

Project 2, Schrödinger's equation for two electrons in a three-dimensional harmonic oscillator well

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1. Introduction

The aim of this project is to solve Schrödinger's equation for two electrons in a harmonic oscillator potential, with, and without a repulsive Coulomb interaction. This is done using the Jacobi rotation method. First for one electron in a harmonic oscillator potential to test the precision of the method, and then for both variations with two electrons.

2. Discretizing the wave equation

To solve this using the Jacobi method, we first have to discretize the equation and rewrite it to a square matrix. The radial part of the wave equation for a single electron in a harmonic oscillator potential reads

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

In our case $V = 1/2kr^2$, with $k = m\omega^2$, and

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

Here E_{nl} is the energy of the harmonic oscillator in three dimensions, and $n = 0, 1, 2, \dots$, $l = 0, 1, 2, \dots$. In this project we will use $l = 0$. We introduce the dimensionless variable $\rho = r/\alpha$ where α is a constant with dimension length. Rewriting equation 2 we end up with

$$-\frac{d^2}{d\rho^2} u(\rho) + \rho^2 u(\rho) = \lambda u(\rho). \quad (3)$$

where

$$\lambda = \frac{2m\alpha^2}{\hbar^2} E, \quad (4)$$

and

$$\alpha = \left(\frac{\hbar^2}{mk} \right)^{1/4}. \quad (5)$$

If we now use that the second derivative of a function u can be written

$$u'' = \frac{u(\rho+h) - 2u(\rho) + u(\rho-h)}{h^2} + O(h^2), \quad (6)$$

where h is our step length, defined as

$$h = \frac{\rho_{\max} - \rho_{\min}}{n_{\text{step}}} \quad (7)$$

giving us

$$\rho_i = \rho_{\min} + ih, \quad i = 0, 1, 2, \dots, n_{\text{step}}. \quad (8)$$

Using this we can rewrite equation 2 to the discretized form

$$-\frac{u_{i+1} - 2u_i + u_{i-1}}{h^2} + V_i u_i = \lambda u_i \quad (9)$$

which is the one we will be using. Solving this numerically, we will define a tridiagonal matrix where

$$d_i = \frac{2}{h^2} + V_i \quad (10)$$

is the diagonal elements, and

$$e_i = -\frac{1}{h^2} \quad (11)$$

is the non-diagonal elements. Finally we can rewrite the Schrödinger equation to

$$d_i u_i + e_{i-1} u_{i-1} + e_{i+1} u_{i+1} = \lambda u_i. \quad (12)$$

This is the equation we will be using Jacobi's method on.

3. Solving the discretized wave equation with Jacobi's method

To solve this we make a program in c++ implementing Jacobi's method. The program can be seen in the github repository linked in the references.

We compare our result with the analytical solutions of the eigenvalues. The lowest solutions are 3, 7 and 11. To get a 4 digit precision of the lowest three, we need $n_{\text{step}} = 200$. The eigenvalues depend on the value of ρ_{\max} , which is expected as ρ_{\max} is the maximum distance from the potential well. In our computation we find that the solutions with $\rho_{\max} = 5$ fits well with the analytical solutions. The number of similarity transformations needed before the non-diagonal elements in the matrix are essentially zero depend on how many n_{step} we choose. With the 4 digit precision we reach a number of 71168 iterations. Trial and error for different values of n reveals that the number of iterations is proportional to n^2 . More precisely the number of iterations needed is approximately $7n^2/4$.

Comparing our algorithm to the one in the armadillo library reveals that the two methods produce exactly the same results. However the armadillo solver is a lot faster than our method. For $n = 100$, our method uses 1.20562 seconds, while armadillo uses 0.004314 seconds.

Next we will study two electrons in a harmonic oscillator well which also interact via a repulsive Coulomb interaction. Setting up the equation for this results in

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr_1^2} - \frac{\hbar^2}{2m} \frac{d^2}{dr_2^2} + \frac{1}{2}kr_1^2 + \frac{1}{2}kr_2^2 \right) u(r_1, r_2) = E^{(2)} u(r_1, r_2). \quad (13)$$

State	$\omega_r = 0.01$	$\omega_r = 0.5$	$\omega_r = 1$	$\omega_r = 5$
1	0.828214	2.23065	4.05706	17.4282
2	2.13595	4.16333	7.90592	36.9753
3	4.15791	6.35172	11.8102	56.6183

Table 1. Excitation energy of the three lowest states in eV.

