

Hamiltonian

We consider both the one-electron and two-electron Hamiltonians in atomic units.

One-Electron System (Hydrogen-like Atom)

$$\hat{H}^{(1)} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$$

This consists of the kinetic energy of the electron and the Coulomb attraction to the nucleus.

Two-Electron System (e.g., Helium Atom)

$$\hat{H}^{(2)} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

Where:

- ∇_i^2 : Laplacian w.r.t. electron i
- r_i : distance from nucleus to electron i
- $\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}$: electron-electron repulsion

Matrix Elements in STO Basis

Let basis functions be:

$$|l, m; \zeta\rangle = r^\ell e^{-\zeta r} Y_{\ell m}(\theta, \phi)$$

We define matrix elements for kinetic, potential, and overlap as:

Kinetic Energy

We define the kinetic energy matrix element as:

$$\langle l_1, m_1; \zeta_1 | \hat{T} | l_2, m_2; \zeta_2 \rangle = \delta_{l_1 l_2} \delta_{m_1 m_2} \cdot t(l_1, \zeta_1, \zeta_2)$$

Let the radial part be $\chi(r) = r^\ell e^{-\zeta r}$. In spherical coordinates, the Laplacian becomes:

$$\nabla^2 \chi(r) = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\chi(r)}{dr} \right) - \frac{\ell(\ell+1)}{r^2}$$

So the expectation value of the kinetic energy is and using integration by part by setting $u = \chi_1(r)$ and $dv = \frac{\partial}{\partial r} (r^2 \frac{\partial \chi_2(r)}{\partial r})$

$$t(\ell_1, \zeta_1, \zeta_2) = -\frac{1}{2} \int_0^\infty \chi_1(r) \nabla^2 \chi_2(r) r^2 dr = \frac{1}{2} \int_0^\infty \nabla \chi_1(r) r^2 \nabla \chi_2(r) dr$$

Computing the derivative of $\chi_i(r)$

$$\frac{\partial \chi_i(r)}{\partial r} = -\zeta_i e^{-\zeta_i r} r^\ell + \ell e^{-\zeta_i r} r^{\ell-1}$$

So the integral becomes

$$t(\ell_1, \zeta_1, \zeta_2) = \frac{1}{2} \int_0^\infty e^{-(\zeta_1 + \zeta_2)r} (\zeta_1 \zeta_2 r^{2\ell+2} - \ell(\zeta_1 + \zeta_2) r^{2\ell+1} + \ell^2 r^{2\ell} - \ell(\ell+1) r^{2\ell}) dr$$

And using gamma function the integral evaluate to

$$t(\ell_1, \zeta_1, \zeta_2) = \frac{1}{2} \left(\zeta_1 \zeta_2 \frac{\Gamma(2\ell+3)}{(\zeta_1 + \zeta_2)^{2\ell+3}} - \ell(\zeta_1 + \zeta_2) \frac{\Gamma(2\ell+2)}{(\zeta_1 + \zeta_2)^{2\ell+2}} + \ell^2 \frac{\Gamma(2\ell+1)}{(\zeta_1 + \zeta_2)^{2\ell+1}} - \ell(\ell-1) \frac{\Gamma(2\ell+1)}{(\zeta_1 + \zeta_2)^{2\ell+1}} \right)$$

Potential Energy

$$\langle l_1, m_1; \zeta_1 | \hat{V} | l_2, m_2; \zeta_2 \rangle = \delta_{l_1 l_2} \delta_{m_1 m_2} \cdot v(l_1, \zeta_1, \zeta_2)$$

Using:

$$v(\ell, \zeta_1, \zeta_2) = -Z \int_0^\infty r^{2\ell+1} e^{-(\zeta_1 + \zeta_2)r} dr = -Z \cdot \frac{\Gamma(2\ell+2)}{(\zeta_1 + \zeta_2)^{2\ell+2}}$$

