

Neural Network Representation for Non-Interacting Kinetic Energy for Atoms and Ionic species

M.Sc. THESIS

By

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A THESIS

*Submitted in partial fulfillment of the
requirements for the award of the degree*

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by

RASHMI S



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INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is presented in the thesis entitled **Neural Network Representation for Non-Interacting Kinetic Energy for Atoms and Ionic species** in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from July, 2025 to May, 2026 under the supervision of **Prof. SATYA S. BULUSU, Professor**, Department of CHEMISTRY, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Rashmi. S.
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This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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(**RASHMI S**)

ABSTRACT

A correct functional expression for the non-interacting kinetic energy $T_s[\rho]$ in terms of the electron density function $\rho(r)$ continues to be a significant problem in OF-DFT. An approximation such as Thomas-Fermi theory will provide a good guess for the value of the kinetic energy, but it will not reproduce the shell structure of an atom, i.e., the various K, L, M, and N shells. The following report presents the construction of a deep learning-based algorithm to approximate the Pauli potential $v_\theta^{NN}([\rho]; r)$ using seven input variables such as the nuclear charge (Z), logarithmic density, and radial Laplacians and gradients of reduced density.

The neural network architecture utilized has seven inputs and predicts the Pauli potential. In order to ensure physical consistency in the predictions made by the model, the following are three crucial considerations that were taken into account. Firstly, the use of SiLU as an activation function ensures smooth predictions. Secondly, the use of Softplus on the output layer ensures that the Pauli potential will always be positive as dictated by physical laws. Lastly, the $1/Z$ weighting was employed during training to account for both light and heavy atoms.

In order to check the applicability of the model in cases involving new atomic species other than those used in training, we tested its effectiveness on new atomic species Arsenic (As), Calcium (Ca), and Potassium (K). Firstly, the neural network makes predictions regarding the Pauli potential of the above atoms. This prediction serves as an input in the self-consistent Numerov approach for calculating the radial probability density of the atom under consideration. The radial probability density thus obtained is then compared with the radial probability density calculated with the help of reference Kohn–Sham density functional theory using the 6-31G basis set. The strong correlation between the two sets of values suggests that the model has accurately predicted the value of the Pauli potential.

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Nomenclature

Symbol	Description
$\rho(r)$	Electron density
μ	Chemical potential (Lagrange multiplier)
$T_s[\rho]$	Non-interacting kinetic energy
$E_H[\rho]$	Hartree energy
$E_{xc}[\rho]$	Exchange-correlation functional
$\nu_{ext}(r)$	External nuclear potential
Z	Nuclear charge
$T_{\nu W}[\rho]$	von Weizsäcker kinetic energy
$T_\theta[\rho]$	Pauli kinetic energy
$\nu_{eff}([\rho]; r)$	Effective local potential
$\nu_\theta([\rho]; r)$	Pauli potential
v_θ^{NN}	Neural network-predicted Pauli potential
v_θ^{ref}	Reference Pauli potential
$t_\theta(r)$	Pauli kinetic energy density
$\phi_i(r)$	Kohn-Sham wavefunctions/orbitals
ϵ_i	Kohn-Sham eigenvalues
MAE_ρ	Mean Absolute Error for radial probability densities

List of Acronyms

ANN	Artificial Neural Network
DFT	Density Functional Theory
HF	Hartree-Fock
KS	Kohn Sham
LDA	Local Density Approximation
MAE	Mean Absolute Error
ML	Machine Learning
MSE	Mean Square Error
NM	Numerov Method
NN	Neural Network
OF-DFT	Orbital-Free Density Functional Theory
RMSE	Root Mean Square Error
XC	Exchange-Correlation

Chapter 1

Introduction

1.1 Overview

Density Functional Theory (DFT) is one of the most foundational and widely utilized electronic structure methods in modern computational chemistry. According to the Hohenberg-Kohn [1] theorem, the ground state energy of an electronic system with multiple electrons is uniquely defined based on the electron density $\rho(r)$. In practical applications, the electron density is usually computed through the solution of the Kohn-Sham (KS) equations involving N orbitals [2]. However, the scaling of the KS-DFT method is $O(N^3)$, limiting its applicability to relatively small biological/-materials systems.

On the other hand, Orbital-Free Density Functional Theory (OF-DFT) reflects the essence of the Hohenberg-Kohn theorem through the solution of only one Euler equation for the density instead of solving a set of N equations. OF-DFT has almost linear scaling properties of ($O(N \ln N)$), which provides a distinct advantage in dealing with massive systems [3–5]. Nonetheless, the expression for non-interacting kinetic energy functional in terms of density is still unknown. One challenge faced in the creation of such functionals involves taking into account the effect of the atomic shells, which comes from the Pauli exclusion principle [6].

In the context of OF-DFT, the kinetic energy functional is generally divided into two parts: the von Weizsäcker (vW) term [7], and a term known as the Pauli kinetic energy. The functional derivative of $T_\theta[\rho]$ with respect to the electron density yields the Pauli potential ($v_\theta^{NN}([\rho]; r)$), which subsequently appears in the Euler equation and plays an important role in the calculation of the self-consistent electron density. Historically, obtaining an accurate description of this potential, without resorting to orbitals [8–10], has been one of the toughest challenges in this domain.

In this research, we propose a neural network architecture based on deep learning to model the Pauli potential of atoms [11]. Our approach utilizes an extensive input feature set that includes seven parameters: nuclear charge (Z), logarithmic density, radial Laplacians, and reduction of density gradients [12]. This ensures that our results are consistent across different types of atoms and enables us to predict the potential directly from the electron density ($v_\theta^{NN}([\rho]; r)$). Finally, the potential based on computed neural networks is included in the self-consistency solution for densities and in the calculation of the non-interacting kinetic energy [13–19].

1.2 Motivation

The traditional quantum chemistry approach, specifically Kohn-Sham Density Functional Theory (DFT), provides good results, although at an increased computational expense as a result of solving for the wavefunction of each electron individually. The orbital free approximation allows much faster computation because one operates not on electrons individually, but directly on the electron density $\rho(r)$, thus avoiding the problem of orbital computations. The idea behind this project is to utilize the power of neural networks to estimate the Pauli potential, allowing for much faster, yet physically accurate, quantum computations.

1.3 Objective

In this work, we seek to establish a neural network model that is able to predict the Pauli potential using a complete set of seven unique input variables. Our objective is for this model to serve as a fast and accurate substitute for the DFT method, such that its results are generalizable to neutral and ionic systems while still retaining their physical validity.

1.4 Organization of the Thesis

This thesis is organized into five chapters and an appendix. This chapter presents a brief overview of Density Functional Theory, and the transition to Orbital-Free DFT and motivation to develop a machine learning surrogate model to predict the Pauli potential and solve the Euler equation for atomic systems. Further, it discusses the motivation and objectives towards developing a machine learning substitute model to predict the Pauli potential and solve the Euler equation for atomic systems.

- **Chapter 2** covers the theory and methods.
- **Chapter 3** the numerical implementation is described, including how the reference data is generated, what the seven input descriptors are, and an explanation of the deep learning neural network architecture and optimization strategy.
- **Chapter 4** contains an overview of the principal results of our model, including its physical validation, and a discussion on the accuracy of the network in predicting Pauli potentials. Notably, the network shows strong extrapolative performance and recovers self-consistent ground-state electron densities (via the Numerov method) for unseen test atoms.
- **Chapter 5** presents the final conclusions of the entire work and describes the future scope.

Chapter 2

Literature Review

2.1 Theory and Method

2.1.1 Schrödinger-Like Equation for Interacting Atomic Systems

In Density Functional Theory, the complex nature of the electronic structure problem, which involves multi-dimensional wave functions, is transformed into one that focuses on the three-dimensional electron density, $\rho(r)$. A vital component of this theory is the Hohenberg-Kohn theorem, which states that for any many-electron system, the true ground-state energy $E[\rho]$ is uniquely related to the electron density, $\rho(r)$ [20, 21]. Using the variational approach for minimizing the energy while holding the total number of electrons constant ($N = \int \rho(\mathbf{r}) d\mathbf{r}$) yields the ground-state density through the Euler-Lagrange equation [22]:

$$\mu = \frac{\delta E[\rho]}{\delta \rho(\mathbf{r})} \quad (2.1)$$

where the Lagrange multiplier μ represents the chemical potential of the system.

The energy described above is analyzed using the Kohn-Sham (KS) framework. The expression can be broken down into its various physical

components:

$$E[\rho] = T_s[\rho] + E_H[\rho] + E_{xc}[\rho] + \int \nu_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} \quad (2.2)$$

This last term corresponds to the coupling of the external nuclear potential given by $\nu_{ext}(\mathbf{r}) = -Z/|\mathbf{r}|$ in case of an atom with nuclear charge Z [?]. The Hartree energy $E_H[\rho]$ takes care of the classical repulsive force between the electron cloud, whereas $E_{xc}[\rho]$ is taken to be the exchange-correlation functional which covers all other non-classical interactions. The quantity $T_s[\rho]$ refers to the kinetic energy of non-interacting particles. In the conventional approach of KS theory, there is no use of an exact density functional for $T_s[\rho]$, and rather N non-interacting single-particle orbitals are introduced.

Despite the fact that KS theory provides highly accurate results, the use of wave functions again creates an extremely significant computational challenge, particularly for complex systems. One way of dealing with this problem is offered by orbital-free density functional theory (OF-DFT), which attempts to cast the entire problem in terms of the density function, requiring that $T_s[\rho]$ be expressed as a density functional. Under OF-DFT, kinetic energy is typically divided into two separate parts:

$$T_s[\rho] = T_{\nu W}[\rho] + T_{\theta}[\rho] \quad (2.3)$$

The first component is the von Weizsäcker kinetic energy [23]:

$$T_{\nu W}[\rho] = \frac{1}{8} \int \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})} d\mathbf{r} \quad (2.4)$$

This term is reflective of the boson-like nature of the system and provides the exact result for cases where the system consists of only one orbital or non-interacting bosons. The second term $T_{\theta}[\rho]$, represents the kinetic energy associated with Pauli's exclusion principle [24–26].

