Physics 367 Scientific Computation Final Project

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1 Motivation

Hartree-Fock (HF), also known as the self-consistent field method, was the earliest and simplest method in electronic structure theory, which tries to describes the motion of electrons in atoms or molecules. Although it has been surpassed by many other more advanced and accurate methods, such as configuration interaction, density functional theory, HF remains useful as a starting point for many calculations. For example, many Quantum Monte Carlo (QMC) calculation use HF wave functions as trial wave functions. The vocabulary of HF, such as closed-shell, open-shell, restricted and unrestricted orbitals, lives on in the electronic structure literature today.

I want to use this project to get hands-on experience with HF as a first step to broaden my understanding of electronic structure theory beyond the niche of QMC (which is very distinct from the rest of the field). Understanding HF is a good springboard to understand other more currently relevant methods like configuration interaction, coupled-cluster and density functional theory, arguably the most popular of all electronic structure methods.

This project aims to find the equilibrium bond length of the helium hydride cation HeH^+ by calculating the molecular energy of HeH^+ over a range of internuclear distances using *restricted*, *closed-shell* Hartree-Fock calculation with the STO-3G basis set.

I also want to use MATHEMATICA's functional and rule-based style of programming as much as possible. Most of this writeup has adapted materials from Szabo and Ostlund [1] which contains a very extensive and accessible discussion of HF (and then goes on to other methods).

2 Physical Problem

2.1 The electronic problem

Suppose we have a system of nuclei and electrons described by position vectors \mathbf{R}_A and \mathbf{r}_i , respectively. The distance between the *i*-th and *j*-th electron is $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, between the *i*-th electron and *A*-th nucleus is $r_{iA} = |\mathbf{r}_i - \mathbf{R}_A|$ and between the *A*-th and *B*-th nuclei is $R_{AB} = |\mathbf{R}_A - \mathbf{R}_B|$. The mass ratio of the *A*-th nucleus to the electron is M_A . The atomic number of the *A*-th nucleus is Z_A .

The non-relativistic time-independent Schrödinger equation for this system is

$$\mathcal{H} \left| \Phi \right\rangle = \mathcal{E} \left| \Phi \right\rangle \tag{1}$$

where in atomic units¹, the full Hamiltonian for N electrons and M nuclei is

$$\mathcal{H} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_{i}^{2} - \sum_{A=1}^{M} \frac{1}{2M_{A}} \nabla_{A}^{2} - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_{A}}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{A=1}^{M} \sum_{B>A}^{M} \frac{Z_{A}Z_{B}}{R_{AB}}$$
(2)

The first and second terms in Eq. (2) are the operators for the kinetic energy of the electrons and nuclei, respectively. The third term represents Coulomb attraction between electrons and nuclei. The fourth and last terms represent the Coulomb repulsion between the electrons and between the nuclei, respectively. The complicated Hamiltonian in Eq. (2) can be simplified with the Born-Oppenheimer approximation: because the nuclei are much heavier than the electrons, they can be assumed to be stationary. This gives us the electronic Hamiltonian:

$$\mathcal{H}_{\text{elec}} = -\sum_{i=1}^{N} \frac{1}{2} \nabla_i^2 - \sum_{i=1}^{N} \sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}}$$
(3)

The total energy in the Born-Oppenheimer approximation is the sum of the electronic energy, obtained by solving Eq. (3), and the nuclear repulsion (the last term in Eq. (2)).

2.2 Terminology

An orbital is a single-electron wave function. A spatial orbital $\psi_i(\mathbf{r})$ is a function of the position vector \mathbf{r} such that $|\psi_i(\mathbf{r})|^2 \, \mathrm{d}\mathbf{r}$ is the probability of finding the electron near \mathbf{r} . In this writeup we sometimes use $\phi(1)$ as a shorthand for $\phi(\mathbf{r}_1)$. Because electrons have spins, each spatial orbital can give rise to two spin orbitals

$$\chi(\boldsymbol{x}) = \begin{cases} \psi(\boldsymbol{r})\alpha(\omega) \\ \psi(\boldsymbol{r})\beta(\omega) \end{cases}$$
(4)

where we have introduced the spin variable ω , spin up function α , spin down function β , and the combined space-spin coordinate $x \equiv r\omega$. The spin functions α and β are orthonormal.

A *Slater determinant* is an antisymmetric linear combination of spin orbitals:

$$|\Psi\rangle = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) & \dots & \chi_k(\boldsymbol{x}_1) \\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) & \dots & \chi_k(\boldsymbol{x}_2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_i(\boldsymbol{x}_N) & \chi_j(\boldsymbol{x}_N) & \dots & \chi_k(\boldsymbol{x}_N) \end{bmatrix}$$
(5)

$$= |\chi_i(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_2)\dots\chi_k(\boldsymbol{x}_N)\rangle$$
(6)

$$= |\chi_i \chi_j \dots \chi_k\rangle \tag{7}$$

where in the last equality we have shortened the notation with the assumption that the electrons label are in the order x_1, \ldots, x_N (although the order actually does not matter). The act of antisymmetrizing a wave function (by forming a Slater determinant) creates *exchange correlation* between electrons i.e. no two electrons of parallel spins can be found in the same region of space. This is the only kind of correlation in HF theory. Motion of electrons of opposite spins is uncorrelated.

