

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 Atomic Units
Mass	Electron Mass (m)	9.109×10^{-31} kg	1
Charge	Elementary Charge (e)	1.602×10^{-19} C	1
Action	Reduced Planck's Constant ($\hbar = \frac{h}{2\pi}$)	1.054×10^{-34} J*s	1
Electric Constant ¹	Coulomb Force Constant ($\frac{1}{4\pi\epsilon_0}$)	8.987×10^9 kg*m ³ *s ⁻² *C ⁻²	1
Length	Bohr Radius (a_0)	5.291×10^{-11} m = 0.529 Å	1
Energy	Hartree (E_h)	4.359×10^{-18} J = 27.211 eV	1

Table 2. Frequently used symbols.

Symbol	Meaning
α	Eigenfunction index
$\{n, l, m\}$	Eigenfunction index for spherically symmetric system
Ψ	Eigenfunction satisfying Kohn-Sham equation
$n(\vec{r})$	Electron density (m ⁻³ units)
$n(r)$	Electron density (m ⁻³ units) expressed in radial direction only
$n_{Radial}(r)$	Radial electron density (m ⁻¹)
$V_{nuc}(\vec{r})$	Electric potential energy due to nucleus
$V_H(\vec{r})$	Electric potential energy due to electron/electron interactions
$V_X(\vec{r})$	Exchange energy
$V_C(\vec{r})$	Correlation energy
N	Number of electrons
f_α	Occupancy of the eigenfunction labeled by α

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.

$$\left(-\frac{1}{2}\nabla^2 + V_{Nuc}(\vec{r}) + V_H(\vec{r}) + V_X(\vec{r}) + V_C(\vec{r})\right)\Psi_\alpha(\vec{r}) = E_\alpha\Psi_\alpha(\vec{r}) \quad (2.1)$$

In Eq. 2.1, the many-bodied Schrödinger equation has been reduced to a one-body Schrödinger equation with a kinetic energy operator $-\frac{1}{2}\nabla^2$. Each Ψ_α solution to Eq. 2.1, can hold two electrons (ignoring spin), and together the Ψ_α give the electron density for N total electrons:

$$n(\vec{r}) = 2 \sum_{\alpha} f_{\alpha} |\Psi_{\alpha}(\vec{r})|^2 \quad (2.2)$$

Physically, E_{α} and Ψ_{α} are sometimes interpreted as molecular orbitals (the energy E_{α} and probability density function $|\Psi_{\alpha}|^2$ 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 $n(\vec{r})$ and the total energy of the system. The various terms in Eq. 2.1 are discussed below.

2.1. Nuclear Potential Energy

$V_{Nuc}(\vec{r})$ is the electric potential energy from the nucleus [5]. The Born approximation, which assumes a stationary nucleus, is used. For a nucleus with Z protons:

$$V_{Nuc}(\vec{r}) = -\frac{Z}{|\vec{r}|} \quad (2.3)$$

2.2 Hartree Potential Energy

$V_H(\vec{r})$ 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:

$$V_H(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' \quad (2.4)$$

The Hartree functional of Eq. 2.4 can be converted into a differential equation using Green's functions. First, notice that $\phi(\vec{r}) = -\int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}'$ is the Green's function solution for Poisson's equation [6], [7]. That is to say, $\phi(\vec{r}) = -\int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}'$ solves the differential equation of Eq. 2.5:

$$\nabla^2\phi(\vec{r}) = 4\pi n(\vec{r}) \quad (2.5)$$

From Poisson's equation [7], ϕ is the *electric potential*, not the *electric potential energy* [5]. The electric potential energy V_H 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:

$$V_H(\vec{r}) = -e\phi(\vec{r}) \quad (2.6)$$

In the atomic units the Hartree potential becomes:

$$V_H(\vec{r}) = e\phi(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' \quad (2.7)$$

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

$$\nabla^2 V_H(\vec{r}) = -4\pi n(\vec{r}) \leftrightarrow V_H(\vec{r}) = \int \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3\vec{r}' \quad (2.8)$$

2.3. Exchange Correlation Potential Energy

$V_{XC}(\vec{r})$ is the exchange correlation energy and accounts for the many bodied electron-electron interactions. V_{XC} is further split into the exchange V_X and correlation energy V_C . 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.

$$V_X(\vec{r}) = \frac{c}{r_s} \quad (2.9)$$

$$\varepsilon_c[n(\vec{r})] = \frac{3}{4} \frac{c}{r_s} \quad (2.10)$$

$$r_s = \left(\frac{3}{4\pi n(\vec{r})} \right)^{\frac{1}{3}} \quad (2.11)$$

$$V_C(\vec{r}) = \varepsilon_c[n(\vec{r})] - \frac{a}{6} \frac{c(x - x_0) - bx x_0}{(x - x_0)P(x)} \quad (2.12)$$

$$\varepsilon_c[n(\vec{r})] = \frac{a}{2} [\ln(D(x) + f_1 Y(x) + f_2 \ln(W(x)) + f_3 Y(x))] \quad (2.13)$$

$$\begin{array}{lll} a = 0.0621814 & x = \sqrt{r_s} & P(x) = r_s + bx + c \\ b = 3.72744 & q = \sqrt{4c - b^2} & D(x) = r_s/P(x) \\ c = 12.9352 & f_1 = 2b/q & Y(x) = \arctan(q/(2x + b)) \\ x_0 = -0.10498 & f_2 = -bx_0/P(x_0) & W(x) = (x - x_0)^2/P(x) \\ & f_3 = 2(b + 2x_0)f_2/q & \end{array} \quad (2.14)$$

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 $n(\vec{r})$ depends on the various potential energies, but the potential energies likewise depend on electron density $n(\vec{r})$.

