

Novel Numerical Solution of Schrodinger Equation for Hydrogen-like Atoms

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Abstract: An improved numerical approach is used to find electron probability distribution around the nucleus and the energy levels for all subshells in Hydrogen-like atoms. This approach exploits the built-in capability of MATLAB to find Eigen values and Eigen vectors and its capability to draw the electron distribution in three dimensions. The space around the nucleus is divided into a large number of finite elements in three dimensions. The size of element is increased with the shell number to cover the space of existence of electron without increasing the number of calculations. Hamiltonian operator matrix was constructed according to Schrodinger equation for the space around the nucleus. The Eigen values for the Hamiltonian operator matrix are found to be the electron energies for each electron subshell around the nucleus. The corresponding Eigen vectors give the value of the wave function of the electron for the corresponding subshell in each spatial element. Three dimensional plots for the square of the magnitude of the wave functions for several subshells are plotted using MATLAB to show the distribution of electron around the nucleus for these subshells. The result of this method shows fabulous coincidence with analytical results for both, energy levels and electron distribution around nucleus.

Keywords: Quantum Chemistry, quantum mechanics, Hamiltonian operator matrix, schrodinger equation, numerical solution

1. Introduction

When you submit Hydrogen-like atom has one electron, Schrodinger equation can be used to find the wave function of the electron and its energy levels^[1];

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)\Psi = E\Psi \quad \text{.....(1)}$$

Where;

V: is the potential energy of the electron

E: is the total energy of the electron

Ψ : is the wave function of the electron

And ∇^2 is the Laplacian operator

Defining $\hat{H} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V\right)$ as the Hamiltonian operator, the above equation can be written as:
 $\hat{H}\Psi = E\Psi \quad \text{.....(2)}$

Analytical solutions for equation (2) are available in literature^[1]. Analytical solutions are perfect for Hydrogen-like atoms, but they can't be simply developed to solve more complicated atoms. Numerical solutions are also available^[2],^[3], but they need massive number of calculations. To reduce the number of calculations, those solutions either work in two dimensions and lose their generality, or increase the size of spatial elements and lose their accuracy. In this paper, we improved our solution^[4] by using MATLAB functions more efficiently and selecting more suitable space for calculation of the wave function which led to more accurate three dimensional plots for the electron's distribution around the nucleus. This also enabled us to study higher electron shells and accurately draw their more complicated shapes, that was enhanced by increasing the sizes of spatial elements with increasing shell number and taking more suitable space of interest. This procedure maintains practical number of calculations with increasing subshell size and keeps generality by working in three dimensions.

2. Theory

Dividing the space into finite elements and considering the functions values at each element as a constant, the functions will be discrete space functions. That will reduce $\hat{H}$ to a square matrix and Ψ to a column vector. As a result, equation (2) will be reduced to an Eigen value problem. In this case, E are the Eigen values of the matrix $\hat{H}$ and Ψ are the associated Eigen vectors.

To demonstrate the calculation of Laplacian operator for discrete functions, let us start with one dimensional Laplacian operator, which can be calculated as follows^[3];

$$\left[\frac{d^2}{dx^2}\right]_{n=1}^N = \frac{\psi_{n+1} - 2\psi_n + \psi_{n-1}}{s^2} \quad \text{.....(3)}$$

Where's is the size of the element.

Then the Laplacian operator on Ψ for one dimensional case is the following tri-diagonal matrix^[5];

$$\frac{1}{s^2} \nabla^2 \Psi = \begin{bmatrix} 2 & -1 & 0 & 0 & & 0 & 0 & 0 \\ -1 & 2 & -1 & 0 & & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & & 0 & 0 & 0 \\ & & -1 & 2 & \ddots & & & \\ & & & \ddots & \ddots & \ddots & & \\ 0 & 0 & 0 & & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & & & -1 & 2 & -1 \\ 0 & 0 & 0 & & & 0 & -1 & 2 \end{bmatrix} \begin{bmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \\ \vdots \\ \psi_n \end{bmatrix} \quad \text{.....(4)}$$

Kronecker tensor product can be used to construct the three dimensional discrete Laplacian operator with respect to the principal axes(x, y and z). The Kronecker tensor product of the three operator's matrices, one for each dimension (x, y and z) with analogous size identity matrices is as follows^[6],^[7];

$$\nabla^2_{x,y,z} = K(K(\nabla^2_{x,I}, I) + K(K(I, \nabla^2_y), I) + K(K(I, I), \nabla^2_z)) \dots (5)$$

Where $K(A, B)$ is the Kronecker tensor product of A and B .