The total energy of the system as described by the OF-DFT approach can be written as a function of electron density and optimized with respect to $\sqrt{\rho(\mathbf{r})}$ to yield a single equation (2.5), reminiscent of Schrödinger's equation:

$$\left(-\frac{1}{2} \nabla^2 + \nu_{eff}([\rho]; \mathbf{r}) \right) \sqrt{\rho(\mathbf{r})} = \mu \sqrt{\rho(\mathbf{r})} \quad (2.5)$$

The effective local potential [27] in this equation is defined as:

$$\nu_{eff}([\rho]; \mathbf{r}) = \nu_{ext}(\mathbf{r}) + \nu_H([\rho]; \mathbf{r}) + \nu_{xc}([\rho]; \mathbf{r}) + \nu_\theta([\rho]; \mathbf{r}) \quad (2.6)$$

In the above equation (2.6), the key variable is the Pauli potential, which is derived by taking the functional derivative of the Pauli kinetic energy with respect to the density:

$$\nu_\theta([\rho]; \mathbf{r}) = \frac{\delta T_\theta[\rho]}{\delta \rho(\mathbf{r})} \quad (2.7)$$

It is this quantity alone that ensures that the Pauli exclusion principle is enforced mathematically, determining the required shell structure of atoms.

Though it may not be possible to derive a general expression for $\nu_\theta([\rho]; \mathbf{r})$ in terms of density exactly [28–31], it is possible to obtain such an expression by reversing the process starting from the exact KS orbital and eigenvalue [32]. In general, a basic physical condition that has to hold in OF-DFT is that both the Pauli kinetic energy density and the associated Pauli potential should always be non-negative quantities. In the past, some methods have tried to calculate the total Pauli energy through the virial theorem, leading to a density-potential relationship:

$$T_\theta[\rho] = -\frac{1}{2} \int \rho(\mathbf{r}) \mathbf{r} \cdot \nabla \nu_\theta([\rho]; \mathbf{r}) d\mathbf{r} \quad (2.8)$$

Nevertheless, it must be stated that describing the energy functional in such a way becomes inherently non-unique and often violates fundamental physical principles, including translational and rotational symmetry. Therefore, a better approach from a theoretical point of view would be to avoid the energy functional completely and concentrate solely on formulating an exact model for the Pauli potential $\nu_\theta([\rho]; \mathbf{r})$.

Chapter 3

Numerical Implementation and Model Evaluation

3.1 Computational Details

The methodology that is used for creating Pauli potential ($v_{\theta}^{NN}([\rho]; r)$) through the use of artificial neural network (ANN) is discussed in this subsection. Consistent with the OF-DFT approach, the reference value of the potential ($v_{\theta}^{ref}([\rho]; r)$) was calculated by making use of the expression (3.1) obtained from KS orbitals and the associated eigenvalue equations. [24] [22]:

$$v_{\theta}([\rho]; r) = \frac{t_{\theta}(r)}{\rho(r)} + \sum_{i=1}^N (\epsilon_N - \epsilon_i) \frac{|\phi_i(r)|^2}{\rho(r)} \quad (3.1)$$

These wavefunctions and energies have been computed via DFT simulations in the framework of the KS-DFT theory through the usage of 6-31G basis set with the help of Gaussian software package.

3.1.1 Dataset Composition and Sampling Strategy

The training and validation dataset is composed of 11 types of chemical elements and ions and consists of a variety of electron environments. These are the following elements and ions: neutral atoms – Li, Be, N, Ne, Mg, P, Ar, Zn, Kr; ions – Be^+ , K^+ . The dataset includes ionic species which are

used to verify the model’s capability of extrapolation on a wider range of possible systems. It should be noted that such a strategy makes it possible to use a rather small number of data points due to optimization purposes without any loss of physical sense. In this case only 2,500 points of each element and ion have been taken into account. Geometric spacing of data points along the x -axis (variable r) in logarithmic scale (*np.geomspace*) was adopted to make the computation more efficient and increase the density of data points in regions of high non-linearity in the vicinity of nucleus, where sharp inter-shell transitions take place, but simultaneously to avoid unnecessary sampling in valence region where the density changes less intensively.

3.1.2 Neural Network Architecture:

The core of the proposed model is the neural network which is designed to understand how the structure and dynamics of the electron cloud in an atom define the Pauli potential. It is implemented as follows:

Initially, the 7 input variables are converted into 256 internal nodes, providing sufficient capacity for pattern learning in the system. The next step includes the application of three successive Residual Blocks. At each iteration, the initial input vector is added to the output from the respective Residual Block. Such an approach makes the learning process more robust because the model learns what correction is required in each Residual Block rather than beginning from scratch each time.

In each of the Residual Blocks, there is one hidden layer which uses the SiLU function as an activation function to provide continuous computation which is needed in case the output needs to be differentiated. As a last step, a Softplus activation function is applied to ensure that the predicted potential is non-negative (as expected in physics). Such a network architecture allows for learning of the atom layers and provides the correct output values for the predicted Pauli potential.

INPUT DESCRIPTORS

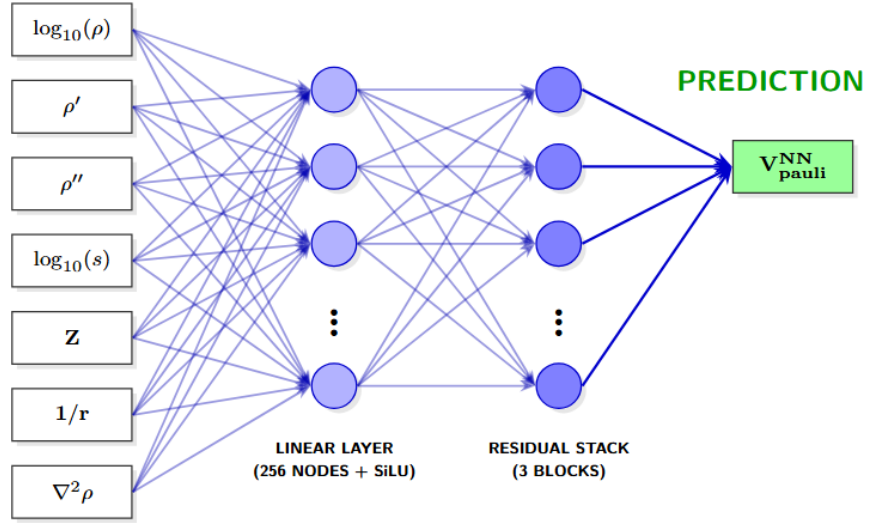


Figure 3.1: Architecture of the Neural Network

3.1.3 Training and Optimization

The concatenated data set was split via random selection, with 80% used for training the weights and optimizing the network parameters and 20% held out as a validation set. The network parameters were optimized using the Adam optimizer and a weighted Mean Squared Error (MSE) loss function. In order to ensure proper learning for atoms of different electronic environments, the loss per point was weighted by $1/Z$, where Z is the atomic number. The physical insight behind such a weighting scheme helps avoid the influence of atoms with large potentials and heavier atoms on the gradients, ensuring good accuracy even for lighter atoms and ions.

The maximum number of epochs considered for training the model was 3,000; however, the training process was terminated manually at 2,200 epochs via the activation of the Early Stopping technique. This technique was utilized by keeping an eye on the loss value associated with the validation data for 150 consecutive epochs to ensure the training process stops in order to prevent overtraining of the model and ensure its generalizability. For achieving convergence without any issue, the Cosine Annealing learning rate schedule was applied in which the initial value of the learn-

ing rate and cycle length (T_{max}) were chosen to be 0.001 and 2,000 epochs respectively. This strategy enables the model to take large steps towards optimal convergence during its early phase of learning and eventually fine tune the same. The final parameter values in the model have been specifically selected at the point where we obtained the lowest validation loss value, thus ensuring optimization of our neural network for accuracy in future OF-DFT calculations.

Chapter 4

Results and Discussion

4.0.1 Evaluation of Learning Dynamics and Convergence

The dynamics of learning were carefully examined through 2,200 training epochs through analysis of the optimization loss. As shown in the figure depicting convergence behavior, both the training loss curve (black solid line) and validation loss curve (red dashed line) experience a fast decrease starting from an initial value of roughly 10^{-1} down to about 10^{-3} for the first 400 training epochs. The quick reduction in early training stages demonstrates that the network quickly captures the key characteristics of the input-to-output mapping.

The essential feature of an effective machine learning model is that it generalizes well to unseen data. From the graph, we can see there is a highly tight relationship between training loss and validation loss from start to finish in the training process. Validation loss always follows training loss but never goes up, which is typically a hallmark of an effectively trained model that has been able to overcome the issue of overfitting.

The optimization loss always stabilizes to within a convergence threshold of 10^{-3} to 10^{-4} . This indicates the optimized weights are well suited for subsequent SCF iterations.

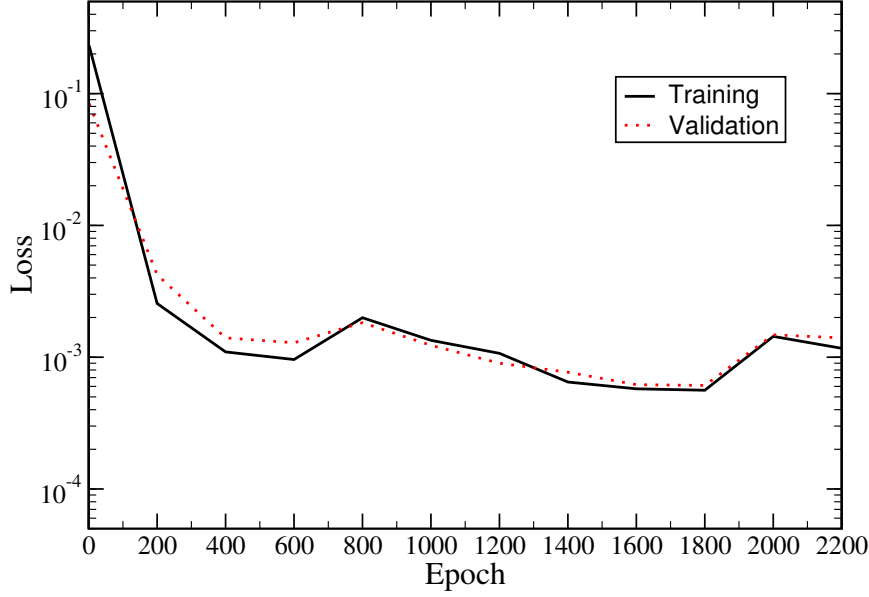


Figure 4.1: Training and Validation Loss Convergence.

