LOCAL DENSITY APPROXIMATION OF SPHERICALLY SYMMETRIC ATOMIC GROUND STATES

BLAŽ STOJANOVIČ

Fakulteta za matematiko in fiziko
Univerza v Ljubljani

The first part of this article discusses the problem of electronic structure and its solutions using density functional theory. First the Hohenberg-Kohn theorems are stated and proved, then the Kohn-Sham auxiliary system is derived using their ansatz and finally different approximations of the exchange correlation functional are discussed. The second part focuses on the numerical implementation of the restricted spherically symmetric local density approximation. This method is then used to calculate atomic ground-states and their first ionisation energies. The results are compared with experimental data and show good agreement.

APROKSIMACIJA LOKALNE GOSTOTE ZA IZRAČUN OSNOVNIH STANJ SFERIČNO SIMETRIČNIH ATOMOV

Članek govori o problemu elektronske strukture in njegove rešitve z uporabo metode gostotnih funkcionalov. Prvi del članka se posveti teoretičnem ozadju, predstavljena in dokazana sta Hohenberg-Kohnova izreka. Za tem je izpeljan Kohn-Shamov sistem enačb in obravnavani so različni približki izmenjalno-korelacijskega funkcionala. V drugem delu je predstaljena numerična implementacija sferično povprečene aproksimacije lokalne gostote. Metoda je uporabljena za izračun atomskih osnovnih stanj in prvih ionizacijskih energij. Na koncu je predstavljena primerjava z eksperimentalnimi vrednostmi.

1. Introduction

In 1929, shortly after Schrödinger's postulated his famous equation, P.M. Dirac was quoted saying that the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are now known. Applying these laws however leads to unsolvable equations and work needs to be done in developing approximate methods in order to solve such problems without excessive computation [1]. In the eighty years that have passed since, along with the developments in computing, many methods for solving the many body Schrödinger equation have been developed and applied to a variety of problems. Perhaps the most popular *ab initio*[1] method, the *Hartree-Fock* method (HF), was proposed in the 1930s [2] and further simplified and popularized in the 1950s by Slater [3, 4]. In the following decades a lot of work was done to develop methods that include electron correlations, which HF neglects. Such approaches are known as post-Hartree-Fock methods, the most famous being *Coupled Cluster* (CC) and *Configuration interaction* (CI) methods.

Perhaps the most important paradigm shift that occurred in the field of computational quantum chemistry in the last century happened in the 1960s, when *Density Functional Theory* (DFT) was put on firm ground in two seminal papers. The 1964 paper co-authored by Hohenberg and Kohn [5] built on the ideas of Thomas [6] and Fermi [7], and showed that the electron density $n(\mathbf{r})$ of the ground state of a quantum many-body system plays an important role and that all properties of the system can be considered as *functionals* of the ground state density. The second paper was the work of Kohn and Sham [8], which replaced the difficult many-body system with an auxiliary system that can be solved more readily. The Kohn-Sham approach forms the basis of most modern DFT approximations that are used for treating electrons in atoms, molecules, condensed matter and chemical processes. Density functional theory represents a shift from a wave function approach, that HF and its descendants use, to a density based approach, where instead of the many body

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[1] From first principles

wave function the electron density plays a central role. This shift began a new era in computational chemistry and culminated in the 1998 Nobel price being in part awarded to Kohn.

In his Nobel lecture [9] Kohn emphasized two different contributions of DFT to physics. Firstly the contribution to understanding, as the density approach provided an alternative line of thought to the truncated Hilbert space of single particle orbitals, which becomes incomprehensible when many Slater determinants are used. Instead it focuses on quantities[2] in real 3-dimensional coordinate space, first and foremost the electron density $n(\mathbf{r})$, which are easily visualizable and provide physical insight into the problem. And secondly, the method is applicable to larger systems than wavefunction based approaches, as the Hohenberg-Kohn formulation is defined completely in terms of $n(\mathbf{r})$, while the Kohn-Sham formulation is defined completely in terms of single particle wave functions ψ_i and $n(\mathbf{r})$ and thus avoids the Van Vleck catastrophe [10].

The rest of this paper is structured as follows. This introduction is followed by the theoretical underpinnings of the method. In the second part a basic numerical implementation is presented and applied to ground state energy calculations of spherically symmetric atoms.

2. Theoretical Background

In the context of electronic structure calculations, which we will focus on, it can be assumed that the nuclei are stationary as their mass is very large in comparison to that of the electrons. This is known as the *Born-Oppenheimer* approximation. In the absence of magnetic fields and ignoring relativistic effects, the Hamiltonian of the system is

$$\hat{H} = \underbrace{-\frac{1}{2}\sum_i \nabla_i^2}_{\text{kinetic energy}} \overbrace{-\sum_{i,I} \frac{Z_i}{|\mathbf{r}_i - \mathbf{R}_I|}}^{\text{electron-nucleus}} \underbrace{+\frac{1}{2}\sum_{i\neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}}_{\text{electron-electron}} \overbrace{+\frac{1}{2}\sum_{I\neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}}^{\text{nucleus-nucleus}}, \tag{1}$$

where $\mathbf{r}_i$ and $\mathbf{R}_I$ are electron and nucleus positions and nucleus charges are denoted by Z_I. We adopted Hartree atomic units $\hbar = m_e = e = \frac{4\pi}{\varepsilon_0} = 1$. We are searching for stationary electronic states, these are described by wave functions $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ and satisfy the stationary many-electron Schrödinger equation

$$\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N). \tag{2}$$

Suppose we are only interested in the ground state of the system. In the wave function picture this is calculated numerically by minimizing the functional of the energy while adhering to the Rayleigh-Ritz minimal principle,

$$E = \min_{\Psi} \langle \Psi | \hat{H} | \Psi \rangle \,. \tag{3}$$

This sort of approach, while very successful for systems with a few electrons, becomes computationally infeasible for larger systems which are of great interest in physics and chemistry. This is due to the parameter search space increasing exponentially. Even ignoring spin effects our wave function has $3N$ continuous variables, say we discretise each of these variables using a p point mesh, we would need p^{3N} mesh points to represent Ψ. On the contrary the electron density of the system

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle \,, \quad \text{where} \quad \hat{n}(\mathbf{r}) = \sum_{i=1,\ldots,N} \delta(\mathbf{r} - \mathbf{r}_i) \tag{4}$$

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[2] Along with $n(\mathbf{r})$ these are the electron exchange correlation hole $n_{\mathrm{xc}}(\mathbf{r}, \mathbf{r}')$ and the linear response function $\chi(\mathbf{r}, \mathbf{r}', \omega)$.

is a function of the three coordinates only and we would need only p^3 mesh points to represent it. This is ultimately the reason for the computational success of DFT. Of course using electron density as the “basic” variable instead of the wave function, has in it of itself no value unless we can calculate all the system properties of interest from it. This issue was resolved by Kohn and Hohenberg in 1964.

