Project 2, Schrödinger's equation for two electrons in a three-dimensional harmonic oscillator well, deadline October 5 (noon)

The aim of this project is to solve Schrödinger's equation for two electrons in a three-dimensional harmonic oscillator well with and without a repulsive Coulomb interaction. Your task is to solve this equation by reformulating it in a discretized form as an eigenvalue equation to be solved with Jacobi's method. To achieve this you will have to write your own code which implements Jacobi's method.

Electrons confined in small areas in semiconductors, so-called quantum dots, form a hot research area in modern solid-state physics, with applications spanning from such diverse fields as quantum nano-medicine to the contruction of quantum gates. You can read about quantum dots at `http://en.wikipedia.org/wiki/Quantum_dot`, which also contains links to several scientific articles. A recent article of interest is the review by Semonin *et al* in Materials Today, volume 15, page 508 (2012).

Here we will assume that these electrons move in a three-dimensional harmonic oscillator potential (they are confined by for example quadrupole fields) and repel each other via the static Colulomb interaction. We assume spherical symmetry.

We are first interested in the solution of the radial part of Schrödinger's equation for one electron. This equation reads

$$-\frac{\hbar^2}{2m}\left(\frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}-\frac{l(l+1)}{r^2}\right)R(r)+V(r)R(r)=ER(r).$$

In our case $V(r)$ is the harmonic oscillator potential $(1/2)kr^2$ with $k=m\omega^2$ and E is the energy of the harmonic oscillator in three dimensions. The oscillator frequency is ω and the energies are

$$E_{nl}=\hbar\omega\left(2n+l+\frac{3}{2}\right),$$

with $n=0,1,2,\dots$ and $l=0,1,2,\dots$.

Since we have made a transformation to spherical coordinates it means that $r\in[0,\infty)$. The quantum number l is the orbital momentum of the electron. Then we substitute $R(r)=(1/r)u(r)$ and obtain

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u(r)+\left(V(r)+\frac{l(l+1)}{r^2}\frac{\hbar^2}{2m}\right)u(r)=Eu(r).$$

The boundary conditions are $u(0)=0$ and $u(\infty)=0$.

We introduce a dimensionless variable $\rho=(1/\alpha)r$ where α is a constant with dimension length and get

$$-\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{d\rho^2}u(\rho)+\left(V(\rho)+\frac{l(l+1)}{\rho^2}\frac{\hbar^2}{2m\alpha^2}\right)u(\rho)=Eu(\rho).$$

We will set in this project $l=0$. Inserting $V(\rho)=(1/2)k\alpha^2\rho^2$ we end up with

$$-\frac{\hbar^2}{2m\alpha^2}\frac{d^2}{d\rho^2}u(\rho)+\frac{k}{2}\alpha^2\rho^2u(\rho)=Eu(\rho).$$

We multiply thereafter with $2m\alpha^2/\hbar^2$ on both sides and obtain

$$-\frac{d^2}{d\rho^2}u(\rho)+\frac{mk}{\hbar^2}\alpha^4\rho^2u(\rho)=\frac{2m\alpha^2}{\hbar^2}Eu(\rho).$$

The constant α can now be fixed so that

$$\frac{mk}{\hbar^2}\alpha^4=1,$$

or

$$\alpha=\left(\frac{\hbar^2}{mk}\right)^{1/4}.$$

Defining

$$\lambda=\frac{2m\alpha^2}{\hbar^2}E,$$

we can rewrite Schrödinger's equation as

$$-\frac{d^2}{d\rho^2}u(\rho)+\rho^2u(\rho)=\lambda u(\rho).$$

This is the first equation to solve numerically. In three dimensions the eigenvalues for $l=0$ are $\lambda_0=3,\lambda_1=7,\lambda_2=11,\dots.$

We use the by now standard expression for the second derivative of a function u

$$u''=\frac{u(\rho+h)-2u(\rho)+u(\rho-h)}{h^2}+O(h^2), \tag{1}$$

where h is our step. Next we define minimum and maximum values for the variable ρ, $\rho_{\mathrm{min}}=0$ and ρ_{max}, respectively. You need to check your results for the energies against different values ρ_{max}, since we cannot set $\rho_{\mathrm{max}}=\infty$.

