Project 2

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THEORY

Schroedinger's Equation for two electrons in a three-dimesnional harmonic oscillator well, noninteracting

The radial part of Schroedinger's equation for one electron reads

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

$V(r)$ 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 $l=0,1,2,\dots$.

Due to the transformation to spherical coordinates $r\in[0,\infty)$. The quantum number l is the orbital momentum of the electron. Substituting $R(r)=(1/r)u(r)$:

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

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

We introduced a dimensionless variable $\rho=(1/\alpha)r$ where α is a constant length:

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

In stipulations of the project, $l=0$. We inserted $V(\rho)=(1/2)k\alpha^2\rho^2$:

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

And multiplied by $2m\alpha^2/\hbar^2$ on both sides:

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

The constant α was fixed after some algebra so that

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

We defined

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

so we were able to rewrite Schroedinger's equation as

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

And evaluate it by considering the canon form of second derivative of a function u

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

where h is defined as our step length. Minimum and maximum values for the variable ρ are $\rho_{\min}=0$ and $\rho_{\max}$ (In our case, we set $\rho_{\max}$ to 7.0).

With a specified number of mesh points, N, h can be defined as, with $\rho_{\min}=\rho_0$ and $\rho_{\max}=\rho_N$,

$$h=\frac{\rho_N-\rho_0}{N}.$$

The value of ρ at a point i is then

$$\rho_i=\rho_0+ih\qquad i=1,2,\dots,N.$$

Rewriting the Schroedinger equation for ρ_i as

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

$V_i=\rho_i^2$ is the harmonic oscillator potential.

The diagonal matrix element is:

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

and the non-diagonal matrix element is:

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

All non-diagonal matrix elements are equal, a constant. The Schroedinger equation is now:

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

u_i is unknown. we rewrote this so we could solve for the matrix eigenvalues.

$$\begin{bmatrix} d_0 & e_0 & 0 & 0 & \dots & 0 & 0 \\ e_1 & d_1 & e_1 & 0 & \dots & 0 & 0 \\ 0 & e_2 & d_2 & e_2 & 0 & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \dots & \dots e_{N-1} & d_{N-1} & e_{N-1} \\ 0 & \dots & \dots & \dots & \dots & e_N & d_N \end{bmatrix} \begin{bmatrix} u_0 \\ u_1 \\ \dots \\ \dots \\ \dots \\ u_N \end{bmatrix} = \lambda \begin{bmatrix} u_0 \\ u_1 \\ \dots \\ \dots \\ \dots \\ u_N \end{bmatrix}. \tag{2}$$

The values of u at the two endpoints are known through the boundary conditions, allowing us to skip the involved rows and columns. we specified the matrix with our values for d_i and e_i

$$\begin{bmatrix} \frac{2}{\hbar^2} + V_1 & -\frac{1}{\hbar^2} & 0 \\ -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_2 & -\frac{1}{\hbar^2} \\ 0 & -\frac{1}{\hbar^2} & \frac{2}{\hbar^2} + V_{N-1} \end{bmatrix} \tag{3}$$

This is the matrix we performed calculations on for the non interacting case

Schroedinger's Equation for two electrons in a three-dimesnional harmonic oscillator well, interacting

We took the case of two electrons in a harmonic oscillator well, but introduced an interaction via the repulsive Coulomb interaction. The single-electron equation:

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

$E^{(1)}$ is the energy within one electron. For two electrons with no repulsive Coulomb interaction, the Schroedinger equation evovles to

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

$$E^{(2)}u(r_1, r_2).$$

To evaluate this further, we introduced the relative coordinate $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ and the center-of-mass coordinate $\mathbf{R} = 1/2(\mathbf{r}_1 + \mathbf{r}_2)$. The radial Schroedinger equation evolved to:

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

By using an ansatz, $u(r, R) = \psi(r)\phi(R)$, the equations for r and R were separated, giving the energy through the sum of the relative energy E_r and the center-of-mass energy E_R:

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

After taking care of this, we added then the repulsive Coulomb interaction between two electrons,

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

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

The r-dependent Schroedinger equation evolved to

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

Through a similar process in the noninteracting case, we were able to introduce a dimensionless variable $\rho = r/\alpha$, and reduce the Schroedinger's equation to:

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

Going further, We defined a new 'frequency'

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

and fixed the constant α to

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

resulting in

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

This further reduced Schroedinger's equation to

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

In our case, we treated ω_r as a parameter reflecting the strength of the oscillator potential, and used the values $\omega_r = 0.01$, $\omega_r = 0.5$, $\omega_r = 1$, and $\omega_r = 5$ in our evaluations.

Implementing an Jacobi Rotation Algorithm

Before we implemented the Jacobi algorithm, first we defined some basic nomenclature. We defined the quantities $\tan\theta = t = s/c$, with $s = \sin\theta$ and $c = \cos\theta$ and

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

Through manipulation of the angle, θ, we got non-diagonal matrix elements of the transformed matrix a_{kl} to become non-zero and consequently, 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 $s = tc$.