Problem 1

Username in GitHub: **bacalfa**
Course files URL: https://github.com/bacalfa/cmu06-640
   All my homework files will be uploaded to the URL above and it can be cloned as follows:

```
git clone git://github.com/bacalfa/cmu06-640
```

Problem 2

Read Chapter 1 in textbook. Key concepts:

- Schrödinger Equation (SE): $H\psi = E\psi$, where H is the Hamiltonian operator and ψ is a set of solutions (eigenstates) of H. Each solution ψ_n has an associated eigenvalue E_n that satisfies the equation.

- When applied to a system characterized by multiple electrons interacting with multiple nuclei, equation (1.1), the ψ in SE is the electronic wave function, which cannot be directly observed, and E is the ground-state energy of the electrons.

- Important quantity in DFT: electron density, $n(\mathbf{r}) = 2 \sum_i \psi_i^*(\mathbf{r})\psi(\mathbf{r})$.

- First theorem of Hohenberg-Kohn: *The ground-state energy from Schrödinger's equation is a unique functional of the electron density.*

- Second theorem of Hohenberg-Kohn: *The electron density that minimizes the energy of the overall functional is the true electron density corresponding to the full solution of the Schrödinger equation.*

- The energy functional contains the following "known" terms: the electron kinetic energies, the Coulomb interactions between the electrons and the nuclei, the Coulomb interactions between pairs of electrons, and the Coulomb interactions between pairs of nuclei. And the "unknown" term is the exchange-correlation functional.

- Kohn-Sham equations have single-electron wave functions as their solutions. Need to be solved self-consistently.

- Different approximations for the exchange-correlation have been proposed, such as the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA), with two most widely used models for the functional: Perdew-Wang (PW91) and Perdew-Burke-Enrzerhof (PBE).

- Hartree-Fock (HF) method is a wave-function-based approach to solve the SE.

- In an HF calculation, we fix the positions of the atomic nuclei and aim to determine the wave function of N-interacting electrons.

- Approximate spin orbitals with (finite) basis set (set of functions) and expansion coefficients.

- The HF method assumes that the exact, N-body wave function of the system can be approximated by a single Slater determinant, in which the N-electron wave function is formed by combining one-electron wave functions in a way that satisfies the antisymmetry principle (*i.e.*, electrons are fermions, so the wave function must change sign if two electrons change places with each other).

- HF method does not correctly describe how electrons influence other electrons. More succinctly, the HF method does not deal with electron correlations.

- Quantum chemistry approaches that are more sophisticated than the HF method for approximately solving the SE capture some part of the electron correlation energy by improving in some way upon one of the assumptions that were adopted in the HF approach.

- Methods based on a single reference determinant are formally known as "post-Hartree-Fock" methods. These methods include configuration interaction (CI), coupled cluster (CC), Møller-Plesset perturbation theory (MP), and the quadratic configuration interaction (QCI) approach.

- Møller-Plesset perturbation theory is based on adding a small perturbation (the correlation potential) to a zero-order Hamiltonian (the HF Hamiltonian, usually). In the Møller-Plesset perturbation theory approach, a number is used to indicate the order of the perturbation theory, so MP2 is the second-order theory and so on.

- Another class of methods uses more than one Slater determinant as the reference wave function. These methods include multiconfigurational self-consistent field (MCSCF), multireference single and double configuration interaction (MRDCI), and N-electron valence state perturbation theory (NEVPT) methods.

- The classification of wave-function-based methods has two distinct components: the level of theory and the basis set. The level of theory defines the approximations that are introduced to describe electron-electron interactions. The second, and equally important, component in classifying wave-function-based methods is the basis set. Using a basis set with more functions allows a more accurate representation of the true solution but also requires more computational effort since the numerical coefficients defining the magnitude of each function's contribution to the net function must be calculated.

Problem 3

Annotations (in red) were added to Section 4 in file `dft-8-31-edits.pdf` and the new file is `dft-bacalfa-edits.pdf`.