Overlap

$$\langle l_1, m_1; \zeta_1 | l_2, m_2; \zeta_2 \rangle = \delta_{l_1 l_2} \delta_{m_1 m_2} \cdot s(l_1, \zeta_1, \zeta_2)$$

$$s(\ell, \zeta_1, \zeta_2) = \int_0^\infty r^{2\ell+2} e^{-(\zeta_1 + \zeta_2)r} dr = \frac{\Gamma(2\ell+3)}{(\zeta_1 + \zeta_2)^{2\ell+3}}$$

Repulsion Integral

$$\langle l_1, m_1; \zeta_1; l_2, m_2; \zeta_2 \mid l_3, m_3; \zeta_3; l_4, m_4; \zeta_4 \rangle$$

Spherical (Angular) Part Using 3j Symbols

We express the angular part of the two-electron repulsion integral using Wigner 3j symbols. The Coulomb operator is expanded as:

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\Omega_1) Y_{lm}(\Omega_2).$$

The angular part of the integral is:

$$A = \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \int Y_{l_1 m_1}(\Omega_1) Y_{lm}^*(\Omega_1) Y_{l_2 m_2}(\Omega_1) d\Omega_1 \cdot \int Y_{l_3 m_3}(\Omega_2) Y_{lm}(\Omega_2) Y_{l_4 m_4}(\Omega_2) d\Omega_2.$$

Each triple product of spherical harmonics is given by:

$$\int Y_{l_1 m_1} Y_{lm}^* Y_{l_2 m_2} d\Omega = \sqrt{\frac{(2l_1 + 1)(2l + 1)(2l_2 + 1)}{4\pi}} \begin{pmatrix} l_1 & l & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l & l_2 \\ m_1 & -m & m_2 \end{pmatrix},$$

$$\int Y_{l_3 m_3} Y_{lm} Y_{l_4 m_4} d\Omega = \sqrt{\frac{(2l_3 + 1)(2l + 1)(2l_4 + 1)}{4\pi}} \begin{pmatrix} l_3 & l & l_4 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_3 & l & l_4 \\ m_3 & m & m_4 \end{pmatrix}.$$

Thus, the full angular factor becomes:

$$A = \sum_{l=0}^{\infty} \sum_{m=-l}^l \sqrt{(2l_1 + 1)(2l_2 + 1)(2l_3 + 1)(2l_4 + 1)} \begin{pmatrix} l_1 & l & l_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l & l_2 \\ m_1 & -m & m_2 \end{pmatrix} \begin{pmatrix} l_3 & l & l_4 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_3 & l & l_4 \\ m_3 & m & m_4 \end{pmatrix}$$

Radial Part of the Two-Electron Repulsion Integral

Define:

$$a = l_1 + l_2 + 2, \quad b = l_3 + l_4 + 2, \quad p = \zeta_1 + \zeta_2, \quad q = \zeta_3 + \zeta_4.$$

The radial integral is:

$$I = \int_0^\infty \int_0^\infty \frac{r_<^l}{r_>^{l+1}} r_1^a r_2^b e^{-pr_1 - qr_2} dr_1 dr_2.$$

We break into two regions.

Region I: $r_1 < r_2$

$$I_1 = \frac{1}{r_2^{l+1}} \int_0^{r_2} dr_1 r_1^{a+l} e^{-pr_1}.$$

With the substitution $t = pr_1$:

$$I_1 = \frac{1}{r_2^{l+1}} \frac{1}{p^{a+l+1}} \gamma(a + l + 1, pr_2),$$

where $\gamma(s, x)$ is the lower incomplete gamma function.

Region II: $r_2 < r_1$

$$I_2 = \int_{r_2}^{\infty} dr_1 r_1^a e^{-pr_1} \frac{r_2^l}{r_1^{l+1}}.$$

With the substitution $t = pr_1$:

$$I_2 = \frac{r_2^l}{p^{a-l}} \Gamma(a - l, pr_2),$$

where $\Gamma(s, x)$ is the upper incomplete gamma function.