If the size of ∇^2_x , ∇^2_y and ∇^2_z matrices are N by N , then, the matrix $(\nabla^2_{x,y,z})$ will be of size N^3 by N^3 .

The nucleus can be considered as a point charge, then, the potential energy of the electron in the space around the nucleus varies as $1/R$, where $R = (x^2 + y^2 + z^2)^{0.5}$, or;

$$V(x,y,z) = -1/R \dots (6)$$

To get the discrete Hamiltonian operator matrix $\tilde{H}$. The above potential energy values were spread over the diagonal of an N^3 by N^3 matrix with zeros elsewhere. Then the resulting matrix is added to the three dimensional discrete Laplacian matrix given by equation (5). So, the $\tilde{H}$ operator matrix will be;

$$\tilde{H} = -0.5 * \nabla^2_{x,y,z} + (-1/R) \dots (7)$$

The Eigen values of the matrix $\tilde{H}$ are the energy levels of electron in the Hydrogen atom. The minimum Eigen value is the ground energy level of the atom (energy of 1s orbital) in atomic units. The accompanying Eigen vector, which contains N^3 elements, is the wave function of that orbital (values of Ψ) at each discrete space element located at (x, y, z) . Then, $|\Psi|^2$ is the probability of finding the electron at any point in space.

Arranging the Eigen values in ascending order, the next four Eigen values of the matrix $\tilde{H}$ are the values of energies of 2S, 2Px, 2Py and 2Pz subshells of the Hydrogen atom. The wave functions for those four subshells are the associated Eigen vectors. Larger space should be considered in this case with larger elements sizes to cover the space in which the electron may exist.

The values of energies of 3S, 3Px, 3Py, 3Pz and the other five 3d subshells in the third orbital of the Hydrogen atom are the next nine Eigen values of the matrix $\tilde{H}$. The associated Eigen vectors are the wave functions of those nine subshells. Space of consideration and element size should be enlarged more to cover the space in which the electron may exist.

3. Results

The ground level energy of the Hydrogen atom, which is the energy of the 1s orbital, was found in atomic units as indicated in the above theory. The effect of changing the number of elements on the accuracy of the calculated energy was tested by taking values of N from 40 to 120. The results are shown in the following table:

