Hartree Fock method for solving the Hydrogen molecule ion

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The SCF Procedure

Step 1: Setting up the problem

Specify a molecule (a set of nuclear coordinates $\{\mathbf{R}\}$, atomic numbers $\{\mathbf{Z}\}$, and number of electrons $\mathbf{N}$) and a basis set ϕ_μ , and the guess values for coefficients.

The molecule we are working with is: H_2^+

Nuclear coordinates: R1 - 0, for R2 - R

Atomic numbers: Z = 1 for both

Number of electrons, N = 1

Basis set: STO-3G, linear combination of 3 gaussian functions of the form

$$\tilde{g}_{1s}(r - R_A) = e^{-\alpha|r-R_A|^2}$$

For 1s orbital of H atom, we used the following exponents for the gaussians:
`0.168856, 0.623913, 3.42525.`

Initial guess for coefficients: We don't require that, we'll see later why

Step 2

Calculate all the required molecular integrals:

$$S_{\mu\nu}, H_{\mu\nu}^{core}, \quad (\mu\nu|\lambda\sigma)$$

In this case, only the overlap and core-Hamiltonian matrices are required since we are dealing with 1-electron system, hence there are no 2-electron interactions (Coulombic or Exchange). So we don't require 2-electron integrals.

THE INTEGRALS!!

MAIN IDEA: Product of two gaussians on different centers, is proportional to another Gaussian with a third center !!

$$\tilde{g_{1s}}(r - R_A) = e^{-\alpha|r - R_A|^2}$$

$$\tilde{g_{1s}}(r - R_A)\tilde{g_{1s}}(r - R_B) = \tilde{K}\tilde{g_{1s}}(r - R_P)$$

$$\tilde{K} = exp[-\alpha\beta/(\alpha + \beta)|R_A - R_B|^2]$$

$$R_P = (\alpha R_A + \beta R_B)/(\alpha + \beta)$$

The exponent of the new Gaussian entered at R_P is

$$p = \alpha + \beta$$

We now evaluate the basic integrals that we need for any a*b initio* calculations which requires contraction of primitive 1s Gaussians. We will evaluate the integrals for normalised functions, and then later normalise as needed.

- Two center overlap integrals:

$$S_{AB} = (A|B) = \int dr_1 \tilde{g}_{1s}(r_1 - R_A)\tilde{g}_{1s}(r_1 - R_B)$$

$$(A|B) = \tilde{K}\int dr_1 \tilde{g}_{1s}(r_1 - R_P) = \tilde{K}\int dr_1 exp[-p|r_1 - r_P|^2]$$

Now let $r = r_1 - R_P,\ dr = dr_1$

$$(A|B) = 4\pi\tilde{K}\int_0^\infty dr r^2 e^{-pr^2}$$

This last integral is just $(\pi/p)^{3/2}/4\pi$, so that

$$(A|B) = [\pi/(\alpha + \beta)]^{3/2} exp[-\alpha\beta/(\alpha + \beta)|R_A - R_B|^2]$$

- The kinetic energy integral:

$$(A \mid -\frac{1}{2}\nabla^2 \mid B) = \int dr_1 \tilde{g}_{1s}(r_1 - R_A)(-\frac{1}{2}\nabla_1^2)\tilde{g}_{1s}(r_1 - R_B)$$

The above integral can be similarly computed as before, after applying the operator, to give:

$$(A \mid -\frac{1}{2}\nabla^2 \mid B) = \alpha\beta/(\alpha + \beta)[3 - 2\alpha\beta/(\alpha + \beta)\mid R_A - R_B\mid^2][\pi/(\alpha + \beta)]^{3/2}exp(-\alpha\beta/(\alpha + \beta)R_A - R_B\mid^2)$$

- Now we consider the nuclear attraction integral:

$$(A \mid -Z_C/r_{1C} \mid B) = \int dr_1 \tilde{g}_{1s}(r - R_A)[-Z_C/\mid r_1 - R_C \mid]\tilde{g}_{1s}(r - R_B)$$

$$= -Z_C \int dr_1 e^{-\alpha \mid r_1 - R_A \mid^2} \mid r_1 - R_C \mid^{-1} e^{-\beta \mid r_1 - R_B \mid^2}$$