4.0.2 Neural Network Predictions for Atoms and Ions

For the thorough validation of both the prediction accuracy and physical validity of the Neural Network, its performance was tested on an extensive set of 11 atomic and ionic species. In this section, detailed results for all eleven system are shown: Lithium (*Li*), Beryllium (*Be*), Nitrogen (*N*), Neon (*Ne*), Magnesium (*Mg*), Phosphorus (*P*), Argon (*Ar*), Zinc (*Zn*), and Krypton (*Kr*), as well as the ions Beryllium ion (Be^+) and Potassium ion (K^+). The choice of atoms and ions is carefully designed such that it covers the second, third, and fourth periods of the periodic table. More specifically, it includes open-shell nonmetals, closed-shell noble gases, s and d-block metals, as well as ions. The 7 input parameters per system were fed into the Neural Network weights to calculate the Pauli potential $v_{\theta}^{NN}([\rho]; r)$ with comparison to the reference values from the 6-31G basis set.

As a first test of the neural network, we start with the lightest second-period elements. This is the simplest task for the model, as it only needs to resolve the major features corresponding to the K and L electronic shells, and to the features of the open valence shells, which the model does well in

Lithium (Li) atom [Figure. 4.2]. Progressing to Beryllium (Be) [Figure 4.3], the network appropriately adjusts to the increased nuclear charge and the consequent subtle contraction of electron density. The high precision exhibited in the predicted Pauli potentials for these light elements is evidenced by their exceptionally low Mean Absolute Errors (MAE_V), which attain values of 2.602×10^{-2} Ha for Lithium and 2.597×10^{-2} Ha for Beryllium.

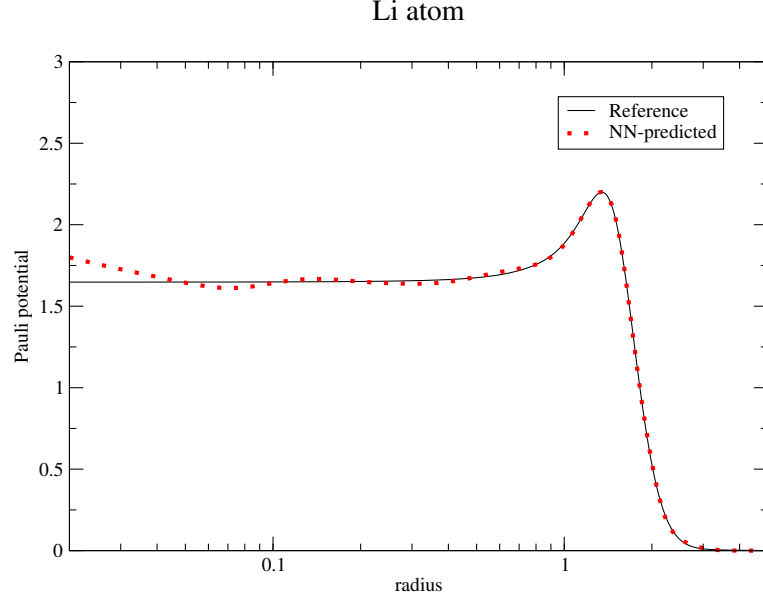


Figure 4.2: Comparison of the reference and NN-based Pauli potentials for Lithium (*Li*) atom

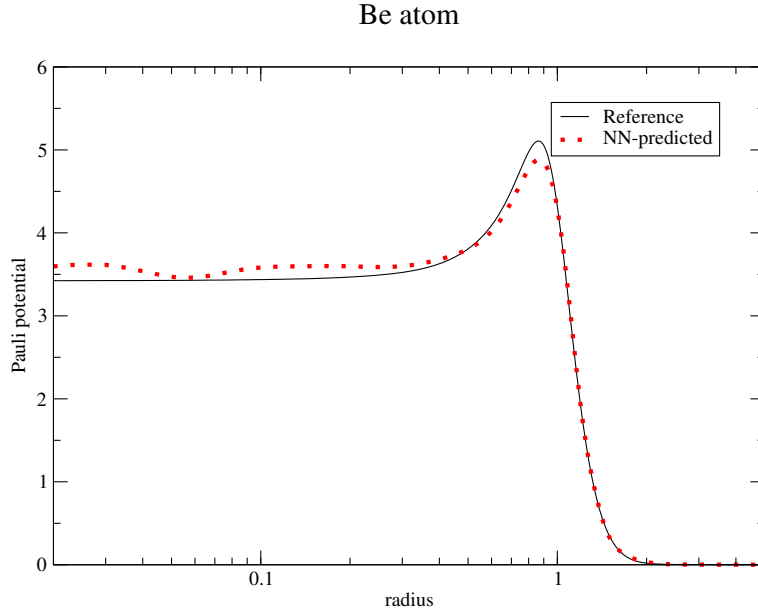


Figure 4.3: Comparison of the reference and NN-based Pauli potentials for Beryllium (*Be*) atom

Progressing through the second period, the accuracy of the model increases considerably since the atomic shell configuration is well-defined, thereby posing a challenge for predicting the fundamental K and L shells of the atom. Being a noble gas with a closed shell configuration ($1s^2 2s^2 2p^6$), Neon (Ne) [Figure 4.4] demonstrates tight valence electrons with a deep potential well close to the nucleus. This particular model correctly predicts this phenomenon, thereby preserving the clear separation of the K and L shells. By contrast, an open shell configuration characteristic for the Nitrogen (N) atom [Figure 4.5] leads to a smooth decay of the valence tail of the Pauli potential. The accuracy of the predicted Pauli potentials of these highly compact atoms can be observed from the very small values of MAE_V obtained as 7.020×10^{-2} Ha for Nitrogen and 6.673×10^{-2} Ha for Neon.

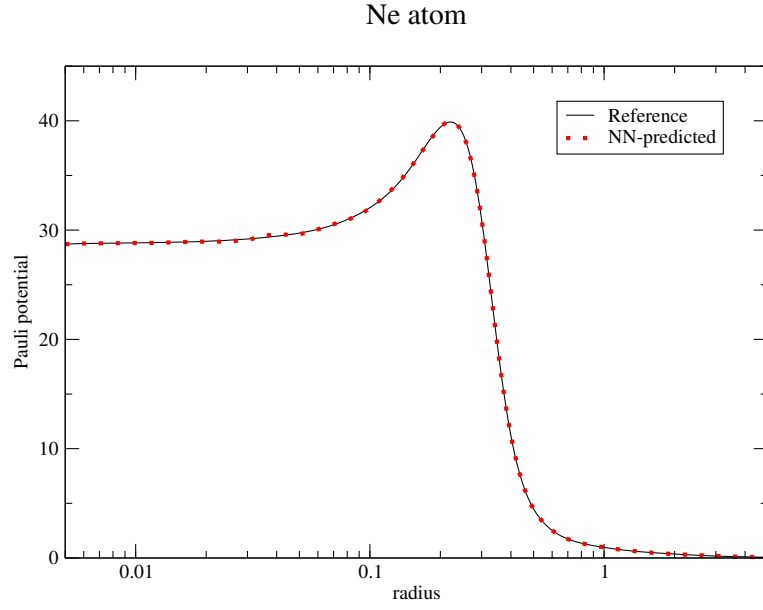


Figure 4.4: Comparison of the reference and NN-based Pauli potentials for Neon (Ne) atom

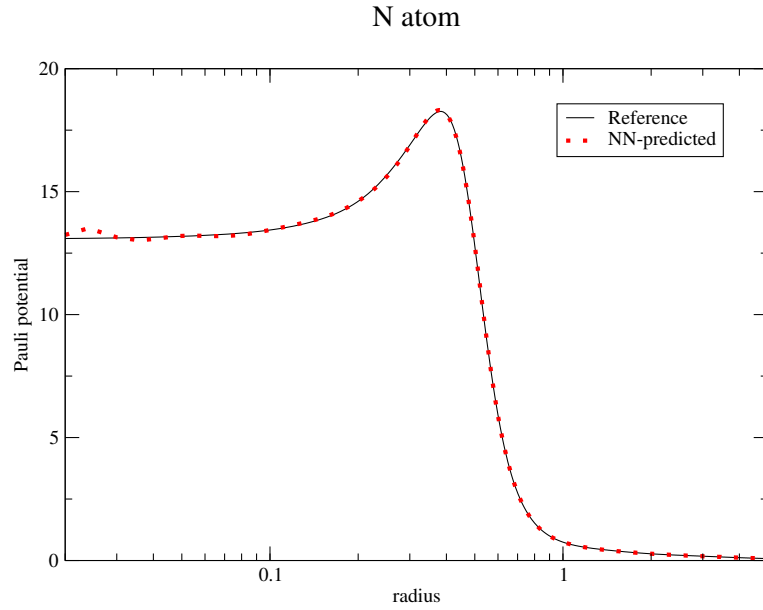


Figure 4.5: Comparison of the reference and NN-based Pauli potentials for Nitrogen (N) atom.

Moving now to the third period, the M shell is added, increasing the complexity of the Pauli potential. In the case of Magnesium (Mg) [Figure 4.6], the model is capable of reproducing the electron density for the whole radial region. With an increasing nuclear charge and approaching the

closed shell of Argon (Ar) atom [Figure 4.7], the size of the electron cloud shrinks. The profile of $v_{\theta}^{NN}([\rho]; r)$ for Argon shows remarkable agreement with reference data in predicting sharp oscillations which distinguish the K, L, and M zones of electrons. Moreover, the model automatically adapts to the compression of the density profile from Phosphorus (P) [Figure 4.8] to Argon without creating any non-physical artifacts.