2.1 Hohenberg-Kohn theorems

Hohenberg and Kohn managed to formulate density functional theory as an exact theory of many-body systems. Their formulation applies to the Hamiltonian (1), and is summarized in two theorems [11]:

Theorem 1. For any system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential $V_{\text{ext}}(\mathbf{r})$ is determined uniquely, up to an additive constant, by the ground state electron density $n_0(\mathbf{r})$.

$$\begin{tikzcd}
V_{\text{ext}}(\mathbf{r}) \arrow[d] & n_0(\mathbf{r}) \arrow[l, "\text{Hohenberg-Kohn}"'] \\
\Psi_i(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \arrow[r] & \Psi_0(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \arrow[u]
\end{tikzcd}$$

Figure 1. The Hohenberg-Kohn theorems *close the loop* between the external potential and ground state density, adapted from [11]

Proof. The theorem is proved by contradiction. Suppose there exist two external potentials V^1_{ext} and V^2_{ext}, that differ by more than a constant and result in the same ground state electron density $n_0(\mathbf{r})$. The potentials give two different Hamiltonians $\hat{H}_1$, $\hat{H}_2$ that lead to two different ground states Ψ_1 and Ψ_2. Under the assumption that the ground states are not degenerate[3] we see that

$$E_1 = \langle\Psi_1|\hat{H}_1|\Psi_1\rangle < \langle\Psi_2|\hat{H}_1|\Psi_2\rangle \tag{5}$$

Rewriting the last term

$$\langle\Psi_2|\hat{H}_1|\Psi_2\rangle = \langle\Psi_2|\hat{H}_2|\Psi_2\rangle + \langle\Psi_2|\hat{H}_1 - \hat{H}_2|\Psi_2\rangle = E_2 + \int (V^1_{\text{ext}}(\mathbf{r}) - V^2_{\text{ext}}(\mathbf{r}))n_0(\mathbf{r})\mathrm{d}\mathbf{r} \tag{6}$$

Hence

$$E_1 < E_2 + \int (V^1_{\text{ext}}(\mathbf{r}) - V^2_{\text{ext}}(\mathbf{r}))n_0(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{7}$$

and completely analogously, starting from the definition of E_2

$$E_2 < E_1 - \int (V^1_{\text{ext}}(\mathbf{r}) - V^2_{\text{ext}}(\mathbf{r}))n_0(\mathbf{r})\mathrm{d}\mathbf{r}. \tag{8}$$

Adding equations (7) and (8) we obtain the contradictory statement

$$E_1 + E_2 < E_2 + E_1 \tag{9}$$

It follows that two such potentials cannot exist.

From the first theorem it follows that the Hamiltonian is fully determined up to a constant shift in energy. As a consequence all wave functions, ground or excited, are determined. Meaning that all properties of the system are completely determined given only the ground state density.

Theorem 2. Energy $E[n]$ can be defined as a universal[4] functional of the electron density $n(\mathbf{r})$ and

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[3] We are following the argument of Hohenberg and Kohn. The theorem can be extended to degenerate states as well. See Levi-Lieb’s alternative formulation of DFT [11].

[4] Independent of the system studied.

is valid for any external potential V_{ext}. The ground state energy of the system is a global minimum of the functional, for any given V_{ext} and the electron density that minimizes $E[n]$ is the ground state electron density $n_0(\mathbf{r})$.

The form of the theorem originally proven by Kohn and Hohenberg is limited to densities $n(\mathbf{r})$ that are ground state densities of the Hamiltonian with some external potential V_{ext}. Thus the densities are V-representable[5], they define a space of possible densities within which we can construct functionals. All properties of the system are uniquely determined if a density $n(\mathbf{r})$ is specified, including the total energy functional

$$E_{\text{HK}}[n] = T[n] + E_{\text{int}}[n] + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r} + E_{\text{II}} \equiv F_{\text{HK}}[n] + \int V_{\text{ext}}(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r} + E_{\text{II}} \tag{10}$$

$$F_{\text{HK}}[n] = T[n] + E_{\text{int}}[n] \tag{11}$$

Where E_{II} is the nucleus interaction energy, we defined the Hohenberg-Kohn functional F_{HK} that includes the internal kinetic and potential energies of the electron system. As such it is universal since both the kinetic energy and interaction energy of the particles are functionals of the density only.

Proof. Let us consider a system with ground electron density $n_0^1(\mathbf{r})$ that as a consequence of the first HK theorem corresponds to the external potential $V_{\text{ext}}(\mathbf{r})$. Using (10) we see that

$$E_{\text{HK}}[n_0^1] = E_1 = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle \,. \tag{12}$$

It follows that by definition of the ground state of $\hat{H}_1$ that the energy of any other state $n_0^2(\mathbf{r})$ is greater,

$$E_1 = \langle \Psi_1 | \hat{H}_1 | \Psi_1 \rangle < \langle \Psi_2 | \hat{H}_1 | \Psi_2 \rangle \,. \tag{13}$$

From (13) we can conclude that the energy calculated using (10), evaluated for the ground state energy $n_0^1(\mathbf{r})$ is lower than the energy evaluated for any other density $n(\mathbf{r})$. Meaning that if the HK funcitonal is known, then minimizing the energy of the system, with respect to variations in all V-representable electron densities, finds the ground state density and energy of the system.

While HK theorems provide an exact theory of many-body problems the issue is that the universal HK functional F_{HK} is not known. Moreover, the theorems do not provide any guidance for finding the functional. As such the essence of DFT becomes the construction of functionals that give useful approximations for certain systems.

2.2 Kohn-Sham auxiliary system

When it comes to the actual implementation of DFT one approach could be the minimization of an explicit energy functional, however this is not the most efficient path. An ansatz for solving the problem was proposed by Kohn and Sham. They assumed that the ground state density of the original interacting system is equal to that of another non-interacting system residing in an effective external potential. The non-interacting system gives rise to independent-particle equations which are exactly solvable[6], while all the many-body terms are included in the effective potential. The sum of the densities of individual orbitals is the total electron density of the system

$$n(\mathbf{r}) = \sum_{\sigma} \sum_{i=1}^{N} |\phi_i^{\sigma}(\mathbf{r}),|^2, \quad \int n(\mathbf{r})\mathrm{d}\mathbf{r} = N. \tag{14}$$

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[5] In Levi-Lieb's formulation, the functional is defined for any density $n(\mathbf{r})$, which is termed as N-representability.

[6] Numerically in practice.