We distinguish two types of spin orbitals. *Restricted* spin orbitals are constrained to have the same spatial function for α (spin up) and β (spin down) spin functions. Given a set of K orthonormal spatial orbitals ψ_i we can form a set of 2K spin orbitals by multiplying each spatial orbital by either the α or β spin function.

$$\chi_{2i-1}(\boldsymbol{x}) = \psi_i(\boldsymbol{r})\alpha(\omega) \tag{8}$$

$$\chi_{2i}(\boldsymbol{x}) = \psi_i(\boldsymbol{r})\beta(\omega) \tag{9}$$

$$1 a_0 = 5.2918 \times 10^{-11} \,\mathrm{m}$$

The unit of energy is Hartree:

$$1 \,\mathrm{Hartree} = \frac{\hbar^2}{m_{\mathrm{e}} a_0^2} = 4.3598 \times 10^{-18} \,\mathrm{J}$$

where $m_{\rm e}$ is the electron mass and e is the elementary charge (also the unit of charge in atomic units).

¹ In atomic units, the unit of length is the Bohr radius:



Figure 1: Two kinds of closed-shell determinants. Note that the spin up and spin down electrons occupy the same set of spatial orbitals. Reprinted from Szabo and Ostlund [1, pp.101-105]



Figure 2: An unrestricted Slater determinant. Note the different spatial orbitals occupied by the spin up and spin down electrons. Reprinted from Szabo and Ostlund [1, pp.101-105]

Determinants formed from them are called restricted determinants like in Fig. 1. In such a determinant, a given spatial orbital ψ_i can be occupied either by a single electron (spin up or spin down) or by two electrons of opposite spins. We can classify restricted determinants according to the number of spatial orbitals that are singly occupied. A determinant in which each spatial orbital is doubly occupied is called a *closed-shell* determinant like in Fig. 1(a). An *open-shell* refers to a spatial orbital that contains a single electron like in Fig. 1(b). One refers to determinants by the number of open shells they contain.

Unrestricted orbitals have different spatial functions for different spins. Given a set of K orthonormal spatial orbitals ψ_i^{α} and another set of K orthonormal spatial orbitals ψ_j^{β} (where the two sets need not be orthogonal to each other), we can form 2K unrestricted spin orbitals

$$\chi_{2i-1}(\boldsymbol{x}) = \psi_i^{\alpha}(\boldsymbol{r})\alpha(\omega) \tag{10}$$

$$\chi_{2i}(\boldsymbol{x}) = \psi_i^\beta(\boldsymbol{r})\beta(\omega) \tag{11}$$

These 2K unrestricted spin orbitals are orthonormal although the α and β spatial orbitals need not be. A determinant formed from these orbitals is called an unrestricted determinant like in Fig. 2.

2.3 The Hartree-Fock approximation

The simplest antisymmetric wave function that can describe the ground state of an N-electron system is a Slater determinant

$$|\Psi_0\rangle = |\chi_1\chi_2\dots\chi_N\rangle \tag{12}$$

The variational principle states that the best wave function of this functional form (i.e. a single Slater determinant) is the one which gives the lowest possible energy

$$E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle \tag{13}$$

The variational flexibility in the wave function in Eq. (12) comes from the choice of the spin orbitals. As we shall see later, a spin orbital in HF is a MO-LCAO: a *Molecular Orbital* that is a Linear Combination of *Atomic Orbitals* centered on atoms in the molecule. By minimizing E_0 with respect to the choice of spin orbitals, we can derive an eigenvalue equation for each spin orbital called the Hartree-Fock (HF) equation

$$f(1)\chi_a(\boldsymbol{x}_1) = \varepsilon_a \chi_a(\boldsymbol{x}_1) \tag{14}$$

where the coordinate x_1 is a dummy variable to show the space-spin dependence of χ_a and f(1) is an effective one-electron operator called the *Fock operator*

$$f(1) = \underbrace{-\frac{1}{2}\nabla_1^2 - \sum_{A=1}^M \frac{Z_A}{r_{1A}}}_{h(1)} + \underbrace{\sum_b \mathscr{J}_b(1) - \mathscr{K}_b(1)}_{v^{\mathrm{HF}}(1)}$$
(15)

where the Coulomb operator and exchange operators are, respectively, defined by their actions on a spin orbital:

$$\mathscr{J}_{b}(1)\chi_{a}(1) = \left[\int \mathrm{d}\boldsymbol{x}_{2}\,\chi_{b}^{*}(2)\,\frac{1}{r_{12}}\,\chi_{b}(2)\right]\chi_{a}(1) \tag{16}$$

$$\mathscr{K}_{b}(1)\chi_{a}(1) = \left[\int \mathrm{d}\boldsymbol{x}_{2}\,\chi_{b}^{*}(2)\,\frac{1}{r_{12}}\,\chi_{a}(2)\right]\chi_{b}(1) \tag{17}$$

Note that the coordinate x_2 in Eqs. (16) and (17) is just a dummy variable. The Coulomb operator $\mathscr{J}_b(1)$ in Eq. (16) gives the averaged Coulomb potential at x_1 due to an electron in χ_b . This is a *local* operator because the result of operating with $\mathscr{J}_b(1)$ on $\chi_a(1)$ only depends on the value of χ_a at just x_1 .