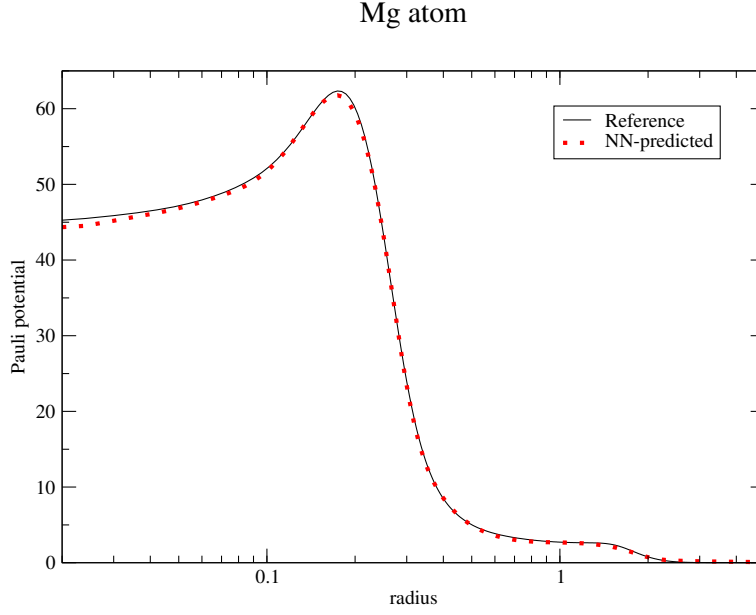


Figure 4.6: Comparison of the reference and NN-based Pauli potentials for Magnesium (Mg)atom

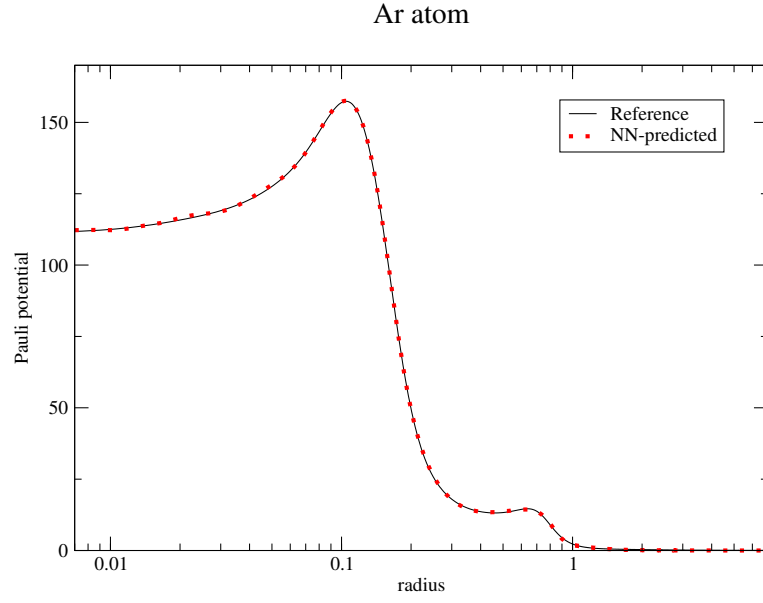


Figure 4.7: Comparison of the reference and NN-based Pauli potentials for Argon (Ar) atom.

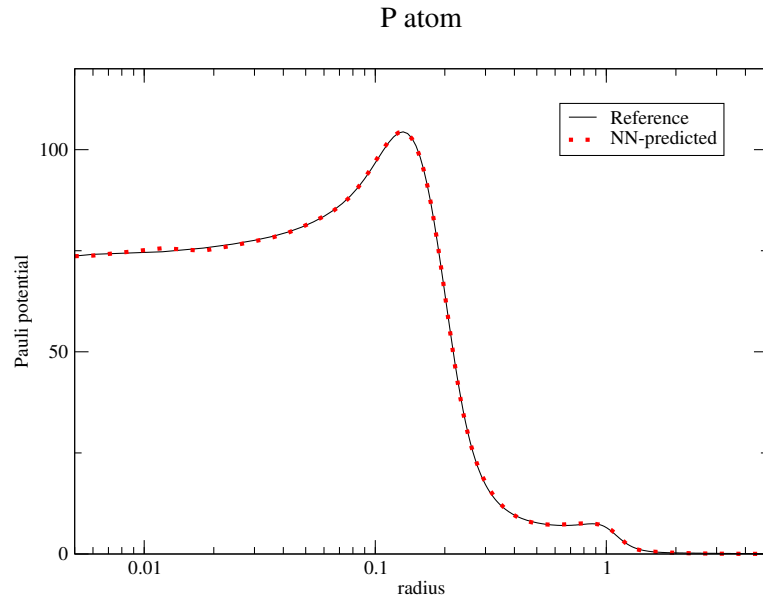


Figure 4.8: Comparison of the reference and NN-based Pauli potentials for Phosphorus (P) atom

Expanding to the fourth period, the inclusion of Zinc (Zn) [Figure 4.9] and Krypton (Kr) [Figure 4.10] examines how well the model can deal with the d-block elements and a more advanced N-shell structure. Zinc presents the difficulty of a completely filled 3d subshell, causing a signifi-

cant change in the gradient of the electron density in the core region. It is shown that the network is highly scalable to these heavier atoms, with a successful prediction of the deep potential wells needed due to the high nuclear charge without being plagued with the error scaling problems of conventional functional approaches. The accuracy of the mapping continues up to the closed-shell Krypton atom, showing the capability of the network in mapping 7 different input features to a more intricate potential surface. The accuracy of the predicted Pauli potential is evident in their very low Mean Absolute Error (MAE_V), achieving 5.169×10^{-2} Ha for Zinc and 7.680×10^{-2} Ha for Krypton.

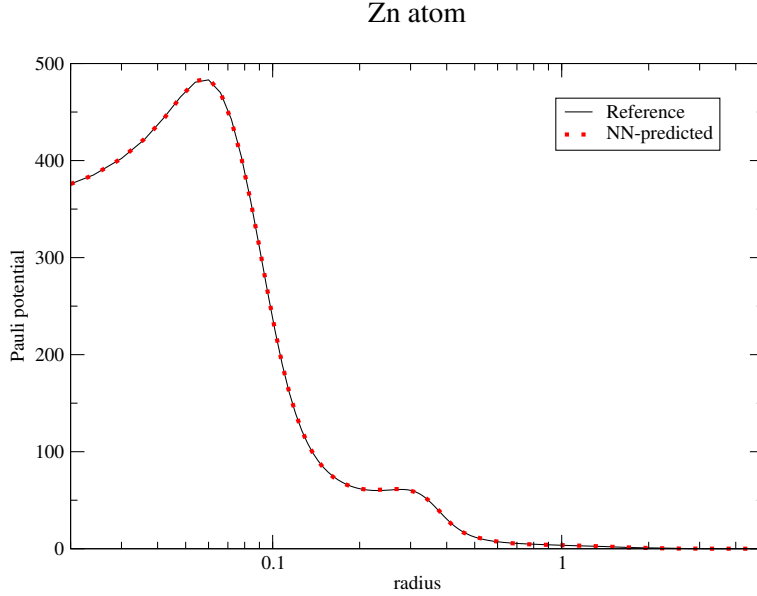


Figure 4.9: Comparison of the reference and NN-based Pauli potentials for Zinc(Zn) atom

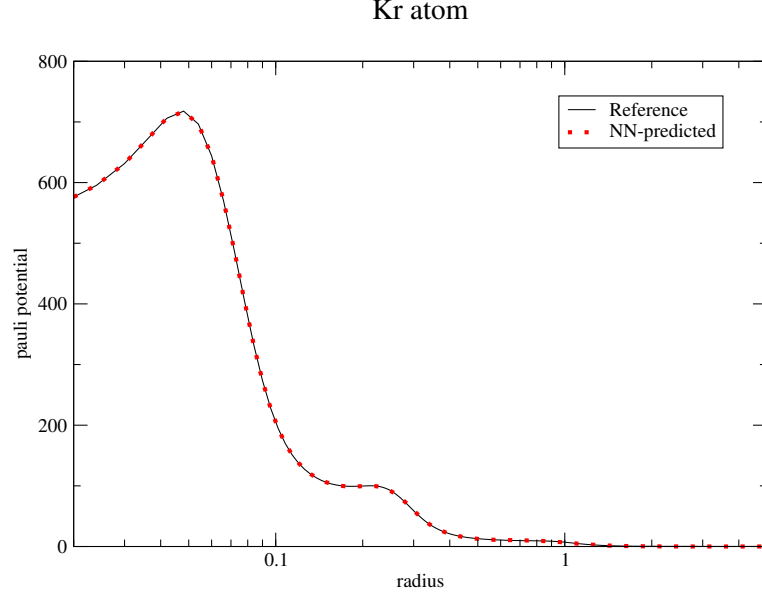


Figure 4.10: Comparison of the reference and NN-based Pauli potentials for Krypton (Kr) atom

A key success in using the residual architecture lies in its ability to generalize beyond neutral systems. However, this generalization remains subject to constraints that mirror those observed in the neutral dataset regime. In the case of the Potassium ion (K^+) [Figure 4.11], isoelectronic to Argon, but with a greater nuclear charge ($Z = 19$), the additional attraction leads to a contraction in the radius of the electron distribution. The neural network shows great prediction accuracy, successfully differentiating between the two isoelectronic systems by adjusting the potentials inwardly depending only on the input descriptor. Such accuracy can be seen from its MAE_V of 3.378×10^{-1} Ha. In contrast, the Beryllium ion (Be^+) [Figure 4.12] behaves like neutral Be, showing a very low MAE_V of 2.382×10^{-2} Ha.