Final Expression

$$I = \int_0^{\infty} (I_1 + I_2) e^{-qr_2} r_2^b dr_2.$$

Verification with Simple Molecules

We use a few simple well known answer to verify the above integral

1s orbital hydrogen

For hydrogen in 1s orbital we set $\zeta_1 = \zeta_2 = 1$, $Z = 1$ and $\ell = 0$

$$t(\ell, \zeta_1, \zeta_2) = \frac{1}{2} \left(\frac{\Gamma(3)}{2^3} \right) = \frac{1}{2} \frac{2!}{8} = \frac{1}{8}$$

$$v(\ell, \zeta_1, \zeta_2) = -\frac{\Gamma(2)}{2^2} = -\frac{1}{4}$$

$$s(\ell, \zeta_1, \zeta_2) = \frac{\Gamma(3)}{2^3} = \frac{2}{8} = \frac{1}{4}$$

to extract $\langle V \rangle$ and $\langle T \rangle$ we need to divide v, t by s , so

$$\langle T \rangle = \frac{1/8}{1/4} = \frac{1}{2}$$

$$\langle V \rangle = \frac{-1/4}{1/4} = -1$$

Thus our energy for ground state hydrogen is

$$E = \frac{1}{2} - 1 = -\frac{1}{2} \approx -13 \text{ eV}$$

Solving generalized Eigenvalue Problem for hydrogen with 2 different ζ_i values

Consider two basis function $\chi_1(r) = r^\ell e^{-\zeta_i r}$ for $i = 1, 2$ $\ell = 0$ and $Z = 1$, we want to solve

$$\mathbf{H}\vec{c} = E\mathbf{S}\vec{c}$$

We construct the \mathbf{S} and \mathbf{H} matrix

$$\begin{aligned} \mathbf{S} &= \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \\ \mathbf{H} &= \begin{bmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{bmatrix} = \begin{bmatrix} T_{11} + V_{11} & T_{12} + V_{12} \\ T_{21} + V_{21} & T_{22} + V_{22} \end{bmatrix} \end{aligned}$$

Take the determinant and setting it to 0

$$\det(\mathbf{H} - ES) = (H_{11} - ES_{11})(H_{22} - ES_{22}) - (H_{12} - ES_{12})^2 = 0$$

Since \hat{H} is hermitian and our basis set is always real so we can freely switch index, and overlap is also symmetric.

Solving the quadratic equation above will yield two different E and thus getting ground state and first excited state

Generalized Eigenvalue Problem for n Slater-Type Orbitals

We now generalize our previous 2×2 case to a basis of n Slater-type orbitals (STOs), all s -type ($\ell = 0$), each with a different exponential decay parameter ζ_i . The basis functions are:

$$\chi_i(r) = e^{-\zeta_i r}, \quad i = 1, 2, \dots, n$$

We construct the $n \times n$ overlap matrix S and Hamiltonian matrix H as follows:

$$\begin{aligned} S_{ij} &= \langle \chi_i | \chi_j \rangle = \int_0^\infty \chi_i(r) \chi_j(r) r^2 dr = \frac{2}{(\zeta_i + \zeta_j)^3} \\ T_{ij} &= \frac{1}{2} \left(\frac{2\zeta_i \zeta_j}{(\zeta_i + \zeta_j)^3} \right) \\ V_{ij} &= \langle \chi_i | V | \chi_j \rangle = - \int_0^\infty \chi_i(r) \chi_j(r) r dr = - \frac{2}{(\zeta_i + \zeta_j)^3} \\ H_{ij} &= T_{ij} + V_{ij} \end{aligned}$$

Thus, we construct:

$$S = \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1n} \\ S_{21} & S_{22} & \cdots & S_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ S_{n1} & S_{n2} & \cdots & S_{nn} \end{bmatrix}, \quad H = \begin{bmatrix} H_{11} & H_{12} & \cdots & H_{1n} \\ H_{21} & H_{22} & \cdots & H_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ H_{n1} & H_{n2} & \cdots & H_{nn} \end{bmatrix}$$

We solve the generalized eigenvalue problem:

$$H\vec{c} = E S \vec{c}$$

to obtain n approximate energy eigenvalues and their corresponding eigenstates expressed in the STO basis.