In contrast, the exchange operator $\mathscr{K}_b(1)$ is a *non-local* operator. Operating with $\mathscr{K}_b(1)$ on $\chi_a(1)$ involves an "exchange" of electron 1 and electron 2 to the right of $1/r_{12}$ in Eq. (17) relative to Eq. (16). This operator is non-local because the result of operating with $\mathscr{K}_b(1)$ on $\chi_a(1)$ depends on the value of χ_a throughout all space, not just at \mathbf{x}_1 .

In Eq. (15), v^{HF} is the average potential experienced by an electron due to the presence of all the other electrons. The essence of the HF approximation is to replace the complicated many-electron problem by a one-electron problem in which electron-electron repulsion is treated in an average way.

The *field* i.e. the HF potential v^{HF} seen by the by an electron depends on the spin orbitals of the other electrons. In other words, the Fock operator depends on its eigenfunctions (through the exchange operator). Thus the HF equation is non-linear and must be solved iteratively by a procedure called the *self-consistent-field* (SCF) method. In SCF we start by making an initial guess at the spin orbitals, calculate the average field v^{HF} seen by each electron and then solve the eigenvalue Eq. (14) for a new set of spin orbitals. Using these new spin orbitals, one can obtain new fields and repeat the procedure until self-consistency is reached i.e. until the fields no longer change and the spin orbitals used to construct the Fock operator are the same as its eigenfunctions.

In restricted HF, the HF equation is solved by introducing a finite set of K spatial basis functions $\phi_{\mu}(\mathbf{r})$, $\mu = 1, \dots, K$. The spatial parts of the spin orbitals with spin up can be expanded in terms of the known set



Figure 3: Occupied (HF ground state) and virtual orbitals. Reprinted from Szabo and Ostlund [1].

of functions ϕ_{μ} . The spatial parts of the spin orbitals with spin down an be expanded in the same way and both expansions substituted into Eq. (13) to obtain matrix eigenvalue equations for the expansion coefficients. In unrestricted HF, the spatial basis functions for spin up and spin down are allowed to be different like in Eqs. (10) and (11).

Regardless of whether restricted or unrestricted HF is used, the solution of the HF eigenvalue Eq. (14) is a set of 2K orthonormal HF spin orbitals $\{\chi_k\}$ with orbital energies $\{\varepsilon_k\}$. The Slater determinant formed from the N spin orbitals with the lowest energies (the *occupied* orbitals) is the HF ground state wave function $|\Psi_0\rangle$ and is the best single-determinant variational approximation to the true ground state of the system. The remaining 2K - N orbitals are called *virtual* orbitals. This is shown in Fig. 3.

The larger and more complete the set of basis functions ϕ_{μ} , the greater is the degree of flexibility in the expansion for the spin orbitals and the lower will be the expectation value $E_{0\text{finite}} = \langle \Psi_0 | H | \Psi_0 \rangle$. Larger and larger basis sets will keep lowering the HF energy $E_{0\text{finite}}$ until a limit is reached, called the Hartree-Fock limit E_0 . The difference between the exact ground state energy \mathcal{E}_0 and the Hartree-Fock limit E_0 is called the *correlation energy*². Finite-size basis sets will always give an energy above this limit.

2.4 The Roothaan equations

To make the HF eigenvalue equation solvable on a computer, we need to be more specific about the form of the spin orbitals. Here we will use a set of restricted closed-shell spin orbitals. Our molecule are thus allowed to only have an even number N of electrons with all electrons paired such that all n = N/2 spatial orbitals are doubly occupied. With this choice of spin orbitals, we can integrate out the spin functions in Eq. (14) to obtain a purely *spatial* HF eigenvalue equation

$$f(1)\psi_j(\boldsymbol{r}_1) = \varepsilon_j\psi_j(\boldsymbol{r}_1) \tag{18}$$

where the spatial HF operator—counterpart to the spin version in Eq. (15)—is now

$$f(1) = \underbrace{-\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{1A}}}_{h(1)} + \sum_a^{N/2} 2J_a(1) - K_a(1)$$
(19)

² The ground state Slater determinant found by HF is only one of the $\binom{2K}{N}$ possible Slater determinants of N electrons from 2K spin orbitals. If one wish to find the exact non-relativistic ground state \mathscr{E}_0 (within the space spanned by finite size of the basis ϕ_{μ}), one can diagonalize the full Hamiltonian in the basis of these $\binom{2K}{N}$ Slater determinants. The lowest eigenvalues is the true ground state energy. This procedure is called *configuration interaction* (CI). HF is essentially diagonalization in the basis of slater determinants.