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 $V_{Nuc}(\vec{r}) + V_H(\vec{r}) + V_{XC}(\vec{r}) = V(\vec{r})$ are spherically symmetric. Because the system is spherically symmetric, spherical coordinates $\vec{r} = r\hat{r} + \theta\hat{\theta} + \phi\hat{\phi}$ can be used. Spherical symmetry implies that the function does not depend on θ or ϕ . *Critically, the assumption is not that the eigenfunction solution Ψ_α is spherically symmetric but rather that the potential energy functions are spherically symmetric.* Due to the Poisson equation solution for V_H , a spherically symmetric V_H requires a spherically symmetric electron density n .

This assumption of spherical symmetry is valid within the hydrogenic orbitals (the wavefunction solutions for the hydrogen atom, the familiar $1s, 2p, 3p$, etc... orbitals). It can also be shown that mathematically, that if all the orbitals of a subshell (e.g. p_x, p_y, p_z or $d_{z^2}, d_{xz}, d_{yz}, d_{xy}, d_{x^2-y^2}$) all filled, then the resulting electron density is spherically symmetric [9]. Pictorially, this is shown in Figure 1 which shows the 5 d orbitals and Figure 2 which shows the sum of all 5 d orbitals.

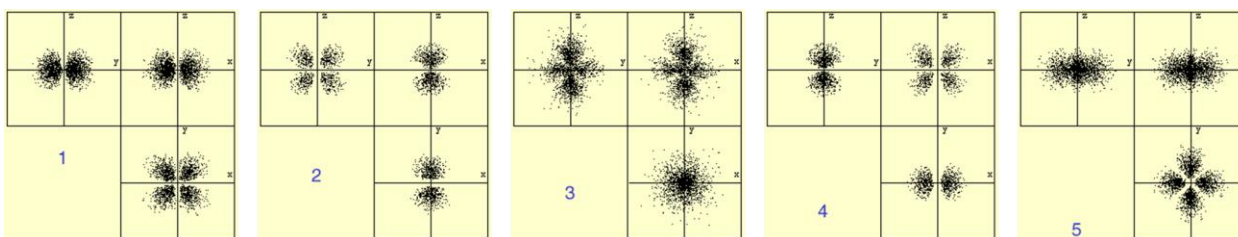


Figure 1. The five d orbitals. The electron density in each orbital is not spherically symmetric.

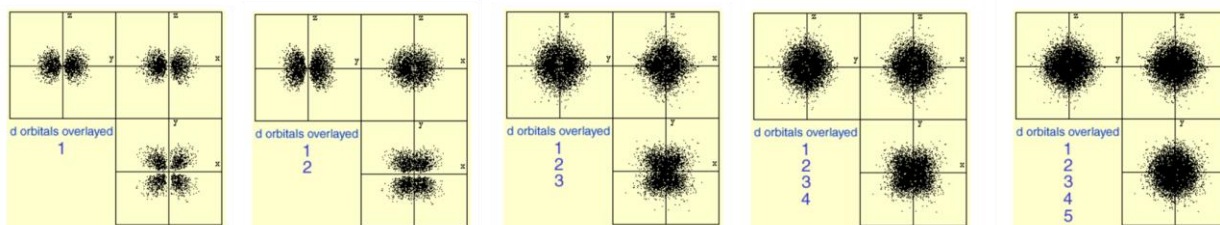


Figure 2. The five d orbitals summed together. When all five d orbitals are added together, the electron density is spherically symmetric.

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

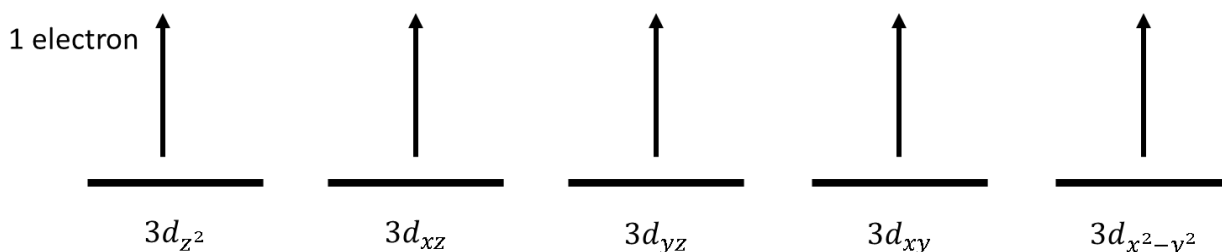


Figure 3. Manganese electronic structure. Manganese has five valence electrons to fully occupy the $3d$ subshell. Each arrow represents one electron.

The orbitals (the $3d$ or $2p$ 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 $3d$ orbitals. In this case, if $1/5^{\text{th}}$ 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.