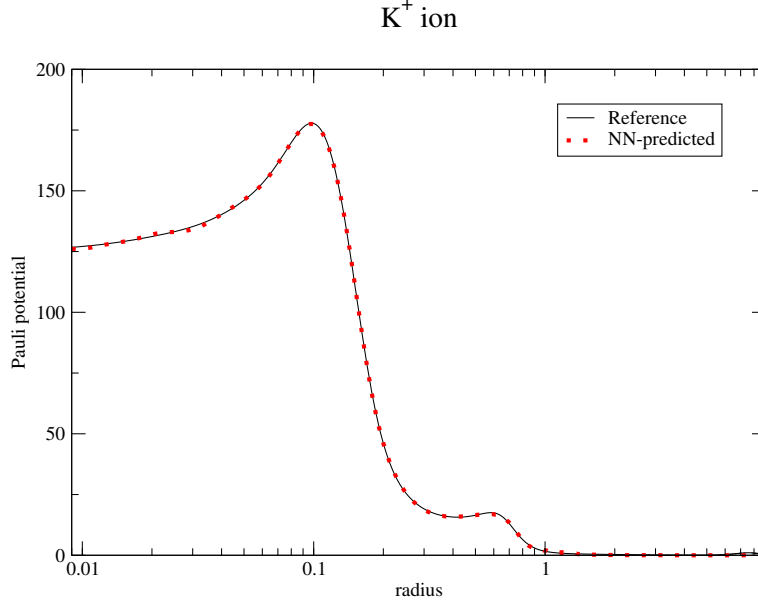


Figure 4.11: Comparison of the reference and NN-based Pauli potentials for Potassium (K^+) ion.

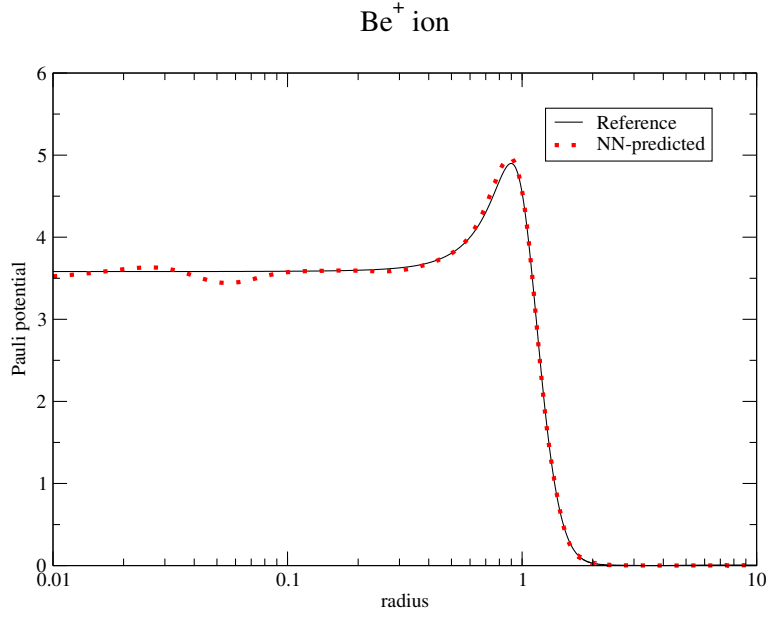


Figure 4.12: Comparison of the reference and NN-based Pauli potentials for Beryllium (Be^+) ion

The precision of the predicted potential was quantified using the Mean Absolute Error (MAE_V), defined as:

$$MAE_V = \frac{1}{N_d} \sum_{i=1}^{N_d} |V_{ref}(r) - V_{NN}(r)| \quad (4.1)$$

where $V_{ref}(r)$ is the reference potential and $V_{NN}(r)$ is the potential predicted by the neural network at each radial grid point r . The calculated MAE_V values for the targeted subset of species are summarized in Table 4.1.

Table 4.1: Mean Absolute Error (MAE_V) for the predicted Pauli potentials.

Species	MAE_V (Ha)	Species	MAE_V (Ha)
Li	2.602×10^{-2}	Mg	7.878×10^{-2}
Be	2.597×10^{-2}	P	5.706×10^{-2}
Be ⁺	2.382×10^{-2}	Ar	8.203×10^{-2}
N	7.020×10^{-2}	K ⁺	3.378×10^{-1}
Ne	6.673×10^{-2}	Zn	5.169×10^{-2}
Kr	7.680×10^{-2}		

Further verification of the physical validity of the proposed model involved the solution of the KS-like radial equation employing the predicted v_{θ}^{NN} . The radial distribution functions ($4\pi r^2 \rho(r)$) for both neutral atoms and ions demonstrate perfect agreement with reference data in terms of locating the local maxima corresponding to electronic shells.

4.0.3 Calculation of Ground-State Densities via the Neural Network Potential

The physical correctness of the proposed Neural Network was tested by solving the ground state electron density for all atomic and ionic species under study, using the predicted Pauli potential ($v_{\theta}^{NN}([\rho]; r)$). Such a process serves as a strong criterion to check that the neural network manages to obtain the Pauli force necessary for density stabilization and correct atomic shell structure.

By using the spherical symmetry of atoms, a three-dimensional density equation was simplified to a one-dimensional differential equation along

the radial direction. In order to solve this numerically-stable, an additional transformation from r to x has been made as $r = x^2$, while the density is expressed as $y(x) = x^{3/2}\sqrt{\rho(x)}$, which brings to mind the following form suitable for use in the Numerov approach:

$$\frac{d^2y}{dx^2} + (\mu - v_{eff}(x))y = 0 \quad (4.2)$$

where μ represents the chemical potential and the effective potential $v_{eff}(x)$ is comprised of the NN-predicted Pauli potential, the nuclear-electron attraction, and the Hartree and exchange terms treated within the Local Density Approximation (LDA) [33].

The radial density probability functions, which have been constructed from $4\pi r^2\rho(r)$, from iterative solutions to this equation for the $v_{\theta}^{NN}([\rho]; r)$ distributions show a remarkable agreement with the respective Kohn-Sham densities for all considered atomic and ionic species. Instead of fitting well only one electronic configuration, this model perfectly describes the structure of the density for the particular physical system. In relation to the second-period atomic and ionic elements: Lithium (Li) [Figure 4.13], Beryllium (Be) [Figure 4.14], Nitrogen (N) [Figure 4.16], and Neon (Ne) [Figure 4.15], the radial densities have correctly captured the fundamental K and L electronic shells with a rather small Mean Absolute Error (MAE_{ρ}) of 2.196×10^{-2} , 2.792×10^{-2} , 8.426×10^{-3} , and 2.952×10^{-2} , respectively. In regards to the third-period atoms: Magnesium (Mg) [Figure 4.17], Phosphorus (P) [Figure 4.19], and Argon (Ar) [Figure 4.18], the proposed model has successfully captured the three peaks of the radial density distribution corresponding to the K, L, and M electronic shells with the respective MAE_{ρ} errors being 6.694×10^{-2} , 2.267×10^{-2} , and 3.348×10^{-2} . Furthermore, for the ionic species, the Beryllium ion (Be^+) [Figure 4.21] yields an MAE_{ρ} of 1.881×10^{-2} , while the Potassium ion (K^+) [Figure 4.20] maintains structural fidelity and accurately reflects the inward radial contraction of the electron cloud relative to its neutral counterparts, recording an MAE_{ρ} of 6.633×10^{-2} . Across all evaluated species, the model successfully captures the proper shell-to-shell transitions and the

correct asymptotic decay.

To quantitatively assess this precision, the Mean Absolute Error (MAE) for the radial probability densities was calculated as follows:

$$MAE_{\rho} = \frac{1}{N_d} \sum_{i=1}^{N_d} |4\pi r_i^2 \rho_{ref}(r) - 4\pi r_i^2 \rho_{NN}(r)| \quad (4.3)$$

The accuracy throughout the entire suite was determined by considering these MAE_{ρ} values. The remarkably small MAE values for the neutral atom and the K^+ ion indicate that the Neural Network generates a reliable potential function. It is evident that the neural network model plays a crucial role in providing a reliable surrogate functional for OF-DFT. This indicates that the neural network model can guide a multi-electron atomic system into its true ground-state density.

Table 4.2: Mean Absolute Error (MAE_{ρ}) for the radial probability densities recovered via the self-consistent Numerov method for all atomic and ionic species.

Species	Radial Density MAE_{ρ}	Species	Radial Density MAE_{ρ}
Li	2.196×10^{-2}	P	2.267×10^{-2}
Be	2.792×10^{-2}	Ar	3.348×10^{-2}
Be ⁺	1.881×10^{-2}	K ⁺	6.633×10^{-2}
N	8.426×10^{-3}	Zn	7.162×10^{-2}
Ne	2.952×10^{-2}	Kr	1.316×10^{-1}
Mg	6.694×10^{-2}		

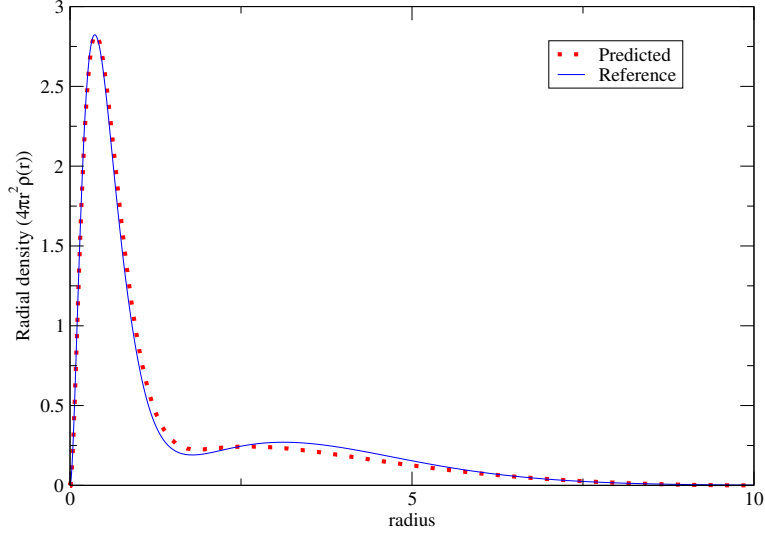


Figure 4.13: Radial probability density for the Lithium (*Li*) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

