

Radial correlation in two-electron atoms

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The purpose of this work is to study the non-relativistic ground-state energy of 2-electron atoms and ions by means of variational methods. We incorporate radial correlation effects considering an open-shell wave function with different spatial orbitals. First, the corresponding analytical expressions for the energy of the system as a function of the variational parameters must be deduced. Then, the energy is minimized following two methods. The results for various values of Z are compared to more sophisticated calculations. Lastly, the magnetic susceptibility and the atomic form factor for these systems, introducing radial correlation, are considered.

I. INTRODUCTION

Given their simplicity, hydrogen atoms and hydrogen-like ions are systems with an exact solution. These systems have been widely covered over the years by physicists. However, for the helium atom and other two-electron ions there is no exact solution and, consequently, they have been a topic of high interest for many years.

The understanding of these systems has been decisive in a variety of fields, such as astrophysics. For example, studying the case for $Z = 1$, that is, the negative hydrogen ion. It plays an important role in the Sun's surface, being crucial to understand its emission and absorption properties [1]. Negative hydrogen also appears to be key in other processes, for instance, for upcoming nuclear fusion machinery [2].

Different methods have been considered in order to obtain a better analytical approximation to the exact energy of 2-electron atoms. Perhaps one of the most well-known is the Hartree–Fock method. Instead of using hydrogen-like orbitals with an effective charge, it determines its functional form with the variational method. Doing so gives an improvement of the energy with respect to the simple variational method, nonetheless, it fails to consider possible correlation effects.

The aim of this paper is to incorporate radial correlation in our calculations. This has been done before in quite a few publications, such as in the works of Eckart [3] or those of Shull and Löwdin [4], with very satisfactory results.

There are many ways to introduce radial correlation into the wave function, but it is not clear for all them what interpretation each term has. The wave function adopted here introduces correlation by simply considering an open-shell wave function with different spatial orbitals, using exponential functions as the orbitals.

Hartree atomic units ($\hbar = e = m_e = 1$) are used throughout this report.

II. THEORETICAL CONSIDERATIONS

In this first section we give a concise theoretical background of the various topics we will be discussing in this work. The results for each module shall be expected in the following section, as well as a brief discussion alongside them.

A. Ground state for two-electron atoms and ions

The non-relativistic electrostatic Hamiltonian for helium-like atoms is given by

$$\mathcal{H} = -\frac{1}{2} \nabla_{\mathbf{r}_1}^2 - \frac{1}{2} \nabla_{\mathbf{r}_2}^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}, \quad (1)$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and Z is the atomic number. The first two terms are the kinetic energy contribution, the following two correspond to the electron-nucleus potential and the last one introduces the electron-electron repulsion.

Since the Hamiltonian does not depend on spin, the wave function can be factorized into spatial and spin functions, where the spin function is appropriately antisymmetrical, $\chi_{0,0}(1, 2)$. We shall focus on the former.

First we will review the simple variational method with one parameter. This method proposes that each electron partially screens the nuclear charge Z , thus we can assume that each electron “sees” an effective nuclear charge $Z_{\text{eff}} < Z$. For instance, if we take as a trial wave function a Slater determinant with analytical hydrogenic orbitals and compute all the matrix elements, we get that the condition of minimum energy is satisfied with $Z_{\text{eff}} = Z - \frac{5}{16}$. We will compare the success of this result with others methods in the following sections.

In the present work, as a trial spatial wave function for these systems we use [1]

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{N} \frac{1}{4\pi} (e^{-ar_1} e^{-br_2} + e^{-br_1} e^{-ar_2}), \quad (2)$$

where \mathcal{N} is the normalization constant whereas a and b are the parameters we want to determine using the variational method. The election of this particular functional

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form arises from the requirement to have a different spatial orbital for each electron, labelling the nuclear charge seen by each of them with a and b , thus breaking the symmetry between them and introducing radial correlation explicitly.

To obtain the matrix elements of \mathcal{H} some integrals need to be solved, in particular the kinetic energy T , the electron-nucleus potential V_{en} and the electron repulsion potential V_{ee} that result in the expectation value of the Hamiltonian

$$E(a, b) = \langle \Psi | \mathcal{H} | \Psi \rangle = T + V_{\text{en}} + V_{\text{ee}}. \quad (3)$$

B. Minimization with two parameters

The variational energy E_{min} is given by the minimization of $E(a, b)$. Minimizing this expression the usual way results in a non-linear system of two equations that cannot be solved analytically, and a numerical resolution is needed. The use of any standard minimization algorithm is enough to obtain the best minimum. We have used a generic two-dimensional simplex subroutine written in the programming language C [5], giving it a precision of 10^{-15} and letting it run for a maximum of 10^6 iterations. It is worth noting that this type of algorithm heavily relies on the initial value given to it.