With a given number of steps, n_{step}, we then define the step h as

$$h=\frac{\rho_{\mathrm{max}}-\rho_{\mathrm{min}}}{n_{\mathrm{step}}}.$$

Define an arbitrary value of ρ as

$$\rho_i=\rho_{\mathrm{min}}+ih \qquad i=0,1,2,\dots,n_{\mathrm{step}}$$

we can rewrite the Schrödinger equation for ρ_i as

$$-\frac{u(\rho_i+h)-2u(\rho_i)+u(\rho_i-h)}{h^2}+\rho_i^2u(\rho_i)=\lambda u(\rho_i),$$

or in a more compact way

$$-\frac{u_{i+1}-2u_i+u_{i-1}}{h^2}+\rho_i^2u_i=-\frac{u_{i+1}-2u_i+u_{i-1}}{h^2}+V_iu_i=\lambda u_i,$$

where $V_i=\rho_i^2$ is the harmonic oscillator potential. Define first the diagonal matrix element

$$d_i=\frac{2}{h^2}+V_i,$$

and the non-diagonal matrix element

$$e_i = -\frac{1}{h^2}.$$

In this case the non-diagonal matrix elements are given by a mere constant. *All non-diagonal matrix elements are equal.* With these definitions the Schrödinger equation takes the following form

$$d_i u_i + e_{i-1} u_{i-1} + e_{i+1} u_{i+1} = \lambda u_i,$$

where u_i is unknown. We can write the latter equation as a matrix eigenvalue problem

$$\left(\begin{array}{ccccccc} d_1 & e_1 & 0 & 0 & \dots & 0 & 0 \\ e_1 & d_2 & e_2 & 0 & \dots & 0 & 0 \\ 0 & e_2 & d_3 & e_3 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & d_{n_{\mathrm{step}}-2} & e_{n_{\mathrm{step}}-1} \\ 0 & \dots & \dots & \dots & \dots & e_{n_{\mathrm{step}}-1} & d_{n_{\mathrm{step}}-1} \end{array}\right) \left(\begin{array}{c} u_1 \\ u_2 \\ \dots \\ \dots \\ \dots \\ u_{n_{\mathrm{step}}-1} \end{array}\right) = \lambda \left(\begin{array}{c} u_1 \\ u_2 \\ \dots \\ \dots \\ \dots \\ u_{n_{\mathrm{step}}-1} \end{array}\right) \tag{2}$$

or if we wish to be more detailed, we can write the tridiagonal matrix as

$$\left(\begin{array}{ccccccc} \frac{2}{h^2}+V_1 & -\frac{1}{h^2} & 0 & 0 & \dots & 0 & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2}+V_2 & -\frac{1}{h^2} & 0 & \dots & 0 & 0 \\ 0 & -\frac{1}{h^2} & \frac{2}{h^2}+V_3 & -\frac{1}{h^2} & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots & \frac{2}{h^2}+V_{n_{\mathrm{step}}-2} & -\frac{1}{h^2} \\ 0 & \dots & \dots & \dots & \dots & -\frac{1}{h^2} & \frac{2}{h^2}+V_{n_{\mathrm{step}}-1} \end{array}\right) \tag{3}$$

Recall that the solutions are known via the boundary conditions at $i = n_{\mathrm{step}}$ and at the other end point, that is for ρ_0. The solution is zero in both cases.

a) Your task here is to write a function which implements Jacobi's rotation algorithm (see Lecture notes chapter 7) in order to solve Eq. (2).

   We Define the quantities $\tan\theta = t = s/c$, with $s = \sin\theta$ and $c = \cos\theta$ and

$$\cot 2\theta = \tau = \frac{a_{ll} - a_{kk}}{2a_{kl}}.$$

   We can then define the angle θ so that the non-diagonal matrix elements of the transformed matrix a_{kl} become non-zero and we obtain the quadratic equation (using $\cot 2\theta = 1/2(\cot\theta - \tan\theta)$

$$t^2 + 2\tau t - 1 = 0,$$

   resulting in

$$t = -\tau \pm \sqrt{1+\tau^2},$$

   and c and s are easily obtained via

$$c = \frac{1}{\sqrt{1+t^2}},$$

   and $s = tc$.

