PHYS-E0412 Computational Physics :: Homework 12

Due date 9.4.2019 at 10 am

Electronic Structure Solver

Many of the algorithms and techniques discussed in the course are usually put together to solve a larger problem. In this exercise we tackle one such problem, the problem of electronic structure. The equations to be solved are similar to those found in density functional theory (DFT):

$$H\phi_i = (T + V_{\text{eff}})\phi_i = \left(-\frac{1}{2}\Delta + V_{\text{eff}}\right)\phi_i = \epsilon_i \phi_i$$

where

$$V_{\text{eff}} = V_{\text{ext}} + V_{\text{H}} + V_{\text{xc}}$$

where V_{ext} is the external potential (from the M nuclei of atoms located at $\mathbf{R_k}$), V_{H} is the electrostatic potential of the electrons known as the Hartree potential, and V_{xc} is the exchange-correlation that depends on the density $\rho = \sum_{i=1}^{N} |\phi_i|^2$ of the N electrons. For practical reasons it is easiest to solve the problem on a finite interval $[0, L]$ using Dirichlet boundary conditions and, e.g., $L = \pi$.

a) Select a discretization of your favorite flavor and use it to obtain the matrix H (and possibly S if you use non-orthogonal basis functions). Use the potentials

$$V_{\text{ext}} = \sum_{k=1}^{M} -85e^{-2(x-R_k)^2}$$

$$V_{\text{H}} = \int \frac{\rho(x')}{|x - x'| + \delta}\, dx'$$

$$V_{\text{xc}} = V_{\text{x}} = -\rho^{1/3}$$

where δ is a small regularizing parameter. Iterate the equations so long that V_{eff} and ρ are self-consistent. Use your solver to compute the ground state density of one nucleus and three electrons ($M = 1, N = 3$) (3 p.)

b) Set up a problem with two nuclei and six electrons ($M = 2, N = 6$). Vary the distance between the two nuclei and compute the total energy of the system as

$$E = \sum_{i=1}^{N} \epsilon_i - \frac{1}{2}\int V_H \rho + \sum_{i=1}^{M}\sum_{j=i+1}^{M} \frac{9.0}{(R_i - R_j)^2}$$

where the last term represents the repulsion between the nuclei. Can you find a minimum of the energy? What is the equilibrium distance? (2 p.)

c) How many hours did you spend working on this exercise?