C. Minimization with one parameter

The minimization of $E(a, b)$ can be also done employing a scaling method and the virial theorem. For instance, for our wave function in Eq. (2) we can set

$$a = \eta(1 + \nu) \quad \text{and} \quad b = \eta(1 - \nu), \quad (4)$$

where η can be referred to as “scale factor” [2], as it appears when the distance variables \mathbf{r}_1 and \mathbf{r}_2 are transferred to a new scale by being rewritten as $\eta\mathbf{r}_1$ and $\eta\mathbf{r}_2$, while ν can be referred as the “splitting factor” since if we take $\nu = 0$ Eq. (2) transforms into a doubly-occupied orbital, but when $\nu \neq 0$ the orbitals are different and each of them has only one electron.

To obtain the minimum of the ground-state energy, we must note that the kinetic and potential energies follow these properties [6] regarding the scale factor η : $V(\eta) = \eta V(1)$ and $T(\eta) = \eta^2 T(1)$, where $T(1)$ and $V(1)$ are the matrix elements of the kinetic energy and potential energy operators setting $\eta = 1$ in our trial wave function, Eq. (2). Then, the expression for the ground state energy is

$$E(\eta) = \eta V(1) + \eta^2 T(1) \quad (5)$$

which minimized with respect to η yields

$$\eta_{\text{min}} = -\frac{V(1)}{2T(1)} \quad \text{and} \quad E_{\text{min}} = -\frac{V^2(1)}{4T(1)}. \quad (6)$$

Once $T(1)$ and $V(1)$ are computed analytically by evaluating two quite straight-forwarded integrals, we can substitute them in the expression for E_{min} , Eq. (6), and then minimize it with respect to ν using any standard method. We have used a one-dimensional simplex algorithm in C. The scale factor is then found through the expression for η_{min} .

D. Magnetic susceptibility

The magnetic susceptibility χ_{m} is a measure of how much a material will become magnetized in an applied magnetic field. Whether χ_{m} is positive or negative will classify this material into two categories: if the material responds with an alignment with the magnetic field, that is, $\chi_{\text{m}} > 0$, it is called paramagnetic. Otherwise, if it responds with an alignment against the magnetic field, $\chi_{\text{m}} < 0$, it is diamagnetic.

The expression for the magnetic susceptibility is

$$\chi_{\text{m}} = -\frac{N_{\text{A}} r_{\text{e}}}{6} N \overline{r^2}, \quad (7)$$

where $N_{\text{A}} = 6.022\,140\,76 \times 10^{23} \text{ mol}^{-1}$ (Avogadro constant), $r_{\text{e}} = 2.817\,940\,3262 \times 10^{-13} \text{ cm}$ (classical electron radius), N is the number of electrons and

$$\overline{r^2} \equiv \left\langle \Psi \left| \frac{1}{N} \sum_{i=1}^N r_i^2 \right| \Psi \right\rangle, \quad (8)$$

where Ψ is the ground-state wave function. We will study the case $Z = 2$, that is, the helium atom. Specifically, we want to see how χ_{m} is affected by radial correlation in the trial wave function.

E. Electronic density and atomic form factor

We will now focus on the electronic density and the atomic form factor of the two-electron systems using our trial wave function. The atomic form factor is deeply connected to the cross sections for radiation interaction processes, that involving elastic collisions between photons and matter being the most obvious, such as Rayleigh scattering. Rayleigh scattering is the process in which a photon is elastically scattered by bound atomic electrons, that is, without the targeted atom being excited. Thus, the state does not change and the incident photon energy is the same as the scattered photon energy. This process is also called coherent because interference effects caused by different parts of the atomic distribution appear.

