# Assignment 6: Explaining the periodic table

## Introduction

In this report, an attempt is made to qualitatively understand general atomic systems by using a mean field approximation. The charge density resulting from the occupied orbitals of an atomic system can be written as

$$\rho(r,\theta,\varphi) = \sum_{n=1}^{N}\sum_{\ell=0}^{n-1}\sum_{m=-\ell}^{\ell} g_{n\ell m}\rho_{n\ell m}(r,\theta,\varphi) \tag{1}$$

where $g_{n\ell m}$ takes the value zero, one or two which is the number of electrons occupying the $(n,\ell,m)$ state, and $\rho_{n\ell m}$ is the charge density of an electron in the $(n,\ell,m)$ state:

$$\begin{aligned}\rho_{n\ell m}(r,\theta,\varphi) &= -e\left|\psi_{n\ell m}(r,\theta,\varphi)\right|^2 \\ &= -eR_{n\ell}^2(r)\left|Y_{\ell m}(\theta,\varphi)\right|^2\end{aligned} \tag{2}$$

where $R$ is the radial wave function and $Y$ are the spherical harmonics. We'll replace the spherical harmonic with its average

$$\begin{aligned}&\left|Y_{\ell m}(\theta,\varphi)\right|^2 \\ &\quad\to \frac{1}{4\pi}\int_{\theta=0}^{\pi}\int_{\varphi=0}^{2\pi}\left|Y_{\ell m}(\theta,\varphi)\right|^2 r^2\sin\theta \mathrm{d}\theta\mathrm{d}\varphi = \frac{1}{4\pi}\end{aligned} \tag{3}$$

so that $\rho_{n\ell m}\to -eR_{n\ell}^2/4\pi$. This enables us to write

$$\rho(r) = -\frac{e}{4\pi}\sum_{n=1}^{N}\sum_{\ell=0}^{n-1} g_{n\ell}R_{n\ell}^2(r) \tag{4}$$

where $g_{n\ell}$ is the number electrons being in a state with principal and azimuthal quantum number $(n,\ell)$ and $\rho(r)$ is to be understood as the approximation of $\rho(r,\theta,\varphi)$ in which we have averaged over the spherical harmonics.

The radial wavefunctions are solutions to

$$\begin{aligned}E_{n\ell}(rR_{n\ell}) &= -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\left(rR_{n\ell}\right)}{\mathrm{d}r^2} \\ &+ \left[\frac{\hbar^2\ell(\ell+1)}{2mr^2} - \frac{Ze^2}{4\pi\epsilon_0 r} - e\varphi_{ee}(r)\right]\left(rR_{n\ell}\right)\end{aligned} \tag{5}$$

where $P_{n\ell} = rR_{n\ell}$ is the reduced radial wavefunction and $\varphi_{ee}(r)$ is a yet unknown electric potential. It is decomposed into two parts

$$\varphi_{ee} = \varphi_{ee}^{dir} + \varphi_{ee}^{exch} \tag{6}$$

where the direct part is the solution to the Poisson equation

$$\frac{\mathrm{d}^2(r\varphi_{ee}^{dir}(r))}{\mathrm{d}r^2} + \frac{r\rho(r)}{\epsilon_0} = 0 \tag{7}$$

with boundary conditions that $r\varphi_{ee}^{dir}$ should vanish at the origin and that $r\varphi_{ee}^{dir}$ should approach $-Ze/4\pi\epsilon_0$ as $r\to\infty$. The exchange part is calculated with the formula

$$\varphi_{ee}^{exch}(r) = \frac{3e}{4\pi\epsilon_0}\left|\frac{3\rho(r)}{8\pi e}\right|^{1/3}. \tag{8}$$

To determine the right $\varphi_{ee}^{dir}$, the system was solved iteratively until it became self-consistent.

## Numerical implementation

The implementation can be summarized with the following steps:

1. Set $\varphi_{ee} = 0$.
2. Calculate $\rho(r)$ by solving (5) for the different $n$ and $\ell$ and calculating the sum in (4).
3. Use $\rho(r)$ to solve Poisson's equation (7) and obtain from it the potential $\varphi_{ee}^{dir}$.
4. Calculate the exchange potential $\varphi_{ee}^{exch}$ using equation (8) and set $\varphi_{ee} = \varphi_{ee}^{dir} + \varphi_{ee}^{exch}$.
5. Repeat from 2. until convergence of energies $E_{n\ell}$.

Atomic units were used (for more details, see end of report).

## Test on helium atom

For helium, the charge distribution takes the simple form

$$\rho(r) = -\frac{e}{4\pi}\cdot 2R_{10}^2(r). \tag{9}$$

Applying the steps above, the energy converges to the value $E_{10} = -0.76$ Hartree (see figure 1). The electric potential $\varphi_{ee}$ after six iterations is plotted in figure 2. To calculate the total energy, the following formula was used:

$$E_{tot} = -2E_{10} - \frac{1}{2}\int_0^{r_{max}} P_{10}^2(r)e\varphi_{ee}\mathrm{d}r \tag{10}$$

The integral above was calculated numerically and found to be equal to $-0.92$ which gies a total energy of $E_{tot} = -1.06$.