From now on the explicit reference to spin σ will be dropped. The total functional of the energy (10) is calculated as

$$E_{\mathrm{HK}}[n] = T_{\mathrm{s}}[n] + E_{\mathrm{h}}[n] + \int V_{\mathrm{ext}}(\mathbf{r})n(\mathbf{r})\mathrm{d}\mathbf{r} + E_{\mathrm{II}} + E_{\mathrm{xc}}[n]. \tag{15}$$

Where T_{s} is the single particle kinetic term, E_{h} is the Hartree term and $E_{\mathrm{xc}}[n]$ is the exchange-correlation term. T_{s} easily expressed in terms of the single-particle orbitals $\phi_i(\mathbf{r})$,

$$T_{\mathrm{s}}[n] = -\frac{1}{2}\sum_{i=1}^{N} \langle \phi_i(\mathbf{r})|\nabla^2|\phi_i(\mathbf{r})\rangle\,. \tag{16}$$

It is important to note that $T_s[n]$ is not an explicit orbital functional, but an implicit density functional $T_s[n] = T_s[\{\phi_i[n]\}]$, as it depends on the whole set of orbitals, each of which is a density functional itself. The Hartree term E_h is expressed as

$$E_{\mathrm{h}}[n] = \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'. \tag{17}$$

We defined the *exchange-correlation* functional $E_{\mathrm{xc}}[n]$ as the difference of the kinetic and internal energy of the true many-body interacting system and the kinetic and internal energy of the auxiliary system

The solution to the non-interacting system can be viewed as the problem of minimization of E_{KS} with respect to the electron density $n(\mathbf{r})$. Remembering that T_{s} is an explicit functional of the orbitals and not the density, instead of varying the density one can vary the independent wavefunctions and apply the chain rule where necessary. The minimization condition becomes

$$\frac{\delta E_{\mathrm{KS}}}{\delta\phi_i^*(\mathbf{r})} = \frac{\delta T_{\mathrm{s}}}{\delta\phi_i^*(\mathbf{r})} + \left[\frac{\delta E_{\mathrm{ext}}}{\delta n(\mathbf{r})} + \frac{\delta E_{\mathrm{h}}}{\delta n(\mathbf{r})} + \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})}\right]\frac{\delta n(\mathbf{r})}{\delta\phi_i^*(\mathbf{r})} = 0, \tag{18}$$

with normalization constraints

$$\langle\phi_i|\phi_j\rangle = \delta_{ij}. \tag{19}$$

Using the relations

$$\frac{\delta T_{\mathrm{s}}}{\delta\phi_i^*(\mathbf{r})} = -\frac{1}{2}\nabla^2\phi_i(\mathbf{r}), \quad \frac{\delta n(\mathbf{r})}{\delta\phi_i^*(\mathbf{r})} = \phi_i^*(\mathbf{r}) \tag{20}$$

and the method of Lagrangian multipliers to handle the constraints, we obtain the Kohn-Sham auxiliary system

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{KS}}(\mathbf{r})\right)\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r}), \tag{21}$$

where we defined the Kohn-Sham effective potential as

$$V_{\mathrm{KS}}(\mathbf{r}) = \frac{\delta E_{\mathrm{ext}}}{\delta n(\mathbf{r})} + \frac{\delta E_{\mathrm{h}}}{\delta n(\mathbf{r})} + \frac{\delta E_{\mathrm{xc}}}{\delta n(\mathbf{r})} = V_{\mathrm{ext}}(\mathbf{r}) + V_{\mathrm{h}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}). \tag{22}$$

Solving the equations gives the ground state electron density and energy of the fully interacting system. One issue that remains is that the exchange correlation potential is not known and needs to be approximated in some way.

2.3 Exchange-Correlation functionals

In their paper Kohn and Sham argued, based on the argument that solids can be considered close to the limit of the homogeneous electron gas, that the exchange correlation functional $E_{\mathrm{xc}}[n]$ can be treated as a local or nearly local functional of the density [8, 9]. Some of the most important and widely used approximations of the exchange correlation functional have this quasi-local form.

LDA - Local Density Approximation

While it is clear that the true form of $E_{\mathrm{xc}}[n]$ is complicated, even relatively simple approximations of it provide satisfactory results. The simplest of all is the local density approximation, which assumes that the exchange-correlation energy at each point is that of a homogenous electron gas with that density. Thus integrating over all space gives the exchange-correlation functional

$$E_{\mathrm{xc}}^{\mathrm{LDA}}[n(\mathbf{r})] = \int n(\mathbf{r})\varepsilon_{\mathrm{xc}}(n(\mathbf{r}))\mathrm{d}\mathbf{r} = \int n(\mathbf{r})\varepsilon_{\mathrm{x}}(n(\mathbf{r}))\mathrm{d}\mathbf{r} + \int n(\mathbf{r})\varepsilon_{\mathrm{c}}(n(\mathbf{r}))\mathrm{d}\mathbf{r}. \tag{23}$$

The exchange part of the energy $\varepsilon_{\mathrm{x}}(n)$, can in fact be calculated analytically [11]

$$\varepsilon_{\mathrm{x}}(n) = -\frac{3}{4}\left(\frac{3}{2\pi}\right)^{\frac{2}{3}}\frac{1}{r_s} \quad \text{where} \quad r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}} \tag{24}$$

r_s is the radius of a sphere that contains one electron. On the other hand $\varepsilon_{\mathrm{c}}(n)$ is not analytically known and determining the correlation energy of a homogenous interacting electron liquid is not a trivial problem in itself. The earliest approaches for calculating $\varepsilon_{\mathrm{c}}(n)$ used perturbation theory[7], but such approaches became obsolete when Quantum Monte Carlo (QMC) became the de-facto standard [13] . Nowadays various parametrizations of the QMC generated data are used, of which we will later compare three [14, 16, 15].

This approximation has proved surprisingly successful, even applied to systems that differ from the electron liquid considerably. One explanation for this is that the error systematically cancels out [11], as LDA overestimates ε_{x} and underestimates ε_{c}.

LSDA - Local Spin Density Approximation

The local density approximation can easily improved upon by taking spin into account. Local spin density approximation can be formulated either in terms of two spin densities $n^{\uparrow}(\mathbf{r})$ and $n^{\downarrow}(\mathbf{r})$

$$E_{\mathrm{xc}}^{\mathrm{LSDA}}[n(\mathbf{r})] = \int n(\mathbf{r})\varepsilon_{\mathrm{xc}}(n^{\uparrow}(\mathbf{r}), n^{\downarrow}(\mathbf{r}))\mathrm{d}\mathbf{r}. \tag{25}$$

LSDA can be extended to non-collinear spins and is as such the most general local approximation. For unpolarized systems it is the same as LDA, as $n^{\uparrow}(\mathbf{r}) = n^{\downarrow}(\mathbf{r}) = n(\mathbf{r})/2$.

GGA - Generalized Gradient Approximation

In the LDA only the knowledge of the density at a certain point is exploited. So naturally, since any real system is not spatially homogenous, it might be useful to include the information about the gradient of the density in the functional. This is exactly what Generalized Gradient Approximations do.

$$E_{\mathrm{xc}}^{\mathrm{GGA}}[n(\mathbf{r})] = \int f(n(\mathbf{r}), |\nabla n(\mathbf{r})|)\mathrm{d}\mathbf{r}. \tag{26}$$

GGAs vary wildly with the choices of functions $f(n, |\nabla n|)$, and there is no consensus at the moment on what the best function is. At the moment the most popular are PBE [17] and BLYP [18]. The main advantage of GGAs over LDA is that they can enforce analytically determined asymptotic properties of the functional [11, 18]. A further generalization of GGA's are meta-GGA's that use the Laplacian of the density as well [11].

