**Implementation of Kohn Sham Solver**

1. Units and Symbols

Hartree atomic units will be used throughout this paper [1]. The relevant units are presented in Table 1 below. Many symbols will be used. The important symbols are presented in

Table 2.

Table 1. Hartree atomic units.

|  |  |  |  |
| --- | --- | --- | --- |
| **Dimension** | **Name** | **SI Units** | **Hartree Atomics Units** |
| Mass | Electron Mass | 9.109\*10-31 kg | 1 |
| Charge | Elementary Charge | 1.602\*10-19 C | 1 |
| Action | Reduced Planck’s Constant | 1.054\*10-34 J\*s | 1 |
| Electric Constant-1 | Coulomb Force Constant | 8.987\*109 kg\*m3\*s-2\*C-2 | 1 |
| Length | Bohr Radius | 5.291\*10-11 m = 0.529 Å | 1 |
| Energy | Hartree | 4.359\*10-18 J = 27.211 eV | 1 |

Table 2. Frequently used symbols.

|  |  |
| --- | --- |
| **Symbol** | **Meaning** |
|  | Eigenfunction index |
|  | Eigenfunction index for spherically symmetric system |
|  | Eigenfunction satisfying Kohn-Sham equation |
|  | Electron density (m-3 units) |
|  | Electron density (m-3 units) expressed in radial direction only |
|  | Radial electron density (m-1) |
|  | Electric potential energy due to nucleus |
|  | Electric potential energy due to electron/electron interactions |
|  | Exchange energy |
|  | Correlation energy |
|  | Number of electrons |
|  | Occupancy of the eigenfunction labeled by |

2. The Kohn-Sham Equation

The derivation of the Kohn-Sham equations [2][3] are beyond the scope of this paper, but the result is shown in Eq. 2.1 below.

In Eq. 2.1, the many-bodied Schrödinger equation has been reduced to a one-body Schrödinger equation with a kinetic energy operator . Each solution to Eq. 2.1, can hold two electrons (ignoring spin), and together the give the electron density for total electrons:

Physically, and are sometimes interpreted as molecular orbitals (the energy and probability density function associated with each molecular orbital) [4], but they are not entirely physical quantities but rather mathematical constructs. The real physical quantity is the electron density and the total energy of the system. The various terms in Eq. 2.1 are discussed below.

*2.1. Nuclear Potential Energy*

is the electric potential energy from the nucleus [5]. The Born approximation, which assumes a stationary nucleus, is used. For a nucleus with prototons:

*2.2 Hartree Potential Energy*

is the Hartree potential energy and is a mean field approximation for the Coulombic energy interaction between two different electrons. The term *mean field* is used because the actual electron densities is unknown. In quantum mechanics, the probability densities are calculated. In this case, the probability densities approximate the electron distribution. Physically, the Hartree potential energy gives the energy of the configuration of electrons. The Hartree potential energy is often written as:

The Hartree functional of Eq. 2.4 can be converted into a differential equation using Green’s functions. First, notice that is the Green’s function solution for Poisson’s equation [6], [7]. That is to say, solves the differential equation of Eq. 2.5:

From Poisson’s equation [7], is the *electric potential*, not the *electric potential energy* [5]. The electric potential energy is the charge multiplied by the electric potential. In this paper, the electron density is solved for, thereby making the electric potential energy or Hartree energy:

In the atomic units the Hartree potential becomes:

Ultimately, Poisson’s equation can be solved to find the Hartree energy:

*2.3. Exchange Correlation Potential Energy*

is the exchange correlation energy and accounts for the many bodied electron-electron interactions. is further split into the exchange and correlation energy . The derivation of these energies is beyond the scope of this paper, but these energies are reproduced below [8]. Many approximations for the exchange correlation potential energy exist. In fact, a large focus of current research efforts are aimed at developing more accurate exchange correlation potentials.

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*2.4. Additional Energies*

Additional energy terms can account for effects such as applied electric or magnetic field and spin. In this paper, any additional energy interactions are ignored. In particular, spin interactions are ignored, and it is assumed that each electron wavefunction can hold two electrons of opposite spin.

*2.5. Computational Solution*

An analytical equation to the Kohn-Sham equation is essentially impossible. To this end, we will use numerical methods to solve the equation. Notice first that a self-consistent solution is needed for Eq. 2.1. Electron density depends on the various potential energies, but the potential energies likewise depend on electron density .

For the computational solution, first the eigenvalue differential equation (Schrödinger’s equation) will be considered. Then Poisson’s equation will be considered. A self-consistency method will then be used to find the numerical solution.

