

# PHYS 1600 Final Project

## Ionization energies of atoms using the Hartree method

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This project uses the Hartree method to find approximate solutions for the Schrödinger equation in multi-electron atoms and ions. By taking the difference between ground state energies of successively ionized species, we get estimates for the ionization energies of each element. The results are compared with available experimental or extrapolated data.

### I. INTRODUCTION

Ionization energy is the minimum amount of energy required to remove the most loosely held electron from a given species. The ionization energy can give insight into the chemical properties of an element since it is related to the stability of chemical bonds that an atom can form. The study of ionization energy is also useful in plasma physics, which deals with ionized gases.

Originally, ionization energy was studied by passing emitted electrons through an electrostatic potential. Because of this, the term ionization potential was used. The two names are now used interchangeably. Today, experimentalists usually use resonance ionization spectroscopy, in which ionization is reached through an intermediate excited state by exposing the atom to photons that are resonant with this state. High-precision results for ionization energies of different atoms have been obtained using laser spectroscopy[1].

The Hartree-Fock method is used in computational physics and chemistry to approximately solve for the stationary states of multi-electron species. It has been widely used to study ionization energies and atomic energy levels in general. In its many variants, it has produced results that agree very well with experiment as well as some useful semiempirical results[2, 3]. This project is based on the original method developed by Douglas Hartree in 1927.

### II. METHOD

The Hartree method assumes that the  $n$ -electron wavefunction is equal to the product of the individual wavefunctions:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \dots \psi_n(\mathbf{r}_n) \quad (1)$$

Each individual electron's wavefunction is solved for by assuming a mean field determined by the probability distribution of every other electron superimposed over the field of the nucleus. Assuming each wavefunction is spherically symmetrical (which can be done if none of the electrons has orbital angular momentum), the angular part  $|Y_j(\theta, \phi)|^2$  in the probability density  $|\psi_j(\mathbf{r})|^2 = |R_j(r)|^2|Y_j(\theta, \phi)|^2$  reduces to just a normal-

ization factor and we get a charge density

$$\rho_j(\mathbf{r}) = -\frac{|R_j(r)|^2}{4\pi}e = -\frac{|u_j(r)|^2}{4\pi r^2}e \quad (2)$$

associated with electron  $j$ .  $u_j(r) = rR_j(r)$  has been introduced for reasons that will be explained. Using Gauss's Law, this means the mean field potential experienced by electron  $i$  is

$$V_i(\mathbf{r}) = -\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{e^2}{4\pi\epsilon_0} \sum_{j \neq i} \left( \int_0^r \frac{|u_j(r')|^2}{r'} dr' + \int_r^\infty \frac{|u_j(r')|^2}{r'} dr' \right) \quad (3)$$

The two integral expressions correspond to the potential due to the charge distribution within radius  $r$  and outside  $r$  respectively.

The reason for introducing  $u(r)$  is that the time-independent Schrödinger equation for  $u_i$  takes the same form as the 1D Schrödinger equation[4]:

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2mr^2} + V_i(r) \right] u_i(r) = E_i u_i(r) \quad (4)$$

The goal of the method is to find  $u_1(r), u_2(r), \dots, u_n(r)$  such that the resulting  $V_i(r)$  are self-consistent, i.e. Eq. 4 is satisfied by the same  $u_i(r)$ .

To solve this problem computationally, initial guesses are made for each  $u_i$ , and the integrals in Eq. 3 are evaluated to give each  $V_i$ . An ODE solver is then used to solve Eq. 4 and get a new set of corrected bound states and energies. The corresponding  $u_i$  are again used to calculate  $V_i$ . This process is continued iteratively until the energies  $E_i$  do not change by more than a small threshold. Once this happens, the potential is assumed to have converged sufficiently and is taken as self-consistent.

The Hartree wave function for the atom is then given by Eq. 1. It may seem reasonable to calculate the total energy as the sum of all  $E_i$  obtained from Eq. 4. This is incorrect because it double-counts the effect of repulsion between each pair of electrons. A simple way to avoid double-counting in the individual electron energies is to subtract the expected value of the second integral term (the integral from  $r$  to  $\infty$ ) in Eq. 3. This means for calculating the energy of every electron, we only include repulsion by electrons that are closer to the origin. The interaction with a particular electron further from the origin is incorporated into that electron's energy term. Once this correction is made to each electron's energy,

they can be added up to give the total energy of the atom or ion. The ionization energy is given by the difference in total energy between the ground states of the ionized species and the species before ionization.