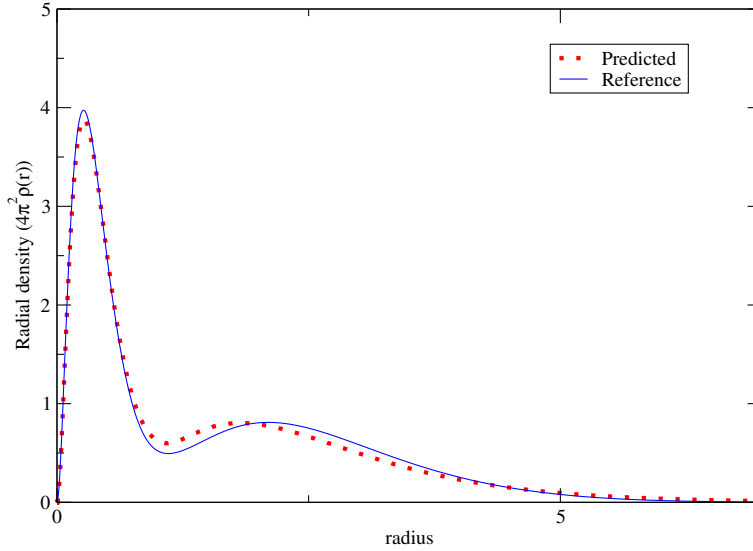


Figure 4.14: Radial probability density for the Beryllium (*Be*) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

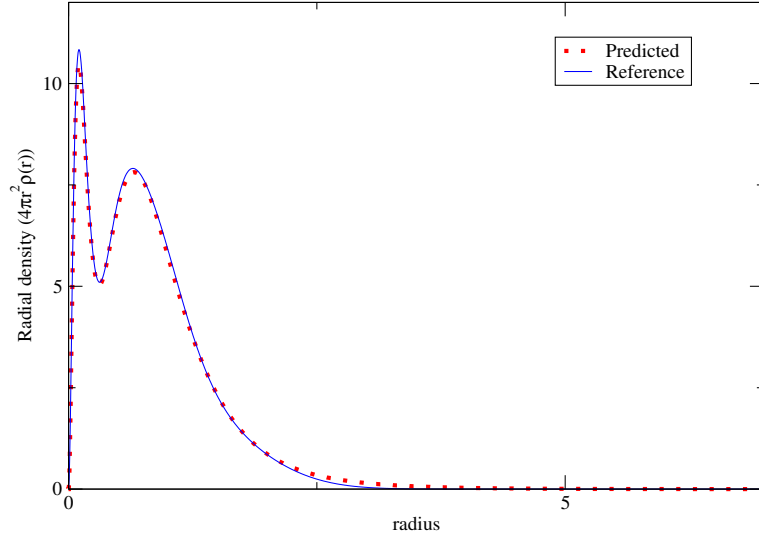


Figure 4.15: Radial probability density for the Ne atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

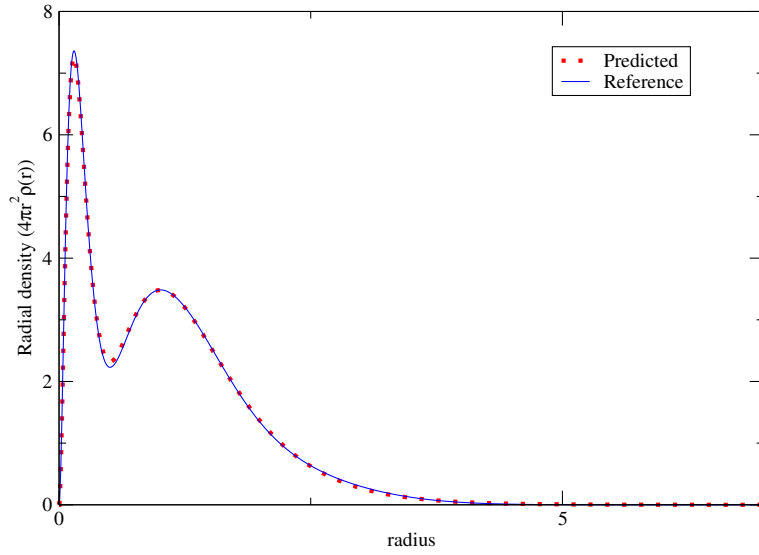


Figure 4.16: Radial probability density for the Nitrogen (N) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

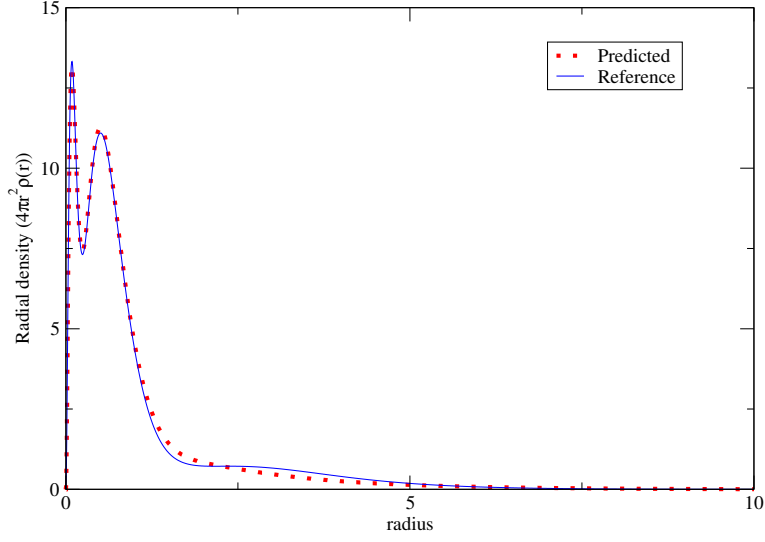


Figure 4.17: Radial probability density for the Magnesium (Mg) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

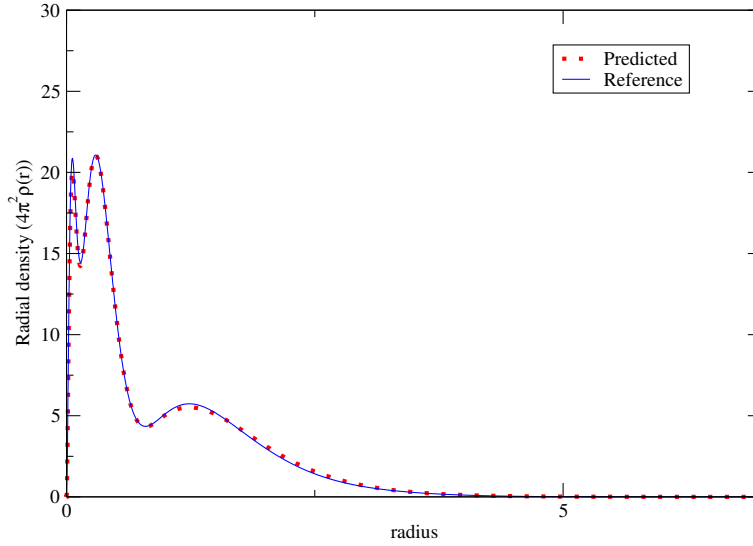


Figure 4.18: Radial probability density for the Argon (Ar) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

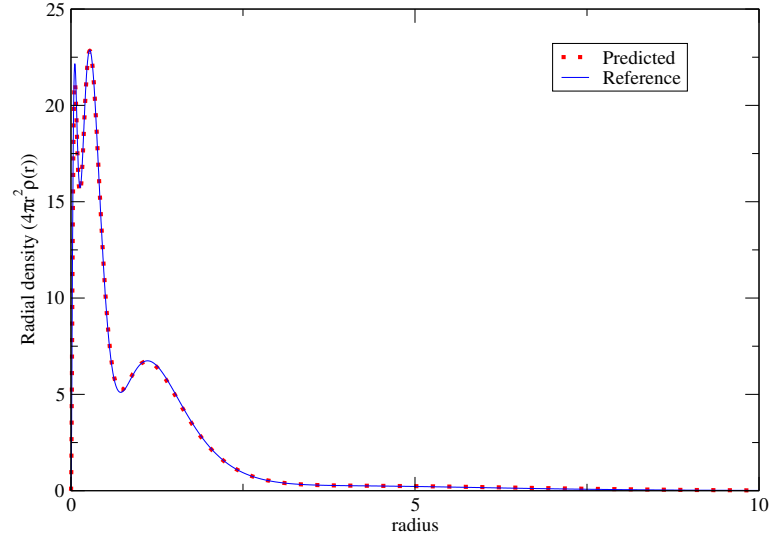


Figure 4.19: Radial probability density for the Phosphorus (P).atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

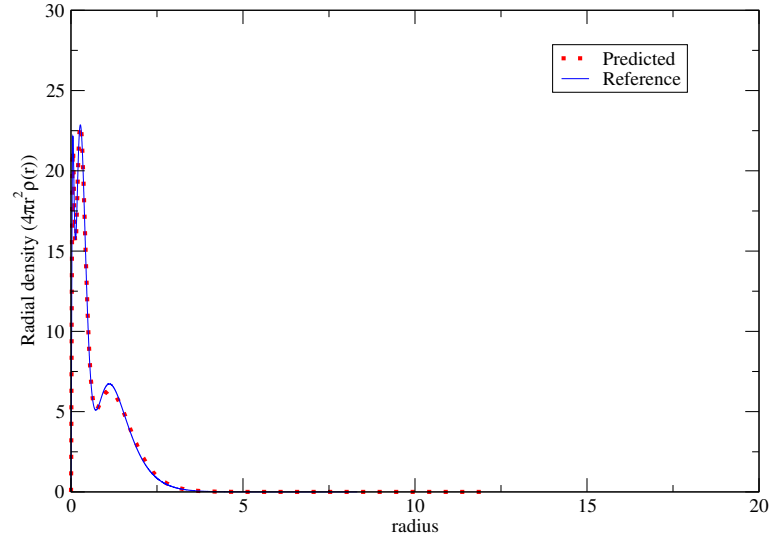


Figure 4.20: Radial probability density for the Potassium ion (K^+) obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