3. Numerical Solution for Eigenvalue Differential Equation

First, assume that the potential energy functions are spherically symmetric. Because the system is spherically symmetric, spherical coordinates can be used. Spherical symmetry implies that the function does not depend on or . *Critically, the assumption is not that the eigenfunction solution is spherically symmetric but rather that the potential energy functions are spherically symmetric*. Due to the Poisson equation solution for , a spherically symmetric requires a spherically symmetric electron density .

This assumption of spherical symmetry is valid within the hydrogenic orbitals (the wavefunction solutions for the hydrogen atom, the familiar , etc… orbitals). It can also be shown that mathematically, that if all the orbitals of a subshell (e.g. or ) all filled, then the resulting electron density is spherically symmetric [9]. Pictorially, this is shown in Figure 1 which shows the 5 orbitals and Figure 2 which shows the sum of all 5 orbitals.

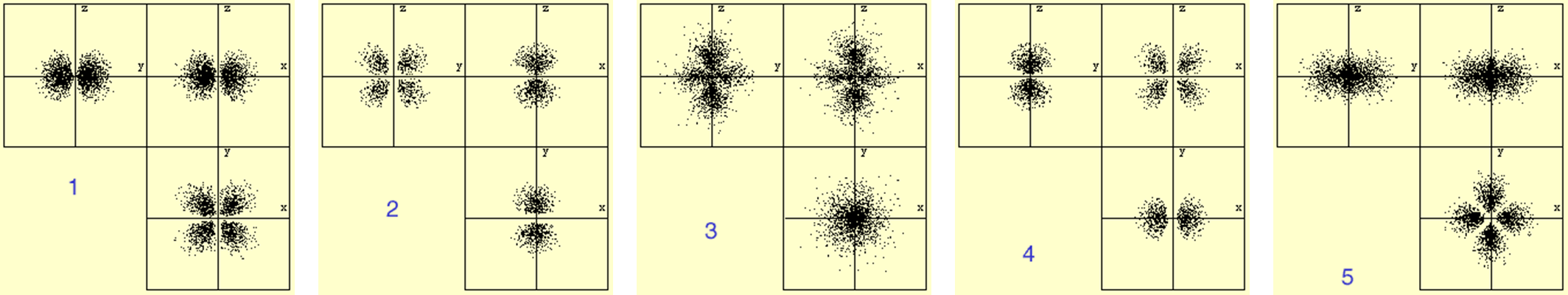


Figure 1. The five d orbitals. The electron density in each orbital is not spherically symmetric.

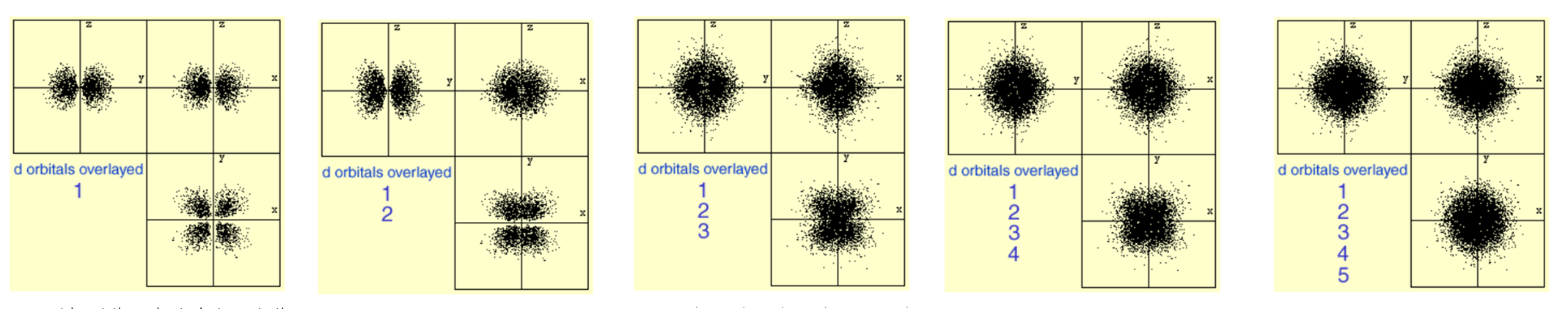


Figure 2. The five d orbtitals summed together. When all five d orbitals are added together, the electron density is spherically symmetric.

Following this, consider the valence electronic structure of manganese, which has 5 electrons to fill the orbitals (Figure 3). Because all 5 orbitals are filled, the electron density should be spherically symmetric.