Note that the sum only runs to N/2 because only half of the spin orbitals are distinct and note the appearance of a factor of 2 in front of the spatial Coulomb operator J compared to Eq. (15). The spatial Coulomb and exchange operators—counterparts to the spin versions in Eqs. (16) and (17)—are defined by their action on a spatial orbital ψ_i :

$$J_a(1)\psi_i(1) = \left[\int \mathrm{d}\mathbf{r}_2 \psi_a^*(2) \,\frac{1}{r_{12}} \,\psi_a(2)\right] \psi_i(1) \tag{20}$$

$$K_a(1)\psi_i(1) = \left[\int \mathrm{d}\mathbf{r}_2\psi_a^*(2)\,\frac{1}{r_{12}}\,\psi_i(2)\right]\psi_a(1) \tag{21}$$

Now we introduce a set of K known basis functions $\phi_{\mu}(\mathbf{r})$ and expand the unknown molecular orbitals as a linear combination of the basis functions (which are almost always atomic orbitals)

$$\psi_i = \sum_{\mu=1}^{K} C_{\mu i} \phi_\mu \tag{22}$$

With this basis we can convert Eq. (18) into a matrix equation called the *Roothaans equation*

$$FC = SC\varepsilon \tag{23}$$

where \boldsymbol{F} is the Fock matrix

$$F_{\mu\nu} = \int \mathrm{d}\boldsymbol{r}_1 \phi^*_{\mu}(1) f(1) \phi_{\nu}(1) \tag{24}$$

and C is the matrix consisting of coefficients from Eq. (22). Thus the *i*-th column of C describe the spatial molecular orbitals ψ_i .

The overlap matrix \boldsymbol{S} has elements:

$$S_{\mu\nu} = \int d\mathbf{r}_1 \phi^*_{\mu}(1) \phi_{\nu}(1)$$
 (25)

To complement the coefficient matrix C, in this calculation we will also use the *density matrix* P whose elements are defined as

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^*$$
(26)

The result of the HF calculation can either be characterized by P or C.

Note that Eq. (22) is not quite in the form of an eigenvalue equation but it would if S were the identity. We can transform into a basis where S is the identity by introducing a matrix X such that $X^{\dagger}SX = 1$ and a matrix $C' = X^{-1}C$ such that C = XC'. With these new matrices, left-multiplying Eq. (22) by X^{\dagger} gives

$$X^{\dagger}FC = X^{\dagger}SC\varepsilon \tag{27}$$

$$\boldsymbol{X}^{\dagger}\boldsymbol{F}(\boldsymbol{X}\boldsymbol{C}') = \boldsymbol{X}^{\dagger}\boldsymbol{S}(\boldsymbol{X}\boldsymbol{C}')\boldsymbol{\varepsilon}$$
⁽²⁸⁾

$$F'C' = C'\varepsilon$$
 let $F' = X^{\dagger}FX$ (29)

Eq. (29) is the pseudo-eigenvalue equation we need to solve. Because F' depends on C', this is a non-linear equation that needs to be solved repeatedly until consistency is achieved i.e. C' does not change anymore according to some criterion.

3 Choice of basis functions

A normalized Gaussian-type functions (GF) that describes a 1s orbital centered on the A-th nucleus is:

$$\phi_{1s}^{\text{GF}}(\alpha, \boldsymbol{r} - \boldsymbol{R}_A) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha |\boldsymbol{r} - \boldsymbol{R}_A|^2}$$
(30)

The same orbital can also be described by a Slater-type function (SF):

$$\phi_{1s}^{SF}(\zeta, \boldsymbol{r} - \boldsymbol{R}_A) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta |\boldsymbol{r} - \boldsymbol{R}_A|^2}$$
(31)

The choice between these two types of basis functions is a tradeoff between qualitative behavior and ease of integral evaluation. Slater functions more correctly describe the the qualitative features of molecular orbitals. At large distances molecular orbitals e.g. the ground state of hydrogen atom decay like $e^{-\zeta r}$ which is of the Slater rather than Gaussian form.

However, most commercial software uses Gaussian functions because in a realistic calculation, if K basis functions are used, one has to evaluate on the order of $K^4/8$ two-electron integrals which are very time-consuming for Slater functions. Gaussian functions are easier to integrate because the product of two Gaussians is another Gaussian.

It turns out that one can, to some extent, avoid this dilemma by using a linear combination of Gaussian functions to approximate a Slater function. This gives rise to an STO-LG basis: each basis function (an atomic orbital) is a *contracted Gaussian function* (CGF) i.e. a linear combination (or *contraction*) of L Gaussian functions (called *Gaussian primitives* and denoted g to distinguish them from the CGF), each having the form in Eq. (30):

$$\phi_{\mu}^{\text{CGF}}(\zeta, \boldsymbol{r} - \boldsymbol{R}_A) = \sum_{p=1}^{L} d_{p\mu} g_p(\alpha_{p\mu}, \boldsymbol{r} - \boldsymbol{R}_p)$$
(32)

(where the index $\mu = 1, 2, ..., K$ enumerates the basis functions) to simulate a Slater-type orbital (STO) with exponent ζ centered on \mathbf{R}_A . Note that each Gaussian function in the contraction in Eq. (32) has its own coefficient and exponent. In principle, each Gaussian primitive in the sum on the RHS can have different centers \mathbf{R}_p but in practice they are almost always equal to \mathbf{R}_A ³ and we shall follow that practice here. In this calculation, we will use a STO-3G basis because according to Szabo and Ostlund [1], L = 3 has been empirically determined to produce nearly all the essential valence features of a Slater orbital. As a shorthand, in this writeup we sometimes refer to the μ -th basis function as just μ .

