

Solving the Schrödinger equation for the Hydrogen atom using Daubechies Wavelet Basis

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2 Introduction

The Schrödinger equation for three dimensions for a potential $1/r$, which is the potential for a hydrogen atom, given $Z=1$, is given as The time independent Schrödinger equation reads as,

$$H\Psi(x, y, z) = E\Psi(x, y, z)$$

Where Ψ is the wave function and \hat{H} is the Hamiltonian operator given by

$$H = \frac{\hat{p}^2}{2m} + V(x, y, z)$$

On substituting the potential function as $1/r$, we obtain the expression

$$2m\hbar^2\left(\frac{1}{\sqrt{x^2 + y^2 + z^2}} - E\right)\Psi = \frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}$$

On representing the Schrödinger equation spherical coordinates, the angular part will remain the same irrespective of the potential taken, whereas the radial equation has to be solved depending on the potential chosen. One can employ various methods to solve the differential equation for the radial part, and obtain the eigenvalues and eigenfunctions. One such procedure to solve such problems as given in [5] states that after setting the boundary conditions, one has to use logarithmic mesh of radial points for integration, and start integrating from a large distance with a trial value of Energy E . After that one has to search for the first bound state at sufficiently negative energy and increase energy in small steps to cover all necessary bound states. This can be done using optimization tools available. After obtaining the bound state energies, $\Psi(r)$ has to be calculated for all bound states. To calculate $\Psi(r)$ standard Ode solving tools like Adam Bashford, Runge-Kutta algorithm or Numerov algorithm can be employed for every value of energy found. Adam bashford method uses an iterative approach to find the wavefunction as an initial value problem (where the value of the function and its derivative is given at a point)

$$\psi(x+h) = \psi(x) + 3/2\psi'(x)h - (1/2)\psi'(x-h)h$$

The Runge Kutta algorithm is a method more accurate than Adam Bashford, but takes more time as it is a multi-step approach

$$\psi_{n+1} = \psi_{n+h}(k1/6 + k2/3 + k3/3 + k4/6) \text{ with}$$

$$k1 = \psi'(x_n, \psi_n)$$

$$k2 = \psi'(x_n + 0.5h, \psi_n + 0.5k1)$$

$$k3 = \psi'(x_n + 0.5h, \psi_n + 0.5k2)$$

$$k4 = \psi'(x_n + h, \psi_n + hk3)$$

Apart from that, one can employ the Numerov algorithm, which helps to reduce the error by an order of the step size chosen. Since the radial part has the equation of form $\psi''(x) = f(x)\psi(x)$ The recursive relation is as follows

$$w_{n+1} - 2w_n + w_{n-1} = h^2 \psi_n f_n + O(h^6)$$

where $w_n = fn(1(h * h/12)fn)$

One drawback lies in the fact that these methods tend to be unstable. There are methods which are more stable, and they involve representing the solution as a linear combination of basis functions. This paper deals with solving the Schrödinger equation of a hydrogen atom in Cartesian form using Daubechies wavelet basis. Doing so, this problem becomes an eigenvalue problem, where eigenvalues are the energy levels of the system, whereas the eigenvectors are the coefficients of the wavelet basis functions using which, we can reconstruct the wave function. The number of eigenvalues obtained or the size of the Hamiltonian matrix will depend on the domain chosen, i.e the range of position coordinates, along x, y and z axis that can be spanned by the basis set. The lowest eigenvalue corresponds to ground state energy, where on taking h and m as 1, we get the value as -0.5Ha.

3 Construction of Wavelet Basis

Choosing wavelets as our basis set poses several advantages over other basis sets as mentioned in Paper [1] such as improvement of accuracy by adding more wavelets, without any numerical instabilities, ensuring different resolutions in different regions and coupling between them and obtaining higher derivative operators easily using the properties of transnational in variance and overlap integrals. There are a family of Daubechies wavelets, each of which is determined by a an order of Daubechies wavelet represented as K, for which the mother wavelet and scaling function lies in the range $[0, 2^K - 1]$. Scaling and wavelet basis functions can be obtained from the mother scaling function and wavelet function using the condition-

$$s(x) = \sum_{n=0}^{n=2K-1} h_n DT^n s(x)$$

So a basis scaling function s_n^k indicates that the the wavelet function has been enlarged by 2^k and shifted towards the left by n. The representation of basis function in terms of the wavelet function (given in Paper [6]) is as follows

$$s_n^k = 2^n s(2^n(x - k))$$

The least possible value of order which we can take for a smooth wavelet function is 3. Since the problem that we are dealing with is symmetric, the range of x at which we initiated to evaluate the energy values are $[-5, 5]$. Keeping the resolution(k) 0, for the basis set to span this range, the basis functions that it contains should have n ranging from -5 to 0. This will give us 6 basis elements. Since the equation that we are dealing with is involves differential operators of order 2 along x, y and z axis, the wave function will depend of position along all the 3 axes respectively. So the wave function that has to be chosen is given below-

$$\psi(x, y, z) = \sum_{i1, i2, i3} s_{i1, i2, i3} \phi(x - i1) \phi(y - i2) \phi(z - i3)$$

where i1, i2, i3 go from -5 to 0. Hence the total number of coefficients $s_{i1, i2, i3}$ obtained are 216. This makes the wave function a vector of size 216, which ensures that the Hamiltonian will be a matrix of size 216X216. Substituting the wave function, we obtain a relation in terms of the coefficients i.e

$$\sum_n H_{mn} c_n = \sum_n E_m c_n$$

where c_n represents s_{i_1, i_2, i_3} with each n representing a particular value of i_1, i_2, i_3 . Using these set of linear equations one can construct the Hamiltonian matrix. The elements of the matrix can be determined by finding the elements of kinetic energy part and then the potential energy part, which is dealt with in the further part of the report.