Explain why we should choose t to be the smaller of the roots. Convince yourself that this choice ensures that $|\theta| \leq \pi/4)$ (and has the effect of minimizing the difference between the matrices $\mathbf{B}$ and $\mathbf{A} \Rightarrow$ so that the iterations goes 'faster')

We need: $|\theta| \leq \pi/4 \Rightarrow \theta \leq \pi/4$ and $\theta \geq -\pi/4$. Start with the first:

$$\begin{aligned} \theta = \arctan t &\leq \pi/4 \\ t &\leq \tan(\pi/4) = 1 \end{aligned}$$

and

$$\begin{aligned} \theta = \arctan t &\geq -\pi/4 \\ t &\geq \tan(-\pi/4) = -1 \end{aligned}$$

so $|t| \leq 1 \Rightarrow -\tau \pm \sqrt{1+\tau^2} \leq 1$. I then look at the case where $\tau > 0$ and try the positive root of t:

$$\begin{aligned} -\tau + \sqrt{1+\tau^2} &\leq -|\tau| + 1 + |\tau| = 1 \\ &\Rightarrow t \leq 1 \Rightarrow \theta \leq \pi/4 \end{aligned}$$

Then try the case when $\tau < 0$ and try the negative root of t:

$$\begin{aligned} -\tau - \sqrt{1+\tau^2} = |\tau| - \sqrt{1+\tau^2} &\geq |\tau| - (1 + |\tau|) = -1 \\ &\Rightarrow t \geq -1 \Rightarrow \theta \geq -\pi/4 \end{aligned}$$

So we see then that when $\tau > 0$ we choose the positive root, and when $\tau < 0$ we choose the negative root to make shure that $|\theta| \leq \pi/4$. This is to make shure that the operations does not make bigger changes to the other elements while making another element zero –> also making shure that we get to the solution faster (or at all?).

b) How many points n_{step} do you need in order to get the lowest three eigenvalues with four leading digits? Remember to check the eigenvalues for the dependency on the choice of $\rho_{\max}$.

How many similarity transformations are needed before you reach a result where all non-diagonal matrix elements are essentially zero? Try to estimate the number of transformations and extract a behavior as function of the dimensionality of the matrix.

You can check your results against the code based on Householder's algorithm, *tqli* in the file lib.cpp. Alternatively, you can use the Armadillo function for solving eigenvalue problems.

Comment your results (here you could for example compute the time needed for both algorithms for a given dimensionality of the matrix).

c) We will now study two electrons in a harmonic oscillator well which also interact via a repulsive Coulomb interaction. Let us start with the single-electron equation written as

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}u(r)+\frac{1}{2}kr^2u(r)=E^{(1)}u(r),$$

where $E^{(1)}$ stands for the energy with one electron only. For two electrons with no repulsive Coulomb interaction, we have the following Schrödinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{dr_1^2}-\frac{\hbar^2}{2m}\frac{d^2}{dr_2^2}+\frac{1}{2}kr_1^2+\frac{1}{2}kr_2^2\right)u(r_1,r_2)=E^{(2)}u(r_1,r_2).$$

Note that we deal with a two-electron wave function $u(r_1,r_2)$ and two-electron energy $E^{(2)}$.

With no interaction this can be written out as the product of two single-electron wave functions, that is we have a solution on closed form.

We introduce the relative coordinate $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$ and the center-of-mass coordinate $\mathbf{R}=1/2(\mathbf{r}_1+\mathbf{r}_2)$. With these new coordinates, the radial Schrödinger equation reads

$$\left(-\frac{\hbar^2}{m}\frac{d^2}{dr^2}-\frac{\hbar^2}{4m}\frac{d^2}{dR^2}+\frac{1}{4}kr^2+kR^2\right)u(r,R)=E^{(2)}u(r,R).$$

The equations for r and R can be separated via the ansatz for the wave function $u(r,R)=\psi(r)\phi(R)$ and the energy is given by the sum of the relative energy E_r and the center-of-mass energy E_R, that is

$$E^{(2)}=E_r+E_R.$$

We add then the repulsive Coulomb interaction between two electrons, namely a term

$$V(r_1,r_2)=\frac{\beta e^2}{|\mathbf{r}_1-\mathbf{r}_2|}=\frac{\beta e^2}{r},$$

with $\beta e^2=1.44$ eVnm.