The exponents $\alpha_{p\mu}$ and coefficients $d_{p\mu}$ are found by least-square fitting and, once determined, remain fixed during the course of a calculation. A linear combination of these basis functions, each over a different atomic nucleus, will give a molecular orbital.

Szabo and Ostlund [1, p.157] gives the following contract coefficients and exponents as the best least-square fit to a 1s Slater-type orbital $\phi_{1s}^{SF}(\zeta' = 1.0, r - R)$:

$$\phi_{1s}^{CGF}(\zeta' = 1.0, \boldsymbol{r} - \boldsymbol{R}) = 0.444635 \, g_{1s}(0.109818, \boldsymbol{r} - \boldsymbol{R}) + 0.535328 \, g_{1s}(0.405771, \boldsymbol{r} - \boldsymbol{R}) + 0.154329 \, g_{1s}(2.22766, \boldsymbol{r} - \boldsymbol{R})$$
(33)

Each Gaussian primitive is of the 1s type⁴ in Eq. (30). If we need to approximate a Slater-type orbital with a different exponent ζ instead of 1.0, we can simply multiply each exponent of the Gaussian primitives in Eq. (33) by a factor of ζ^2 . Note that although these CGF's are approximations of Slater-type functions, once their functional forms are fixed, there is no further approximation in the calculation besides the HF approximation. The coefficients $d_{p\mu}$ and exponents $\alpha_{p\mu}$ for a variety of types of basis e.g. STO-3G, 4-31G, 6-31G* and 6-31G** are widely available.

As suggested by Szabo and Ostlund [1], we use a STO-3G basis function with $\zeta = 2.0925$ to be the first basis function, a 1s atomic orbital centered on the He atom:

$$\phi_1(\zeta = 2.0925, \boldsymbol{r} - \boldsymbol{R}_{\rm He}) = 0.444635 \, g_{1\rm s}(0.480844, \boldsymbol{r} - \boldsymbol{R}_{\rm He}) + 0.535328 \, g_{1\rm s}(1.776691, \boldsymbol{r} - \boldsymbol{R}_{\rm He}) + 0.154329 \, g_{1\rm s}(9.753934, \boldsymbol{r} - \boldsymbol{R}_{\rm He})$$
(34)

³ One instance where different centers \mathbf{R}_p within a single contraction might be useful is when we need to approximate a 2p-orbital by two 1s Gaussian lobes of opposite sign placed a small distance apart.

⁴ Usually only 1s, 2p, 3d Gaussian primitives are used because the molecular integrals for these primitives can be simplified. A 2s or 3s basis function will then be a contraction of 1s primitives. A 3p basis function will be a contraction of 2p primitives and so on. Because only 1s orbitals are occupied in He and H, it is reasonable to put a 1s basis function on He and another on H. However, for heavier atoms, we might need to put more than one basis functions on that atom to account for higher orbitals like 2s, 2p and so on.



Figure 4: Diagram showing the coordinate system for the calculation. The He atom is labeled 1 and the H atom labeled 2. Reprinted from Szabo and Ostlund [1]

and another STO-3G basis function with $\zeta = 1.24$, a 1s atomic orbital centered on the H atom, as the second basis function:

 $\phi_{2}(\zeta = 1.24, \boldsymbol{r} - \boldsymbol{R}_{\rm H}) = 0.444635 \, g_{1\rm s}(0.168856, \boldsymbol{r} - \boldsymbol{R}_{\rm H}) + 0.535328 \, g_{1\rm s}(0.623913, \boldsymbol{r} - \boldsymbol{R}_{\rm H}) + 0.154329 \, g_{1\rm s}(3.42525, \boldsymbol{r} - \boldsymbol{R}_{\rm H})$ (35)

The setup is shown in Fig. 4

4 Evaluation of molecular integrals

Suppose that we have an integral $I_{\mu\nu}$ that involves two basis functions ϕ_{μ}^{CGF} and ϕ_{ν}^{CGF} and we know how to evaluate the corresponding integral I_{pq} for any two primitive Gaussians g_p and g_q , then the integral over the basis functions can be easily computed:

$$I_{\mu\nu} = \sum_{p=1}^{L} \sum_{q=1}^{L} d_{p\mu}^* d_{q\nu} I_{pq}$$
(36)

Similarly, integrals involving four basis functions can also be reduced to integrals involving four Gaussian primitives.

As a shorthand notation, in this section we sometimes use the letter A to denote the normalized Gaussian primitive centered at \mathbf{R}_A with exponent α , B the normalized Gaussian primitive centered at \mathbf{R}_B with exponent β and so on.