In order to calculate the atomic form factor, first we need to obtain the expression for the electronic density, given by

$$\rho(\mathbf{r}) = \int \dots \int |\Psi(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)|^2 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N. \quad (9)$$

The atomic form factor $F(\mathbf{q})$ [7] for an atom with atomic number Z is defined as

$$F(\mathbf{q}) = \left\langle \Psi_0 \left| \sum_{j=1}^Z \exp(i\mathbf{q} \cdot \mathbf{r}_j) \right| \Psi_0 \right\rangle, \quad (10)$$

where Ψ_0 is the ground-state wave function, the sum covers the Z atomic electrons and \mathbf{q} is the momentum transfer vector with modulus q . The atomic form factor can be also expressed as the Fourier integral of the total electron density $\rho(\mathbf{r})$

$$F(\mathbf{q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{q} \cdot \mathbf{r}) d^3\mathbf{r}. \quad (11)$$

Considering the spherical symmetry of the atom, the angular part of the integral can be computed analytically and we get the simplified expression

$$F(q) = \int_0^\infty \rho(r) j_0(qr) 4\pi r^2 dr, \quad (12)$$

where $j_0(x) = (\sin x)/x$ is the spherical Bessel function of the first kind and order 0.

$F(q)$ is a monotonously decreasing function of q , going from $F(0) = Z$ to $F(\infty) = 0$, in such a way that it favors the before-mentioned Rayleigh scattering towards small angles.

III. RESULTS AND DISCUSSION

A. Ground-state energy

The first calculation made in order to obtain the ground-state energy is the normalization constant, that results in

$$\mathcal{N} = \left[\frac{1}{8a^3b^3} + \frac{8}{(a+b)^6} \right]^{-1/2}. \quad (13)$$

We also need expressions for the kinetic energy, the electron-nucleus potential and the electron-electron potential, and after doing some calculations, we attain the following

$$T = \mathcal{N}^2 \left[\frac{a^2 + b^2}{16a^3b^3} + \frac{8ab}{(a+b)^6} \right], \quad (14)$$

$$V_{\text{en}} = -\mathcal{N}^2 Z \left[\frac{a+b}{8a^3b^3} + \frac{8}{(a+b)^5} \right], \quad (15)$$

$$V_{\text{ee}} = \mathcal{N}^2 \left[\frac{a^2 + 3ab + b^2}{8a^2b^2(a+b)^3} + \frac{5}{2} \frac{1}{(a+b)^5} \right]. \quad (16)$$

With these expressions we finally obtain the expectation value of the Hamiltonian, Eq. (3). Defining $\alpha = a + b$ and $\beta = ab$, the energy for the ground state reads

$$E(a, b) = \frac{8\beta^3\alpha^6}{\alpha^6 + 64\beta^3} \left[-Z \left(\frac{\alpha}{8\beta^3} + \frac{8}{\alpha^5} \right) + \frac{a^2 + b^2}{16\beta^3} + \frac{8\beta}{\alpha^6} + \frac{a^2 + 3\beta + b^2}{8\beta^2\alpha^3} + \frac{5}{2\alpha^5} \right]. \quad (17)$$

As a way of checking that this expression is correct, we can make the substitution $a = b = Z_{\text{eff}}$ in Eq. (17) and then confirm that it becomes the result for the simple variational method with same orbital electrons $E_{Z_{\text{eff}}} = -Z_{\text{eff}}^2$. Indeed, the expression found satisfies this simple condition. Furthermore, this result is in full accord with calculations made similarly by other researchers [1–4, 8].

B. Minimization of the energy

The two-parameter function $E(a, b)$, once we minimize it employing the simplex subroutine, leads for $Z = 1$ to the best minimum $E_{\text{min}} = -0.513\,303$ for $a = 1.0392$ and $b = 0.2832$. The interpretation of this result is that since H^- is weakly bound, one electron is close the nucleus while the other one is far from it, that is, an almost un-screened hydrogen atom and a very loose electron, hence the small ionization potential.

TABLE I: Ground-state energies $E_{Z_{\text{eff}}}$ obtained from the simple variational method, E_{HF} obtained from the Hartree–Fock method, E_{nr} the non-relativistic energies and E_{min} obtained from Eq. (17) for different values of Z with optimized parameters a and b .

Z	$E_{Z_{\text{eff}}}$	E_{HF}	E_{nr}	E_{min}	a	b
1	-0.4727	-0.48793	-0.52775	-0.51330	1.039	0.283
2	-2.8477	-2.86168	-2.90372	-2.87566	2.183	1.189
3	-7.2227	-7.23642	-7.27991	-7.24875	3.295	2.079
4	-13.5977	-13.61130	-13.65557	-13.62297	4.390	2.985
5	-21.9727	-21.98624	-22.03097	-21.99755	5.474	3.901

The results for other values of Z are presented in Table I. It shows a collection of energies obtained from different methods: two taking radial correlation into account and two without it. These last two are $E_{Z_{\text{eff}}}$, the energy derived from the simple variational method and E_{HF} , the energy obtained from the Hartree–Fock method. The other two are the exact non-relativistic energy E_{nr} [2] and E_{min} , the energy obtained using our trial wave function, Eq. (17). The table includes the values for a and b obtained for each minimization of Eq. (17).

