

## Assignment 6: Explain the Periodic Table

deadline Thursday May 5 2022

In this assignment you will combine the program you wrote in Assignment 5 (hydrogen atom) and in Assignment 4 (Poisson's equation) to get a qualitative picture of general atomic systems. For this we will set up a so-called mean-field potential that approximates the field created by all the electrons. In this way we reduce the true many-body problem to a set of one-particle problems. We will further assume that the average potential is spherically symmetric. Since all electrons move in the potential created by all the other electrons we need to solve this system iteratively until *self-consistence*.

We write the single particle three-dimensional wave function as

$$\Psi(r, \theta, \phi) = R_{n\ell}(r)Y_{\ell m}(\theta, \phi) = \frac{P_{n\ell}(r)}{r}Y_{\ell m}(\theta, \phi). \quad (1)$$

The separation into radial and angular wave functions is possible since we assume a central symmetric potential. The functions  $Y_{\ell m}(\theta, \phi)$  are Spherical Harmonics (see e.g. Arfken and Weber). The Hamiltonian to be used is the hydrogen-like one plus an (unknown) electronic potential  $V_{ee}(r)$

$$H = \frac{\mathbf{p}^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} + eV_{ee}(r) = -\frac{\hbar^2\nabla^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} + eV_{ee}(r). \quad (2)$$

As for the hydrogen atom the relation

$$\nabla^2 \left( \frac{P_{n\ell}(r)}{r} Y_{\ell m}(\theta, \phi) \right) = \frac{1}{r} \left( \frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{\hbar^2 r^2} \right) P_{n\ell}(r) Y_{\ell m}(\theta, \phi) \quad (3)$$

gives the equation for the radial part of the wave function:

$$\left( -\frac{\hbar^2}{2m_e} \frac{d^2}{dr^2} + \frac{\hbar^2 \ell(\ell+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} + eV_{ee}(r) \right) P_{n\ell}(r) = E_{n\ell} P_{n\ell}(r). \quad (4)$$

This is effectively a one-dimensional equation. The boundary conditions are that the functions,  $P_{n\ell}(r)$ , have to vanish in the origin, and all bound states go to zero when  $r \rightarrow \infty$ . If  $V_{ee}(r)$  was known the equation could be solved just as the pure hydrogen-like equation. The steps are thus; first the radial functions are expanded in B-splines (of order  $k$  and defined on a knot sequence with  $N_p$  knot points)

$$P_{n\ell}(r) = \sum_{i=2}^{N_p-k-1} c_i B_{i,k}(r), \quad (5)$$

where the first and last B-spline have been removed in accordance with the boundary conditions. Then Eq. 4 is expressed in matrix form, as a generalized eigenvalue problem

$$\mathbf{H}\mathbf{c} = E_{n\ell}\mathbf{B}\mathbf{c}. \quad (6)$$

The elements of the matrix  $\mathbf{H}$  are

$$H_{ij} = \int_0^{r_{max}} B_{j,k}(r) H B_{i,k}(r) dr = \int_0^{r_{max}} B_{j,k} \left( -\frac{\hbar^2}{2m_e} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r} + eV_{ee}(r) \right) B_{i,k}(r) dr \quad (7)$$

and those of  $\mathbf{B}$

$$B_{ij} = \int_0^{r_{max}} B_{j,k}(r) B_{i,k}(r) dr. \quad (8)$$

The B-splines are supposed to be defined on a knotsequence from zero to  $r_{max}$  where the latter should be large enough that it is a good approximation to assume the bound orbitals to be zero outside it. The only difference compared to the solution of the hydrogen Hamiltonian is the presence of the

electronic potential in Eq. 7.

### How to get the electronic potential?

Solve first Eq. 4 with  $V_{ee}(r) = 0$ . Calculate the electronic radial charge density (averaged over the angular parts) from the *occupied* orbitals  $P_{n\ell}$ :

$$\rho(r) = e \sum_i^{N_{\text{occ}}} \int \frac{1}{4\pi} \Psi_i^*(r, \theta, \phi) \Psi_i(r, \theta, \phi) d\Omega = e \sum_i^{N_{\text{occ}}} \left( \frac{P_{n_i \ell_i}(r)}{r} \right)^2 \frac{1}{4\pi} \int Y_{\ell_i m_i}^*(\theta, \phi) Y_{\ell_i m_i}(\theta, \phi) d\Omega = \frac{1}{4\pi} \sum_j^{\text{occ. orbitals}} e N_j \left( \frac{P_{n_j \ell_j}(r)}{r} \right)^2, \quad (9)$$