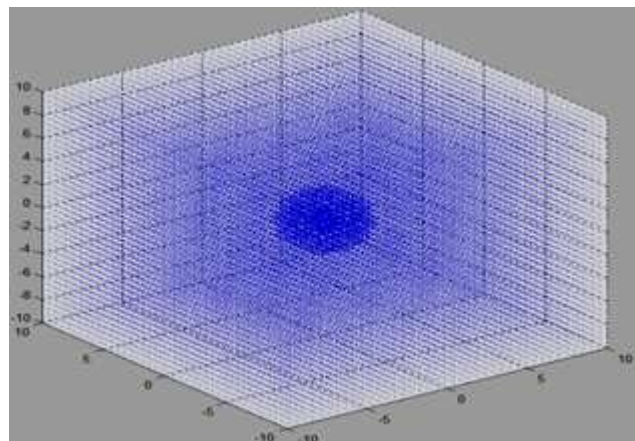


Figure 1: probability distribution $(|\Psi|^2)$ for the 1S orbital

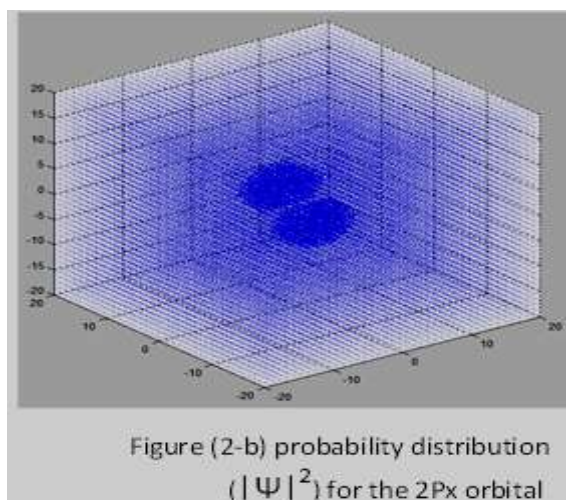
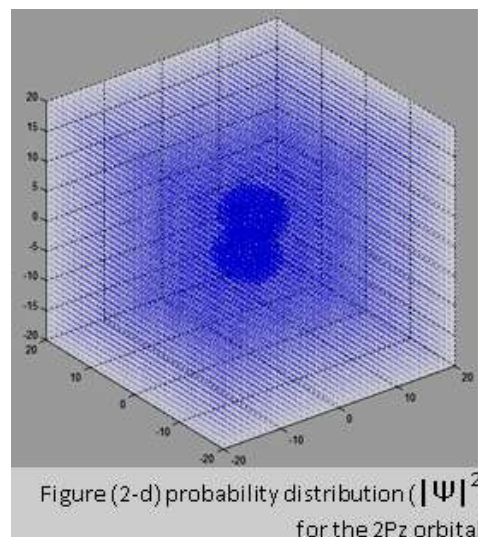
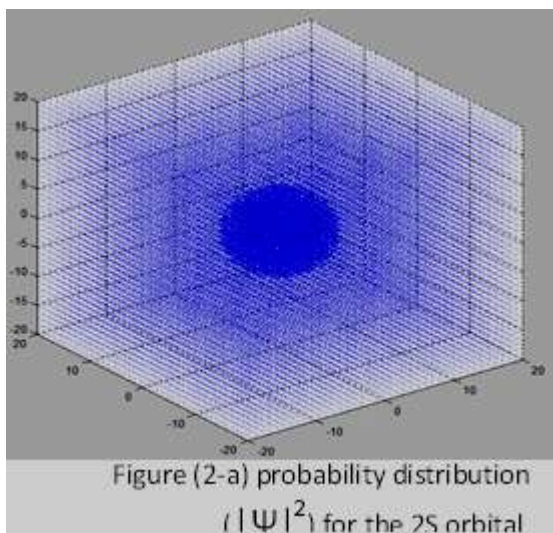
Number of elements "N" in one dimension	Calculated Energy	error
40	-0.48893	2.21%
60	-0.49484	1.03 %
80	-0.49698	0.60 %
100	-0.49799	0.40 %
120	-0.49854	0.29 %

The results are in good agreement with the theoretical value of (-0.5000) and the error is obviously decreasing with increasing number of elements. The space of consideration is 10 units from the nucleus in the x , y and z directions. The wave function of the 1s orbital at each point in the considered space, $\Psi(x, y, z)$, was also found using the method shown in the above theory. Probability of finding the electron at any point in the considered space, $(|\Psi|^2)$, is shown in figure (1). This figure agrees with the figures found in literature^[8] and it is more realistic because it shows that the electron has some possible existence outside the 1s sphere.

The next four Eigen values of the matrix $\tilde{H}$ were calculated, their values were approximately equal. They represent the energies of the 2S, 2Px, 2Py and 2Pz subshells. Their calculated values are shown in the following table with the true theoretical values for comparison; the value of N is 100:

Subshell	Calculated Value	Theoretical Value	% Error
2S	-0.1239	-0.125	0.88 %
2Px	-0.1252	-0.125	0.16 %
2Py	-0.1252	-0.125	0.16 %
2Pz	-0.1252	-0.125	0.16 %