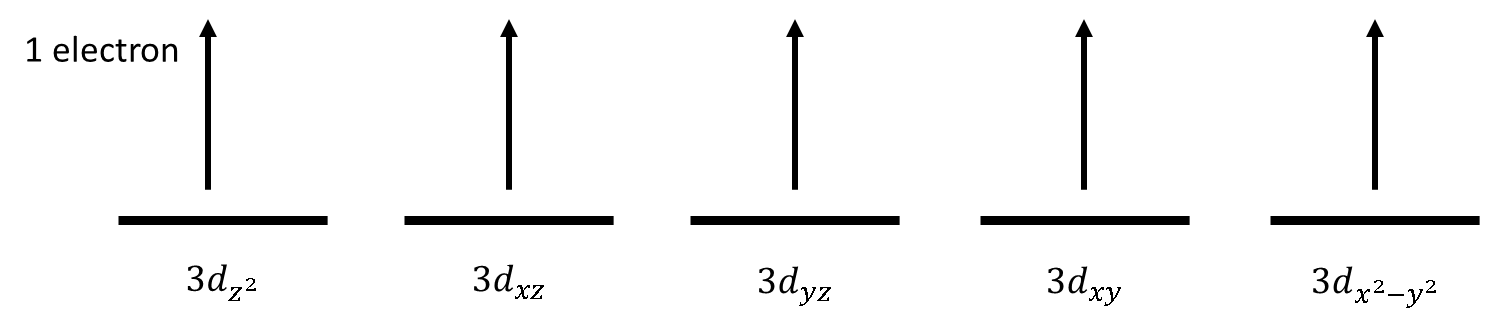


Figure 3. Manganese electronic structure. Manganese has five valence electrons to fully occupy the 3d subshell. Each arrow represents one electron.

The orbitals (the or orbitals, for example), however, are energetically degenerate, meaning they all have the same energy. So even if there are not enough electrons to fill all the orbitals of a subshell, one can imagine that each subshell is partially filled. For example, consider scandium,, which only has one valence electron in the orbitals. In this case, if 1/5th of an electron fills each orbital, then the resulting electron density is spherically symmetric (Figure 4). This type of partial occupancy is employed in this paper: if there are several orbitals of the same energy, then each degenerate orbital is partially filled.

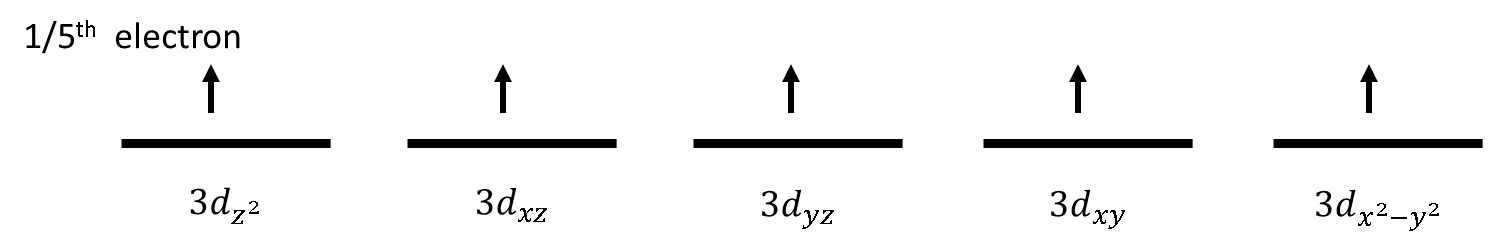


Figure 4. Scandium electronic structure. Scandium only has one valence electron, but the 3d subshell can still be fully occupied. Each arrow represents 1/5th electron.

This symmetry property of the wavefunctions comes from the angular solution to the Schrödinger equation (the spherical harmonics). Because the same spherical harmonics are used for the spherically symmetric Kohn-Sham equation, the same properties remain. Therefore, the assumption of spherical symmetry is appropriate.

*3.1. Schrödinger’s Equation in Spherical Coordinates*

The Laplace operator in spherical coordinates is [10]:

The Kohn-Sham equation (Eq. 2.1) with is:

Guessing a separable solution and assuming leads to [9]:

Eq 3.3 leads to two independent differential equations:

Eq. 3.4 and 3.5 arise from the fact that the left-hand sides of these two equations must equal a constant for Eq. 3.3 to be satisfied. If the left-hand sides of Eq 3.4 and 3.5 did not equal constants, then the addition of Eq 3.4 and 3.5 would not lead to Eq. 3.3, whose right-hand side is 0. In Eq. 3.4 and 3.5 is a constant.