Comparison: Hydrogenic $\zeta = \frac{Z}{n}$ vs. Even-Tempered Basis

We now compare the exact hydrogenic values of ζ for a hydrogen atom ($Z = 1$) with an even-tempered Slater-type basis. The hydrogenic $1s$ orbital has the exact form:

$$\chi_{1s}(r) = e^{-Zr}, \quad \text{so } \zeta = Z = 1$$

Hydrogenic Orbital Energy (Exact $\zeta = Z$)

From earlier, we showed:

$$\langle T \rangle = \frac{1}{2}, \quad \langle V \rangle = -1, \quad E = -\frac{1}{2}$$

Even-Tempered STO Basis

In the even-tempered approach, we choose a geometric progression of exponents:

$$\zeta_i = \alpha \beta^{i-1}, \quad i = 1, \dots, n$$

Common choices are:

$$\begin{aligned} \alpha &= 0.3, & \beta &= 2.0 \\ \Rightarrow \zeta &= [0.3, 0.6, 1.2, 2.4, \dots] \end{aligned}$$

This allows flexible radial coverage and is useful for compact basis set generation. The resulting basis functions are:

$$\chi_i(r) = e^{-\zeta_i r}$$

Numerical Comparison via Generalized Eigenvalue Problem

We construct the Hamiltonian and overlap matrices using the previously defined expressions:

$$\begin{aligned} S_{ij} &= \frac{2}{(\zeta_i + \zeta_j)^3}, & T_{ij} &= \frac{\zeta_i \zeta_j}{(\zeta_i + \zeta_j)^3}, & V_{ij} &= -\frac{2}{(\zeta_i + \zeta_j)^2} \\ H_{ij} &= T_{ij} + V_{ij} \end{aligned}$$

Then we solve the generalized eigenvalue problem:

$$H\vec{c} = E S \vec{c}$$

Interpretation

- When using only one STO with $\zeta = 1$, we recover the exact result.
- Even-tempered sets allow flexibility, but convergence is slower — more functions are needed for comparable accuracy.
- For practical quantum chemistry, even-tempered STOs provide a compact and numerically efficient alternative, especially in correlated or molecular calculations where exact hydrogenic forms aren't available.

Energy Convergence with Increasing Basis Size

Letting $n = 1, 2, \dots, 10$, and using even-tempered ζ_i , one can plot the lowest eigenvalue vs. n and observe convergence toward -0.5 Hartree.

Hartree–Fock for a Two-Electron System in a Non-Orthonormal Basis

We consider a Slater determinant in the singlet case:

$$\Psi^{\text{HF}}(x_1, x_2) = \varphi(\mathbf{r}_1) \varphi(\mathbf{r}_2) \Xi(\sigma_1, \sigma_2),$$

where the spatial orbital is expanded in a non-orthonormal basis $\{|\chi_\mu\rangle\}$,

$$|\varphi\rangle = \sum_{\mu} C_{\mu} |\chi_{\mu}\rangle.$$

Because the basis is non-orthonormal, we impose the constraint

$$\langle \varphi | \varphi \rangle = \sum_{\mu\nu} C_{\mu}^{*} C_{\nu} S_{\mu\nu} = 1, \quad S_{\mu\nu} = \langle \chi_{\mu} | \chi_{\nu} \rangle.$$