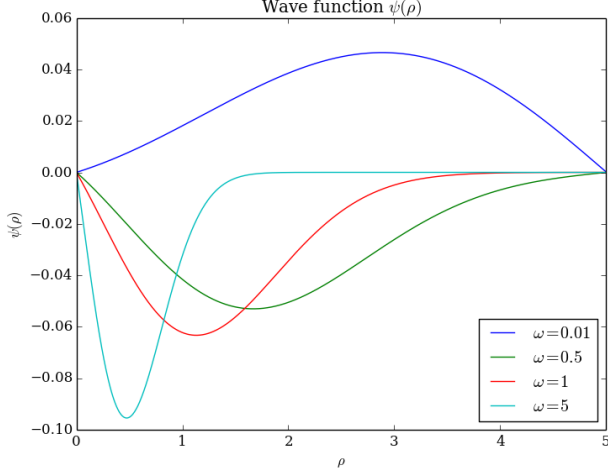


Fig. 1. Wavefunction with different ω_r .

To make this mess look nicer we change coordinates to the center of mass coordinate R , and make the equation dimensionless by multiplying with some constants, arriving at the final equation for the system

$$-\frac{d^2}{d\rho^2}\psi(\rho) + \omega_r^2 \rho^2 \psi(\rho) + \frac{1}{\rho} = \lambda \psi(\rho), \quad (14)$$

where

$$\omega_r^2 = \frac{1}{4} \frac{mk}{\hbar^2} \alpha^4, \quad \alpha = \frac{\hbar^2}{m\beta e^2}, \quad \lambda = \frac{m\alpha^2}{\hbar^2} E.$$

Looking at equation 3 we see that we will be solving the same equation again, only this time the potential term takes on a different form. This means that we can reuse our code from the one electron case to this one.

We treat ω_r as a strength parameter for the oscillator potential, and will study our case for different values of ω_r . The lowest energies for the different ω values are tabulated in table 3. Studying the table shows that the excitation energies increase with higher ω , which is logical since the potential is proportional with ω . The potential well gets deeper with higher oscillator strength, making it harder to get out of the potential.

Figure 3 shows the wavefunction for different ω_r , while figure 3 shows the probability distribution. Here ρ represents the coordinate of the mass center of the two electrons. As ω_r increases, the probability of finding the mass center in the potential well increases. In short, bigger ω gives a deeper well, which in turn increases the probability that the electrons are located in the potential well.

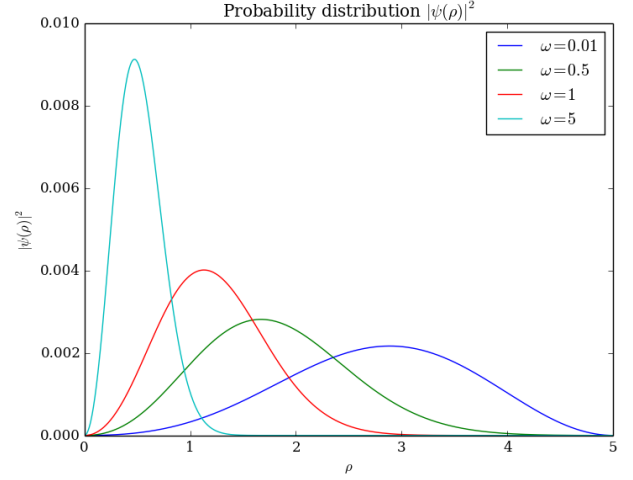


Fig. 2. Probability distribution of ψ .

4. Conclusions

In this project we've seen how the Saha and Boltzmann distributions control the ionization and energy levels of elements. We tried using this to study Ca^+K and $\text{H}\alpha$ lines. We saw that even though there is a lot less Calcium in the sun, the Ca^+K lines was much stronger because of its lower ionization energy. We also saw how the Planck function in combination with the Voigt profile can be used to model spectral lines. This was achieved by using a reversing layer model, where the temperatures of the surface of the sun and the reversing layer controlled whether or not we got absorption or emission lines. With this we were also able to create growth curves, which in turn could be used to approximate the Coloumb damping parameter for solar iron lines by comparing with measurements.

5. References

Rutten, R. J.: 1991, The Generation and Transportation of Radiation, Sterrekundig Instituut Utrecht, The Netherlands