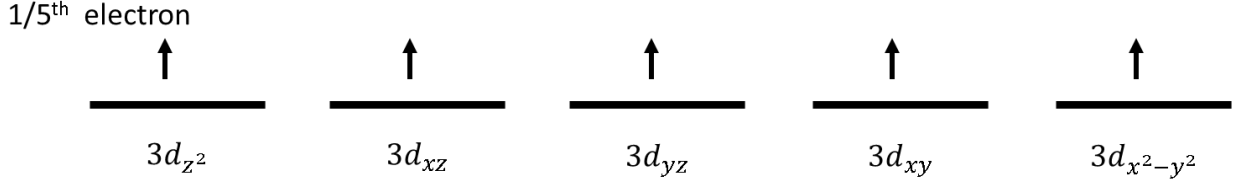


Figure 4. Scandium electronic structure. Scandium only has one valence electron, but the $3d$ subshell can still be fully occupied. Each arrow represents $1/5^{\text{th}}$ electron.

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]:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \quad (3.1)$$

The Kohn-Sham equation (Eq. 2.1) with $V_{Nuc}(\vec{r}) + V_H(\vec{r}) + V_X(\vec{r}) + V_C(\vec{r}) = V(\vec{r})$ is:

$$\left(-\frac{1}{2} \nabla^2 + V(\vec{r}) \right) \Psi_\alpha(\vec{r}) = E_\alpha \Psi_\alpha(\vec{r}) \quad (3.2)$$

Guessing a separable solution $\Psi_\alpha(\vec{r}) = R_\alpha(r) Y_\alpha(\theta, \phi)$ and assuming $V(\vec{r}) = V(r)$, $\frac{\partial V}{\partial \theta} = \frac{\partial V}{\partial \phi} = 0$ leads to [9]:

$$\frac{1}{R_\alpha} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R_\alpha}{\partial r} \right) - 2[V(r) - E_\alpha] + \frac{1}{Y_\alpha} \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial Y_\alpha}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y_\alpha}{\partial \phi^2} \right] = 0 \quad (3.3)$$

Eq 3.3 leads to two independent differential equations:

$$\frac{1}{R_\alpha} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R_\alpha}{\partial r} \right) - 2[V(r) - E_\alpha] = l(l+1) \quad (3.4)$$

$$\frac{1}{Y_\alpha} \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial Y_\alpha}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y_\alpha}{\partial \phi^2} \right] = -l(l+1) \quad (3.5)$$

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 l is a constant.

The solution of Eq. 3.5 for Y is $Y_m^l(\theta, \phi)$ which are the spherical harmonics, a set of orthonormal functions [11]. m is constrained as: $m = -l, \dots, 0, \dots, l$. l is constrained as: $l = 0, 1, 2, \dots, \infty$. For a value of l , there are $2l + 1$ possible m values. The constraint of $l = 0, 1, 2, \dots, \infty$ also holds for the differential equation of Eq. 3.4.

Now the radial equation Eq. 3.4 $\left(\frac{1}{R_\alpha} \frac{d}{dr} \left(r^2 \frac{dR_\alpha}{dr} \right) - 2[V(r) - E_\alpha] = l(l + 1) \right)$ must be solved. If the substitution of $u(r) = rR(r)$ is made, Eq. 3.4 simplifies to (switching from the α index to $\{n, l\}$ index):

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + V(r) + \frac{l(l + 1)}{2r^2} \right] u_{n,l}(r) = E_{n,l} u_{n,l}(r) \quad (3.6)$$

The boundary conditions for $u_{n,l}$ are $u_{n,l}(r = 0) = 0$ and $u_{n,l}(r = \infty) = 0$. These boundary conditions are necessary to ensure a finite value for the wavefunction. For each l value there will be a set of solutions $\{u_{n,l}(r), E_{n,l}\}$. So the wavefunctions and energies are indexed by the quantum numbers $\{n, l\}$ as: $u_{n,l}$ and $E_{n,l}$. The smallest l gives the lowest energy solutions.

One solution method for Eq. 3.6, which is of the form $\hat{H}_l u_{n,l} = E_{n,l} u_{n,l}$ (\hat{H}_l 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 $V(r) = -\frac{1}{r}$ is solved. The numerical eigenenergy values (Table 3 and Figure 5) agree with the analytical solution $\left(E_n = -\frac{13.61}{n^2} \text{ eV} \right)$. 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
$n = 1$	1s	-13.6028 eV	-13.6100 eV
$n = 2$	2s	-3.4014 eV	-3.4025 eV
$n = 3$	3s	-1.5075 eV	-1.5122 eV

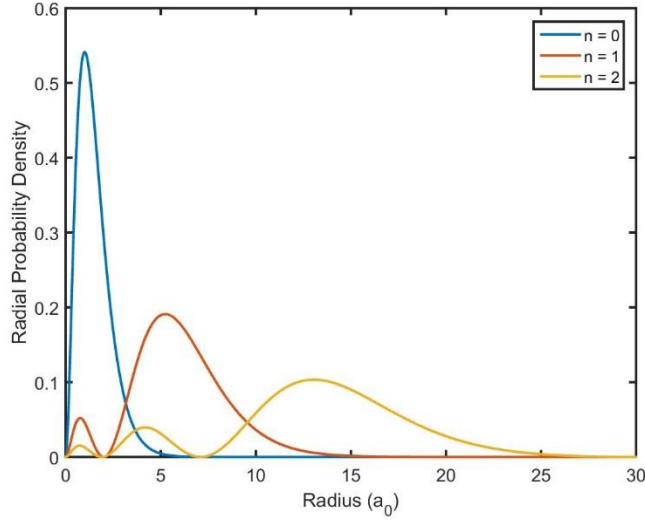


Figure 5. Numerical solutions for the radial probability density of the hydrogen atom.