The implementation for this project[5] initializes each  $u_i$  to zero. `scipy.integrate.odeint` is used to solve Eq. 4. In the first iteration, the probability density of all electrons is zero and so  $V_i(\mathbf{r}) = -Ze^2/4\pi\epsilon_0 r$ . This means the solutions of Eq. 4 are simply the bound states of Hydrogen-like species. Although these wavefunctions can be solved for exactly, starting with the solution of the Hydrogen atom was a useful way to verify the accuracy of the method.

To evaluate the new  $V_i(r)$  once the  $u_i$  are no longer zero, cumulative integrals of  $|u_i(r)|^2$  and  $|u_i(r)|^2/r$  are needed (Eq. 3). The solver `integrate.odeint` only gives the value of  $u_i(r)$  at a discrete set of points. But when solving for the next batch of  $u_i$ , `integrate.odeint` requires as input a function describing the Schrödinger equation for arbitrary  $r$ . So an estimate of  $V_i(r)$  is needed for continuously varying  $r$ . To achieve this, `scipy.integrate.cumulative_trapezoid` was used to calculate the cumulative integrals at all points where  $u_i$  was evaluated by the solver. For  $r$  in between these points, linear interpolation was used. Linear interpolation introduces errors of order  $h^2$  (for step size  $h$ ). This justifies the use of the trapezoidal rule rather than Simpson's rule or any other method of integration with error smaller than  $h^2$ , since the error would still be dominated by the  $h^2$  term.

The Pauli Exclusion Principle is also an important consideration. The Hartree method itself does not impose the general condition that the overall wavefunction be antisymmetric. But the Pauli principle can be respected by treating the electrons differently based on their quantum numbers. Two electrons in the same orbital must share all the same quantum numbers except spin, and there are only two possible values for the spin of an electron. So to satisfy the Pauli principle, at most two electrons (assumed to have opposite spin) should be allowed to share the same  $u_i$ .

Finally, since Eq. 4 is an eigenvalue equation, the shooting method was used to find values of  $E_i$  that satisfy the condition  $u_i(r) = 0$  at the origin. This is a necessary condition for the wave function to be normalizable[4]. In each case, the smallest allowed value of  $E_i$  was chosen to get the ground state of the species. If none of the  $E_i$  changed by more than  $10^{-7}$  at a given iteration, convergence was taken to be achieved.

### III. RESULTS AND DISCUSSION

Fig. 1 shows the obtained ground-state  $u(r)$  for each electron in the atoms of interest: those of the first four elements. Because the method used requires the potential to be spherically symmetric, it cannot be applied to heavier atoms which have electrons of non-zero orbital

angular momentum. The figure shows the energy associated with each  $u(r)$ . As mentioned, each  $u(r)$  is available to at most two electrons. Fig. 2 shows the same results for some ionized species.

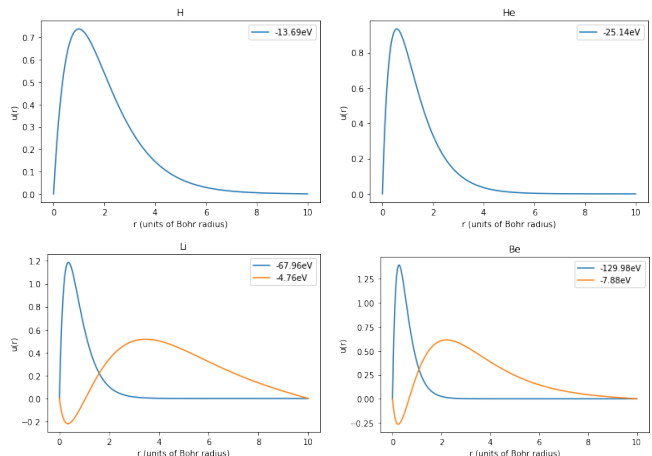


FIG. 1.  $u(r)$  and associated energies for electrons in atoms of the first four elements. The unit length is the Bohr radius=52.9pm

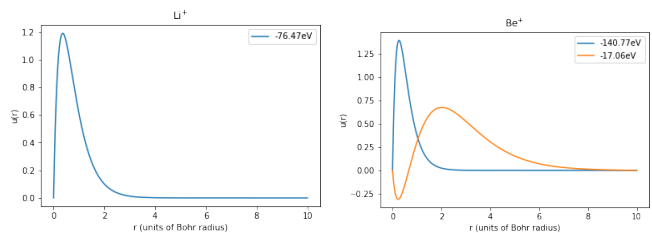


FIG. 2.  $u(r)$  and associated electron energies for some of the ions studied

To calculate the total energy, the correction term discussed previously was subtracted from each electron's energy to avoid double-counting. The change in the total energy when the number of electrons is reduced by one

