

Mathematical Background

A bound state of an object in quantum mechanics is generally considered to be represented by a *wavefunction* $|\psi\rangle$, which is a vector in an infinite-dimensional vector **space*** of wavefunctions, describing all possible states of the system. Mathematicians know the vector spaces in question as L^2 spaces, which come equipped with a natural *inner product*

$$\langle\psi|\phi\rangle = \int \psi^* \phi \, d\tau,$$

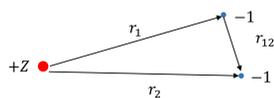
generalizing the dot product in familiar finite-dimensional vector spaces. The quantum mechanical description of reality is inherently probabilistic, in the following way. Observable quantities such as energy, position, and momentum are represented by Hermitian operators, or linear operators $T: L^2 \rightarrow L^2$ so that $\langle\psi|T\phi\rangle = \langle T\psi|\phi\rangle$. If the state of a system is described by ψ , then the *expected value* of the observable quantity is $\langle\psi|T\psi\rangle$. In that way, we may interpret the real-valued function $\psi^*\psi = |\psi|^2$ as the probability density function describing the probability of finding the system in any given state. From this we also get the normalization condition $\langle\psi|\psi\rangle = 1$, so that our probabilities add to unity.

The vector space nature of this description naturally allows us to superpose wavefunctions together, an important feature of the theory. In nonrelativistic systems describable by (potentially) state-dependent and time-independent potential energies U and kinetic energy operator T , wavefunctions which describe the system must satisfy the Schrödinger Equation $H\psi = (T + U)\psi = E\psi$, where E is the energy of the system.

The Problem

We wish to analyze a system of two electrons, each with spatial+spin coordinates ξ_j for $j = 1, 2$, in a stationary nuclear field. Coulombic potential energies go as r^{-1} , so in natural units electron j lies in an attractive coulomb potential $-Zr_j^{-1}$ and a repulsive electron-electron potential r_{12}^{-1} , where $Z = 2$ is the atomic number of Helium. The answer we seek is a function $\psi(\xi_1, \xi_2)$ satisfying

$$\left(-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1} - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_2} + \frac{1}{r_{12}}\right)\psi = (H_1^0 + H_2^0 + V_{12})\psi = E\psi,$$



the Schrödinger equation for our system. The presence of a potential depending on the spatial coordinates of both electrons significantly complicates the problem. So, we make simplifying assumptions to the model and use reasonable assumptions as to the functional form of the solution, then solve for the corresponding parameters which provide the best fit to the actual behavior of the solutions. Here, we use a method of approximation called the Hartree-Fock method.

Reduction of the Problem

In the Hartree-Fock (HF) method, we assume that we may write ψ as a combination of single-electron functions ϕ_j which depend on the spatial coordinates of only a single electron, called orbitals. The specific form we use, $\psi = |\phi_i(\xi_j)|$ is a determinant of a matrix because this automatically satisfies certain symmetry properties that the full wavefunction must possess. We may also integrate over the spins of the particles, since we know they will have opposite spins in the ground state orbital.

We can then use a mathematical tool called calculus of variations to find a condition for finding the “best fit” of functions of this form to our system, from which we produce the Hartree Fock equation

$$(H + J)\phi = \epsilon\phi,$$

Where $H = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$ is the core Hamiltonian and $J = \int \phi^*(2)r_{12}^{-1}\phi(2)$ is the potential arising from the interaction of the two electrons.

Quantum Mechanics in Practice: Calculating the Ionization Energy of Helium

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Abstract:

Quantum mechanics is a phenomenal tool for modeling the physical world; its predictive power is unparalleled among other quantitative theories in physics. However, the mathematical formalism is a painfully abstract beast that requires considerably more effort than classical theories to extract useful answers in most cases. Here, we will present a method of approximating the quantum-mechanical state of the two nonrelativistic electrons in the ground state of Helium. An exact solution to this motion is unknown because obtaining it involves a PDE over a six-dimensional phase space. However, experience has shown that we can formulate a reasonable guess which converges to a fairly accurate approximation in only a few iterations.

Basis Functions and Hilbert Space

The L^2 space from which wavefunctions come is also a type of space called a Hilbert space. An advantage of this structure is that by only considering functions of the form $\sum c_i \phi_i$ for a fixed set of basis functions $\{\phi_i\}$, we may use the tools of linear algebra to deduce the particular linear combination we need. As the linear span of the basis we use grows larger, approaching completeness, we are better able to represent more orbital shapes than before. Choosing these basis functions wisely can significantly improve computation time.

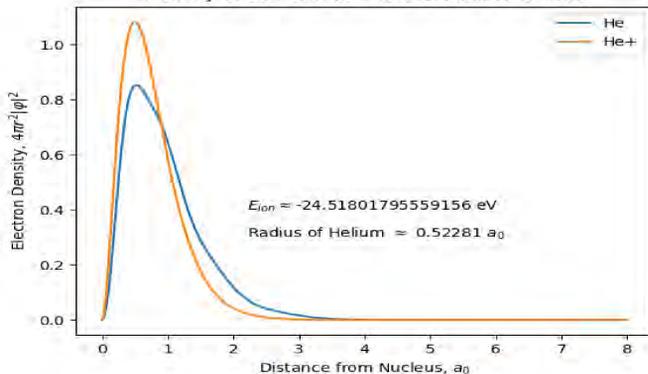
Since we expect the ground state to be spherically symmetric, we use spherical basis functions $\phi_\alpha(r) = (2\alpha\pi^{-1})^{3/4} \exp(-\alpha r^2)$, which are normalized but not orthogonal. Using this form, the HF equations yield