The solution of Eq. 3.5 for is which are the spherical harmonics, a set of orthonormal functions [11]. is constrained as: . is constrained as: . For a value of , there are possible values. The constraint of also holds for the differential equation of Eq. 3.4.

Now the radial equation Eq. 3.4 must be solved. If the substitution of is made, Eq. 3.4 simplifies to (switching from the index to index):

The boundary conditions for are and . These boundary conditions are necessary to ensure a finite value for the wavefunction. For each value there will be a set of solutions . So the wavefunctions and energies are indexed by the quantum numbers as: and . The smallest gives the lowest energy solutions.

One solution method for Eq. 3.6, which is of the form ( is a linear differential operator) is called basis set expansion (Appendix A) [12]. In this method, the solution to the differential equation is written as a linear combination of orthonormal functions. The linear combination coefficients can then be found through a simple matrix eigenvalue solver (Appendix A).

*3.2. Schrödinger’s Equation for the Hydrogen Atom*

To test the implementation, a hydrogen atom with potential energy function is solved. The numerical eigenenergy values (Table 3 and Figure 5) agree with the analytical solution . Further the calculated wavefunctions agree with analytically determined wavefunctions.

Table 3. Numerical and analytical eigenenergies for the hydrogen atom.

|  |  |  |  |
| --- | --- | --- | --- |
| Energy Level | Orbital | Numerical Energy | Analytical Energy |
|  | 1s | -13.6028 eV | -13.6100 eV |
|  | 2s | -3.4014 eV | -3.4025 eV |
|  | 3s | -1.5075 eV | -1.5122 eV |

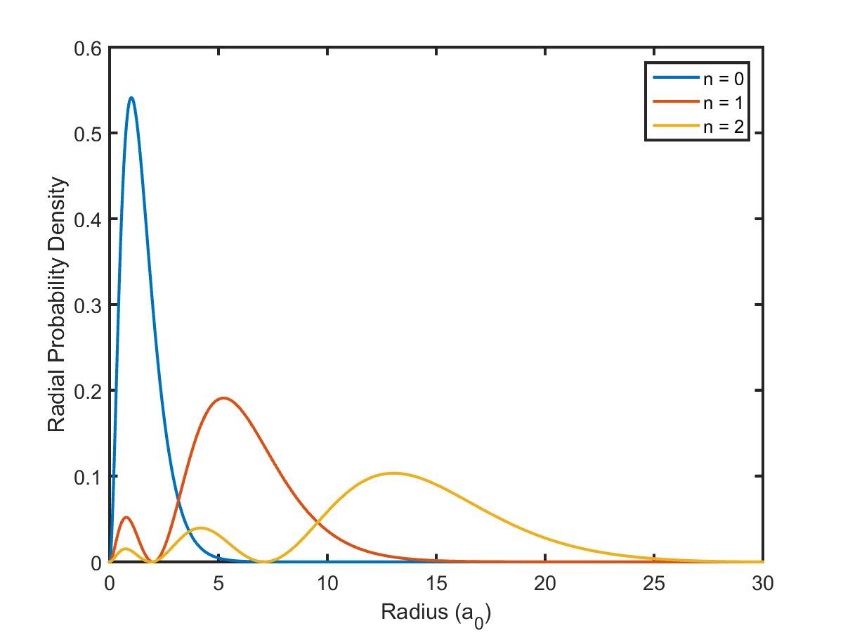


Figure 5. Numerical solutions for the radial probability density of the hydrogen atom.

Ultimately, the total solution is indexed by three quantum numbers as:

For each , there are several solutions to Eq. 3.6. Further for each value, . The energy of a solution only depends on as This means there are degenerate solutions with the energy level . This will be important when the electron density is calculated.

*3.3. Electron Density*

The electron density is obtained by summing over all the allowed eigenfunctions . Notice that the index has been replaced with in Eq. 3.9. and are both indices for the eigenfunction.

is the occupancy of each and is constrained as . The spherical harmonics are orthonormal (the tilde means the complex conjugate):

Or when and :

Due to the spherical symmetry of the problem, does not depend on the angular components: To find note that Eq 3.12 must be true:

Expanding both sides of Eq. 3.12 gives:

is the occupation number that describes the probability that an eigenfunctions described by the quantum numbers is occupied. is subject to the constraint that there are electrons in the total system:

In Eq. 3.15, and do not depend on the index and becomes . The factor comes from the degeneracy of the state that has energy . is assigned according to Aufbau principle. The lowest energy eigenfunctions are filled first. The factor of 2 in Eq. 3.15 comes from the spin degeneracy of electrons.