Element and order	Result	Reference value[6]
H I	13.69eV	13.60eV
He I	23.60eV	24.59eV
He II	54.77eV	54.42eV
Li I	4.75eV	5.39eV
Li II	74.94eV	75.64eV
Li III	123.23eV	122.45eV
Be I	7.53eV	9.32eV
Be II	17.05eV	18.21eV
Be III	153.66eV	153.90eV
Be IV	219.08eV	217.72eV

TABLE I. Successive ionization energies of the first four elements

then gives the ionization energy of a species. Table I shows the successive ionization energies obtained using this method. The results are compared with reference values[6], some of which are experimental and some are semiempirical calculations.

The expected numerical error in  $V_i(r)$  with a step size of  $h = 0.001 \times (\text{Bohr Radius})$  is of the order of  $3 \times 10^{-5} \text{ eV}$ . The difference between the result obtained and the reference values is outside this range for all the species. But with a few exceptions, the agreement is still reasonable and the successive ionization energies show the correct trend. The results are also able to capture some of the chemical properties of these elements. For example, Helium has the highest first ionization energy, which indicates its inertness. Sharp increases in higher order ionization energies also suggest the favorability of  $\text{Li}^+$  and  $\text{Be}^{2+}$  compared to  $\text{Li}^{2+}$  and  $\text{Be}^{3+}$ , which is consistent with the chemical valencies of these two elements.

For a given element, the deviations from the reference values were largest for the first ionization energy and showed a generally decreasing trend with higher orders of ionization. This means the accuracy of the calculated energies worsens with increasing number of electrons, which is to be expected. By making the assumption that the atomic wavefunction is a Hartree product (Eq. 1), the method ignores exchange interactions between electrons, which become more significant as the number of electrons and overlap of their wavefunctions increases. Also, relativistic effects like the spin-orbit and spin-spin interactions were ignored, but these would have a very small effect on the ionization energies. Judging from the scale of the errors recorded, they can likely be attributed to the lack of exchange energy terms, along with some numerical error.

Some difficulty was encountered in enforcing the Pauli Exclusion Principle. Because of the two possible values of the spin, as mentioned earlier, both the electrons in Helium can share the same orbital. In fact, because of this symmetry in Helium, only a single wavefunction needs to be solved for in each iteration. For Lithium and Beryllium, the situation is more complicated. For the third electron, it had to be determined whether the eigenstate that should be accepted should be the one with the lowest possible energy or the second-lowest. The potential experienced by this electron must be different from that of the other two. This is particularly clear if the wavefunctions were initialized to the eigenstates of Hydrogen,

putting this electron in the  $2s$  orbital and the others in the  $1s$  orbital. But on trying the method with this initialization and the rootfinder configured to find the lowest energy available for the third electron, it was found that all three electrons converge to the same state, contradicting the Pauli principle. This suggests that putting the third electron in the ground state of the mean field potential does not give a stable solution (at least not one that satisfies the Pauli principle). So for the third electron, the rootfinder was set to find the first excited state instead, which obviously did not converge to a solution with all three electrons in the same state.

#### IV. CONCLUSION

This project shows that the basic Hartree method is reasonably accurate for atoms of the first four elements. The calculated ionization energies give some explanation for Helium's inertness as a noble gas, and Lithium and Beryllium's metallic nature. The radial wavefunctions shown in Figs. 1 and 2 also contain information about the size of atoms and ions, the relative size of shells and the location of nodes. These properties were not directly related to the goal of finding ionization energies but may have other interesting interpretations.

The Hartree method has been superseded by the Hartree-Fock method, in which the solution is given by combining single-electron wavefunctions using a so-called Slater determinant rather than the Hartree product. This enforces the antisymmetry of the wavefunction and gives a more accurate picture including exchange interactions. An obvious next step to improve the accuracy of this project would be to implement the Hartree-Fock method.

Another shortcoming of the particular implementation used is the high amount of numerical error. To simplify the computation, the trapezoidal rule was used to evaluate all necessary integrals and linear interpolation was used to estimate functions at points where they were not explicitly calculated. This fixes the numerical error to be proportional to the square of the step size. In the future, the code could be improved to use more accurate integration methods, while still being able to evaluate the potential at as many points as required by the ODE solver.

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