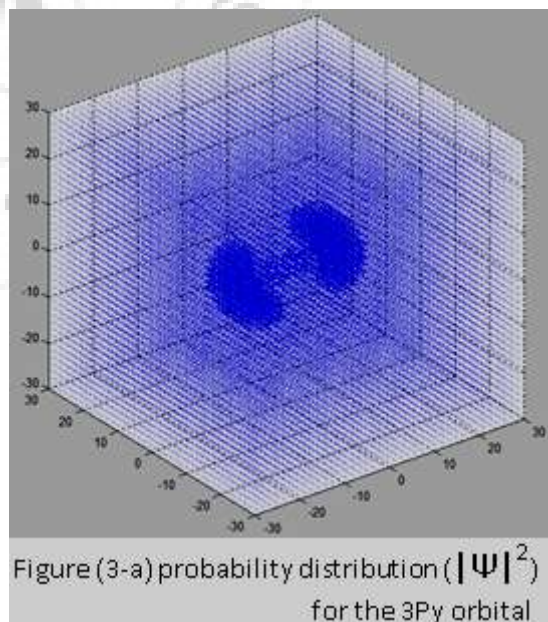
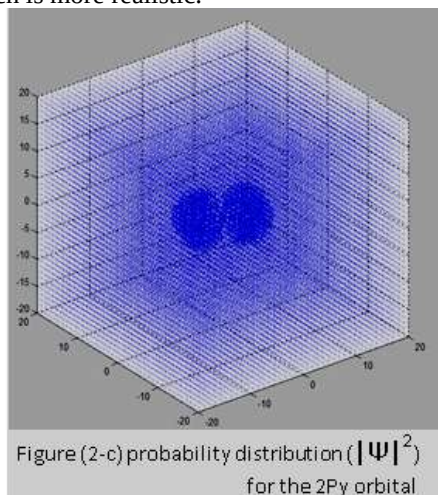
The space of consideration for the above calculations is 20 units from the nucleus in all directions, this space is divided



The next nine Eigen values range from -0.0558 to -0.0547 which are in good agreement with the theoretical value of (-0.0556). These are the energies of 3S, 3Px, 3Py, 3Pz and the other five 3d subshells in the third orbital of the Hydrogen atom. The associated Eigen vectors, which are the wave functions of those nine subshells, are calculated and the figures of $|\Psi|^2$ for some of them are shown in figure (3 a-g).

One can continue and calculate energies and electron's distribution for higher shells, but this will take a lot of pages of this paper, so we will finalize that with the electron's distribution for the 4Px subshell shown in figure (4). All these results prove the amazing accuracy of this method in calculating energy and electron's probability distribution, because all the figures show very good coincidence with the figures found in literature^[8].

into N^3 ($100^3 = 10^6$) elements. The corresponding Eigen vectors are the wave functions of the above four subshells. These wave functions were calculated and the 3D plots of $|\Psi|^2$ are shown in figure (2 a-d). These figures are similar to the figures found in literature^[8]. The difference is that these figures are not aligned with the coordinate axes x, y and z and this is normal because the electron distributions of the Px, Py and Pz subshells are nominally considered to be aligned with the principal axes. But these figures show that they are aligned with any, randomly selected three orthogonal axes, which is more realistic.