The problem of finding the values is not as trivial as it seems because theft-cited *1s, 2s, 2p, 3s, 3p, 4s, 3d,…* Aufbau principle cannot be assumed to hold. Similarly, the electron density is (the factor of 2 in Eq. 2.18 comes from the fact that each eigenfunction can hold two electrons):

An important distinction must be made between the electron density and the radial electron density . The electron density is the density of electrons in all of space (units of m-3). The radial electron density is the number of electrons a certain radius away from the nucleus (units of m-1). The radial electron density is defined as:

4. Numerical Solution to Poisson’s Equation

Now the Poisson equation will be considered:

Again, a spherical coordinate system can be used and assuming spherical symmetry of and , only the radial components of the Laplacian are retained:

Eq. 4.2 can be rewritten as:

with in Eq. 4.3. The differential equation in Eq 4.3, , can be solved using Numerov’s method.

*4.1. Numerov’s Method for Poisson’s Equation*

For a differential equation of the form,

Numerov’s method gives the following sixth-order approximation [13]:

For Poisson’s equation, Numerov’s method uses the following substitutions:

Therefore Numerov’s method takes the form:

Numerov’s method requires two initial conditions and ( is an arbitrary positive number). The solution obtained from Numerov’s method will be labeled as . The particular solution does not necessarily satisfy boundary conditions, rather boundary conditions will be applied using undetermined coefficients in the homogenous solution , which satisfies Eq. 4.8.

The general solution is . The coefficients and in Eq. 4.8 are found using boundary conditions. First to make the electric potential energy finite at , the boundary condition of Eq. 3.9 is necessary:

The electric potential energy of an electron of charge a distance away from a point charge is . In the Hartree units this electric potential energy is , where is (the point charge divided by the fundamental charge). In the Kohn-Sham simulations, the electron density at a distance far away from the origin (the nucleus) can be considered as a point charge. Therefore, the boundary condition becomes:

In Eq. 4.10, is a distance far from the origin and is the number of electrons in the atom:

*4.2. Testing the Numerical Solution to Poisson’s Equation*

The described method was used to solve a system with the electron density shown in Figure 6a. The solution is shown in Figure 6b. The numerical derivative is shown in Figure 7a and matches with in Figure 7b. Further and , confirming the boundary conditions are satisfied. These analyses show that the numerical method works correctly.