4.1 Overlap matrix

The elements of the overlap matrix S is given in Eq. (25). From Szabo and Ostlund [1, p. 412], the integral for any pair of normalized 1s Gaussian primitives is⁵

$$(A|B) = \int \mathrm{d}\boldsymbol{r}_1 \, g_{1\mathrm{s}}(\alpha, \boldsymbol{r}_1 - \boldsymbol{R}_A) g_{1\mathrm{s}}(\beta, \boldsymbol{r}_1 - \boldsymbol{R}_B) \tag{37}$$

$$= \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \left(\frac{\pi}{\alpha+\beta}\right)^{3/2} \exp\left[-\frac{\alpha\beta}{\alpha+\beta}|\boldsymbol{R}_A - \boldsymbol{R}_B|^2\right]$$
(38)

4.2 Core Hamiltonian matrix

The core Hamiltonian matrix H^{core} is the sum of the kinetic and nuclear attraction matrices:

$$\boldsymbol{H}^{\text{core}} = \boldsymbol{T} + \boldsymbol{V}^{\text{nucl}} \tag{39}$$

The kinetic matrix \boldsymbol{T} has entries

$$T_{\mu\nu} = \int \mathrm{d}\boldsymbol{r_1}\phi_{\mu}^*(1) \left[-\frac{1}{2}\nabla_1^2\right]\phi_{\nu}(1) \tag{40}$$

which can be evaluated for any pair of normalized 1s Gaussian primitives:

$$\left(A \left| -\frac{1}{2} \nabla^2 \right| B \right) = \int d\mathbf{r}_1 g_{1s}(\alpha, \mathbf{r}_1 - \mathbf{R}_A) \left[-\frac{1}{2} \nabla^2 \right] g_{1s}(\beta, \mathbf{r}_1 - \mathbf{R}_B)$$

$$= \left(\frac{2\alpha}{\pi} \right)^{3/4} \left(\frac{2\beta}{\pi} \right)^{3/4} \frac{\alpha\beta}{\alpha + \beta} \left[3 - \frac{2\alpha\beta}{\alpha + \beta} |\mathbf{R}_A - \mathbf{R}_B|^2 \right] \left(\frac{\pi}{\alpha + \beta} \right)^{3/2} \exp\left(-\frac{\alpha\beta}{\alpha + \beta} |\mathbf{R}_A - \mathbf{R}_B|^2 \right)$$

$$(41)$$

$$(42)$$

The nuclear attraction matrix V^{nucl} has entries

$$V_{\mu\nu}^{\rm nucl} = \int d\mathbf{r}_1 \, \phi_{\mu}^*(1) \left[-\sum_C \frac{Z_C}{|\mathbf{r}_1 - \mathbf{R}_C|} \right] \phi_{\nu}(1) \tag{43}$$

From Szabo and Ostlund [1, p.415], for the C-th nucleus and a pair of normalized 1s Gaussian primitives, the integral is 6

$$\left(A\left|-\frac{Z_C}{r_{1C}}\right|B\right) = \int \mathrm{d}\boldsymbol{r}_1 \, g_{1s}(\alpha, \boldsymbol{r}_1 - \boldsymbol{R}_A) \left[-\frac{Z_C}{|\boldsymbol{r}_1 - \boldsymbol{R}_C|}\right] g_{1s}(\beta, \boldsymbol{r}_1 - \boldsymbol{R}_B) \tag{44}$$

$$= \begin{cases} -\left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \left(\frac{2\pi}{\alpha+\beta} Z_C\right) \exp\left[-\frac{\alpha\beta}{\alpha+\beta} |\mathbf{R}_A - \mathbf{R}_B|^2\right] & \text{if } \mathbf{R}_P = \mathbf{R}_C \\ -\left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \left(\frac{2\pi}{\alpha+\beta} Z_C\right) \times \exp\left[-\frac{\alpha\beta}{\alpha+\beta} |\mathbf{R}_A - \mathbf{R}_B|^2\right] \\ \times F_0\left[(\alpha+\beta) |\mathbf{R}_P - \mathbf{R}_C|^2\right] & \text{if } \mathbf{R}_P \neq \mathbf{R}_C \end{cases}$$
(45)

where the function F_0 is related to the built-in standard error function Erf in MATHEMATICA by

$$F_0(t) = \frac{1}{2} \left(\frac{\pi}{t}\right)^{1/2} \operatorname{Erf}(\sqrt{t})$$
(46)

and

$$\boldsymbol{R}_{P} = \frac{\alpha \boldsymbol{R}_{A} + \beta \boldsymbol{R}_{B}}{\alpha + \beta} \tag{47}$$

 $[\]frac{1}{5}$ The expressions for integrals of Gaussians primitives here differ slightly from Szabo and Ostlund [1] because the formulas in the text are for *unnormalized* Gaussian primitives.