First we combine the two gaussians to obtain a single Gaussian at R_P

$$(A \mid Z_C/r_{1C} \mid B) = -Z_C \tilde{K} \int dr_1 e^{-p \mid r - R_P \mid^2} \mid r_1 - R_C \mid^{-1}$$

The above integral is calculated by replacing the quantity in the integral by its Fourier transform and applying the Fourier Integral Theorem. The final value of the integral is:

$$(A \mid -Z_C/r_{1C} \mid B) = -2\pi/(\alpha + \beta) Z_C exp[-\alpha\beta/(\alpha + \beta) \mid R_A - R_B \mid^2] \times F_0[(\alpha + \beta) \mid R_P - R_C \mid^2]$$

where
$$F_0(t) = t^{-1/2} \int_0^{t^{1/2}} dy^{-y^2} = \frac{1}{2}(\pi/t)^{1/2} erf(t^{1/2})$$

Reformulating the Eigenvalue Equation

The Roothan equations are non linear and hence they have to be solved in an iterative manner

$$F(C)C = SC\epsilon$$

If S were a unit matrix (if the basis functions were orthonormal), then we would have the form of a usual matrix eigenvalue equation.

If we have a set of non-orthogonal basis functions, then it is always possible to find a transformation matrix X such that:

$$X^{+}SX = 1$$

It can be shown that $X = Us^{-1/2}$, satisfies the above equation.

$$X'SX = (Us^{-1/2})^{+}S(Us^{-1/2}) = s^{-1/2}U^{+}SUs^{-1/2}$$

$$= s^{-1/2}ss^{-1/2} = 1$$

Considering a new coefficient matrix C' connected to the old coefficient matrix C by:

$$C' = X^{-1}C \longrightarrow C = XC'$$

Substituting into Roothan Equations

$$FXC' = SXC'\epsilon$$

Multiplying on the left by X'

$$(X'FX)C' = (X'SX)C'\epsilon$$

Define a new matrix F'

$$F' = X^+FX$$

Then, $$\boxed{F'C' = C'\epsilon}$$

These are the **transformed Roothan Equations** that can be solved for C' by diagonalising F'. This is the eigenvalue problem that we have to solve.

Step 3

Now with that context, we'll start solving the eigenvalue problem.

Diagonalise the overlap matrix **S** and obtain a transformation matrix **X**.

$$X = Us^{-1/2}$$

where U is a unitary matrix such that

$$U^+SU = s$$

where s is a diagonal matrix of the eigenvalues of S.

Step 4: Obtain a guess at the density matrix P

Step 5: Calculate the matrix G from the density matrix P and the two electron integrals

$$(\mu\nu \,|\, \lambda\sigma)$$

Step 6: Add G to the core-Hamiltonian to obtain the Fock matrix:

$$F = H^{core} + G$$

$$G = \sum_{\mu\nu} \sum_{\lambda\sigma} P_{\lambda\sigma}[(\mu\nu \,|\, \sigma\lambda) - \frac{1}{2}(\mu\lambda \,|\, \sigma\nu)]$$

In this case, P matrix will not be there as there aren't any 2-electron integrals, thus we skip the above steps. Hence the Fock matrix will be equal to core-Hamiltonian only and thus it is independent of coefficients and it therefore remains constant.

Step 7: Calculate the transformed Fock matrix: $F' = X^+FX$

Step 8: Diagonalise F' to obtain C' and ϵ. We get 6 eigenvalues and eigenvectors, out of which we take the coefficient vector with the minimum eigenvalue, because we are computing ground state energies.

Step 9: Calculate the new coefficients: $C = XC'$

**Step 10**: Form new density matrix P using the new C's obtained.

Step 11: Determine whether the procedure has converged or not, i.e. determine whether the new density matrix of Step 10 is the same as the previous density matrix within a specified criterion. If the procedure has not converged, return to Step 5 with a new density matrix.