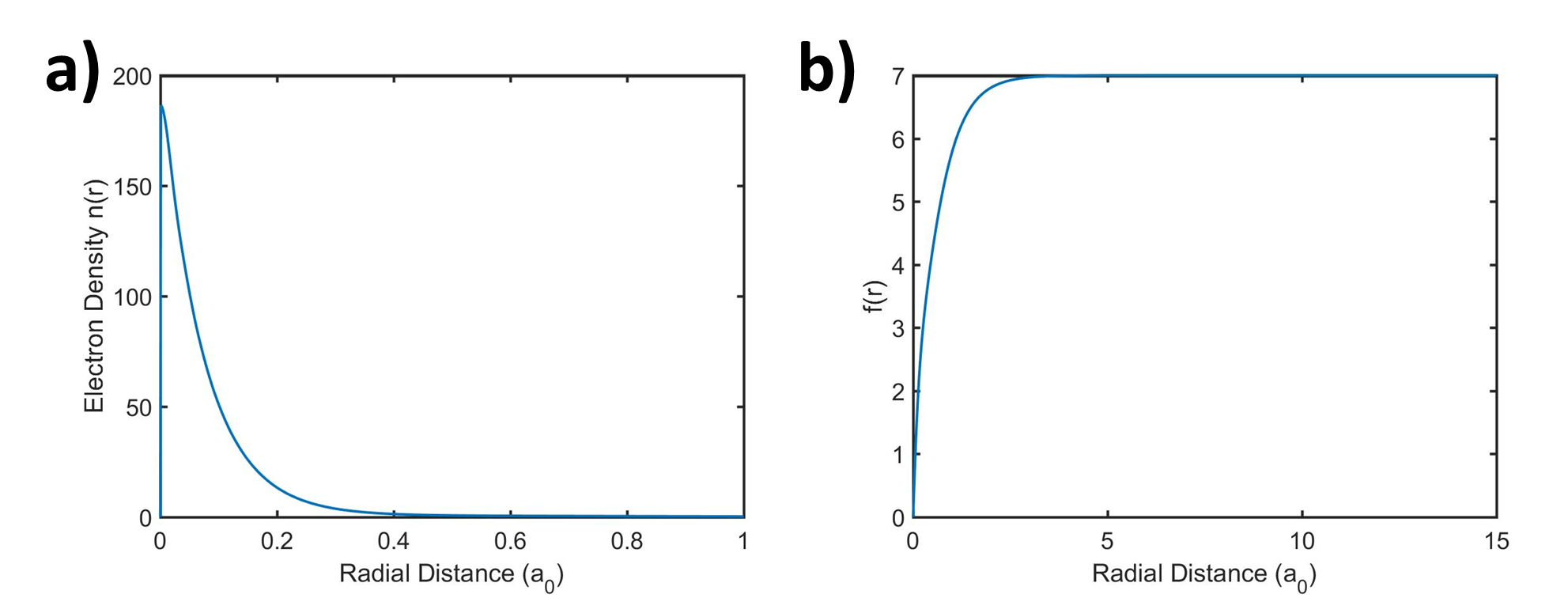


Figure 6. a) The electron density . b) The solution obtained numerically.

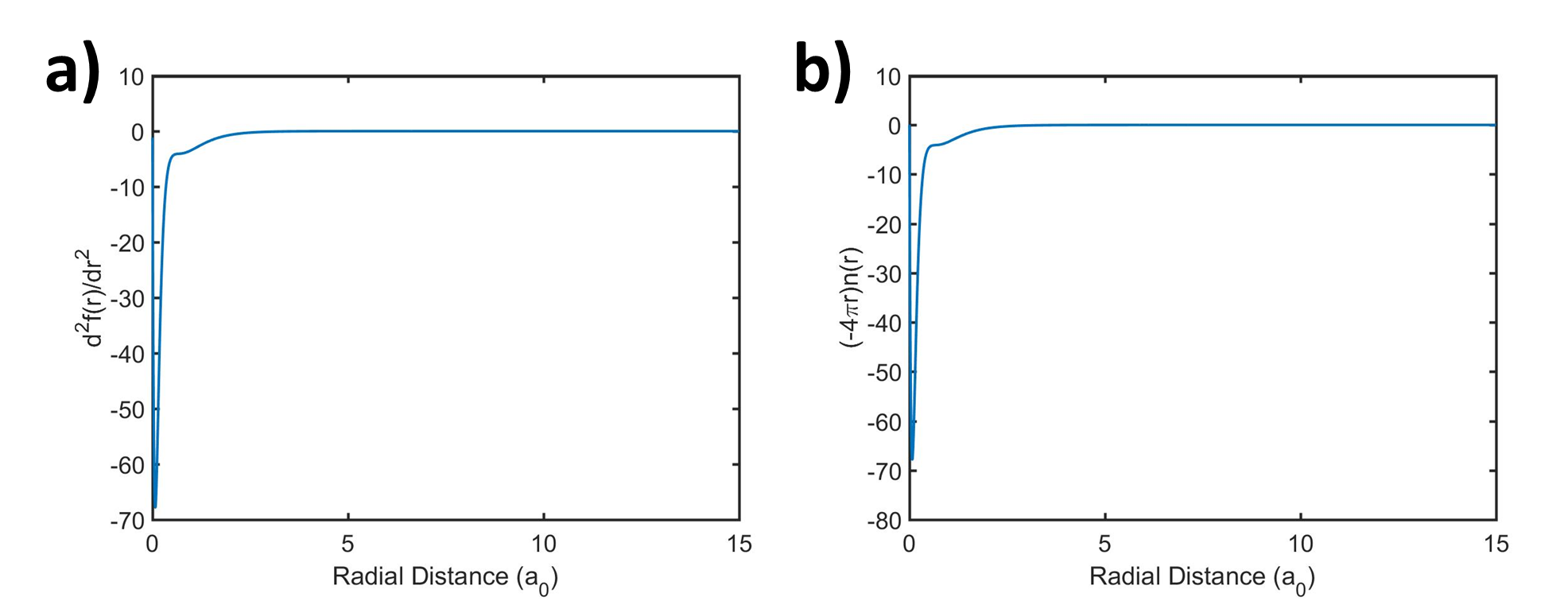


Figure 7. a) The left-hand side of Eq. 3.3 obtained using a numerical derivative. b) The right-hand side of Eq. 3.3 .

