

Lausanne HW

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This is your homework for the week.

HALF HARMONIC OSCILLATOR

Consider the half harmonic oscillator, with potential

$$v(x) = \begin{cases} \frac{1}{2}x^2 & x > 0 \\ \infty & x \leq 0 \end{cases} \quad (0.1)$$

1. Eigenvalues and vectors:

With the Schrodinger equation in atomic units,

$$-\frac{1}{2} \frac{d^2}{dx^2} \phi(x) + v(x)\phi(x) = \epsilon \phi(x), \quad (0.2)$$

solve the following:

(a) Give the eigenfunctions of the SE, in terms of the regular harmonic oscillator eigenfunctions.

Hint: $\phi_j(x=0) = 0$ for the half harmonic oscillator

(b) Write out the first three energy eigenvalues and eigenfunctions, and make a plot (or cartoon) of the eigenfunctions.

Hint: Remember to normalize the eigenfunctions.

(c) Determine the kinetic energy values for the first three eigenfunctions.

2. Electronic densities:

Considering a system of N non-interacting, same-spin (or single occupation) electrons, determine the density for this system with $N=1, 2$, and 3 .

(a) Write out the analytic formulas for the densities.

(b) Make a plot (or cartoon) of these densities.

(c) Write out the total kinetic energy for these systems.

3. Thomas-Fermi approximation: *A statistical description of the electrons*

Based on the density alone, Thomas and Fermi showed that one could approximate the kinetic energy of a system of same-spin electrons by

$$T_s^{\text{TF}}[n] = \frac{\pi^2}{6} \int dx n^3(x) \quad (0.3)$$

Evaluate $T_s^{\text{TF}}[n]$ on the exact densities found in problem 2a, and compare to the kinetic energies of 2c. Give % errors.

4. Self-consistent TF: *Pure DFT*

One can minimize the TF energy, $E^{\text{TF}}[n] = T_s^{\text{TF}}[n] + V[n]$, by taking the functional derivative.

$$\begin{aligned} \mu &= \frac{\delta E}{\delta n(x)} = \frac{\delta T_s}{\delta n(x)} + v(x) \\ &= \frac{\pi^2}{2} (n^{\text{TF}}(x))^2 + v(x) \end{aligned} \quad (0.4)$$

(a) Using this equation, find the TF density, $n^{\text{TF}}(x)$, in terms of μ , the chemical potential, and the external potential $v(x)$.

(b) When $v(x) > \mu$, the TF density must become zero – classically no particles have energy above μ , so the TF density must be zero there.

For the half harmonic oscillator, determine μ for when $N = 1$. Then repeat for $N = 2$ and 3 .

Hint: The integrated density must equal N .

(c) Using the μ values found in problem 4b, plot the TF densities, and plot against the true densities.

Do the TF densities satisfy the boundary conditions?

(d) Determine $T_s^{\text{TF}}[n^{\text{TF}}]$. Give percentage errors from the true T_s .

(e) Is the $T_s^{\text{TF}}[n^{\text{TF}}]$ closer to the true T_s than $T_s^{\text{TF}}[n]$ (from problem 3)? Why or why not?

5. Conceptual questions:

(a) List and describe two things that make a KS calculation different than a pure DFT calculation like TF.

(b) Is the non-interacting KE always positive? If not, give an example where it wouldn't be.

(c) How can the TF kinetic energy be so close and yet so far? Comment on the following:

- What kind of accuracies are necessary in chemistry vs. physics calculations, and how does TF measure up?
- What does TF theory miss?