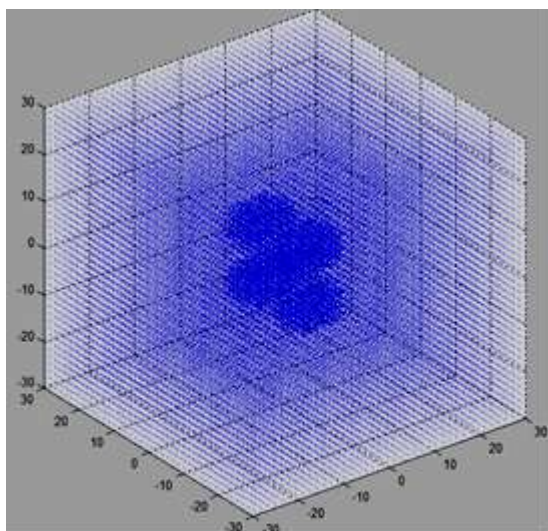


Figure (3-b) probability distribution ($|\Psi|^2$)
for the 3dyz orbital

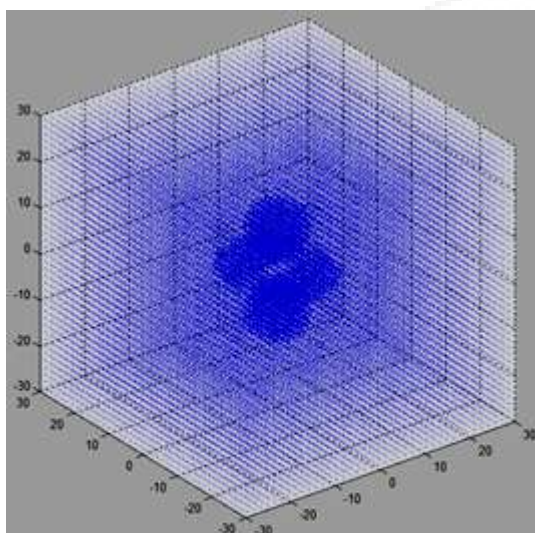


Figure (3-c) probability distribution ($|\Psi|^2$)
for the 3dz² orbital

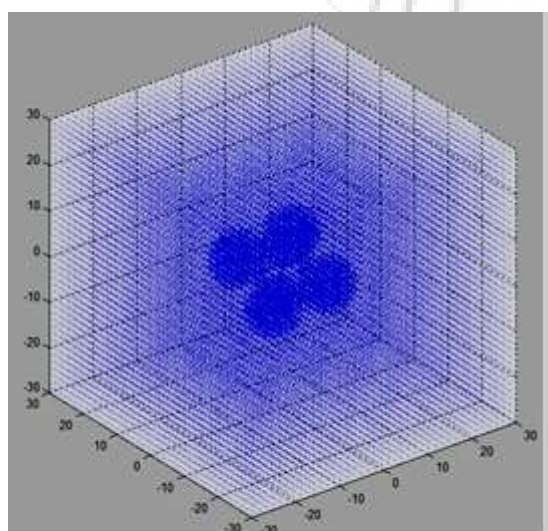


Figure (3-d) probability distribution ($|\Psi|^2$)
for the 3dx²-y² orbital

4. Conclusion

The agreement of the values of electron's energy with the true theoretical values was great. When suitable space is considered for a certain shell and the number of spatial elements in each dimension is larger than 60, the error is less than 1%, which is excellent for a numerical solution. The error can be reduced more, by increasing the number of elements.

The figures of distribution of electron around the nucleus for all the considered subshells are in great agreement with the distribution figures found in literature. They are really better than those figures because they show the distribution in a more realistic manner showing that the electron has probable existence in regions outside the geometrical shapes shown in literature.

The main advantage of this method is that it agrees with the available methods of solutions and it shows great coincidence for all the considered subshells of electron's orbitals. This method can also be evolved to find the solutions for multi electron atoms by modifying the potential energy term. The potential energy due to the repulsion between electrons in multi electron atoms should be added, so the potential energy matrix should be reconstructed for this purpose. Then the solution will proceed in the same sequence.

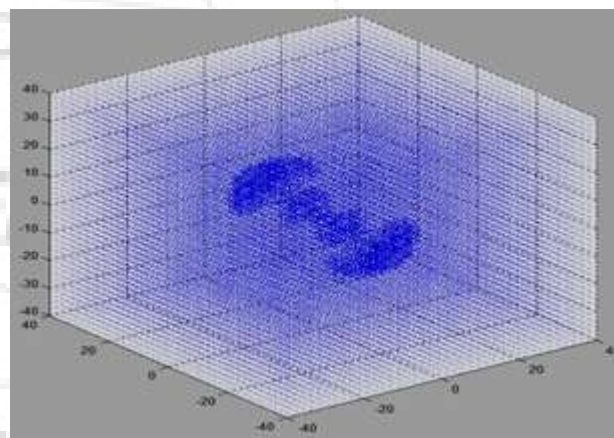


Figure 4: probability distribution ($|\Psi|^2$) for the 4Px orbital

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