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[7] Namely random phase approximation [12].

3. Numerical implementation

3.1 LDA for atomic calculations

In the second part of this paper we will be implementing LDA for calculations of ground states of atoms. This sort of computation is much simpler than DFT calculations for solids, where this is often just the first step in the computation, like in the Linearized Augmented Planewave (LAPW) Method.

The problem is usually solved in spherical coordinates. The Kohn-Sham single state wave-functions are written as

$$\phi_{nlm}(\mathbf{r}) = \frac{1}{r} u_{nl}(r) Y_{lm}(\theta, \phi), \tag{27}$$

where $Y_{lm}(\theta, \phi)$ are normalized spherical harmonics. When working with atoms it is often convenient treat the problem as spherically symmetric, and independent of spin [11]. We derive the potential by a spherical average over any non-spherical terms and average all the spin states so that orbital densities are the same for each spin state. This sort of calculation is referred to as restricted and is often sufficiently accurate. In the case of closed shell atoms (noble gases) it is in fact exact.

Using the Laplacian in the spherical coordinates, Kohn-Sham equations (21) for the restricted case can be reduced to radial equations for each principal quantum number n

$$-\frac{1}{2}\frac{d^2}{dr^2} u_{nl}(r) + \left(\frac{l(l+1)}{2r^2} + V_{\mathrm{KS}}(r) - \varepsilon_{nl} \right) u_{nl}(r) = 0. \tag{28}$$

The electron density then becomes

$$n(\mathbf{r}) = \sum_{n,l}^{\text{occuppied}} 2(2l+1) \frac{|u_{nl}(r)|^2}{r^2}. \tag{29}$$

Finally the expression for the total energy E_{KS} can be simplified by making use of the eigenvalues ε_{nl} and thus avoiding differentiation of individual orbitals for kinetic energy calculations. We see that

$$\varepsilon_i = \langle \phi_i | T_{\mathrm{s}} + V_{\mathrm{KS}} | \phi_i \rangle \to T_{\mathrm{s}}[n] = \sum_i \varepsilon_i - \int V_{\mathrm{KS}}(\mathbf{r}) n(\mathbf{r}) \mathrm{d}\mathbf{r} \tag{30}$$

which we can use to rewrite the total energy functional as

$$E = \sum_{n,l}^{\text{occuppied}} 2(2l+1)\varepsilon_{nl} + \int 4\pi r^2 n(r) \left[V_{\mathrm{ext}} + \varepsilon_h + \varepsilon_{\mathrm{xc}} - V_{\mathrm{KS}} \right] \mathrm{d}r, \tag{31}$$

where $\varepsilon_h(\mathbf{r}) = \frac{1}{2} \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}\mathbf{r}'$ is the Hartree energy density.

This sort of approach should work well for closed-shell atoms or atoms which are nearly spherically symmetric. If additional accuracy is required, one can perform the spin unrestricted calculation which allows for spin dependence of potentials and orbitals or perform the fully unrestricted calculation. In the fully unrestricted calculation for atoms, the density $n(r, \theta)$ and exchange-correlation potential $V_{\mathrm{xc}}(r, \theta)$ are cylindrically symmetric. This can be resolved with clever expansions of the potentials and by performing angular integrals of $V_{\mathrm{xc}}(r, \theta)$ numerically [11], but is tedious to implement.

3.2 Self consistency loop

Once the explicit expression for the energy functional is known the Kohn-Sham equations can be solved. As the Kohn-Sham functional is dependent on the density, the equations (22), (28) and (29)

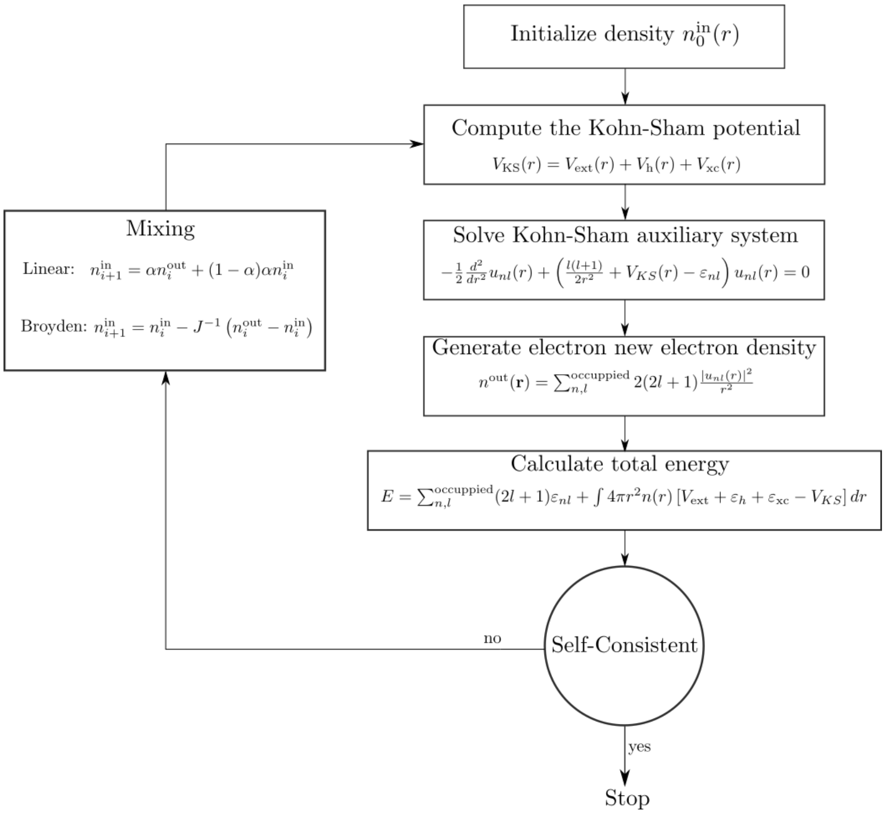

Figure 2. Schematic of the self consistency loop for the spherically restricted problem. When the loop is finished one uses the energy eigenvalues ε_{nl}, Kohn-Sham orbitals u_{nl} and the electron density obtained to calculate various response functions (i.e. properties) of the system.

form a system of nonlinear coupled equations. A standard approach for solving such systems is to iterate until self-consistency between $V_{\text{KS}}(\mathbf{r})$ and $n(\mathbf{r})$ is achieved. The flowchart showing such a calculation can be seen on Figure 2. We start with an initial guess of the electron density, solve the Kohn-Sham equations and obtain a new density and we stop when these are sufficiently "similar". Each step in the self consistency loop brings with it numerical considerations, which we will now examine in more detail.