where the sum over  $i$  goes over all electrons in the atom, but that over  $j$  goes over all occupied orbitals (defined by  $n$  and  $\ell$ ) and  $N_j$  is the occupation number for each such sub-shell  $n_j \ell_j$  (with maximum occupation number  $2(2\ell_j + 1)$ , when the sub-shell is filled). Check that

$$\int \rho(r) dV = 4\pi \int \rho(r) r^2 dr = N_{\text{occ}} \quad (10)$$

before you proceed. Use then  $\rho(r)$  on the right-hand side of Poisson's equation (Assignment 4) to get the potential  $V_{ee}(r)$  created by the charge distribution. We will call this part  $V_{ee}^{\text{dir}}(r)$ , to distinguish it from the exchange part discussed below. Poisson's equation gives,

$$\nabla^2 V_{ee}^{\text{dir}}(r) = \frac{1}{r} \frac{\partial^2 \varphi(r)}{\partial r^2} = -\frac{4\pi \rho(r)}{4\pi \epsilon_0}, \quad (11)$$

and as in Assignment 4 you can expand  $\varphi$  in B-splines i.e.

$$V_{ee}^{\text{dir}}(r) = \frac{1}{r} \varphi(r) = \frac{1}{r} \sum_{m=2}^{N_{p'} - k_{\text{ord}}} \chi_m B_{m,k'}(r). \quad (12)$$

and obtain it through the collocation method. As before the boundary conditions are that  $\varphi$  is zero at  $r = 0$ , because of that the first B-spline is removed, and for large distances  $\varphi \rightarrow e N_{\text{occ}}$ . Note that you do not need to use the same B-spline set as in Eq. 5 above. When you have obtained  $V_{ee}^{\text{dir}}(r)$  you can solve Eq. 6 again. For this you have of course to calculate the contributions to the matrix elements in Eq. 7, i.e.

$$\int B_{j,k}(r) \left\{ \frac{1}{r} \sum_m \chi_m B_{m,k'}(r) \right\} B_{i,k}(r) dr \quad (13)$$

Add also the approximate exchange potential (see below),  $V_{ee}(r) = V_{ee}^{\text{dir}}(r) + V_{ee}^{\text{exch}}(r)$ . Repeat until convergence. Easiest is to check the convergence of the orbital energies  $E_{n\ell}$ . This is a so-called *self consistent* method.

### Pauli principle and exchange interaction

So far we have accounted for the classical potential from a charge distribution. For the electron-electron interaction we have thus not accounted for the Pauli principle. As a first approximation of the so called exchange interaction between the electrons you can use the approximate exchange potential suggested by Slater (Phys. Rev. 81, 385, 1951)

$$V_{ee}^{\text{exch}}(r) = -3 \left( \frac{3\rho(r)}{e8\pi} \right)^{1/3} \frac{e}{4\pi\epsilon_0}. \quad (14)$$

which you add to Eq. 4 giving:

$$\left( -\frac{\hbar^2}{2m_e} \frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{2m_e r^2} - \frac{Ze^2}{4\pi\epsilon_0 r} + eV_{ee}^{\text{dir}}(r) + eV_{ee}^{\text{exch}}(r) \right) P_{n\ell}(r) = E_{n\ell} P_{n\ell}(r). \quad (15)$$

The form of the exchange potential as  $\sim \rho^{1/3}$  is derived from a free-electron gas model. If you search on the internet you will find a few slightly different suggestions for the constants. Depending on the system studied different choices might be optimal. Again, add the contribution from the exchange potential to the matrix elements in Eq. 7, i.e.

$$\frac{e}{4\pi\epsilon_0} \int B_{j,k}(r) \left\{ -3 \left( \frac{3\rho(r)}{e8\pi} \right)^{1/3} \right\} B_{i,k}(r) dr. \quad (16)$$

Note that since the sum over occupied states in Eq. 9 goes over all occupied orbitals, each electron is allowed to interact with itself. In more refined approximations, like e.g. the Hartree-Fock approximation, the exchange interaction cancels this “self-interaction” exactly, but the approximate local exchange in Eq. 14 cancels it only approximately. This approximation is more severe for systems with few electrons. You should expect your model to work better for atoms with many electrons.