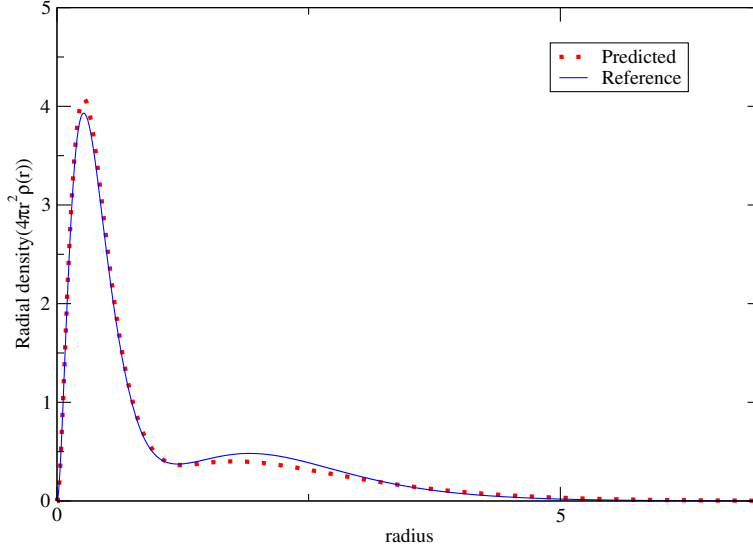


Figure 4.21: Radial probability density for the Beryllium (Be^+) ion obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

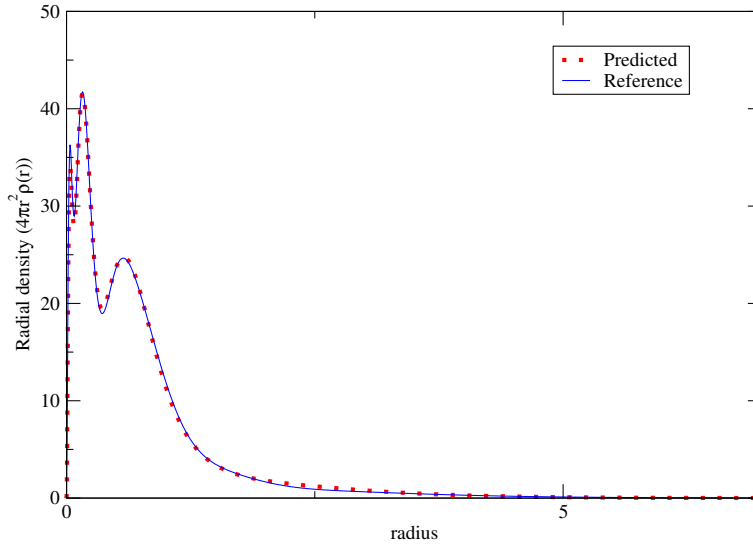


Figure 4.22: Radial probability density for the Zinc (Zn) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

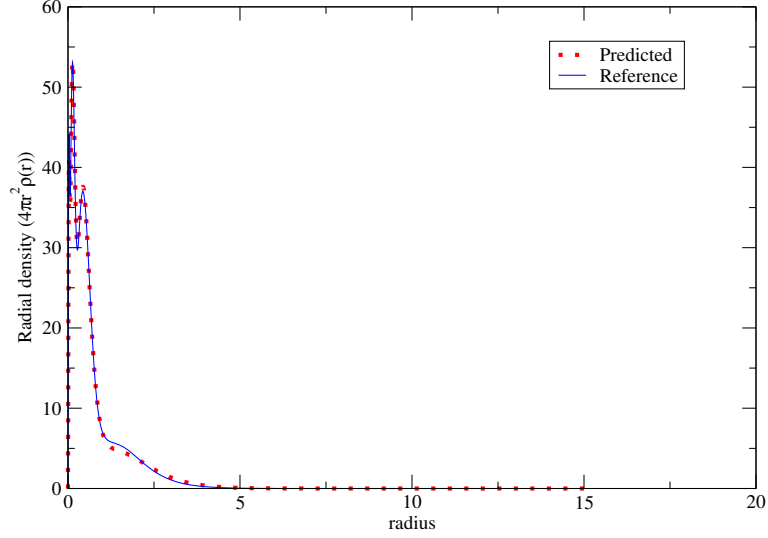


Figure 4.23: Radial probability density for the Krypton (Kr) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

4.0.4 Calculation of $T_s[\rho]$ from Neural Network Predicted Pauli Potentials

In order to test the overall accuracy of the Neural Network, the predicted Pauli potentials ($v_{\theta}^{NN}([\rho]; r)$) have been employed to calculate the total non-interacting kinetic energy (T_s) of each atom considered. In this orbital-free approach, the total kinetic energy is given by the addition of the analytical form of von Weizsäcker ($T_{vW}[\rho]$) and the Pauli kinetic energy produced from the Neural Network output ($T_{\theta}^{NN}[\rho]$).

$$T_s^{NN}[\rho] = T_{vW}[\rho] + T_{\theta}^{NN}[\rho] \quad (4.4)$$

The predictive performance was quantitatively verified against exact Kohn-Sham reference data using the percentage relative difference ($\% \Delta T$):

$$\% \Delta T = \frac{|T_s^{ref} - T_s^{NN}|}{T_s^{ref}} \times 100 \quad (4.5)$$

The examination of the results shown in Table 4.3 reveals that the neural network has an outstanding level of accuracy throughout the whole

span of atomic numbers. In the case of the smallest system, Lithium (*Li*), the network demonstrates slightly higher relative error, which is around 0.84%. Notably, despite the increasing complexity of the systems, the relative errors are extremely small; for heavier atoms such as Zinc (*Zn*) and Krypton (*Kr*), the $\% \Delta T$ values are below 0.06%.

The high accuracy obtained at multiple length scales shows that the neural network was able to effectively understand the physics behind the interaction of light and heavy atoms without falling into the error scaling problem associated with conventional functionals. The consistently small errors observed for the ions, such as Be^+ and K^+ , demonstrate that the model is capable of maintaining its efficacy under various electronic conditions. Thus, it can be concluded that the neural network can be used as an alternative to estimate non-interacting kinetic energy.

Table 4.3: Comparison of reference (T_s^{ref}) and predicted (T_s^{NN}) non-interacting kinetic energies with associated percentage relative errors ($\% \Delta T$).

Species	T_s^{ref} (Ha)	T_s^{NN} (Ha)	$\% \Delta T$
Li	7.3765	7.4385	0.841%
Be	14.5243	14.5240	0.002%
Be^+	14.1113	14.0178	0.663%
N	53.9536	53.8650	0.164%
Ne	127.9484	128.5438	0.465%
Mg	199.5396	199.1204	0.210%
P	341.3173	340.6052	0.209%
Ar	525.5945	526.2672	0.128%
K^+	598.0302	599.1641	0.190%
Zn	1774.9955	1775.7362	0.041%
Kr	2749.9369	2749.4899	0.016%

4.0.5 Test Atoms

After verifying the validity of the Pauli potential derived by the artificial neural network on the training set, it is essential to assess the ability of the developed model to generalize its predictive capability. For this purpose, the trained artificial neural network was used to make predictions for the following three test atoms that were not part of the training set: Potassium (*K*), Calcium (*Ca*), and Arsenic (*As*).

Using the learned optimized network weights, the Pauli potentials $v_{\theta}^{NN}([\rho]; r)$ for the new species were obtained. The similarity between predicted Pauli potential $v_{\theta}^{NN}([\rho]; r)$ and the reference Pauli potential $v_{\theta}^{ref}([\rho]; r)$ evaluated by the 6-31G basis set is clearly shown in Figures [4.24][4.26][4.28]. This proves that the neural network has indeed learned the physical nature of the kinetic energy functional, rather than simply memorizing the training data set.

The physical validity of these potentials can be verified by their ability to produce correct non-interacting kinetic energies (T_s) and electron densities for the ground state. The performance of this model, using non-interacting kinetic energy, is given in Table 4.4 for the chosen test cases.

Table 4.4: Non-interacting kinetic energy results for test atoms: comparison between reference (T_s^{ref}) and Neural Network (T_s^{NN}) predictions.

Species	T_s^{ref} (Ha)	T_s^{NN} (Ha)	% ΔT
K	598.1915	599.3092	0.1868%
Ca	675.6428	677.12109	0.2182%
As	2233.4602	2223.9629	0.4252%

By employing the predicted potential $v_{\theta}^{NN}([\rho]; r)$ density profile, we have obtained the self-consistent electron densities of these newly discovered atoms using the radial Euler equation. The radial probability densities $4\pi r^2 \rho(r)$, as seen, demonstrate great consistency with the exact Kohn-Sham densities, correctly distinguishing the different atomic shells of these

unknown species. The predicted density profile for Calcium [Figure 4.27] shows somewhat higher deviations compared to those of Potassium [Figure 4.25] and Arsenic [Figure 4.29]. Such specific deviation demonstrates the dependence of the density recovery procedure from the accuracy of the potential predicted by the neural network. Namely, it shows that the quality of the final density can only be as accurate as the underlying neural network potential. In conclusion, the results have successfully demonstrated the ability of the proposed functional to transfer its performance to new atomic systems, as well as its reliability as an alternative to compute non-interacting kinetic energy in orbital-free density functional theory.