3.2.1 Initializing the electron density

Before any calculations are performed one must choose an initial electron density. In certain types of calculations the initial density guess is very important, for example in magnetic solids [11]. However, when it comes to atom ground state calculations the simplest way is often the best and that is to guess that the density is similar to that of the H atom

$$n_0(r) = \frac{1}{64\pi}\exp(-\frac{Z}{2}r), \quad \text{for which} \quad \int_0^\infty 4\pi r^2 n_0(r)\mathrm{d}r = Z \tag{32}$$

where Z is the number of electrons. For us this will suffice, but it is important to note that when it comes to solving more complex problems there exist semi-empirical methods for guessing the initial density, a popular approach used in quantum chemistry is the Extended Hückel Method [19].

3.2.2 Computing the Kohn-Sham potential

Once we have our initial density we need to calculate the Kohn-Sham potential, while this step is done in each iteration of the calculation it is not the most computationally intensive step, as we will see it boils down to solving an ordinary differential equation[8]. The Kohn-Sham is the sum of the external $V_{\mathrm{ext}}[n]$, Hartree $V_{\mathrm{h}}[n]$ and exchange-correlation $V_{\mathrm{xc}}[n]$ potentials. Calculating $V_{\mathrm{xc}}[n]$ and $V_{\mathrm{ext}}[r]$ poses no real problem as explicit form for the external potential for nucleus with charge Z is known,

$$V_{\mathrm{ext}}[r] = -\frac{Z}{r} \tag{33}$$

and explicit parametrizations of the exchange-correlation exist, these are discussed in more detail in appendix A. As both V_{ext} and V_{KS} diverge when $r \to 0$ some care needs to be taken. Usually, the point at $r = 0$ is omitted from calculations and the information at the origin is approximated using extrapolation from neighbouring points.

The Hartree potential

$$V_{\mathrm{h}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathrm{d}\mathbf{r}' \tag{34}$$

could be obtained by means of direct integration of the above expression. A much more common approach is to solve the Poisson equation that we obtain from Gauss' law

$$\nabla^2 V_{\mathrm{h}}(\mathbf{r}) = -4\pi n(\mathbf{r}) \tag{35}$$

in spherically symmetric situations one can use the substitution $U_{\mathrm{h}} = rV_{\mathrm{h}}$ to obtain the ODE

$$\frac{\mathrm{d}^2}{\mathrm{d}r^2} U_{\mathrm{h}} = -4\pi r n(r). \tag{36}$$

The boundary conditions are obtained from two observations:

1. Hartree potential at $r = 0$ is finite $\to U_{\mathrm{h}}(0) = 0$.
2. Expansion of (34) gives $V_{\mathrm{h}} \sim \frac{1}{r} \int n(\mathbf{r}')\mathrm{d}\mathbf{r}' \to U_{\mathrm{h}}(\infty) = \mathrm{Z}$

In practice, a maximum radius r_{max} has to be chosen to make the domain finite. We assume that electrons reside near the nucleus and as such $\int_0^{r_{\mathrm{max}}} n(r)\mathrm{d}r = Z$. The problem could be solved by the shooting method, but can be simplified into an initial value problem. Because we know the solution of the homogeneous equation $\frac{\mathrm{d}^2}{\mathrm{d}r^2} U_h^{hom} = 0 \to U_h^{hom} = \alpha r$, we only need to solve an initial value problem $U_h^{part}(0) = 0$, $\frac{\mathrm{d}}{\mathrm{d}r} U_h^{part}(0) = 1$ for the particular solution and fix the boundary conditions with the homogeneous solution.

$$U_{\mathrm{h}}(r) = U_{\mathrm{h}}^{\mathrm{part}}(r) - r \left(\frac{Z - U_{\mathrm{h}}^{\mathrm{part}}(r_{\mathrm{max}})}{r_{\mathrm{max}}} \right). \tag{37}$$

The solution is readily obtained with a numerical integration scheme. The most straightforward approach is to use a uniform radial grid with Numerov method. In DFT however, it is often beneficial to use grids that are denser near the origin [11]. Because electrons are located mostly near the nucleus this is where more accuracy is needed. A popular choice is a logarithmic grid [20], which can be defined as

$$r_i = -a \ln(1 - x_i^M), \quad x_i = \frac{2i-1}{2N}, \quad \text{for} \quad i = 1, \dots N \tag{38}$$

where m and a are free parameters that characterize the grid. A logarithmic grid has the disadvantage of extending the problem from $0 \leq r \leq \infty$ to $-\infty \leq r \leq \infty$ in practice this is dealt with a series expansion near the origin as detailed in [21].

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[8] In the non spherically-symmetric case the ODE becomes a partial differential equation

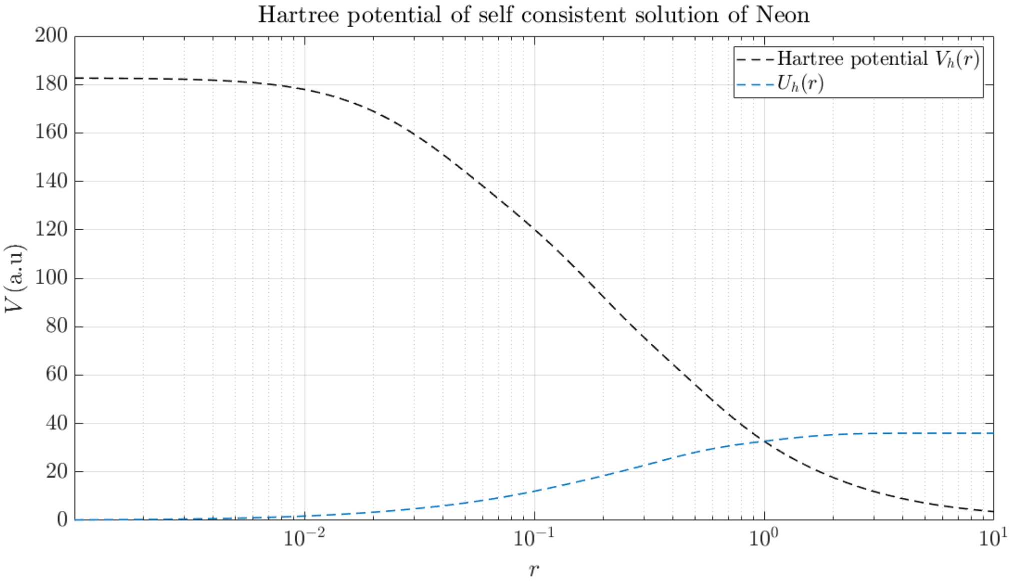

Figure 3. Hartree potentital of self consistent solution of Neon, calculated using an uniform grid with 10^4 points and Numerov integration, $r_{\max} = 10$.