These results bear out the importance of general spatial correlation, in our particular case, radial correlation. When the nuclear charge increases, the correlation energy between electrons of opposite spins becomes less important. It is observed that introducing the splitting orbitals, the energy obtained has a better upper bound than the energy calculated by the simple variational method, for instance. It can also be observed that while the Hartree–Fock energies present an improvement with respect to those obtained from the simple variational method, they also fail to give a better upper bound for $Z = 1$. This brings out the importance of taking correlation into account, as the Hartree–Fock method does not consider it.

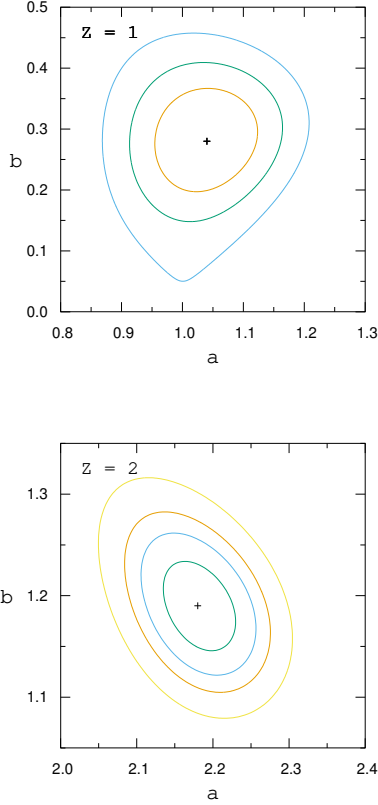


FIG. 1: Contour plots of $E(a, b)$, Eq. (17), for $Z = 1$ (top) and $Z = 2$ (bottom). The contour lines (from outer to inner) are $-0.50, -5.06, -0.51$ for $Z = 1$ and $-2.871, -2.873, -2.874, -2.875$ for $Z = 2$.

TABLE II: Ground-state energies E_{\min} obtained through the scaling method with their corresponding η_{\min} and ν_{\min} as well as the derived parameters a and b .

Z	E_{\min}	η_{\min}	ν_{\min}	a	b
1	-0.513 303	0.6612	0.5717	1.0391	0.2832
2	-2.875 662	1.6859	0.2950	2.1831	1.1885
3	-7.248 750	2.6869	0.2263	3.2949	2.0709
4	-13.622 966	3.6872	0.1904	4.3895	2.9848
5	-21.997 540	4.6873	0.1677	5.4734	3.9012

The minimum, displayed in Fig. 1 with a cross, undoubtedly requires $a \gg b$ (or vice-versa), i.e. two very different orbitals. Several values of the energy have been drawn in these figures and it is clearly seen how each level approaches more the minimum.

As mentioned above, there is an alternative way of minimizing the energy through a one-parameter function. The numerical results for this method are listed in Table II. We can see that the minimized energy and the parameters a and b match with very small relative error to those found with the two-parameter function (Table I).

C. Magnetic susceptibility

In order to obtain the magnetic susceptibility first we need to compute the expected value for r^2 . Making use of Eq. (8) we end up with the expression

$$\overline{r^2} = N^2 \left[\frac{3}{16} \frac{a^2 + b^2}{a^5 b^5} + \frac{96}{(a+b)^8} \right]. \quad (18)$$

For our particular case, we input $N = 2$ for the number of electrons. First, we can take the standard effective nuclear charge Z_{eff} for both a and b with $Z = 2$. Doing so we arrive at the value

$$\chi_m = -1.67 \times 10^{-6} \text{ cm}^3/\text{mol}.$$

If we input the optimised parameters $a = 2.1832$ and $b = 1.1885$ for $Z = 2$ (Table I), we get

$$\chi_m = -1.95 \times 10^{-6} \text{ cm}^3/\text{mol}.$$

As it is well known, helium is diamagnetic. The experimental value is [9]

$$\chi_m = -2.02 \times 10^{-6} \text{ cm}^3/\text{mol}$$

and it is observed that the value obtained with our trial wave function has a small relative difference with it, whereas the one obtained with Z_{eff} differs more.