Hartree–Fock Lagrangian

The Hartree–Fock energy functional is

$$E^{\text{HF}}[C] = 2\langle \varphi | \hat{h} | \varphi \rangle + \langle \varphi \varphi | \hat{v}_{ee} | \varphi \varphi \rangle - \langle \varphi \varphi | \hat{v}_{ee} | \varphi \varphi \rangle_{\text{ex}},$$

and the corresponding Lagrangian is

$$\mathcal{L}[C, C^{*}] = E^{\text{HF}}[C] - \lambda (\langle \varphi | \varphi \rangle - 1).$$

In the basis expansion this becomes

$$\mathcal{L}[C, C^{*}] = 2 \sum_{\mu\nu} C_{\mu}^{*} C_{\nu} h_{\mu\nu} + \sum_{\mu\nu\lambda\sigma} C_{\mu}^{*} C_{\nu}^{*} C_{\lambda} C_{\sigma} [(\mu\nu|\lambda\sigma) - (\mu\nu|\sigma\lambda)] - \lambda \left(\sum_{\mu\nu} C_{\mu}^{*} C_{\nu} S_{\mu\nu} - 1 \right).$$

Stationary Condition

Taking the derivative with respect to C_{μ}^{*} gives

$$\sum_{\nu} \left(h_{\mu\nu} + \sum_{\lambda\sigma} D_{\lambda\sigma} [(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)] \right) C_{\nu} = \lambda \sum_{\nu} S_{\mu\nu} C_{\nu},$$

with the density matrix

$$D_{\lambda\sigma} = \sum_p n_p C_{\lambda p} C_{\sigma p}^{*},$$

where n_p are orbital occupation numbers (not restricted to integers).

Roothaan–Hall Equations

Defining the Fock matrix

$$F_{\mu\nu} = h_{\mu\nu} + \sum_{\lambda\sigma} D_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma) \right],$$

the Hartree–Fock equations take the form of a generalized eigenvalue problem,

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon},$$

to be solved self-consistently.

SCF Loop Implementation Steps

1. Define parameters ζ_i, m_i, l_i, Z , and the number of electrons.
2. Build the single-particle Hamiltonian H_{core} and the overlap matrix S .
3. Initialize the density matrix D from the eigenvectors of H_{core} (the core Hamiltonian guess), and set the reference energy $E_{\text{old}} = 0$.
4. For each SCF iteration:
 - (a) Construct the Coulomb and exchange matrices J and K from D and the electron repulsion integrals (ERI).
 - (b) Form the Fock matrix:

$$F = H_{\text{core}} + J - \frac{1}{2}K,$$

and symmetrize it to ensure Hermiticity.

- (c) Solve the generalized eigenvalue problem:

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon},$$

to obtain molecular orbital (MO) coefficients C and orbital energies ε .

- (d) Select the occupied orbitals C_{occ} according to the number of electrons and build a new density matrix:

$$D_{\text{new}} = 2C_{\text{occ}}C_{\text{occ}}^T.$$

- (e) Compute the electronic energy:

$$E_{\text{one}} = \text{Tr}[DH_{\text{core}}], \quad E_{\text{two}} = \frac{1}{2}\text{Tr}[D(J - \frac{1}{2}K)],$$

$$E_{\text{total}} = E_{\text{one}} + E_{\text{two}}.$$

(f) Check convergence using:

$$\Delta E = |E_{\text{total}} - E_{\text{old}}|, \quad \Delta D = \|D_{\text{new}} - D\|.$$

If both are below the threshold, stop the iteration.

(g) Update $D \leftarrow D_{\text{new}}$ and $E_{\text{old}} \leftarrow E_{\text{total}}$.