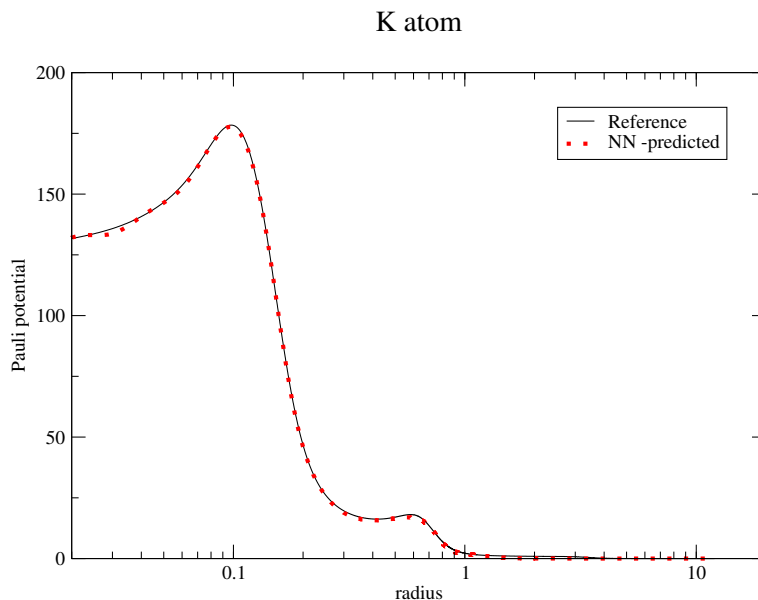


Figure 4.24: Comparison of the reference and NN-based Pauli potentials for Potassium (K) atom

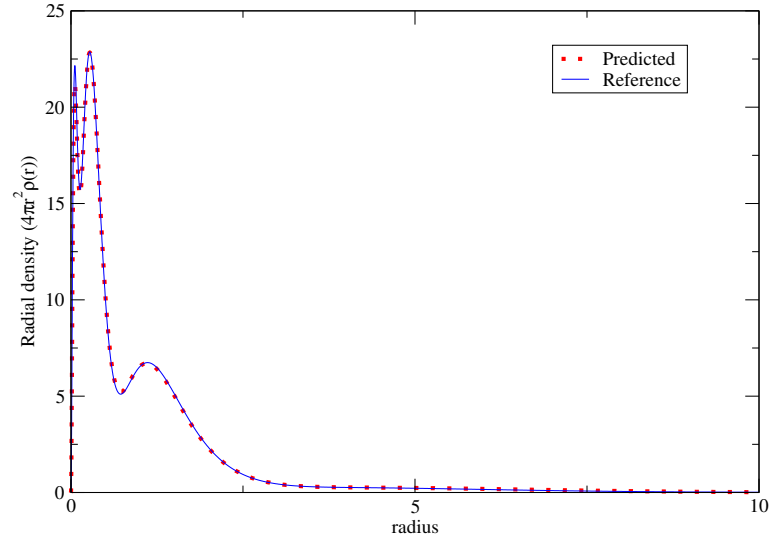


Figure 4.25: Radial probability density for the Potassium (K) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

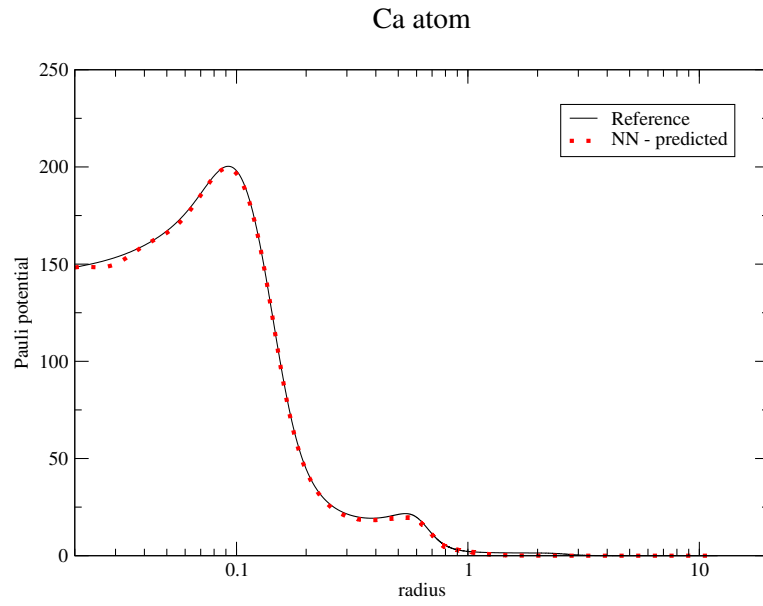


Figure 4.26: Comparison of the reference and NN-based Pauli potentials for Calcium (Ca) atom

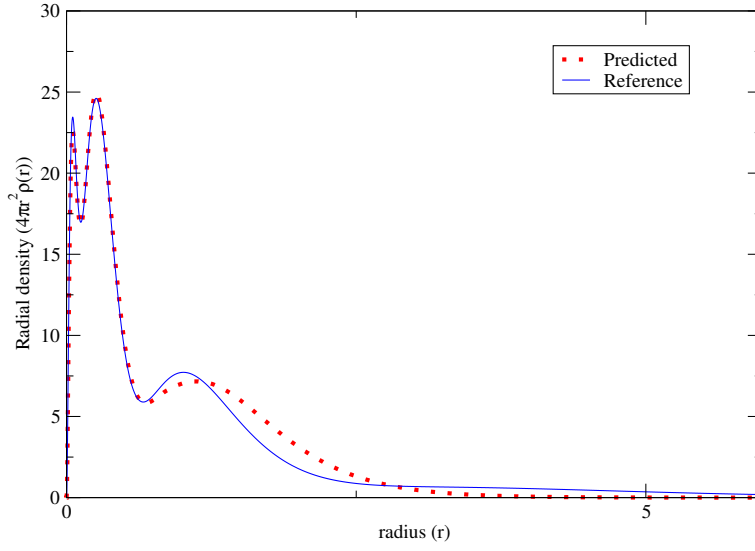


Figure 4.27: Radial probability density for the Calcium (*Ca*) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

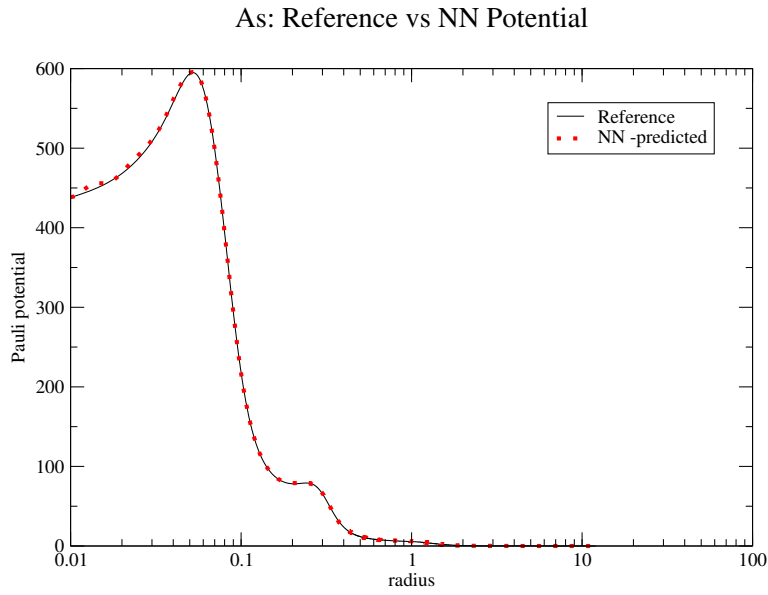


Figure 4.28: Comparison of the reference and NN-based Pauli potentials for Arsenic (*As*) atom

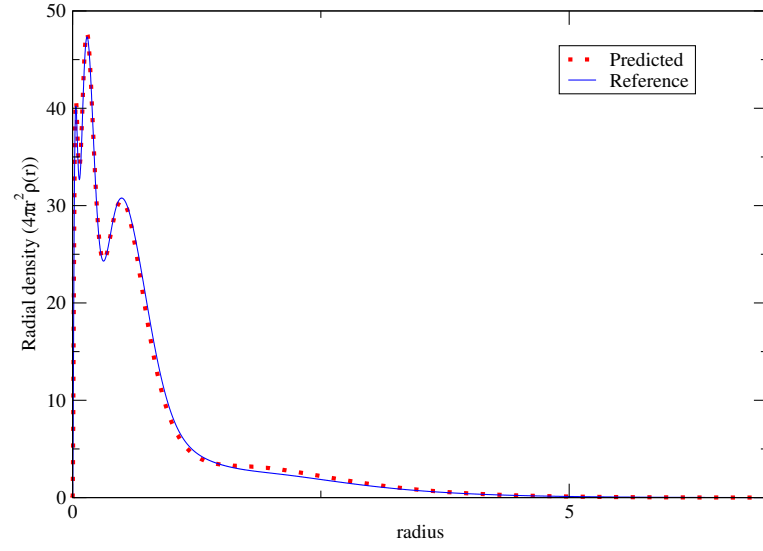


Figure 4.29: Radial probability density for the Arsenic (*As*) atom obtained from KS-DFT calculations using the 6-31G basis set and from Eq. (4.2) using $v_{\theta}^{NN}([\rho]; r)$

Chapter 5

Conclusion and Future Scope

5.1 Conclusion

In this study, a deep learning-based neural network has been successfully implemented to predict the Pauli potential ($v_{\theta}^{NN}([\rho]; r)$). Seven selected input features, such as the nuclear charge (Z), logarithmic density, radial Laplacian, and density gradients, are directly used by the neural network to predict the Pauli potential, which is then employed to calculate the non-interacting kinetic energy (T_s). The architecture of the neural network was deliberately engineered to guarantee a robust training process and valid physical output values within different electronic systems, ranging from neutral atoms to ions.

The predictions show a good level of accuracy based on the Mean Absolute Errors (MAE_V) of the predicted Pauli potentials, which have been found to fall within the 10^{-2} Ha order of magnitude when applied to the main dataset. An important aspect of this research is the efficiency of the model in the case of the heavier elements, where the model was found to be able to produce relative percentage errors ($\% \Delta T$) less than 0.06% for elements like Zn and Kr . Using the model in an SCF calculation using the Numerov approach produced the correct probability densities for these elements.

Additionally, extrapolative generalization was evident from the ability of the model to predict the electronic characteristics of unknown atoms outside the range of those used in the training process. When new test atoms were provided, the network maintained its accuracy, resulting in kinetic energy percent errors of 0.4252%, 0.2182%, and 0.1868% for arsenic (As), calcium (Ca), and potassium (K) respectively. Taken together, these results confirm that the neural network is capable of learning the complex function mapping from the chosen physical properties—the nuclear charge and density-related properties to the Pauli potential, and not just fitting to the training data. Through generating accurate Pauli potentials, the model becomes a powerful alternative for use in determining the non-interacting kinetic energy of OF-DFT.

5.2 Future Scope

Despite its high efficiency in estimating the Pauli energy and non-interacting kinetic energy of individual atoms using one-dimensional coordinates, the existing neural network leaves room for many possible future endeavors. One of the key goals in such cases is to scale the approach up to three dimensions so that it can be applied to realistic molecules.

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