3.2.3 Solving the Kohn-Sham auxiliary system

Having obtained the Kohn-Sham potential we can now solve the auxiliary system (28). This is the most computationally expensive step of the loop. Because we are solving for the ground state we are tasked with calculating enough lowest energy eigenfunctions to store all of the electrons in the systems, accounting for degeneracy of the state ε_{nl}

$$\text{degeneracy}(\varepsilon_{nl}) = 2(2l + 1) \tag{39}$$

We know the bound states satisfy $u_{nl}(0) = 0$ and are generally defined for $r \in [0, \infty)$. To numerically solve the problem we must restrict ourselves to a finite computational domain as we have done when computing the KS potential. The asymptotic behaviour of u_{nl} for $r \to \infty$ can be calculated and used to obtain values $u_{nl}(r_{\max})$ and $u_{nl}(r_{\max} - \Delta r)$, Δr is the discretization step. In our application we will use[9]

$$u_{nl}(r) \sim re^{-Zr}. \tag{40}$$

What remains is a boundary value problem that we will solve using a variant of the shooting method. We will be solving the initial value problem by integrating from $r_{\max}$ towards 0, this is numerically more stable than the other way around. We will not be changing the initial slope however, since we know it from (40). We will be changing the energy ε_{nl}, when we will use an eigenvalue the boundary condition at $r = 0$ will be satisfied. We will start the search for energy eigenvalues at some lower bound[10] ε_{min} and coarsely scan the region with step $\Delta\varepsilon$ until we find the root, then we use Brent's method to find the zero more accurately. This process is repeated with different values of n and l until enough states are obtained. Four states of Argon are presented on Figure 4, note that the orbitals are mostly localized to $r < 1$,

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[9] Inspired by the solution to Hydrogen atom.

[10] There is no general guideline for choosing the lower bound energy. An educated guess can be made from experimental data or simpler models. One such approach is to consider the energy of a single electron around a nucleus with charge Z.

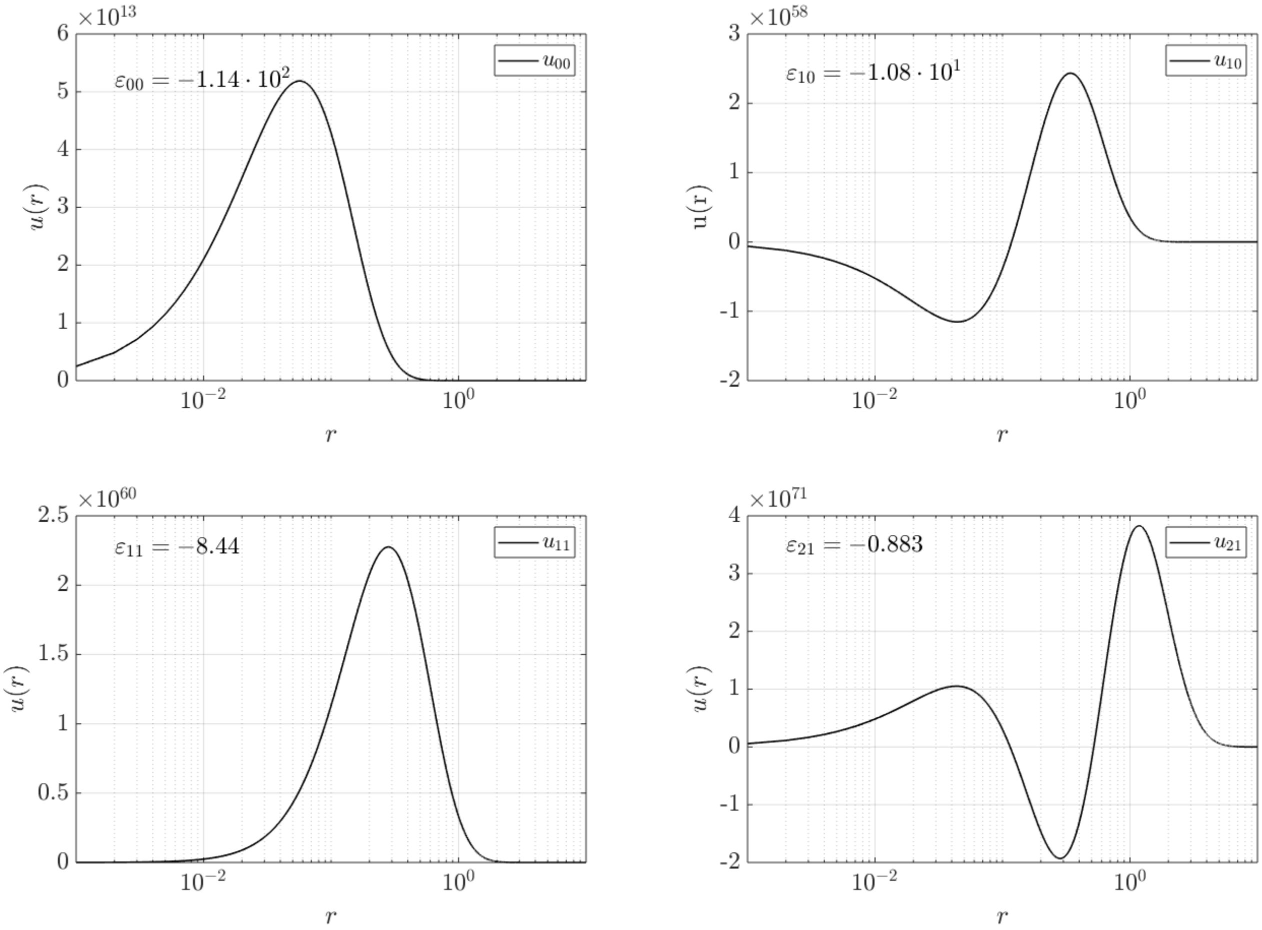

Figure 4. Four lowest energy orbitals of Argon, and their respective energy eigenvalues.

3.2.4 Calculating the total energy

Calculating the total energy boils down to performing the integral in (31) numerically. The equation can be rearranged slightly to obtain

$$E = \sum_{n,l}^{\text{occuppied}} 2(2l+1)\varepsilon_{nl} + \int_{o}^{r_{\max}} 4\pi r^2 n(r) \left[-\frac{1}{2}\frac{U_{\mathrm{h}}(r)}{r} + (\varepsilon_{nl} - V_{\mathrm{xc}}) \right] \mathrm{d}r, \tag{41}$$

The integrals are evaluated with standard numerical integration schemes without any issues. Once the ground state energies from two subsequent iterations are close enough the loop is terminated.