**Step 12**: If the procedure has converged, then use these final C, P, F matrices to compute other values of interest, namely Energy.

Step 13: Repeat the above SCF procedure at different values of **R** and compute the energy to plot the potential energy surface.

Since we don't have P matrix in our computation, the Fock matrix is fixed and so is its Eigenvalues and Eigenvectors (coefficients). Thus we get the required coefficients in one iteration only.
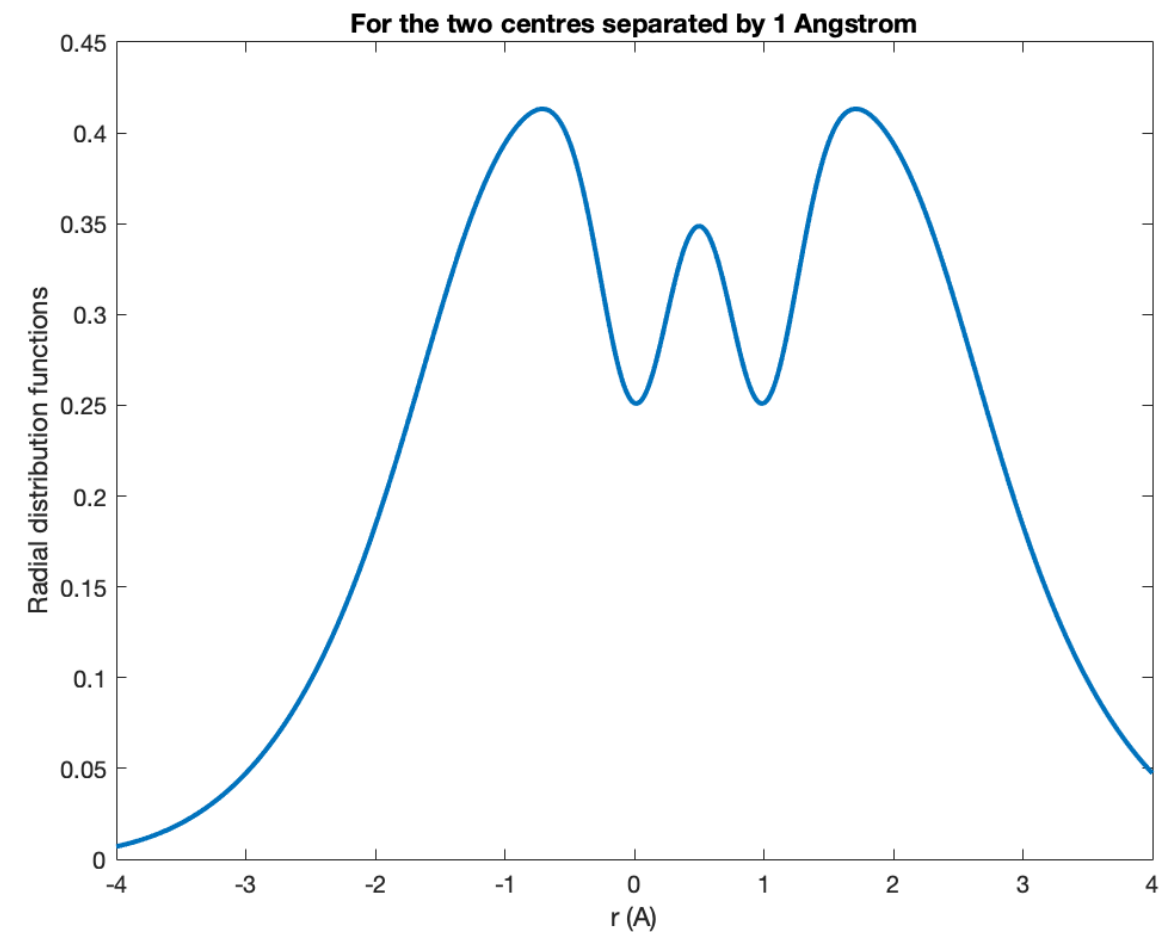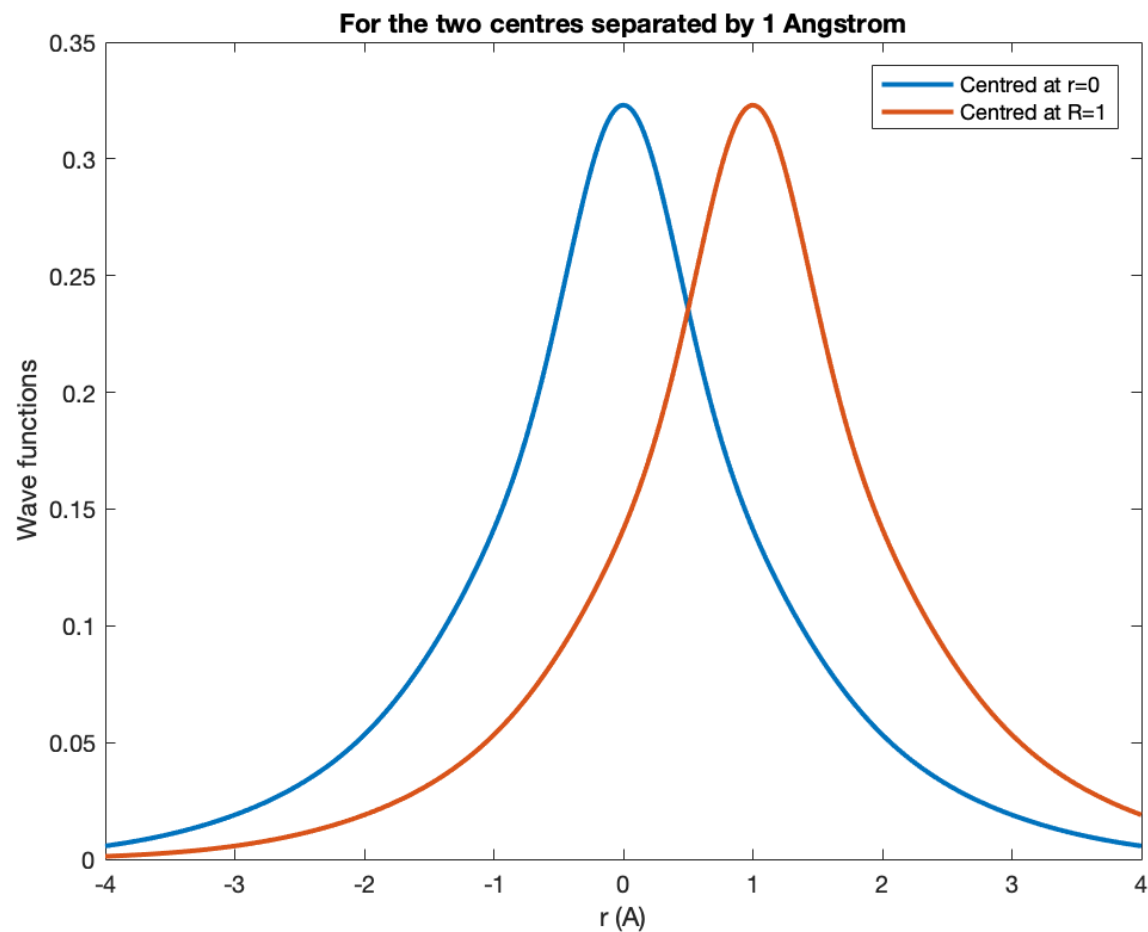
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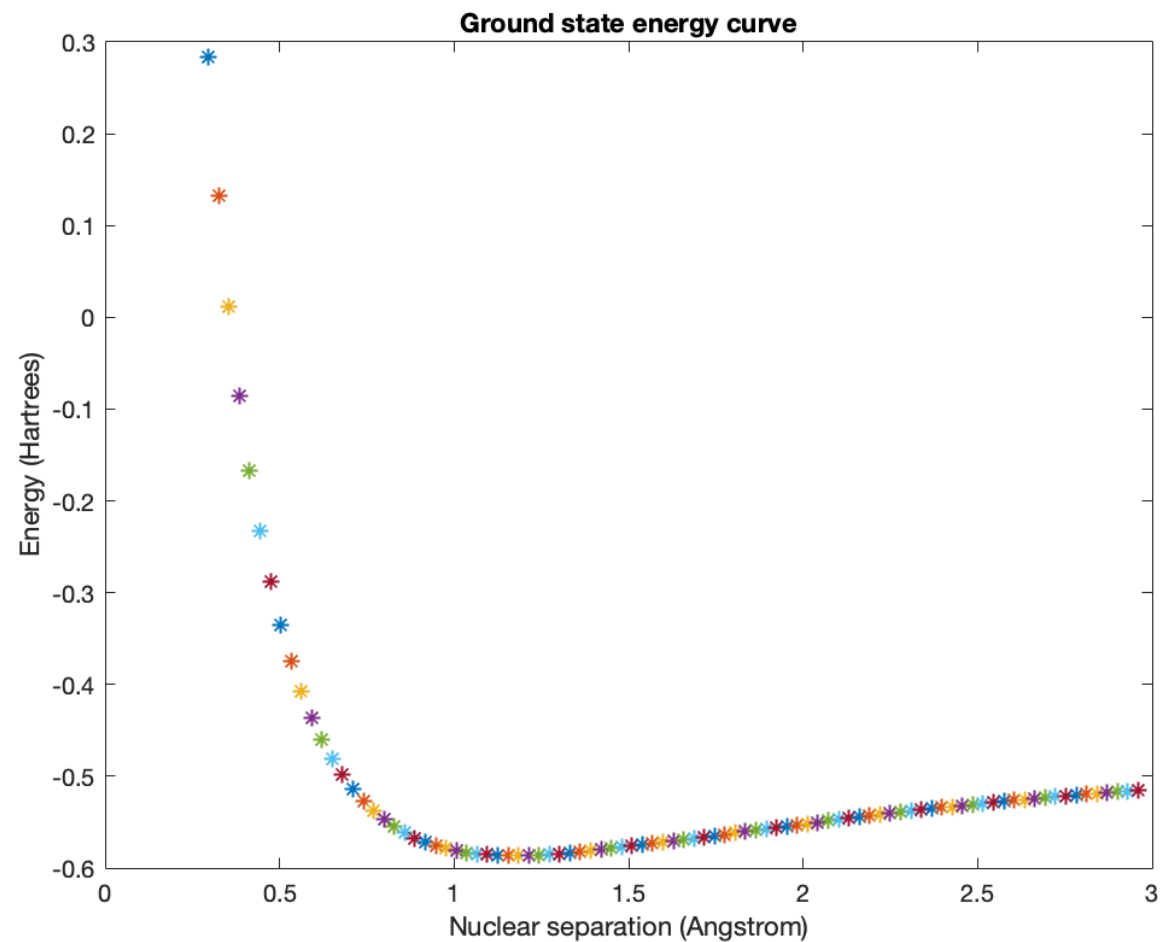
Results from HF/STO-3G code
Minimum Energy = -0.5864 Hartrees
Bond Length = 1.0580 Å
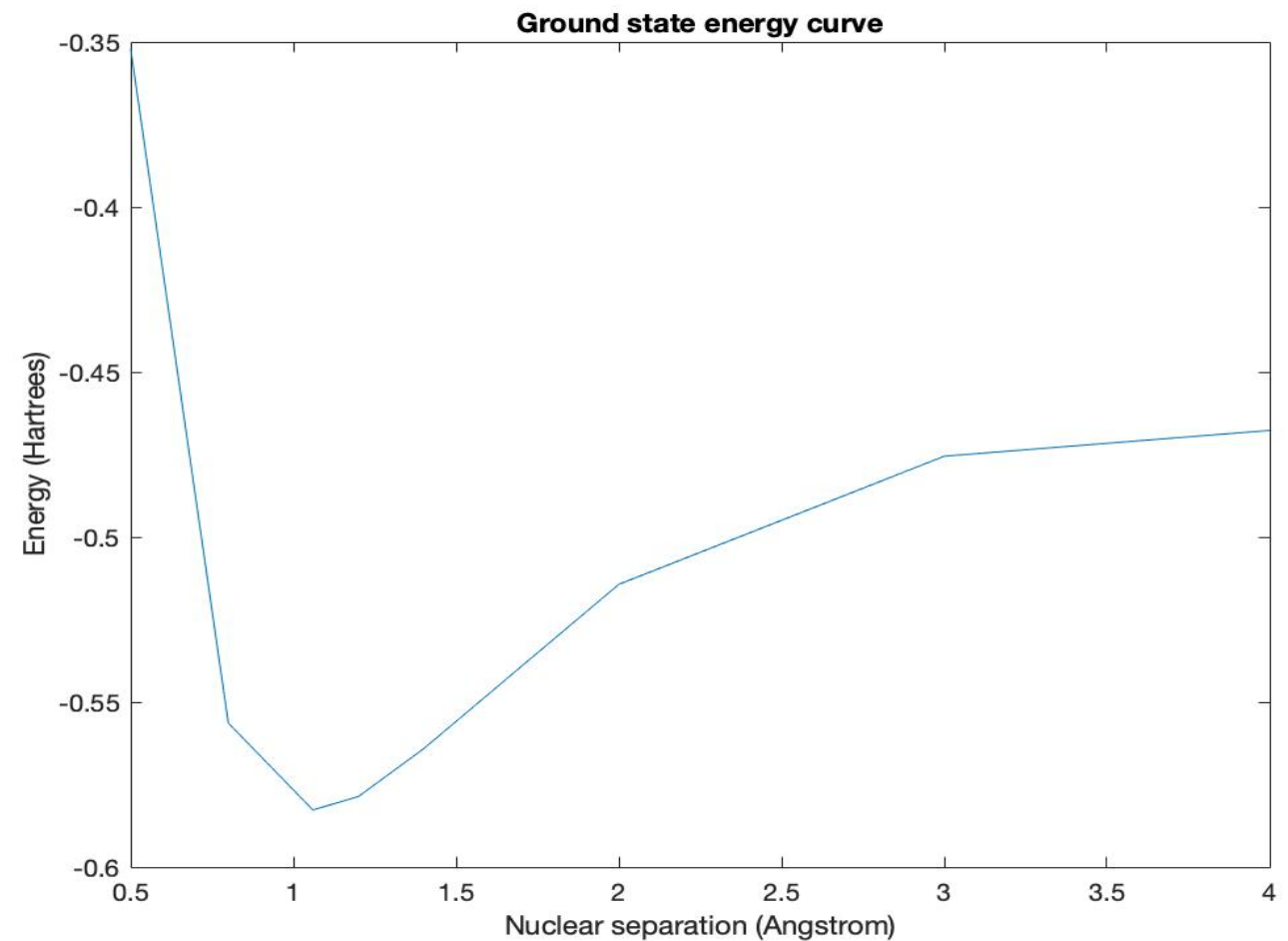
Results for HF/STO-3G using Gaussian
Minimum energy = -0.5827
Bond Length = 1.06 Å

Literature results[1]: Equilibrium energy = -0.1029 Hartrees
Bond Length = 1.06 Å

RESULTS

Coefficients for the Wave Functions:
(0.0848   0.1232   0.1150), (0.0848   0.1232   0.1150)

Radial distribution function

Individual Contribution

Code, Literature survey, Presentation: Equal Contribution

References

1. chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/
   Book%3A_Quantum_States_of_Atoms_and_Molecules_(Zielinksi_et_al.)/
   10%3A_Theories_of_Electronic_Molecular_Structure/
   10.04%3A_The_Case_of_H%E2%82%82%E2%81%BA

2. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory, by Attila
   Szabo and Neil S. Ostlund, Dover Publications, ISBN-10: 0486691861