PHYS 511: Computational Modeling and Simulation - Fall 2016
Assignment #4, due Friday November 18, before class

Galerkin (Rayleigh-Ritz) approach to solve an eginevalue problem

1. Consider the stationary Schröedinger equation for an electron moving a spherically-symmetric potential $V(r)$ (here $\mathbf{r} = (x, y, z)$ and $r = \sqrt{x^2 + y^2 + z^2}$). It has the following form:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi. \tag{1}$$

In the above equation $\hbar$ is the Plank constant divided by 2π, m is the mass of the electron, and E is the energy of the electron. $\psi(\mathbf{r}) = \psi(x, y, z)$ is the unknown wave function (can be complex). For attractive potentials (this requires $\frac{\partial V}{\partial r} > 0$, because in the classical sense the direction of the force acting on the electron, given by $\mathbf{F} = -\nabla V$, is towards the center located at the origin) this equation may allow solutions only for some discrete values of E. Thus, the stationary Schrödinger equation is an eigenvalue problem. The lowest such value of E is called the ground state energy and the corresponding wave function is called the ground state wave function.

Due to spherical symmetry of $V(r)$ the solutions can be represented as products of the radial part, R_{nl}, of the wave function and spherical harmonics, Y_l^m:

$$\psi(\mathbf{r}) = R_{nl}(r)Y_l^m(\theta, \phi), \qquad n = 1, 2, 3\ldots, \quad l = 0, 1, 2\ldots, \quad m = -l, \ldots, l, \tag{2}$$

where r, θ, and ϕ are electron coordinates in the spherical coordinate system. Thus, in order to solve the Schrödinger equation for a spherically symmetric potential one only needs to find R_{nl}. Equation (1) is then reduced to a 1D eigenvalue problem (which can be further reduced to a Sturm-Liouville form):

$$-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]R = ER \tag{3}$$

Next, to make things more convenient, we introduce new dimensionless coordinates, $r \leftarrow \frac{r}{a_B}$ (constant $a_B = \frac{\hbar^2}{me^2}$, which has the dimension of length, is called the Bohr radius. e is the charge of the electron). In these new coordinates the radial Schrödinger equation becomes:

$$HR = ER, \tag{4}$$

where the Hamiltonian operator in the case $l = 0$ (quantum number l is zero for the ground state) is

$$H = -\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + V(r). \tag{5}$$

2. In this assignment we will be solving the Schrödinger equation for the ground state of the hydrogen atom, i.e. our potential in dimensional units is $V(r) = -\frac{1}{r}$ and

$$H = -\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} - \frac{1}{r}. \tag{6}$$

To do that we will be using the variational method in conjunction with the Galerkin approach (which in quantum mechanics is traditionally called the Rayleigh-Ritz method). Our task will be to approximate the radial part of the wave function, $R(r)$, as a linear combination of N basis functions:

$$R(r) = \sum_{i=1}^{N} c_i\,\varphi(r). \tag{7}$$

The basis functions will be Gaussians,

$$\varphi_i = \exp(-a_i r^2), \tag{8}$$

where parameter a_i is unique for each function. We can vary linear coefficients c_i in (7) to minimize the trial energy, ε (the energy computed within our approximate method). Note that the variational method in quantum mechanics says the trial energy ε can never exceed the exact ground state energy, $E_{\rm gr}$, that is $\varepsilon \leq E_{\rm gr}$. Moreover, it can be shown that the problem of finding the minimum of ϵ with respect to linear coefficients c_i is equivalent to solving the generalized eigenvalue problem with $N \times N$ matrices $\mathcal{H}$ (Hamiltonian matrix) and $\mathcal{S}$ (overlap matrix):

$$\mathcal{H}c = \varepsilon \mathcal{S}c, \tag{9}$$

where matrix elements of $\mathcal{H}$ and $\mathcal{S}$ are given by

$$\mathcal{H}_{ij} = \iiint \varphi_i^* H \varphi_j d\mathbf{r} = 4\pi \int_0^\infty \varphi_i^* H \varphi_j r^2 dr, \qquad \mathcal{S}_{ij} = \iiint \varphi_i^* \varphi_j d\mathbf{r} = 4\pi \int_0^\infty \varphi_i^* \varphi_j r^2 dr.$$

The asterix $(*)$ stands for complex conjugation and can be omitted if the basis functions are real.