Problem 4

The Python code is in file `hw01.py`. The graph generated is shown below.
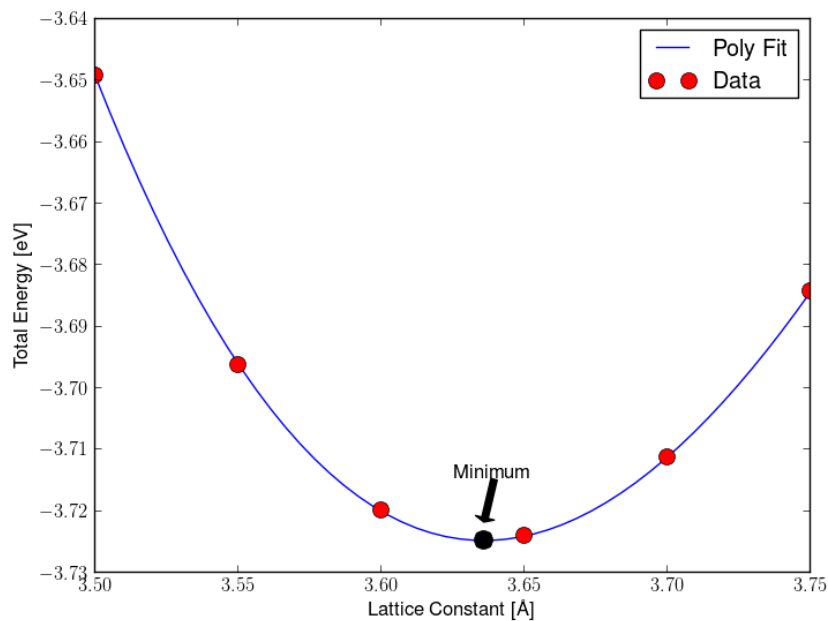
Figure 1: Graphical results for Problem 4.

Problem 5

The Python code is in file `hw01.py`. The graph generated is shown below. Using different initial guesses leads to different solutions, since `fsolve` uses a Newton-based optimization method to find a zero of the nonlinear equation and its convergence depends on the initial guess. For example, for $x_0 = 1.5$, the solution obtained is $x^* = 1.6180$.
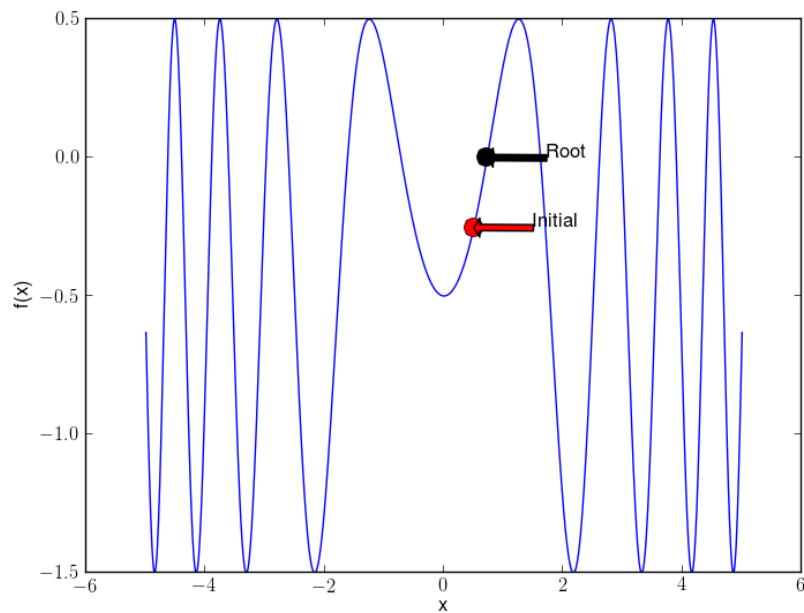
Figure 2: Graphical results for Problem 5.

Problem 6

The Python code is in file `hw01.py`. Solution of linear system $Ax = b$:

$$x = \begin{bmatrix} 4.65 \\ 1.8417 \\ -1.15 \\ -0.3417 \end{bmatrix}$$