D. Electronic density and atomic form factor

Introducing our trial wave function, Eq. (2), in the above-mentioned expression for $\rho(\mathbf{r})$, Eq. (9), and taking $\alpha = a+b$ and $\beta = ab$ we get the following electron density

$$\rho(\mathbf{r}) = \frac{1}{4\pi} \frac{2\alpha^3}{\alpha^6 + 64\beta^3} \left[a^3 \alpha^3 e^{-2ar} + 16\beta^3 e^{-\alpha r} + b^3 \alpha^3 e^{-2br} \right]. \quad (19)$$

To make sure the calculation is right, it has to follow the normalization condition $\int_0^\infty \rho(r) 4\pi r^2 dr = N$, which indeed it does. Once we have this result we can finally compute it into Eq. (12) and obtain, once again taking $\alpha = a+b$ and $\beta = ab$, the following expression

$$F(q) = \frac{4\alpha^3}{\alpha^6 + 64\beta^3} \left[\frac{4a^4\alpha^3}{(q^2 + 4a^2)^2} + \frac{32\beta^3\alpha}{(q^2 + \alpha^2)^2} + \frac{4b^4\alpha^3}{(q^2 + 4b^2)^2} \right]. \quad (20)$$

This expression is in complete accord with reference [10]. Doing the simple substitution $a = b = Z_{\text{eff}}$ we recover the atomic form factor for hydrogenic orbitals multiplied by 2, which supports its correctness.

The representation of $F(q)$ can be observed in Fig. 2, along with the atomic form factor obtained from a radially correlated Hartree-Fock wave function [7]. The

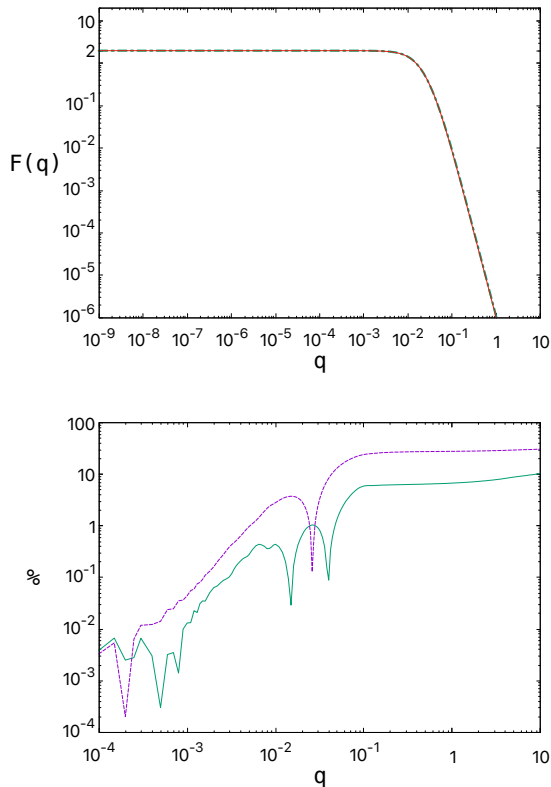


FIG. 2: Top: Atomic form factor of He obtained from a Hartree–Fock wave function with correlation [7] (dashed curve) and from Eq. (20) (solid curve). Bottom: Relative difference, in %, between the Hartree–Fock form factor and the one obtained from the wave function (2) with a and b from Table II (solid curve) or taking $a = b = Z_{\text{eff}}$ (dashed curve).

two curves are very close to each other as, in fact, our radial correlation also gives a good approximation for the atomic form factor. Taking a look at the figure below, one can notice that there is, overall, a smaller relative

difference between the Hartree–Fock form factor and ours than with the one obtained from Z_{eff} . For small values of q , this difference is negligible, while for larger values it quickly starts to increase.

IV. CONCLUSIONS

Introducing radial correlation in the trial wave function for two-electron atoms, even if it is just implicitly, has a great impact in the corresponding ground-state energy. It is more noticeable for smaller values of Z . In fact, radial correlation gives a bound that allows H^- to exist. This means that correlation effects are greater in these two-electron systems than in other many-electron atoms.

The minimization of the energy can be achieved using two different methods: a two-parameter method or a one-parameter one. The relative error between both results is very small.

Radial correlation also contributes to improving the result for the magnetic susceptibility, better than just using the simple variational method with Z_{eff} .

The electron density and therefore, the atomic form factor, also get improved introducing our trial wave function. For smaller values of the momentum transfer it follows quite exactly the desired form.

In this work we have focused on radial correlation, which has been proved to be a good approach, but one could also add angular correlation to the wave function, which may prove to also have very satisfactory results [2, 11].

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