3.2.5 Mixing

In principle one can update either the potential V_{KS} or the density $n(r)$ each iteration, but the density is a clear choice, it is uniquely defined as opposed to the potential. We are left with the task of obtaining a new electron density n_{i+1}^{in} from the previous densities n_i^{in} and n_i^{out}. The simplest approach is to simply use the output density of the previous iteration

$$n_{i+1}^{\mathrm{in}} = n_i^{\mathrm{out}}, \tag{42}$$

this can cause large charge oscillations and is not used often in practical calculations [23]. Linear mixing is a more prevalent approach

$$n_{i+1}^{\mathrm{in}} = \alpha n_i^{\mathrm{out}} + (1-\alpha) n_i^{\mathrm{in}}. \tag{43}$$

It can be seen as crude version of the steepest descent for minimizing the energy and is the best choice in the absence of other information [11]. The choice of α greatly influences the convergence towards self-consistency. As a general rule, for “small enough” values of α the procedure is relatively safe, but the convergence is slow. The problem of choosing α has been studied in depth [25], but is beyond the scope of this article. In our calculations we will be using $\alpha = 0.3$.

Another popular approach is using Broyden’s method [24], which approximates the Jacobian inverse J^{-1} from past iterations and changes the density in an iteration in a direction orthogonal to all previous directions[11]. Consider the function

$$\mathbf{F}[n^{\text{in}}] = n^{\text{out}}, \tag{44}$$

self-consistency will be achieved when

$$\mathbf{F}[n^{\text{in}}] = n^{\text{in}}. \tag{45}$$

As such the problem of achieving self consistency can be reformulated as minimizing the norm of the residual $\mathbf{R}$

$$\mathbf{R}[n] = \mathbf{F}[n] - n. \tag{46}$$

Defining the Jacobian $\mathbf{J}$ as

$$\mathbf{J} = \frac{\delta \mathbf{R}}{\delta n} \tag{47}$$

one can then use the Newton-Ralphson method to minimize the residual by iterating

$$n_{i+1}^{\text{in}} = n_i^{\text{in}} + \mathbf{J}^{-1}(n_i^{\text{out}} - n_i^{\text{in}}). \tag{48}$$

Broyden found a way to effectively calculate the Jacobian and thus the method bears his name. The main advantages of this approach are speed and stability, one of the downsides is that one has to store the inverse of the Jacobian matrix, but this too can be avoided [24]. For implementation details see appendix of [11]. For the purposes of our implementation linear mixing will suffice.

4. Results

4.1 Closed shell atoms

The radial Schrödinger equation (28) is exact for closed-shell atoms, thus we expect good estimates of the ground state energy. Ground state electron densities for the first four noble gases are shown in Figure 5. When compared to experimantal values from [22], the errors range from around 2.5% for Helium to 0.6% for Argon.

4.2 Non spherically symmetric atoms

The radial Schrödinger equation (28) assumes spherical symmetry, but can be used for atoms that do not have a full outer shell. This is often done in practice due to ease of implementation and computational complexity. Nevertheless LDA in this form proves reasonably successful for atoms with open outer shells, as can be seen on Figure 6a.

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[11] This is a general characteristic of Krylov subspace methods.

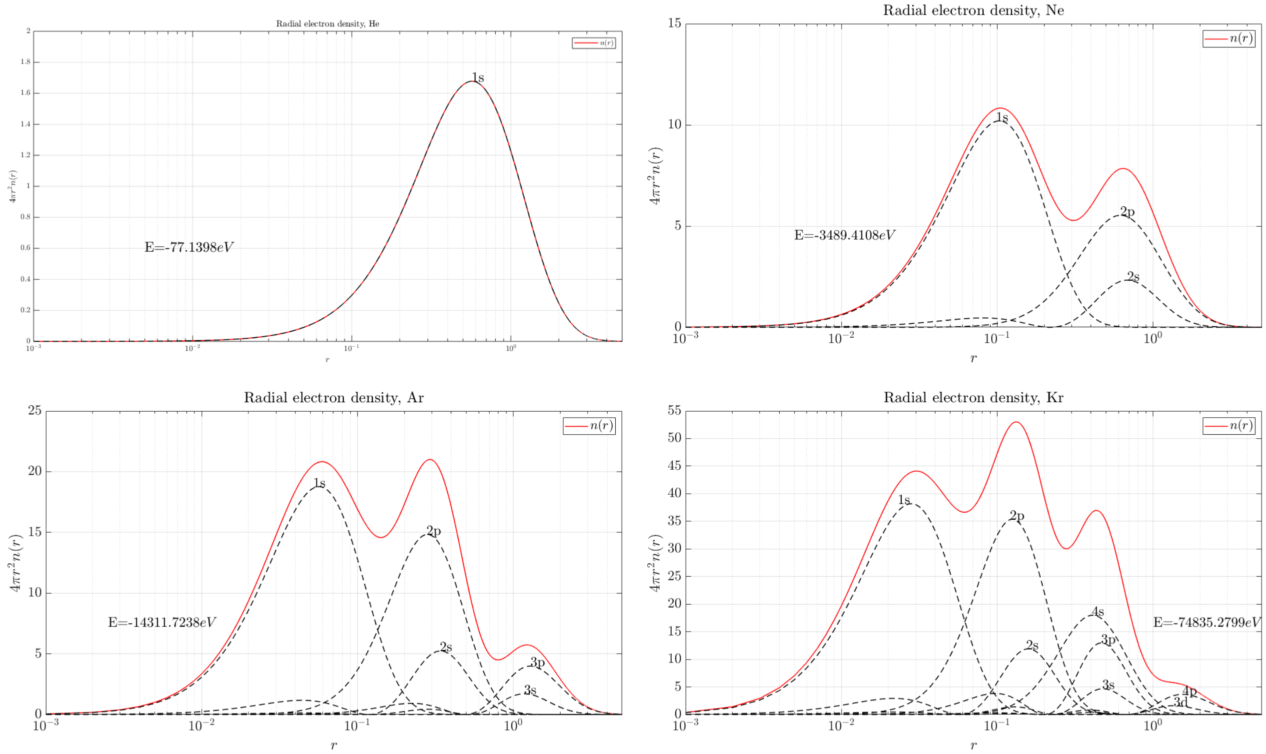
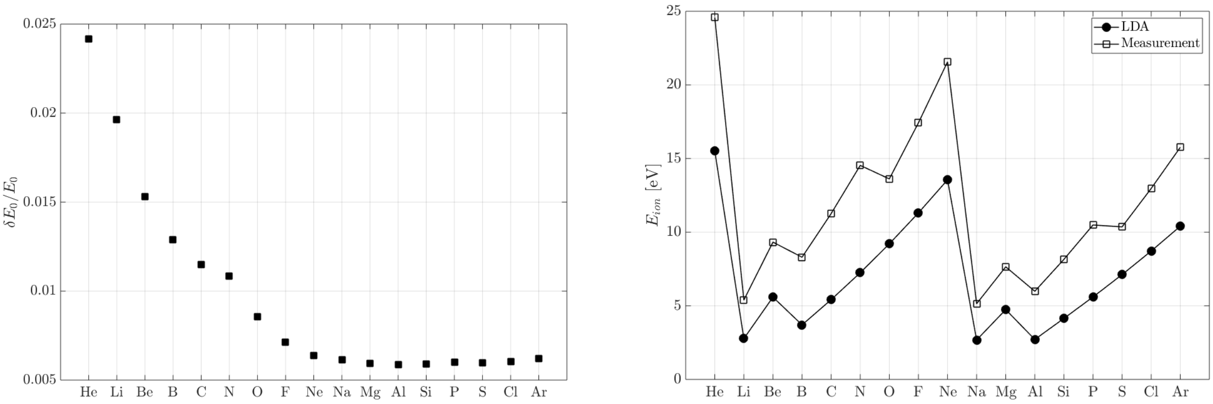


Figure 5. Radial electron density of the first four noble gases. The Kohn-Sham wave functions u_{nl} are named using standard subshell notation ($s \to p \to d \to f \ldots$) and are scaled according to their degeneracy i.e. the density of each state contains all electrons in that subshell. The calculations were performed using $N = 10^4$ points, $r_{\max} = 10$, Numerov integration on a regular grid and Vosko-Wilk-Nusair parametrization of the correlation potential [14].