$$\mathbf{FC} = \epsilon\mathbf{SC}, \quad (1)$$

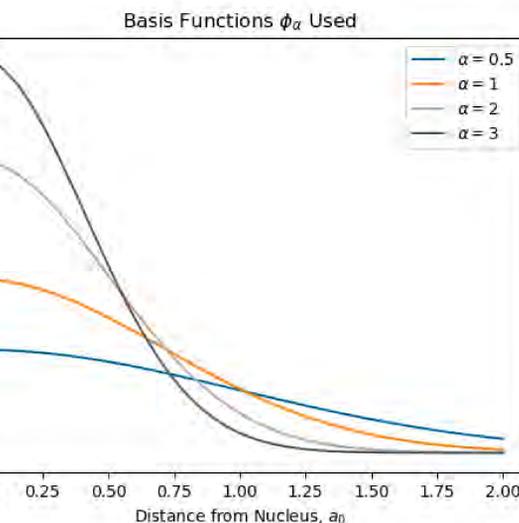
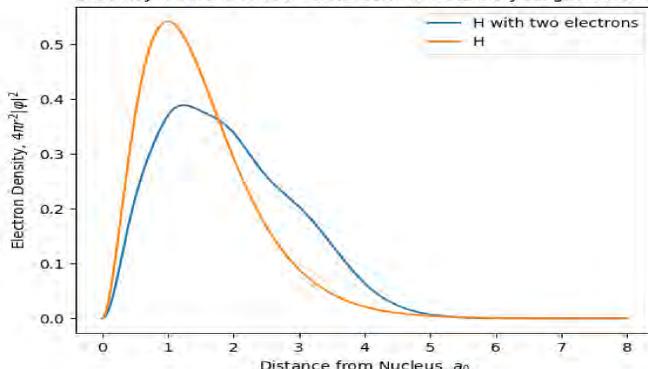
where $\mathbf{F} = (F_{ij}) = (\langle\phi_i|H + J|\phi_j\rangle)$ is the Fock matrix, $\mathbf{C} = (c_i)$ is the coefficient column vector, $\mathbf{S} = (S_{ij}) = (\langle\phi_i|\phi_j\rangle)$ is the overlap matrix, and ϵ is the single-electron energy eigenvalue. The integrals are performed over 3d space. Choosing Gaussians allows us to compute most of these expressions by hand, maximizing the efficiency of the program. The procedure followed during the calculation is detailed to the right.

In the results presented here, 8 basis functions with α values evenly distributed between 0.15 and 2.4 were used, and the iteration was performed until the Euclidean norm of the difference between the coefficient vectors became less than 0.001.

Density of the Ground State Orbital of Helium



Density of the Ground State Orbital of the Hydrogen Anion

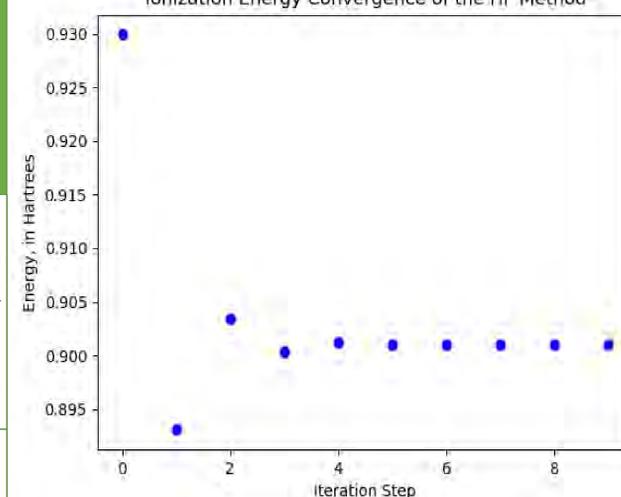


Results

The result of the calculation is a spherically symmetric orbital ϕ , expressed as a linear combination of Gaussian basis functions. We can use this to estimate various properties of the system we are analyzing; here we will focus on atomic radius and ionization energy. To the left are shown the ground state orbitals of helium (on top) and hydrogen (bottom) with one and two electrons populating them. This shows that the lower radius of helium is due to the increased strength of the nuclear well. Qualitatively, this also shows how the introduction of a second electron into an s-orbital affects it: the electrons spread out radially somewhat because of the added repulsive energy of the interacting electron clouds.

The calculated orbitals are plotted in radial units of the classical Bohr radius, a_0 . The estimated ionization energy of helium was found to be 24.51 eV, in good agreement with the reference value of 24.6 eV [2]. The radius of the neutral helium atom was found to be 0.523 times the Bohr radius, also in acceptable agreement with most sources, although definitions of atomic radius vary.

Ionization Energy Convergence of the HF Method



Iterative Process

- Setup:
- Calculate overlap integrals $S_{ij} = \langle\phi_i|\phi_j\rangle$
 - Calculate core Hamiltonian matrix $\langle\phi_i|H|\phi_j\rangle$
 - Initialize calculation of interaction matrix $\langle\phi_i|J|\phi_j\rangle$

Begin:

- Guess initial coefficients (c_j)

Loop:

- From prior coefficients, calculate \mathbf{F}
- Solve the generalized eigenvalue problem (1) for new coefficients and eigenvalues

No

Check:
Have results converged?

Yes

If the results have converged, we may stop the loop and consider the resultant wavefunction the self-consistent solution to equation (1)

Acknowledgements and References

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References:

- [1] Davydov, A. S. (1976). *Quantum mechanics* (2nd ed.). Oxford: Pergamon Press.
- [2] David R. Lide (ed), *CRC Handbook of Chemistry and Physics, 84th Edition*. CRC Press. Boca Raton, Florida, 2003; Section 10, Atomic, Molecular, and Optical Physics; Ionization Potentials of Atoms and Atomic Ions