Ultimately, the total solution $\Psi_{n,l,m}$ is indexed by three quantum numbers $\{n, l, m\}$ as:

$$\Psi_{n,l,m}(\vec{r}) = R_n^l(r)Y_m^l(\theta, \phi) \quad (3.7)$$

$$R_n^l = \frac{u_{n,l}}{r} \quad (3.8)$$

For each $l = 0, 1, 2, 3, \dots, \infty$, there are several $n = 1, 2, \dots$ solutions to Eq. 3.6. Further for each l value, $m = -l, \dots, 0, \dots, l$. The energy of a solution $\Psi_{n,l,m}$ only depends on $\{n, l\}$ as $E_{n,l}$. This means there are $2l + 1$ degenerate solutions $\Psi_{n,l,m}$ with the energy level $E_{n,l}$. 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 Ψ_α . Notice that the α index has been replaced with $\{n, l, m\}$ in Eq. 3.9. α and $\{n, l, m\}$ are both indices for the eigenfunction.

$$n(\vec{r}) = \sum_{\alpha} f_{\alpha} |\Psi_{\alpha}(\vec{r})|^2 = \sum_{n,l,m} f_{n,l,m} |\Psi_{n,l,m}(\vec{r})|^2 = \sum_{n,l,m} f_{n,l,m} |R_n^l(r)Y_m^l(\theta, \phi)|^2 \quad (3.9)$$

$f_{n,l,m}$ is the occupancy of each $\Psi_{n,l,m}$ and is constrained as $0 \leq f_{n,l,m} \leq 1$. The spherical harmonics $Y_m^l(\theta, \phi)$ are orthonormal (the tilde means the complex conjugate):

$$\int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} [\widetilde{Y_m^l(\theta, \phi)}] Y_{m'}^{l'}(\theta, \phi) \sin(\theta) d\theta d\phi = \delta_{ll'} \delta_{mm'} \quad (3.10)$$

Or when $l = l'$ and $m = m'$:

$$\int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} |Y_m^l(\theta, \phi)|^2 \sin(\theta) d\theta d\phi = 1 \quad (3.11)$$

Due to the spherical symmetry of the problem, $n(\vec{r})$ does not depend on the angular components: $n(\vec{r}) = n(r)$. To find $n(r)$ note that Eq 3.12 must be true:

$$\int n(\vec{r}) dV = \int n(r) dV \quad (3.12)$$

Expanding both sides of Eq. 3.12 gives:

$$\begin{aligned} \int n(\vec{r}) dV &= \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \int n(\vec{r}) r^2 dr \sin(\theta) d\theta d\phi \\ &= \int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \int \sum_{n,l,m} f_{n,l,m} |R_n^l(r) Y_m^l(\theta, \phi)|^2 r^2 dr d\theta d\phi = \\ &= \int \sum_{n,l,m} f_{n,l,m} |R_n^l(r)|^2 r^2 dr \\ &\int_{\phi=0}^{\phi=2\pi} \int_{\theta=0}^{\theta=\pi} \int n(r) r^2 dr \sin(\theta) d\theta d\phi = 4\pi \int n(r) r^2 dr \\ 4\pi \int n(r) r^2 dr &= \int \sum_{n,l,m} f_{n,l,m} |R_n^l(r)|^2 r^2 dr \quad (3.13) \end{aligned}$$

$$n(r) = \frac{1}{4\pi} \sum_{n,l,m} f_{n,l,m} |R_n^l(r)|^2 = \sum_{n,l,m} f_{n,l,m} \frac{|u_{n,l}|^2}{4\pi r^2} \quad (3.14)$$

$f_{n,l,m}$ is the occupation number $0 \leq f_{n,l,m} \leq 1$ that describes the probability that an eigenfunctions described by the quantum numbers n, l, m is occupied. $f_{n,l,m}$ is subject to the constraint that there are N electrons in the total system:

$$N = 2 \sum_{n,l} (2l + 1) f_{n,l} \quad (Eq. 3.15)$$

In Eq. 3.15, $f_{n,l,m}$ and $E_{n,l}$ do not depend on the m index and $f_{n,l,m}$ becomes $f_{n,l}$. The $2l + 1$ factor comes from the degeneracy of the $\Psi_{n,l,m}$ state that has energy $E_{n,l}$. $f_{n,l}$ 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 $f_{n,l}$ values is not as trivial as it seems because theft-cited $1s, 2s, 2p, 3s, 3p, 4s, 3d, \dots$ 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):

$$n(r) = 2 \sum_{n,l} f_{n,l} (2l + 1) \frac{|u_{n,l}|^2}{4\pi r^2} \quad (3.16)$$