Adding this term, the r-dependent Schrödinger equation becomes

$$\left(-\frac{\hbar^2}{m}\frac{d^2}{dr^2}+\frac{1}{4}kr^2+\frac{\beta e^2}{r}\right)\psi(r)=E_r\psi(r).$$

This equation is similar to the one we had previously in (a) and we introduce again a dimensionless variable $\rho=r/\alpha$. Repeating the same steps as in (a), we arrive at

$$-\frac{d^2}{d\rho^2}\psi(\rho)+\frac{1}{4}\frac{mk}{\hbar^2}\alpha^4\rho^2\psi(\rho)+\frac{m\alpha\beta e^2}{\rho\hbar^2}\psi(\rho)=\frac{m\alpha^2}{\hbar^2}E_r\psi(\rho).$$

We want to manipulate this equation further to make it as similar to that in (a) as possible. We define a 'frequency'

$$\omega_r^2=\frac{1}{4}\frac{mk}{\hbar^2}\alpha^4,$$

and fix the constant α by requiring

$$\frac{m\alpha\beta e^2}{\hbar^2} = 1$$

or

$$\alpha = \frac{\hbar^2}{m\beta e^2}.$$

Defining

$$\lambda = \frac{m\alpha^2}{\hbar^2}E,$$

we can rewrite Schrödinger's equation as

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2\rho^2\psi(\rho) + \frac{1}{\rho} = \lambda\psi(\rho).$$

We treat ω_r as a parameter which reflects the strength of the oscillator potential.

Here we will study the cases $\omega_r = 0.01$, $\omega_r = 0.5$, $\omega_r = 1$, and $\omega_r = 5$ for the ground state only, that is the lowest-lying state.

With no repulsive Coulomb interaction you should get a result which corresponds to the relative energy of a non-interacting system. Make sure your results are stable as functions of ρ_{max} and the number of steps.

We are only interested in the ground state with $l = 0$. We omit the center-of-mass energy.

You can reuse the code you wrote for (a), but you need to change the potential from ρ^2 to $\omega_r^2\rho^2 + 1/\rho$.

Comment the results for the lowest state (ground state) as function of varying strengths of ω_r.

For specific oscillator frequencies, the above equation has answers in an analytical form, see the article by M. Taut, Phys. Rev. A 48, 3561 - 3566 (1993). The article can be retrieved from the following web address `http://prola.aps.org/abstract/PRA/v48/i5/p3561_1`.

d) In this exercise we want to plot the wave function for two electrons as functions of the relative coordinate r and different values of ω_r. With no Coulomb interaction you should have a result which corresponds to the non-interacting case. Plot either the function itself or the probability distribution (the function squared) with and without the repulsion between the two electrons. Varying ω_r, the shape of the wave function will change.

We are only interested in the wave function for the ground state with $l = 0$ and the two first excited states with the same symmetry and omit again the center-of-mass motion.

You can choose between three approaches; the first is to use the existing *tqli* function. Here the eigenvectors are obtained from the matrix $z[i][j]$, where the index j refers to eigenvalue j. The index i points to the value of the wave function in position ρ_j. That is, $u^{(\lambda_j)}(\rho_i) = z[i][j]$.

The eigenvectors are normalized. Plot then the normalized wave functions for different values of ω_r and comment the results.

Another alternative is to add a piece to your Jacobi routine which also returns the eigenvectors. This is the more difficult part. You will also need to normalize the eigenvectors.

Finally, the armadillo function *eig_ sys* can be used to find eigenvalues and eigenvectors.

e) Here you are asked to implement unit tests in either your C++ program or your Fortran program. For C++ users, please follow the guidelines on how to install unit tests with c++ on the webpage. For Fortran user, the software package Fortran Unit Test Framework (FRUIT), `sourceforge.net/projects/fortranxunit`. These issues will be discussed in more detail at the lab and lectures during week 38.

f) This exercise is optional and is meant more as a challenge. Implement the iterative Lanczos' algorithm discussed in the lecture notes and compute the lowest eigenvalues as done in exercise c) above. Compare your results and discuss faults and merits of the iterative method versus direct methods like Jacobi's method.