4 Kinetic energy

Using the advantage of the fact that wavelets are zero at the boundary conditions, The kinetic energy term matrix constructed using wavelet basis consists of elements which represent the integrals given below.

$$Ki, j, k; i', j', k' = 0.5 * \iiint \phi_{i',j',k'}(x, y, z)(\partial_x^2 + \partial_y^2 + \partial_z^2)\phi_{i,j,k}(x, y, z) dx dy dz$$

Let us take an integral called $T_{i_1,i'_1}(x)$

$$T_{i_1,i'_1}(x) = \int dx \phi(x - i_1) \partial_x^2 \phi(x - i'_1)$$

The integral $T_{i_1}(x)$ can be written as

$$\begin{aligned} T_{i_1,i'_1}(x) &= [\phi_i(x - i_1) \partial_x \phi_i, (x - i'_1)]_0^\infty - \int dx \partial_x \phi(x - i_1) \partial_x \phi(x - i'_1) \\ &= - \int dx \partial_x \phi(x - i_1) \partial_x \phi(x - i'_1) \end{aligned}$$

Now the advantage of the integral $T_{i_1}(x)$ is that it shows translation invariance. (Proof has been given in Paper [3]) i.e

$$T_{i_1,i'_1}(x) = T_{i_1-i'_1,0}(x)$$

$$\begin{aligned} Ki, j, k; i', j', k' &= 0.5 * (T_{i_1-i'_1,0}(x) \delta(i_2 - i'_2) \delta(i_3 - i'_3) \\ &+ T_{i_2-i'_2,0}(y) \delta(i_1 - i'_1) \delta(i_3 - i'_3) + T_{i_3-i'_3,0}(z) \delta(i_1 - i'_1) \delta(i_2 - i'_2)) \end{aligned}$$

So on computing eleven integrals, we can represent all other elements in the matrix by just calculating the difference between i_1 and i'_1 , i_2 and i'_2 and i_3 and i'_3 . Since l goes from -4 to 4, the integrals with l lying outside this range would be 0. Using this property, the kinetic energy operator matrix can be obtained.

5 Representation of $1/r$ as a sum of Gaussians

When we try calculating the potential energy matrix element, we obtain the matrix elements as

$$V_{i,j,k;i',j',k'} = \iiint \phi_{i',j',k'}(x,y,z) V(x,y,z) \phi_{i,j,k}(x,y,z) dx dy dz$$

Now calculating each of the element as a three dimensional integral would end up giving a very high computational complexity, while calculating the elements. But if the potential term can be made separable, then the time and complexity can be reduced. Paper [1] suggests a method to represent $1/r$ as a sum of gaussians. The gaussian form is obtain comes from the identity

$$1/r = \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-r^2 e^{2s} + s} ds$$

On discretizing this integral, one obtains a finite representation of $1/r$ as a sum of 89 terms containing 2 coefficient each, which could be obtain by optimizng them

$$1/r = \sum_l w_l e^{-r^2 \gamma_l}$$

With the 89 optimized values of w_l and γ_l , $1/r$ can be represented in the interval from 10^{-9} to 1 with an relative error of 10^{-8} Now the integral can be made separable, making it a product of 3 one dimensional integrals, along x,y and z axis respectively.

6 Potential Energy

Potential energy Matrix elements after representing $1/r$ as a sum of gaussians, can be written as

$$V_{i,j,k;i',j',k'} = \sum_l w_l \int \phi_{i'}(x) e^{-\gamma_l x^2} \phi_i dx \int \phi_{j'}(y) e^{-\gamma_l y^2} \phi_j dy \int \phi_{k'}(z) e^{-\gamma_l z^2} \phi_k dz$$

One can also save time by using the fact that the potential matrix is a real symmetric matrix. Hence we can reduce the computation as the number of elements that have to calculate are $N^6/2 + N^3$, rather than Calculation of $N^6(N^3 \times N^3 \text{matrix})$ elements.

7 Results

On taking Daubechies 3 wavelet basis, and the range of x from -5 to 5, the Hamiltonian matrix obtained would be of size 216X216. On finding the eigenvalues of this matrix, we get results which are close to the actual values. Out of all the 216 values, 2 of them are positive, and The lowest eigenvalue is -0.38Ha, Now this being the least possible case, the method can be made more accurate by adjusting several factors and parameters

1)Increasing the range of x - As of now, the range of x , is not sufficient and is in fact very small to cover the potential function. Increasing the range of x would ensure that the results would try converging towards the actual values. The maximum range after which the eigenvalues change negligibly can also be determined.

2)Increasing the number of data points -The number of data points used were 1209. This can be increased for better precision 3)Resolution of the basis functions-The resolution was set as 0, while performing these calculations. Increasing the resolution could be evaluated as well.

4)Level of wavelet-The higher the level(K), smoother the wavelet function. Smoothness of wavelets, can lead us to an accurate result. Another advantage is that the range of x will increase with the increase in level of K

These 4 parameters could be evaluated to obtain accurate eigenvalues. Since increasing these parameters would make it computationally heavy and time taken, advanced software tools like high performance clusters could be used.

8 Conclusion

This report first looked at the how using wavelet basis for solving Schrödinger equations, can turn out to be effective. Then it delved in finding the kinetic energy operator using translation invariance, and potential energy operator representing $1/r$ in a separable form. Finally it suggested methods to obtain more accurate results.

1

¹<https://github.com/nitish22066/Solving-the-Schr-dinger-equation-for-Hydrogen-atom-using-Daub>

9 References

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