An important distinction must be made between the electron density n and the radial electron density n_{radial} . 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:

$$n_{radial}(r) = 2 \sum_{n,l} f_{n,l} (2l + 1) |u_{n,l}|^2 \quad (3.17)$$

4. Numerical Solution to Poisson's Equation

Now the Poisson equation will be considered:

$$\nabla^2 V_H(\vec{r}) = -4\pi n(\vec{r}) \quad (4.1)$$

Again, a spherical coordinate system can be used and assuming spherical symmetry of $V_H(\vec{r})$ and $n(\vec{r})$ ($V_H(\vec{r}) = V_H(r)$, $\frac{\partial V_H}{\partial \theta} = \frac{\partial V_H}{\partial \phi} = 0$, $n(\vec{r}) = n(r)$, $\frac{\partial n}{\partial \theta} = \frac{\partial n}{\partial \phi} = 0$), only the radial components of the Laplacian ($\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$) are retained:

$$\frac{d^2}{dr^2} (rV_H) = \frac{d}{dr} \left[\frac{d}{dr} (rV_H) \right] = \frac{d}{dr} \left[V_H + r \frac{dV_H}{dr} \right] = 2 \frac{dV_H}{dr} + r \frac{d^2 V_H}{dr^2} = -4\pi n(r) \quad (4.2)$$

Eq. 4.2 can be rewritten as:

$$\frac{d^2}{dr^2} (rV_H) = \frac{d^2}{dr^2} (f(r)) = (-4\pi r)(n(r)), \quad (4.3)$$

with $f(r) = rV_H(r)$ in Eq. 4.3. The differential equation in Eq 4.3, $\frac{d^2}{dr^2} (f(r)) = (-4\pi r)(n(r))$, can be solved using Numerov's method.

4.1. Numerov's Method for Poisson's Equation

For a differential equation of the form,

$$\frac{d^2 y(r)}{dr^2} = -g(r)y(r) + s(r), \quad (4.4)$$

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

$$\begin{aligned} y(r + \Delta r) \approx & \left(1 + \frac{(\Delta r)^2}{12} g(r + \Delta r) \right)^{-1} \left[2y(r) \left(1 - \frac{5(\Delta r)^2}{12} g(r) \right) \right. \\ & - y(r - \Delta r) \left(1 + \frac{(\Delta r)^2}{12} g(r - \Delta r) \right) \\ & \left. + \frac{(\Delta r)^2}{12} (s(r + \Delta r) + 10s(r) + s(r - \Delta r)) \right] \quad (4.5) \end{aligned}$$

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

$$g(r) = 0, s(r) = (-4\pi r)(n(r)), y(r) = f(r) \quad (4.6)$$

Therefore Numerov's method takes the form:

$$f(r + \Delta r) \approx 2f(r) - f(r - \Delta r) + \frac{(\Delta r)^2}{12} [s(r + \Delta r) + 10s(r) + s(r - \Delta r)] \quad (4.7)$$

Numerov's method requires two initial conditions $f(r = 0) = 0$ and $f(r = \Delta r) = -\delta$ (δ is an arbitrary positive number). The solution obtained from Numerov's method will be labeled as f_p . The particular solution does not necessarily satisfy boundary conditions, rather boundary conditions will be applied using undetermined coefficients in the homogenous solution f_h , which satisfies Eq. 4.8.

$$\frac{d^2 f_h(r)}{dr^2} = 0 \rightarrow y_H = Ar + B \quad (4.8)$$

The general solution is $f = f_p + f_h$. The coefficients A and B in Eq. 4.8 are found using boundary conditions. First to make the electric potential energy $V_H = \frac{f}{r}$ finite at $r = 0$, the boundary condition of Eq. 3.9 is necessary:

$$f(r = 0) = 0 \quad (4.9)$$

The electric potential energy of an electron of charge e a distance r away from a point charge Q is $V_H = e \frac{Q}{r}$. In the Hartree units this electric potential energy is $V_H = \frac{\Omega}{r}$, where Ω is $\frac{Q}{e}$ (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:

$$f(r = L) = rV_H = \Omega \quad (4.10)$$

In Eq. 4.10, L is a distance far from the origin ($L \gg 0$) and Ω is the number of electrons N in the atom:

$$\Omega = \int n(\vec{r}) dV = \int n(r) r^2 dr = N \quad (4.11)$$

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 $f(r)$ is shown in Figure 6b. The numerical derivative $\left(\frac{d^2 f}{dr^2}\right)$ is shown in Figure 7a and matches with $(-4\pi r)n(r)$ in Figure 7b. Further $f(r = 0) = 0$ and $f(r = 15a_0) = \int n(r) r^2 dr = 7$, confirming the boundary conditions are satisfied. These analyses show that the numerical method works correctly.