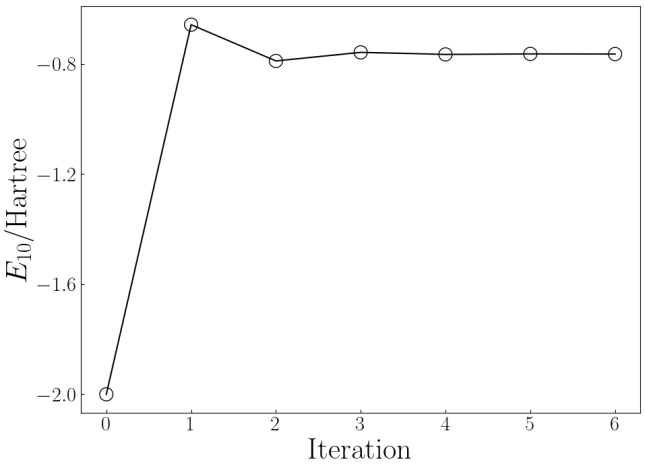



**Figure 1:** The energy $E_{10}$ as a function of iteration step for the helium atom. The energy converges to a value $E_{10} = -0.76$ Hartree.

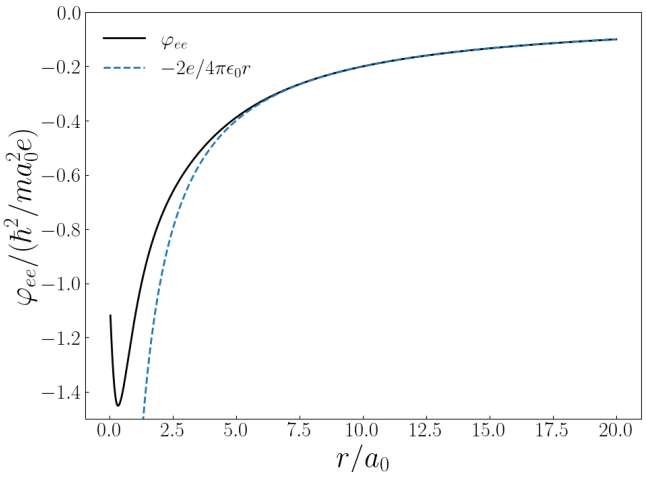
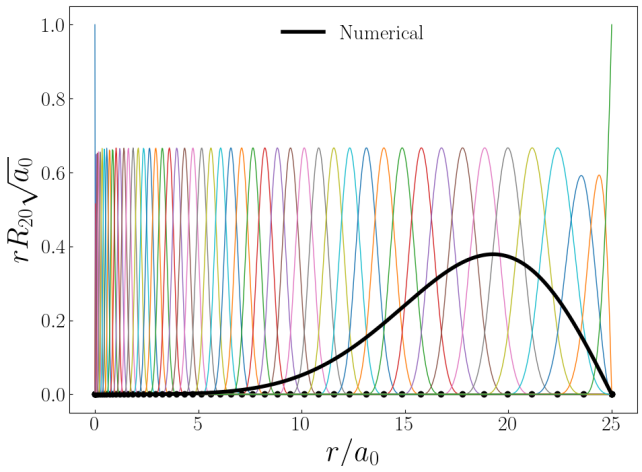



**Figure 2:** The electric potential $\varphi_{ee}$ for the helium atom after six iterations. The potential should converge to the Coulomb potential for large $r$.

## Other atoms

The method seemed to work fine for the Helium atom but I didn't get it to work for Neon. The problem was that when I was solving for $rR_{n\ell}$ with a non-zero $\varphi_{ee}$, I got unbound solutions in the iteration, like this one:




I haven't been able to locate the problem yet, but it could be a sign error somewhere or that I'm implementing the Poisson equation incorrectly.

## Units

Defining $u_{n\ell}$ to be the numerical solution to $rR_{n\ell}$ and making the substitutions

$$\xi = r/a_0, \quad E' = E/(\hbar^2/a_0^2 m), \quad u = a_0^{1/2} r R_{n\ell}, \tag{11}$$

the radial function becomes

$$-\frac{1}{2}u'' + \left[\frac{\ell(\ell+1)}{2\xi^2} - \frac{mea_0^2}{\hbar^2}(\varphi_C + \varphi_{ee})\right] u = E'u. \tag{12}$$

The direct part of $\varphi_{ee}$ is the solution to the Poisson equation:

$$(r\varphi_{ee}^{dir})'' + r\rho(r)/\epsilon_0 = 0. \tag{13}$$

Now, define

$$\hat{\varphi}_{ee}^{dir} = \frac{\varphi_{ee}^{dir}}{\hbar^2/(ma_0^2 e)} \tag{14}$$

and set $\sigma = \rho/B$ where $B$ is to be determined. Making these substituions, and setting $r = a_0\xi$, we get

$$(\xi\hat{\varphi}_{ee}^{dir})'' + \frac{4\pi a_0^3}{e} B\sigma(\xi)\xi = 0. \tag{15}$$

So if we let $B = e/(4\pi a_0^3)$, we get

$$(\xi\hat{\varphi}_{ee}^{dir})'' + \xi\sigma(\xi) = 0. \tag{16}$$

The Coulomb part is always the same,

$$\hat{\varphi}_C = \frac{\varphi_C}{\hbar^2/(ma_0^2 e)} = \frac{Z}{\xi}. \tag{17}$$