Note that the generalized eigenvalue equation (9) has N solutions, $\varepsilon_1, \ldots, \varepsilon_N$ (all of which are implicit functions of Gaussian parameters a_i). The smallest ε corresponds to the ground state energy. Also note that matrices $\mathcal{H}$ and $\mathcal{S}$ are symmetric (or hermitian if basis functions were complex). Moreover, it can be shown that matrix $\mathcal{S}$ is positive definite.

In our particular case these matrix elements can be easily evaluated when φ_i's are Gaussians (8). They expressions are:

$$\mathcal{H}_{ij} = \frac{3\pi^{3/2} a_i a_j}{(a_i + a_j)^{5/2}} - \frac{2\pi}{a_i + a_j}, \qquad \mathcal{S}_{ij} = \frac{\pi^{3/2}}{(a_i + a_j)^{3/2}}. \tag{10}$$

3. Write a Python program (`as04.py`) that uses expansion (7) with N ranging from 1 to 4 to determine variational upper bounds to the exact ground state energy. In this program you should determine not only the optimal values of linear coefficients c_i by solving (9), but also minimize the energies with respect to nonlinear parameters of the gaussians, a_i.

   Useful hints:

   (a) The exact analytic solution for the ground state of hydrogen atom is $E = -\frac{1}{2}$ and $R(r) = 2\,e^{-r}$ (which gives $\psi = RY_0^0 = \frac{1}{\sqrt{\pi}} e^{-r}$). You can do a sanity check: if any of the eigenvalues you obtain when solving (9) happen to be smaller than $-\frac{1}{2}$, then that means you did something wrong. As you increase the number of terms N in expansion (7), the trial energy should approach $-\frac{1}{2}$ from above.

   (b) To solve the generalized eigenvalue problem you can use function `scipy.linalg.eigh` from `scipy` library. To find a minimum of a function you can use `scipy.optimize.minimize` from the same library. When doing that you will need to provide an initial guess for parameters a_i of the Gaussians. For $N = 4$ something like `[0.2, 0.5, 1.0, 2.0]` should be a reasonable initial guess. In fact, any positive values should be acceptable as an initial guess. You will also need to pick the minimization algorithm/method used. In principle, all of them should work. You can use, for instance, `Nelder-Mead`. In order to actually minimize the trial energy you will need to write your own function that takes nonlinear parameters a_i as an input argument. Make sure this function works properly. For example, it should never return a trial energy smaller than $-\frac{1}{2}$.

(c) To initialize matrices it is convenient to call function `numpy.zeros` from `numpy` library.

(d) For a single-term Gaussian expansion the result can actually be obtained analytically: $\varepsilon = -\frac{4}{3\pi} \approx -0.424413$ and $a_1 = \frac{8}{9\pi} \approx 0.282942$. You can use this data to verify that your program works properly.

4. If you want to do an *optional* bonus task then plot all trial wave functions you obtained (up to $N = 4$) and compare them on the same plot to the exact analytic solution. You should see that your trail wave functions (7) approach the exact solution as N gets larger. Note that in order to plot the trial wave functions (linear combinations of Gaussians) you will need to determine not only the lowest eigenvalues ε in (9), but also the corresponding linear coefficients c_i (the corresponding eigenvector). A properly normalized eigenvector can be computed with `scipy.linalg.eigh`. To do the plotting you can use `matplotlib` library.

5. Include the results of your calculations (trial energy and the values of parameters a_i) in file `report.txt` and place it, along with your Python source code and plots (if you generate any) in directory `as04` in your google drive directory shared with the instructor.