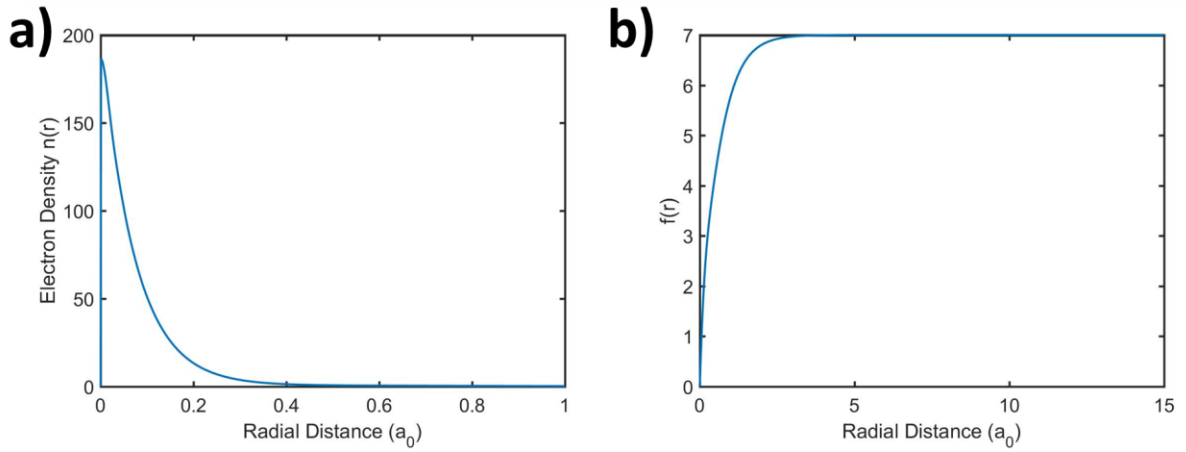


Figure 6. a) The electron density $n(r)$. b) The solution $f(r)$ obtained numerically.

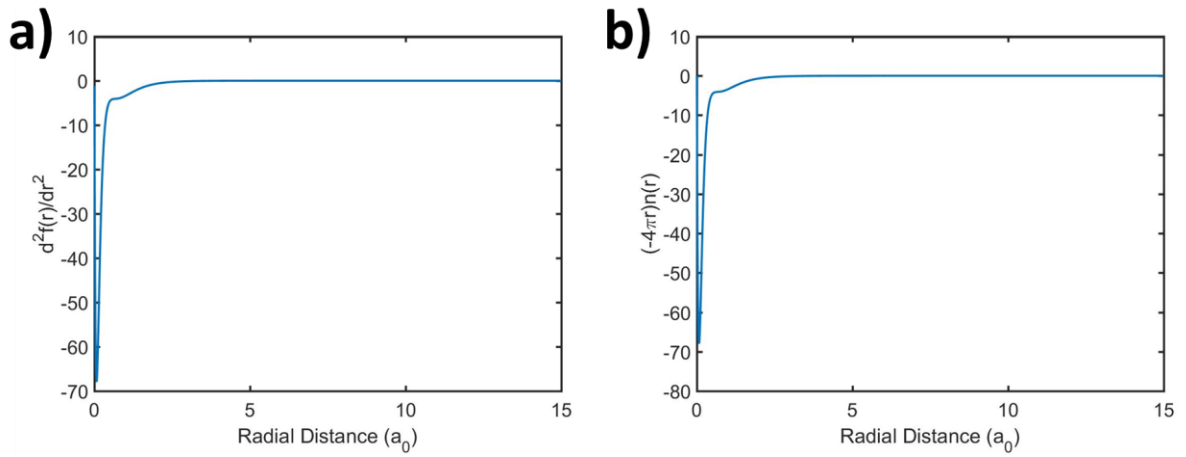


Figure 7. a) The left-hand side of Eq. 3.3 $\left(\frac{d^2f}{dr^2}\right)$ obtained using a numerical derivative. b) The right-hand side of Eq. 3.3 $(-4\pi r)n(r)$.

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 n_{IN} 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 n_{OUT} . If the difference between n_{IN} and n_{OUT} is less than the convergence criterion, the solver is finished. Otherwise, the two solutions n_{IN} and n_{OUT} are mixed into a new input electron density guess, and the iterative algorithm begins anew.

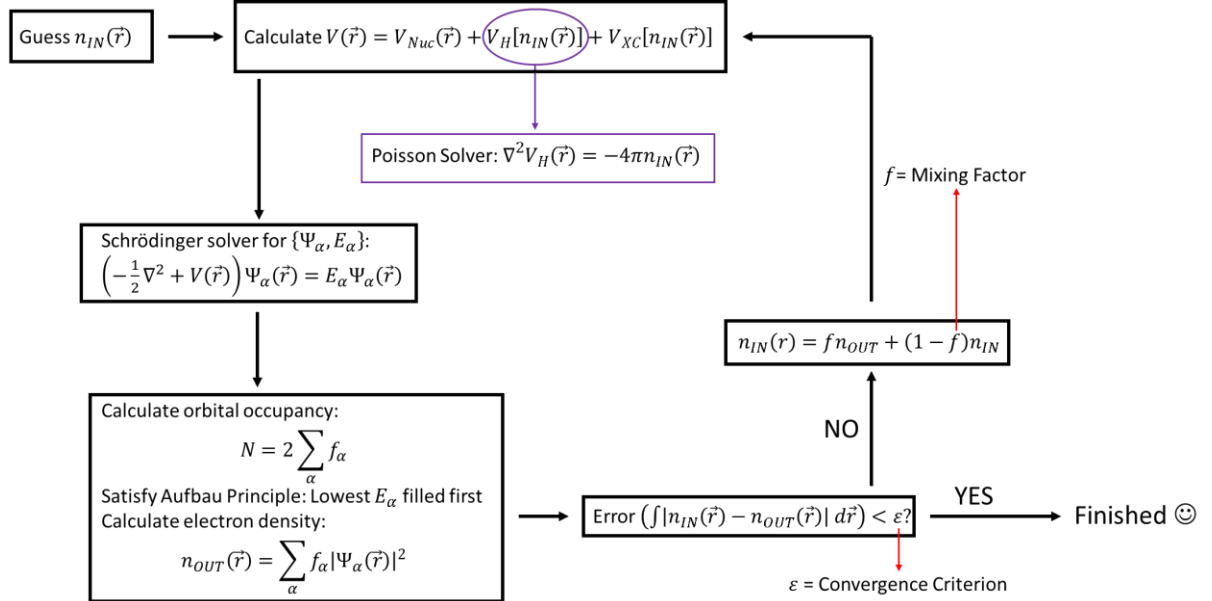


Figure 8. Self-consistent algorithm for the Kohn-Sham equation.

