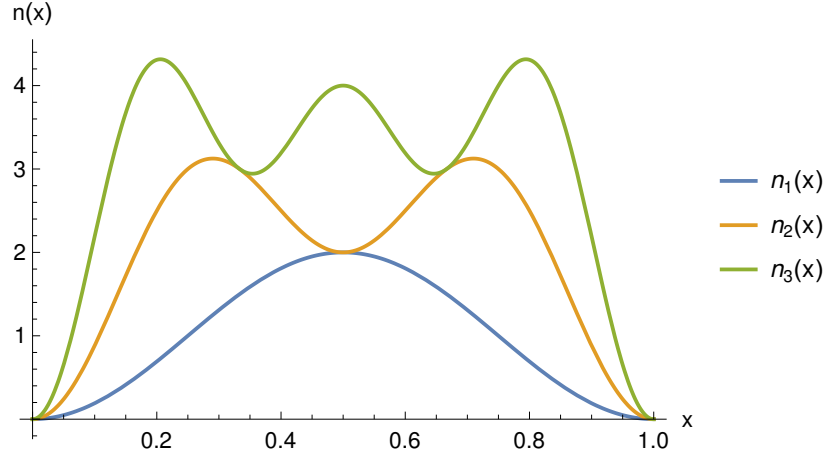


Figure 2: Densities for 1, 2, and 3 fermions same-spin are plotted.

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 minimizing 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.

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

$$\frac{\delta L}{\delta n} = \frac{\delta T^{\text{TF}}[n]}{\delta n} - \mu = 0 \quad (12)$$

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

$$\mu = \frac{\pi^2 N^2}{2} \quad (14)$$

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

$$n(x) = N. \quad (15)$$

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 $N = 1, 2, 3$.

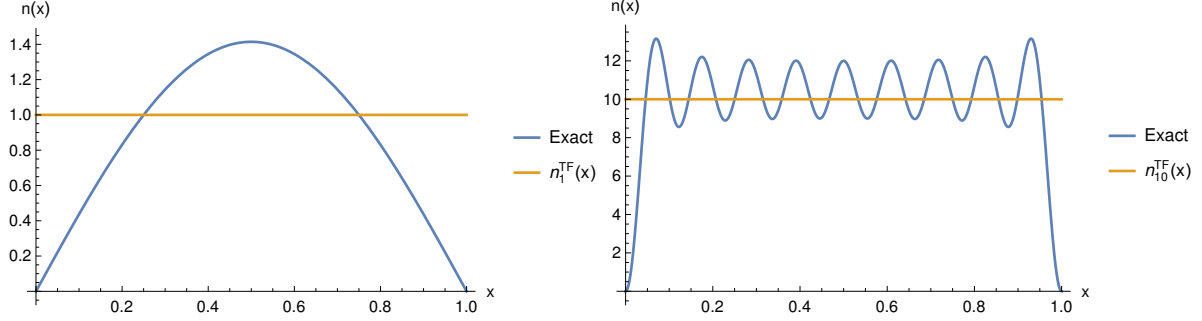


Figure 3: Thomas-Fermi minimizing density and exact density given for 1 and 10 particles.

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 .)

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

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

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

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 .

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

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

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

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 .

$$\begin{aligned} T_N &= 2 \frac{\pi^2}{6} \int_0^{\sqrt{2N}} dx \left(\frac{\sqrt{2(N - \frac{1}{2}x^2)}}{\pi} \right)^3 \\ &= \frac{N^2}{4} \\ V_N &= \frac{N^2}{4} \\ E_N &= \frac{N^2}{2} \end{aligned}$$

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

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

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?

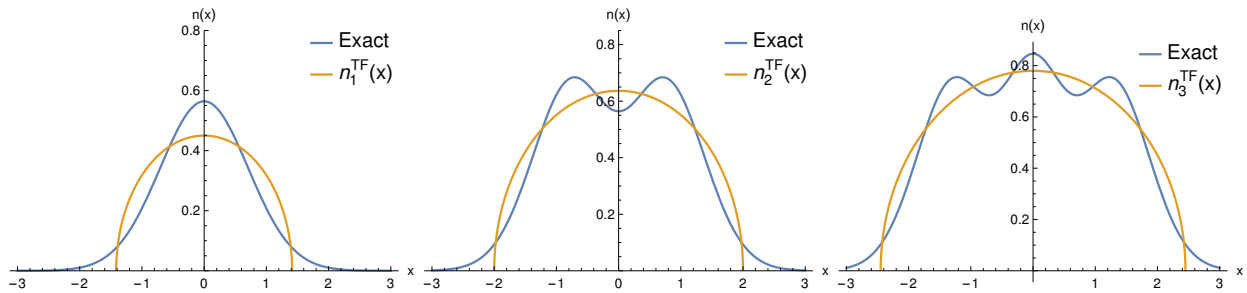


Figure 4: Exact and the approximate densities of the harmonic well for 1, 2, and 3 particles (from left to right).

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.

$$E_N^{TF} = -NV_0(1 - y + y^2/3) \quad (22)$$

$$\frac{dE_N^{TF}}{d\alpha} = 0 \quad (23)$$

$$\alpha = \frac{2N}{3} \quad (24)$$

Therefore, the individual eigenvalues are $E_N^{TF} = -\frac{Nv_0}{4}$.

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?