A final remark is that what we do in this assignment is a primitive version of *Density functional theory* (DFT). It can in fact be proven that the exact ground state energy of a quantum system is a *functional* of the charge density <http://journals.aps.org/pr/abstract/10.1103/PhysRev.140.A1133>., although the form of this functional is not known. The article above is cited over 25 000 times and the method was awarded the Nobel price in Chemistry 1998. The exchange potential is a first approximation of the so called exchange-correlation potential. Modern Quantum Chemistry uses refined version of it, depending e.g. also of the gradient of the charge density, to address large molecules. It is worth noting that the approach works better for large systems with a lot of electrons and thus atoms is in fact quite a hard test.

### Convergence

When using iterative schemes a common problem is oscillations; the system changes too much and then changes back - also too much in the next iteration. This is like when the shower is too cold - one increases the hot water a lot - and then it gets too hot. A way to handle this is to slow down the changes. In every iteration you get a new  $V_{ee}^{new}(r)$ , but instead of using it directly you use a mixture of it and the potential from the last iterations

$$V_{ee}^{new}(r) \Rightarrow (1 - \eta)V_{ee}^{new}(r) + \eta V_{ee}^{old}(r), \quad (17)$$

where  $0 < \eta < 1$ , a typical value can perhaps be  $\eta = 0.4$  Before you start the new iteration you redefine  $V_{ee}^{old}(r)$

$$V_{ee}^{old}(r) \Rightarrow V_{ee}^{new}(r) \quad (18)$$

Try this if you have problems with the convergence (which you will most likely have).

### What to investigate?

Use the method to calculate the ionization energy of different elements. You should not expect to reproduce the experimental values ( find them here <http://www.nist.gov/pml/data/asd.cfm> ), but you should be able to explain the large binding energies in the rare gases, and the small binding energies in the alkalis. You should also be able to see the order in which the orbitals are filled. Try for example potassium; the first 18 electrons are placed like in argon, but should the nineteenth electron be placed in  $n = 3 \ell = 2$  or  $n = 4 \ell = 0$ ? Do you remember Hund’s rule? You do not really need them since your program should be able to give an answer. Does the conclusion hold if you try a potassium-like ion (higher Z but still 19 electrons)?

### How to calculate the ionization energy

When you perform a calculation as above you find an *orbital energy* for each quantum state  $n\ell$ . In fact the orbital energy gives a first rough estimate of the binding energy. But what you really want is the difference in total energy,  $\Delta_{\text{ion}} = E_{\text{atom}} - E_{\text{ion}}$ . It might be tempting to just add the orbital energies to get the total energy, but then you would double count since the energy of orbital  $a$  includes

the interaction with orbital  $b$ , and that of  $b$  includes the interaction with  $a$ . Adding them obviously double counts the interaction. Instead you calculate the total energy as

$$E_{total} = \sum_i^{N_{occ}} \left\{ E_{nl}^i - \frac{1}{2} \int P_{nl}^i(r) V_{ee}(r) P_{nl}^i(r) dr \right\}. \quad (19)$$

If you have saved the matrix with the elements in Eq. 13 and Eq. 16 this easy to calculate.

## Units

For calculations on atomic systems it is practical to write programs in Hartree units. The base units are then:

$$\begin{aligned} \text{lenght : } a_0 &= \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} \approx 0.5 \cdot 10^{-10} \text{ m} \\ \text{mass} &= m_e \approx 9.1 \cdot 10^{-31} \text{ kg} \\ \text{energy : 1Hartree} &= \frac{m_e e^4}{(4\pi\epsilon_0)^2 \hbar^2} = \frac{\hbar^2}{a_0^2 m_e} \approx 27.211 \text{ eV} \\ \text{time} &= \frac{(4\pi\epsilon_0)^2 \hbar^3}{m_e e^4} = \frac{a_0^2 m_e}{\hbar} \approx 2.42 \cdot 10^{-17} \text{ s}. \end{aligned}$$

The energy unit is twice the binding energy in the ground state of hydrogen. The time unit is the classical orbiting time for a particle with the kinetic energy of the ground state electron in an orbit with radius  $a_0$ . With these units the natural constants is not needed in the calculation itself, but you can of course chose to display results (for example energies) in some other unit which you feel more comfortable with. If you define a dimensionless variable  $z = r/a_0$  you can rewrite Eq.4 as a dimensionless equation with (dimensionless) eigenvalues

$$E_{nl} \frac{a_0^2 m_e}{\hbar^2}. \quad (20)$$

## An example

Check your method on helium and neon. In helium both electrons occupy the  $1s$  state and the hydrogen-like solution will give an orbital energy of  $-2$  Hartree. After the procedure above you should have an orbital energy of around  $-0.74$  Hartree and a total energy of around  $-2.70$  Hartree ( and thus an ionization energy of  $\sim 0.70$  Hartree). The total energy is calculated as  $2 \times (-0.74) - 2 \times (-1.23)/2$  a.u. Where 1.23 is the expectation value of the electronic potential. We divide with two as indicated in Eq. 19 and multiply with two because there are two  $1s$ -electrons. One way to understand that this is approximately correct is to note that the electronic potential changes the orbital energy with 1.26 a.u. (it goes from  $-2$  a.u. without electron-electron interaction to  $\sim 0.74$ ), thus the expectation value of the electronic potential should be more or less that. You might need around 30 iterations for convergence.