5. Self-Consistency

As explained earlier, a self-consistent solution is necessary. To this end, an iterative approach (Figure 8) was used. In this algorithm, an initial electron density is guessed. This electron density guess allows the potential energies to be calculated. The Schrödinger equation can then be solved to obtain the electron density . If the difference between and is less than the convergence criterion, the solver is finished. Otherwise, the two solutions and are mixed into a new input electron density guess, and the iterative algorithm begins anew.

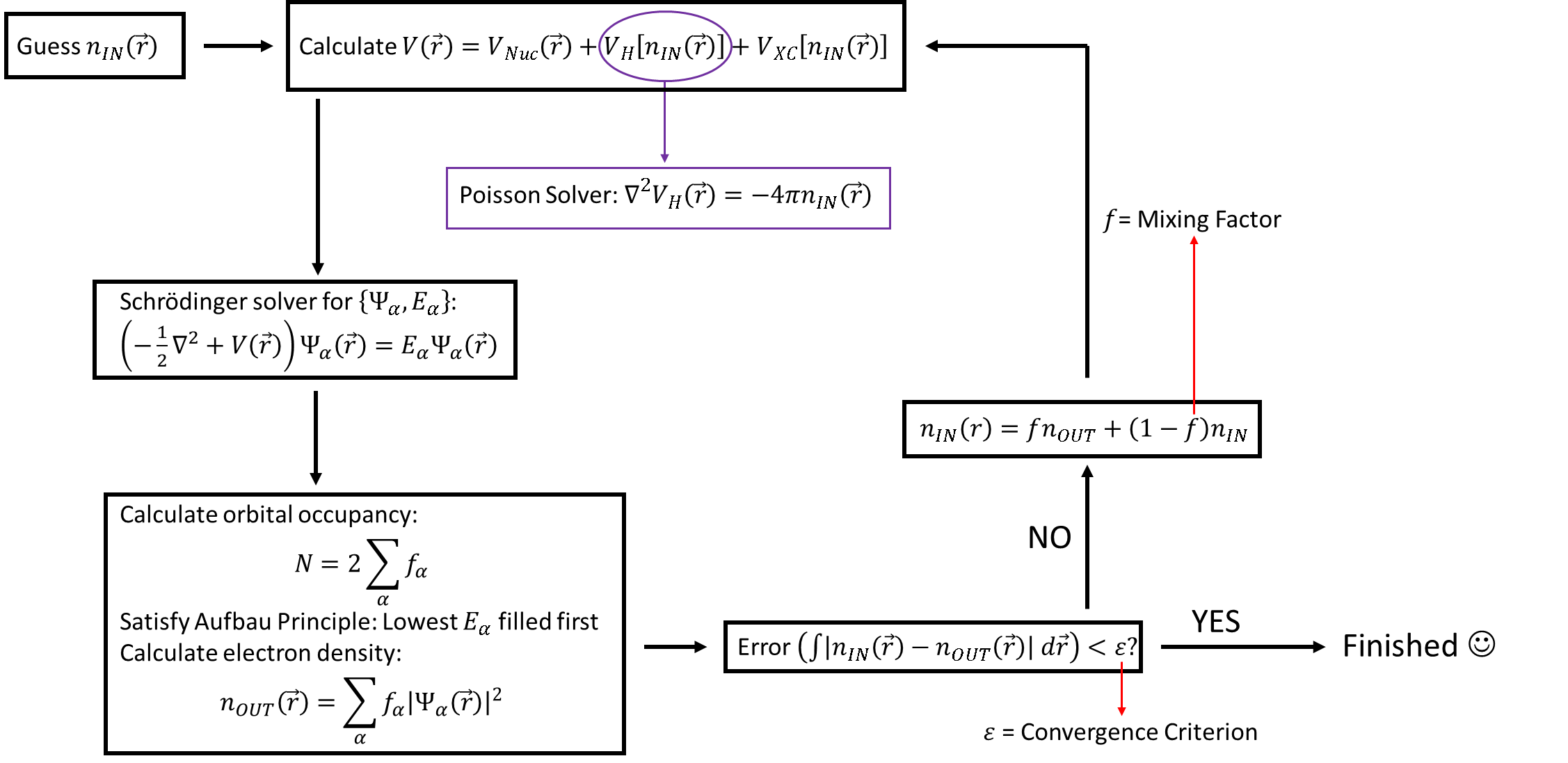
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Figure 8. Self-consistent algorithm for the Kohn-Sham equation.

6. Total Energy

Here, the total energy of the system is calculated. As explained earlier, *the Kohn-Sham orbital energies are not the total energy of the system.* The total energy is given below [8]. The bracket notation indicates that the energies are functionals: the energy is a function of another function.