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 $[n]$ indicates that the energies are functionals: the energy is a function of another function.

$$E_{total}[n] = E_{kinetic}[n] + E_{nuc}[n] + E_{Hartree}[n] + E_{exchange}[n] + E_{correlation}[n] \quad (6.1)$$

$$E_{kinetic}[n] = \sum_{\alpha} f_{\alpha} \int \widetilde{\Psi_{\alpha}(\vec{r})} \left(-\frac{1}{2} \nabla^2 \right) \Psi_{\alpha}(\vec{r}) dV \quad (6.2)$$

The kinetic energy can be simplified using the Kohn-Sham equation $\left(-\frac{1}{2} \nabla^2 \Psi_{\alpha}(\vec{r}) = E_{\alpha} \Psi_{\alpha}(\vec{r}) - V(\vec{r}) \Psi_{\alpha}(\vec{r}) \right)$ and the normalization criterion $\left(\int \widetilde{\Psi_{\alpha}(\vec{r})} \Psi_{\alpha}(\vec{r}) dV = \int |\Psi_{\alpha}(\vec{r})|^2 dV = 1 \right)$:

$$\begin{aligned} E_{kinetic}[n] &= \sum_{\alpha} \int f_{\alpha} \widetilde{\Psi_{\alpha}(\vec{r})} [E_{\alpha} \Psi_{\alpha}(\vec{r}) - V(\vec{r}) \Psi_{\alpha}(\vec{r})] dV \\ &= \sum_{\alpha} \left(\int f_{\alpha} E_{\alpha} \widetilde{\Psi_{\alpha}(\vec{r})} \Psi_{\alpha}(\vec{r}) dV - \int f_{\alpha} V(\vec{r}) \widetilde{\Psi_{\alpha}(\vec{r})} \Psi_{\alpha}(\vec{r}) dV \right) \\ &= \sum_{\alpha} \left(f_{\alpha} E_{\alpha} - \int f_{\alpha} V(\vec{r}) |\Psi_{\alpha}(\vec{r})|^2 dV \right) \\ &= \left(\sum_{\alpha} f_{\alpha} E_{\alpha} \right) - \int V(\vec{r}) \left(\sum_{\alpha} f_{\alpha} |\Psi_{\alpha}(\vec{r})|^2 \right) dV \\ &= \left(\sum_{\alpha} f_{\alpha} E_{\alpha} \right) - \int V(\vec{r}) n(\vec{r}) dV \quad (6.3) \end{aligned}$$

$$E_{kinetic}[n] = \left(\sum_{\alpha} f_{\alpha} E_{\alpha} \right) - \int V(\vec{r}) n(\vec{r}) dV \quad (6.4)$$

$$E_{nuc}[n] = \int V_{nuc}(\vec{r}) n(\vec{r}) dV \quad (6.5)$$

$$E_{Hartree}[n] = \frac{1}{2} \int V_H(\vec{r}) n(\vec{r}) dV \quad (6.6)$$

$$E_{exchange}[n] = \int \varepsilon_X[n(\vec{r})] n(\vec{r}) dV \quad (6.7)$$

$$E_{correlation}[n] = \int \varepsilon_C[n(\vec{r})] n(\vec{r}) dV \quad (6.8)$$

$\varepsilon_X[n(\vec{r})]$ and $\varepsilon_C[n(\vec{r})]$ were previously defined in Appendix A, Section 2. The total energy simplifies to:

$$E_{total}[n] = \left(\sum_{\alpha} f_{\alpha} E_{\alpha} \right) + \int \left(V_{nuc} + \frac{1}{2} V_H + \varepsilon_X + \varepsilon_C - V \right) n(\vec{r}) dV \quad (6.9)$$

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Appendix B. Basis Set Expansion Method

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

Let $\{f_i(x)\}$ be a set of orthogonal functions such that:

$$\int f_m^* f_n dx = \delta_{m,n} = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases} \quad (B1)$$

Included in $\{f_i(x)\}$ are the functions f_1, f_2, \dots, f_N . There are N total functions in the set. The eigenfunctions for an infinite square well (sine waves of varying frequency) were used for the simulations:

$$f_i(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{i\pi}{a}x\right), i = 1, 2, 3 \dots N, \quad (B2)$$

where a 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:

$$\hat{H}\psi_i(x) = E_i\psi_i(x), \quad (B3)$$

where the Hamiltonian operator is:

$$\hat{H} = -\frac{1}{2} \left(\frac{2}{r} \frac{d}{dr} + \frac{d^2}{dr^2} \right) + V_{Nuc}(r) + V_H(r) + V_{XC}(r) \quad (B4)$$

Let ψ_i be a linear combination of the orthogonal functions. A set of functions $\{\psi_i\}$ will satisfy Schrödinger's equation and i is used to index through this set. Each ψ_i will have a different set of coefficients $\{c_n\}$, where the coefficients are used to construct the linear combination:

$$\psi_i(x) = c_{1,i}f_1 + c_{2,i}f_2 + c_{3,i}f_3 + \dots c_{N,i}f_N = \sum_n c_{n,i}f_n(x). \quad (B5)$$

For each ψ_i there is also a corresponding eigenenergy E_i .