5. Report the one-electron and two-electron contributions, as well as the final molecular orbital coefficient matrix.

Newton–Raphson Optimization of Even–Tempered Exponents

1. Even–tempered exponents

We define a set of n Slater type orbital exponents as

$$\zeta_i(\alpha_0, \beta) = \alpha_0 \beta^{i-1}, \quad i = 1, 2, \dots, n,$$

with constraints

$$\alpha_0 > 0, \quad \beta > 1.$$

2. Objective function

Let $E(\{\zeta_i\})$ denote the Hartree–Fock total energy obtained from an SCF procedure using the basis defined by $\{\zeta_i\}$. We define the objective function

$$f(\alpha_0, \beta) = E(\{\zeta_i(\alpha_0, \beta)\}_{i=1}^n).$$

The optimization problem is then

$$\min_{\alpha_0 > 0, \beta > 1} f(\alpha_0, \beta).$$

3. Finite difference derivatives

Let step sizes in each direction be h_α and h_β .

First derivatives (gradient):

$$\frac{\partial f}{\partial \alpha_0} \approx \frac{f(\alpha_0 + h_\alpha, \beta) - f(\alpha_0 - h_\alpha, \beta)}{2h_\alpha}, \quad (1)$$

$$\frac{\partial f}{\partial \beta} \approx \frac{f(\alpha_0, \beta + h_\beta) - f(\alpha_0, \beta - h_\beta)}{2h_\beta}. \quad (2)$$

Second derivatives (Hessian):

$$\frac{\partial^2 f}{\partial \alpha_0^2} \approx \frac{f(\alpha_0 + h_\alpha, \beta) - 2f(\alpha_0, \beta) + f(\alpha_0 - h_\alpha, \beta)}{h_\alpha^2}, \quad (3)$$

$$\frac{\partial^2 f}{\partial \beta^2} \approx \frac{f(\alpha_0, \beta + h_\beta) - 2f(\alpha_0, \beta) + f(\alpha_0, \beta - h_\beta)}{h_\beta^2}, \quad (4)$$

$$\frac{\partial^2 f}{\partial \alpha_0 \partial \beta} \approx \frac{f(\alpha_0 + h_\alpha, \beta + h_\beta) - f(\alpha_0 + h_\alpha, \beta - h_\beta) - f(\alpha_0 - h_\alpha, \beta + h_\beta) + f(\alpha_0 - h_\alpha, \beta - h_\beta)}{4h_\alpha h_\beta}. \quad (5)$$

By Schwarz's theorem, the mixed derivative is symmetric:

$$\frac{\partial^2 f}{\partial \alpha_0 \partial \beta} = \frac{\partial^2 f}{\partial \beta \partial \alpha_0}.$$

4. Newton–Raphson update

Let

$$\mathbf{x} = \begin{bmatrix} \alpha_0 \\ \beta \end{bmatrix}, \quad \nabla f(\mathbf{x}) = \begin{bmatrix} \partial f / \partial \alpha_0 \\ \partial f / \partial \beta \end{bmatrix}, \quad H(\mathbf{x}) = \begin{bmatrix} \partial^2 f / \partial \alpha_0^2 & \partial^2 f / \partial \alpha_0 \partial \beta \\ \partial^2 f / \partial \beta \partial \alpha_0 & \partial^2 f / \partial \beta^2 \end{bmatrix}.$$

The Newton–Raphson step is

$$\Delta \mathbf{x} = -H(\mathbf{x})^{-1} \nabla f(\mathbf{x}).$$

Update rule:

$$\mathbf{x}_{k+1} = \mathbf{x}_k + \Delta \mathbf{x}.$$

5. Constraints and stability

- If $\alpha_0 \leq 0$ or $\beta \leq 1$, reject the step or apply a backtracking line search.
- In practice, one may add a small ridge term λI to H to stabilize the inversion:

$$H_{\text{reg}} = H + \lambda I.$$

- Stop when

$$\|\nabla f(\mathbf{x})\| < \varepsilon \quad \text{or} \quad |\Delta \mathbf{x}| < \delta \quad \text{or} \quad |f_{k+1} - f_k| < \eta.$$