In the code we calculate V_C^{nucl} for each nucleus C and then sum up the result

$$\boldsymbol{V}^{\text{nucl}} = \sum_{C} \boldsymbol{V}_{C}^{\text{nucl}} \tag{48}$$

4.3 Two-electron integrals

The two-electron integral is defined as

$$(\mu\nu|\lambda\sigma) = \int \mathrm{d}\mathbf{r}_1 \mathbf{r}_2 \,\phi_\mu^*(1)\phi_\nu(1) \,\frac{1}{r_{12}} \,\phi_\lambda^*(2)\phi_\sigma(2) \tag{49}$$

From Szabo and Ostlund [1, p.416], this integral can be evaluated for any pair of normalized 1s Gaussian primitives

$$(AB|CD) = \int d\mathbf{r}_1 d\mathbf{r}_2 \ g_{1s}(\alpha, \mathbf{r}_1 - \mathbf{R}_A) g_{1s}(\beta, \mathbf{r}_1 - \mathbf{R}_B) \frac{1}{r_{12}} g_{1s}(\gamma, \mathbf{r}_2 - \mathbf{R}_C) g_{1s}(\delta, \mathbf{r}_2 - \mathbf{R}_D)$$
(50)

$$= \begin{cases} \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \left(\frac{2\gamma}{\pi}\right)^{3/4} \left(\frac{2\delta}{\pi}\right)^{3/4} \frac{2\pi^{5/2}}{(\alpha+\beta)(\gamma+\delta)\sqrt{\alpha+\beta+\gamma+\delta}} \\ \times \exp\left[-\frac{\alpha\beta}{\alpha+\beta}|\mathbf{R}_{A}-\mathbf{R}_{B}|^{2}-\frac{\gamma\delta}{\gamma+\delta}|\mathbf{R}_{C}-\mathbf{R}_{D}|^{2}\right] \\ \times F_{0}\left[\frac{(\alpha+\beta)(\gamma+\delta)}{\alpha+\beta+\gamma+\delta}|\mathbf{R}_{P}-\mathbf{R}_{Q}|^{2}\right] & \text{if } \mathbf{R}_{P} \neq \mathbf{R}_{Q} \qquad (51) \\ \left(\frac{2\alpha}{\pi}\right)^{3/4} \left(\frac{2\beta}{\pi}\right)^{3/4} \left(\frac{2\gamma}{\pi}\right)^{3/4} \left(\frac{2\delta}{\pi}\right)^{3/4} \frac{2\pi^{5/2}}{(\alpha+\beta)(\gamma+\delta)\sqrt{\alpha+\beta+\gamma+\delta}} \\ \times \exp\left[-\frac{\alpha\beta}{\alpha+\beta}|\mathbf{R}_{A}-\mathbf{R}_{B}|^{2}-\frac{\gamma\delta}{\gamma+\delta}|\mathbf{R}_{C}-\mathbf{R}_{D}|^{2}\right] & \text{if } \mathbf{R}_{P} = \mathbf{R}_{Q} \end{cases}$$

where F_0 is defined in Eq. (46), \mathbf{R}_P is defined in Eq. (47) and

$$\boldsymbol{R}_{Q} = \frac{\gamma \boldsymbol{R}_{C} + \delta \boldsymbol{R}_{D}}{\gamma + \delta} \tag{52}$$

5 Algorithm

- 1. Specify a molecule i.e. a set of nuclear coordinates $\{R_A\}$, atomic numbers $\{Z_A\}$ and number of electrons N.
- 2. Specify a basis set whose members describe the atomic orbitals.
- 3. Calculate matrices \boldsymbol{S} and $\boldsymbol{H}^{\text{core}}$ and two-electron integrals $(\mu\nu|\lambda\sigma)$ according to Section 4. \boldsymbol{S} and $\boldsymbol{H}^{\text{core}}$ both have size $K \times K$.
- 4. Obtain a transformation matrix X that satisfies $X^{\dagger}SX = 1$. One way to obtain X is canonical orthogonalization. Suppose U diagonalizes S

$$U^{\dagger}SU = s \tag{53}$$

and $s^{-1/2}$ contains the inverse square root of the diagonal elements of s then the matrix X is given by

$$\boldsymbol{X} = \boldsymbol{U}\boldsymbol{s}^{-1/2} \tag{54}$$

 \boldsymbol{X} has size $K \times K$.

⁶ Szabo and Ostlund [1] neglected to consider the case where $\mathbf{R}_P = \mathbf{R}_C$ which causes division by zero in Eq. (45) because the argument to the function F_0 is zero. The same comment applies to Eq. (51) when $\mathbf{R}_P = \mathbf{R}_Q$.

5. Guess an initial density matrix P.

P, which has size $K \times K$, is defined in Eq. (26). A not uncommon starting point (which we use here) is to let P be the zero matrix, meaning our initial guess is that there is no electron-electron interaction.