In neon you will start with orbital energies of  $-50.0$  Hartree ( the  $1s$  orbital), and  $-12.5$  Hartree (the  $n = 2$  orbitals). After convergence you should have (approximately)  $-31.4$  ( $1s$ ),  $-1.53$  ( $2s$ ), and  $-0.68$  ( $2p$ ) Hartree. The expectation value of the electronic potential is  $\langle V_{ee} \rangle \sim 2 \times 9.25$  a.u. for  $1s$  ( and the contribution to the total energy thus:  $-[(2 \times 9.25)/2] \times 2$ , according to Eq. 19). For  $2s$  the expectation value is  $\sim 2 \times 4.85$  a.u., and for  $2p \sim 2 \times 4.86$  a.u. For the ion all the numbers change slightly.

This can be summarized like this:

Ne	Orbital energy (Hartree)	$\langle -V_{ee}/2 \rangle$ (Hartree)	occupation number	Total (Hartree)
1s	-31.43	-9.25	2	-81.36
2s	-1.53	-4.85	2	-12.77
2p	-0.68	-4.86	6	-33.26
Sum				-127.39

Ne <sup>+</sup>	Orbital energy (Hartree)	$\langle -V_{ee}/2 \rangle$ (Hartree)	occupation number	Total (Hartree)
1s	-32.35	-8.79	2	-82.28
2s	-2.29	-4.56	2	-13.72
2p	-1.43	-4.69	5	-30.64
Sum				-126.64

The electron probability density in Neon

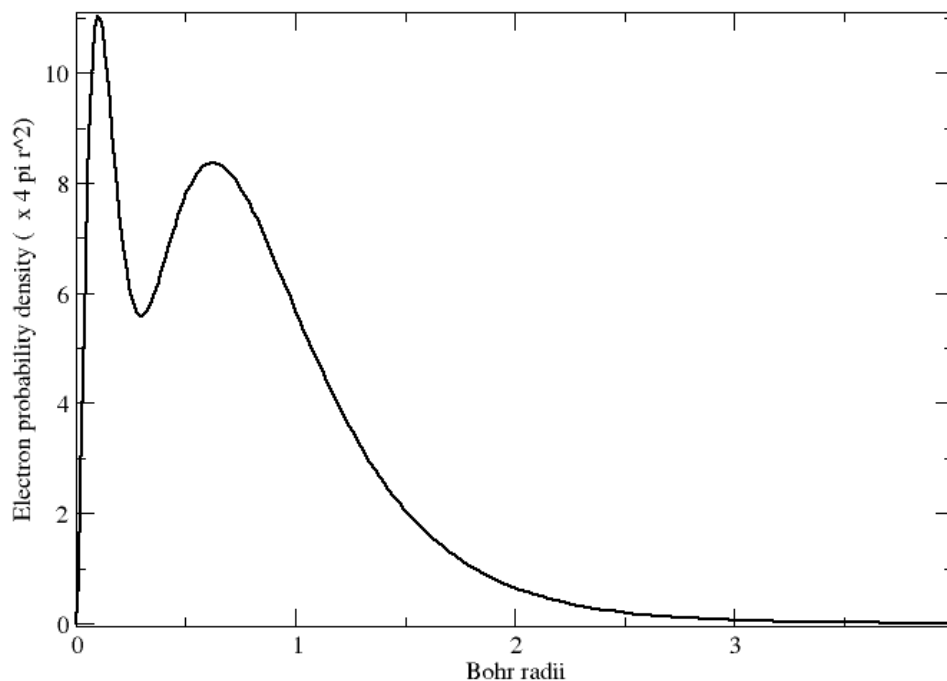


Figure 1: The plot shows  $4\pi r^2 \rho(r)$  where  $\rho(r)$  is the radial electron probability density in Neon obtained with Slater exchange. The area under the curve gives the charge of ten electrons.