(a) Relative error of the ground state energies calculated with LDA

(b) Ionisation energies

Figure 6. A comparison of the LDA approximation ($r_{\max} = 10, \Delta r = 0.001$) for atoms with experimental values. Experimental data obtained from [22]

While the eigenvalues ε_{nl} generally have no physical meaning, the eigen energy of the highest occupied Kohn-Sham orbital approximates the first (vertical) ionisation energy. This is stated by DFT-Koopmans' theorem, which is DFT's counterpart of the theorem that was originally formulated for closed-shell Hartree-Fock theory. Ionisation energy approximation can be seen on figure 6b. From the ionisation energies we observe another interesting characteristic of the spherically averaged calculation. Since atomic orbitals in s-shells are spherical no information is lost when spherical averaging. Hence our calculation correctly describes the decreases in ionisation energy from Be→B and Mg→Al. That is not the case with p-shells and that is why we do not obtain the decreases in ionisation energies from N→O and P→S.

4.3 Different Correlation functional parametrisations

As mentioned in 2.3there exist many parametrisations of the correlation functional. In our calculation we used one of the simplest variants, the spin restricted version of the Vosko-Wilk-Nusair. Table 1 shows a comparison between our calculation, two of its simplest improvements, the spin unrestricted calculation and the calculation corrected for self-interaction of orbitals SIC-LSDA by Perdew and Zunger [15].

Atomic ground state energies [eV]				
Atom	E^{LDA}	E^{LSDA}	$E^{SIC-LSDA}$	Experiment
H	-12.1	-13.0	-13.6	-13.6
He	-77.1	-77.1	-79.4	-79.0
Li	-199.6	-202.2	-199.8	-204.2
Be	-393.1	-393.0	-399.8	-399.1
B	-662.4	-662.5	-672.0	-670.8
N	-1470.1	-1472.7	-1488.9	-1485.3
F	-2626.5	-2696.6	-2720.7	-2713.5
Ne	-3489.4	-3488.9	-3517.6	-3508.1
Na	-4393.0	-4392.6	-4426.1	-4414.7
Mg	-5418.8	-5418.3	-5456.4	-5443.21
Al	-6566.5	-6566.0	-6608.8	-6594.0
P	-9250.4	-9251.1	-9303.7	-9285.1
Ar	-14311.7	-14310.5	-14378.3	-14354.6

Table 1. A comparison of ground state energy calculations with different methods. Our spin restricted calculation E^{LDA} is compared to a spin unrestricted approach E^{LSDA} as originally described in [14] and a self-interaction corrected functional $E^{SIC-LSDA}$. Data obtained from [15] .

As seen when accounting for self-interaction of orbitals one obtains much more accurate estimates of the ground state energies. But perhaps the most glaring improvement is in the estimates of ionisation energies. As seen in 6b the local density approximation systematically underestimates the ionisation energies by around 40%.

Ionisation energies [eV]				
Atom	$-\varepsilon^{LDA}$	$-\varepsilon^{LSDA}$	$-\varepsilon^{SIC-LSDA}$	I_1
H	6.4	7.3	13.6	13.6
He	15.5	15.5	25.8	24.6
Li	0.92	3.2	5.4	5.4
N	7.2	8.3	14.9	14.5
Na	2.7	3.1	5.1	5.1
P	5.6	6.3	10.0	10.5
Ar	10.4	10.4	15.8	15.8

Table 2. A comparison of first ionisation energy calculations with different methods. Data obtained from [15].

As can be seen in tables 1 and 2, the local density approximation provides good approximations of the ground state energies, but fails to do so for the first ionisation energies. The reason is the *self-interaction error* of an electron with itself in the exchange term. Accounting for self-interaction gives much better results, as can be seen in the $\varepsilon^{SIC-LSDA}$ column of table 2.

5. Conclusion

In the article, we discussed one of the most influential methods in computational quantum chemistry, density functional theory. We briefly presented the theoretical underpinnings of the method, the Hohenberg-Kohn theorems, and the Kohn-Sham ansatz. We focused on the numerical intricacies of the problem and the different ways one can approximate the Kohn-Sham functional. We implemented a simple variant of DFT, the local density approximation and used it to calculate the ground-state energies and ionization energies of different atoms. Furthermore, we compared the results to both experimentally obtained data and data obtained with improved numerical methods and showed that LDA is reasonably effective at obtaining ground state energies of atoms.

This article just barely scratches the surface when it comes to DFT, we have omitted the discussion on how to effectively design new functionals with desired properties or how to use DFT for excited states, molecules and solids. Neither have we mentioned extensions of DFT that allow studying dynamics of many-body systems. Nevertheless, LDA is a good starting point, and is sometimes even one of the steps in larger DFT computations. Moreover, it is relatively simple to implement, as opposed to its extensions. All of the computer code used to generate both the results and plots in this paper is available online.

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A Vosko-Wilk-Nusair parametrization of the correlation potential

As mentioned various parametrizations of the correlation functional exist. In the Vosko-Wilk-Nusair parametrization the correlation functional is expressed as

$$\begin{aligned}\varepsilon_{\mathrm{c}}(x) = \frac{A}{2}\bigg[\log\left(\frac{x^2}{X(x)}\right) + \frac{2b}{Q}\arctan\left(\frac{Q}{2x+b}\right) - \\ - \frac{bx_0}{X(x_0)}\left\{\log\left(\frac{(x-x_0)^2}{X(x)}\right) - \frac{2b+4x_0}{Q}\arctan\left(\frac{Q}{2x+b}\right)\right\}\bigg] \quad (49)\end{aligned}$$

where $x(n) = \sqrt{\left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}}$, $X(x) = x^2 + bx + c$, $Q = \sqrt{4c - b^2}$ and the parameters are $A = 0.0621814$, $x_0 = -0.10498$, $b = 3.72744$ and $c = 12.9352$. The potential is expressed as

$$V_{\mathrm{c}}(x) = \varepsilon_c - \frac{A}{6}\frac{c(x-x_0) - bx_0x}{X(x)(x-x_0)}. \quad (50)$$