6. Calculate the matrix \boldsymbol{G} from the density matrix \boldsymbol{P} and the two-electron integrals $(\mu\nu|\lambda\sigma)$. The matrix \boldsymbol{G} of size $K \times K$ has elements

$$G_{\mu\nu} = \sum_{\lambda,\sigma=1}^{K} P_{\lambda\sigma} \left[(\mu\nu|\sigma\lambda) - \frac{1}{2} (\mu\lambda|\sigma\nu) \right]$$
(55)

7. Add G to the core-Hamiltonian matrix H^{core} to obtain the Fock matrix $F = H^{\text{core}} + G$. Calculate the ground state electronic energy as given by Szabo and Ostlund [1, p.150]:

$$E_{\rm elec} = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\nu\mu} (H_{\mu\nu}^{\rm core} + F_{\mu\nu})$$
(56)

$$=\frac{1}{2}\operatorname{Tr}[\boldsymbol{P}(\boldsymbol{H^{\operatorname{core}}}+\boldsymbol{F})]$$
(57)

Note that this formula must use the same density matrix P that was used to form F. Thus if we want to calculate this quantity every iteration to monitor the convergence of the energy, the calculation must be done immediately after forming a new F i.e. in step 7, not after forming a new P in step 11.

- 8. Calculate the transformed Fock matrix $F' = X^{\dagger}FX$.
- 9. Diagonalize F' to obtain the diagonal matrix ε and matrix C' whose columns are the eigenvectors of F'.

$$F'C' = C'\varepsilon \tag{58}$$

- 10. Calculate matrix C = XC'.
- 11. Form a new density matrix P from C.

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^{*}$$
(59)

where N is the total number of electrons (which is required to be even for a closed-shell calculation).

- 12. Calculate G from P and the two-electron integrals in same manner as step 6.
- 13. Calculate F and the ground state electronic energy in the same manner as step 7.
- 14. If the difference between this energy and the one previously obtained is less than 10^{-6} Hartree, terminate the calculation. If not, return to step 8.
- 15. Use the resultant solution, represented by C, P and F, to calculate physical quantities of interest. In this case, since we only want the total energy, we can just add the nuclear-nuclear repulsion to the converged electronic energy obtained in step 13:

$$E_{\rm tot} = E_{\rm elec} + \sum_{A} \sum_{B>A} \frac{Z_A Z_B}{R_{AB}} \tag{60}$$

6 Results

From Fig. 5, the equilibrium bond length of HeH⁺ is approximately $1.4 a_0$. At this approximate bond length, the total energy is $E_{\text{tot}} = -2.85994$ Hartree which agrees with Szabo and Ostlund [1] and differs from the exact result by 0.1 Hartree. The coefficient matrix is

$$\boldsymbol{C} = \begin{pmatrix} 0.796586 & -0.809136\\ 0.335298 & 1.08482 \end{pmatrix}$$
(61)

and the corresponding orbital energies are

$$\boldsymbol{\varepsilon} = \begin{pmatrix} -1.625 & 0\\ 0 & -0.050431 \end{pmatrix} \tag{62}$$

which means the 2 spatial molecular orbitals are

$$\psi_1(\mathbf{r}) = 0.796586 \,\phi_1(\mathbf{r} - \mathbf{r}_{\rm He}) + 0.335298 \,\phi_2(\mathbf{r} - \mathbf{r}_{\rm H}) \tag{63}$$

$$\psi_2(\mathbf{r}) = -0.809136\,\phi_1(\mathbf{r} - \mathbf{r}_{\rm He}) + 1.08482\,\phi_2(\mathbf{r} - \mathbf{r}_{\rm H}) \tag{64}$$

where the basis functions ϕ_1 and ϕ_2 were defined in Eqs. (34) and (35). The energies in ε tell us that because ψ_1 has lower energy, it is the bonding molecular orbital whereas ψ_2 is the anti-bonding molecular orbital.

Because we use restricted spin orbitals, the spin molecular orbitals are just the spatial molecular orbitals combined with either spin up or spin down.

$$\chi_1(\boldsymbol{x}) = \psi_1(\boldsymbol{r})\alpha(\omega) \tag{65}$$

$$\chi_2(\boldsymbol{x}) = \psi_1(\boldsymbol{r})\beta(\omega) \tag{66}$$

$$\chi_3(\boldsymbol{x}) = \psi_2(\boldsymbol{r})\alpha(\omega) \tag{67}$$

$$\chi_4(\boldsymbol{x}) = \psi_2(\boldsymbol{r})\beta(\omega) \tag{68}$$

Because HeH⁺ has 2 electrons, the ground state wave function is the Slater determinants formed from the two spin orbitals having the lowest energy. This is easily seen to be χ_1 and χ_2 . Thus the ground state wave function of HeH⁺ is

$$\Psi_0 = \frac{1}{\sqrt{2}} [\chi_1 \chi_2 - \chi_1 \chi_2] \tag{69}$$

7 Future work

- Extend the program to more basis sets. This will require changing the integral evaluation rules for Gaussian primitives and modifying the code to allow for multiple basis functions centered on the same atom.
- Eliminate as many procedural parts of the program as possible.
- Make the program parallel so that it can run on a cluster.

References

¹A. Szabo and N. S. Ostlund, *Modern quantum chemistry: introduction to advanced electronic structure theory* (Dover Publications, Mineola, New York, 1989).



Figure 5: Molecular energy curve as a function of internuclear distance for HeH^+ .