Multiplying both sides of Eq. B3 by f_k ,

$$f_k \hat{H}\psi_i(x) = f_k E_i \psi_i(x), \quad (B6)$$

and integrating both sides of Eq. B6,

$$\int f_k \hat{H}\psi_i(x) dx = \int f_k E_i \psi_i(x) dx = E_i \int f_k \psi_i(x) dx \quad (B7)$$

In Eq. B7, the term E_i is a constant.

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

$$E_i \int f_k \psi_i(x) dx = E_i \int f_k \sum_n c_{n,i} f_n(x) dx = E_i \int \sum_n c_{n,i} * f_k f_n(x) dx = E_i c_{k,i} \quad (B8)$$

Eq. B8 evaluates to $E_i c_{k,i}$ because of the orthogonality of the functions $\{f_i(x)\}$. For all values other than $i = k$, the integral is zero.

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

$$\begin{aligned} \int f_k \hat{H} \psi_i(x) dx &= \int f_k \hat{H} \sum_n c_{n,i} f_n(x) dx = \int \sum_n c_{n,i} * f_k \hat{H} f_n(x) dx \\ &= \sum_n c_{n,i} \int f_k \hat{H} f_n(x) dx. \quad (B9) \end{aligned}$$

Denoting

$$\int f_k \hat{H} f_n(x) dx = H_{k,n} \quad (B10)$$

Then combining Eq.s B7 through B10 yields:

$$\sum_n c_{n,i} H_{k,n} = E_i c_{k,i} \quad (B11)$$

The index k of $H_{k,i}$ refers to the f_k function originally used to multiply the linear combination wavefunction. f_k belongs to the set of orthogonal functions $\{f_i(x)\}$, so $k = 1, 2, \dots, N$ where N is the total number of elements in $\{f_i(x)\}$. Because the f_k chosen in Eq. B6 is arbitrary, Eq. B11 can be explained into

$$c_{1,i} H_{1,1} + c_{2,i} H_{1,2} + c_{3,i} H_{1,3} + \dots + c_{N,i} H_{1,N} = E_i c_{1,i} \quad (B12)$$

$$c_{1,i} H_{2,1} + c_{2,i} H_{2,2} + c_{3,i} H_{2,3} + \dots + c_{N,i} H_{2,N} = E_i c_{2,i} \quad (B12)$$

$$c_{1,i} H_{3,1} + c_{2,i} H_{3,2} + c_{3,i} H_{3,3} + \dots + c_{N,i} H_{3,N} = E_i c_{3,i} \quad (B12)$$

...

$$c_{1,i} H_{N,1} + c_{2,i} H_{N,2} + c_{3,i} H_{N,3} + \dots + c_{N,i} H_{N,N} = E_i c_{N,i} \quad (B12)$$

If $\vec{c}_i = [c_{1,i}, c_{2,i}, c_{3,i}, \dots, c_{N,i}]$

and $\mathbf{H} = \begin{bmatrix} H_{1,1} & H_{1,2} & H_{1,3} & \dots & H_{1,N} \\ H_{2,1} & H_{2,2} & H_{2,3} & \dots & H_{2,N} \\ H_{3,1} & H_{3,2} & H_{3,3} & \dots & H_{3,N} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ H_{N,1} & H_{N,2} & H_{N,3} & \dots & H_{N,N} \end{bmatrix}.$

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

$$\mathbf{H} \vec{c}_i = E_i \vec{c}_i \quad (B13)$$

The resulting matrix will be of size $N \times N$. $N = 200$ 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 $\{E_i\}$ and $\{\vec{c}_i\}$.

The resulting allowed wavefunctions can be found by:

$$\psi_i = \vec{c}_i \cdot \vec{f}, (B15)$$

where $\vec{f} = [f_1, f_2, f_3, \dots, f_N]$. The set of $\{E_i\}$ is the allowed eigenvalues for the eigenvalue differential equation.

The boundary conditions $\psi_i(x = 0) = 0$ and $\psi_i(x = x_{end}) = 0$ are naturally satisfied because the set of orthogonal functions used have $\psi_i(x = 0) = 0$ and $\psi_i(x = x_{end}) = 0$.

Sine Wave Basis Functions

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

$$f_i(r) = \sqrt{\frac{2}{a}} \sin\left(\frac{i\pi}{a} r\right), i = 1, 2, 3 \dots N (B16)$$

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

$$\begin{aligned} u_{n,l}(r) &= 0 \\ u_{n,l}(r = a) &= 0 \end{aligned}$$

The Hamiltonian operator is:

$$\begin{aligned} \hat{H}_l &= -\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + V(r) = \hat{T} + \hat{V} \\ \hat{T}f_i(r) &= \sqrt{\frac{1}{2a}} \left(\frac{i\pi}{a}\right)^2 \sin\left(\frac{i\pi}{a} r\right) + \frac{l(l+1)}{2r^2} \sqrt{\frac{2}{a}} \sin\left(\frac{i\pi}{a} r\right) (B17) \end{aligned}$$