The kinetic energy can be simplified using the Kohn-Sham equation and the normalization criterion :

and were previously defined in Appendix A, Section 2. The total energy simplifies to:

7. References

[1] “Atomic Units.” [Online]. Available: https://en.wikipedia.org/wiki/Atomic\_units.

[2] W. Kohn and L. J. Sham, “Self-Consistent Equations Including Exchange and Correlation Effects,” *Phys. Rev.*, vol. 140, no. 4A, pp. A1133--A1138, Nov. 1965.

[3] P. Hohenberg and W. Kohn, “Inhomogeneous Electron Gas,” *Phys. Rev.*, vol. 136, no. 3B, pp. B864–B871, Nov. 1964.

[4] R. Stowasser and R. Hoffmann, “What Do the Kohn−Sham Orbitals and Eigenvalues Mean?,” *J. Am. Chem. Soc.*, vol. 121, no. 14, pp. 3414–3420, Apr. 1999.

[5] “Electric Potential Energy.” [Online]. Available: https://en.wikipedia.org/wiki/Electric\_potential\_energy.

[6] “Green’s Function Solution to Poisson’s Equation.” [Online]. Available: http://mathworld.wolfram.com/GreensFunctionPoissonsEquation.html.

[7] “Poisson Equation.” [Online]. Available: https://en.wikipedia.org/wiki/Poisson%27s\_equation#Electrostatics.

[8] Z. Romanowski, “NUMERICAL SOLUTION OF KOHN – SHAM EQUATION FOR ATOM,” *ACTA Phys. Pol. B*, vol. 38, no. 10, pp. 3263–3286, 2007.

[9] D. J. Griffiths, *Introduction to Quantum Mechanics*, 2nd ed. Upper Saddle River, NJ: Pearson Prentice Hall, 2005.

[10] “LaPlace Equation in Spherical Coordinates.” [Online]. Available: http://mathworld.wolfram.com/LaplacesEquationSphericalCoordinates.html.

[11] “Spherical Harmonics.” [Online]. Available: https://en.wikipedia.org/wiki/Spherical\_harmonics.

[12] G. S. Beddard, “Solution of the Schrödinger Equation for One-Dimensional Anharmonic Potentials: An Undergraduate Computational Experiment,” *J. Chem. Educ.*, vol. 88, no. 7, pp. 929–931, Jul. 2011.

[13] “Numerov’s Method.” [Online]. Available: https://en.wikipedia.org/wiki/Numerov%27s\_method.

**Appendix B. Basis Set Expansion Method**

This algorithm was used to solve the eigenvalue differential equation [12].

Let be a set of orthogonal functions such that:

Included in are the functions There are total functions in the set. The eigenfunctions for an infinite square well (sine waves of varying frequency) were used for the simulations:

where is the length of the infinite box, which is equal to the length of the potential function simulated.

The Schrödinger Equation is an eigenvalue differential equation of the form:

where the Hamiltonian operator is:

Let be a linear combination of the orthogonal functions. A set of functions will satisfy Schrödinger’s equation and is used to index through this set. Each will have a different set of coefficients , where the coefficients are used to construct the linear combination:

For each there is also a corresponding eigenenergy

Multiplying both sides of Eq. B3 by ,

and integrating both sides of Eq. B6,

In Eq. B7, the term is a constant.

Remember is a linear combination, so the rightmost side of Eq. B7 simplifies to:

Eq. B8 evaluates to because of the orthogonality of the functions For all values other than the integral is zero.

The left hand side of Eq. B8 can also be expanded:

Denoting

Then combing Eq.s B7 through B10 yields:

The index of refers to the function originally used to multiply the linear combination wavefunction. belongs to the set of orthogonal functions so where is the total number of elements in Because the chosen in Eq. B6 is arbitrary, Eq. B11 can be explained into

If

and

The problem in Eq. B12 turns into an eigenvalue problem:

The resulting matrix will be of size . is more than sufficient, and MATLAB can easily solve the matrix eigenvalue problem of A.13. The solutions to Eq. B13 will be a set of and {

The resulting allowed wavefunctions can be found by:

where The set of is the allowed eigenvalues for the eigenvalue differential equation.

The boundary conditions and are naturally satisfied because the set of orthogonal functions used have and

Sine Wave Basis Functions

For the basis set expansion, the basis functions are the solutions to the 1D infinite well:

The functions can be proven to be orthonormal through integration. These basis functions naturally cause the following boundary conditions:

The Hamiltonian operator is: