

Project 4: MacMurchie-Davidson scheme

Elisa Rebolini

Institut Laue Langevin, Grenoble, France, rebolini@ill.fr

November 20, 2025

You can work in groups of up to three people. We expect that you will use Git to work collaboratively on your project. We expect the following files and structure in your submission:

- A LICENSE file specifying the license for your code.
- An AUTHORS file listing the names of all contributors.
- A README.md file providing a brief description of the directory structure and the project.
- An INSTALL.md file with clear instructions on how to compile and run the program.
- A tests directory containing tests to ensure that the program behaves as expected.
- (Optional) A doc directory for additional documentation, if the project requires more detail than the README.md file can provide.
- A src directory containing all the source files of your program.

The one-electron integrals considered in this homework can be written as

$$O_{\mu\nu} = \langle \chi_\mu | \hat{O} | \chi_\nu \rangle = \int \chi_\mu(\mathbf{r}) \hat{O}(\mathbf{r}) \chi_\nu(\mathbf{r}) d\mathbf{r} \quad (1)$$

where the integration is over the full space of Cartesian coordinates, \hat{O} is a one-electron operator and χ_μ and χ_ν are atomic orbitals (AOs). The aim of this homework is to write a program to compute the overlap matrix for a diatomic molecule using the MacMurchie-Davidson algorithm. In the following a comprehensive summary of the main equations is given, which were extracted from the book Molecular Electronic-Structure Theory by Trygve Helgaker, Poul Jørgensen and Jeppe Olsen. The relevant pages of the book are given as reference in the git repository of the project.

1 Contracted spherical-harmonic Gaussians

1.1 Primitive Cartesian GTOs

Let's consider a calculation where the AOs are taken as linear combinations of real-valued primitive Cartesian Gaussian-Type orbitals (GTOs) of the form

$$G_{ijk}(\mathbf{r}, a, \mathbf{A}) = x_A^i y_A^j z_A^k \exp(-ar_A^2), \quad \mathbf{r}_A = \mathbf{r} - \mathbf{A} \quad (2)$$

centred on the nuclei positions. The position of the electron with respect to the nucleus \mathbf{A} is the vector $\mathbf{r}_A = (x_A, y_A, z_A)$ of norm r_A . The Gaussian exponent a is a real positive number, the Cartesian quantum numbers i, j, k and integers, greater than or equal to zero and their sum gives the total angular momentum quantum number

$$l = i + j + k. \quad (3)$$

The full set of GTOs of a given total angular momentum quantum number l and of the same exponent a constitutes a shell. The number of Cartesian GTOs in such a shell is given by

$$N_l^c = \frac{(l+1)(l+2)}{2} \quad (4)$$

The Cartesian GTOs can be factorized in the three directions

$$G_{ijk}(\mathbf{r}, a, \mathbf{A}) = G_i(x, a, A_x) G_j(y, a, A_y) G_k(z, a, A_z), \quad (5)$$

where, for instance,

$$G_i(x, a, A_x) = x_A^i \exp(-ax_A^2) \quad (6)$$

which simplifies a lot the calculation of integrals over Cartesian GTOs.

The primitive Cartesian GTOs are mostly used in fixed linear combinations $\chi_\mu(\mathbf{r})$. A typical AO thus consists of a linear combination of primitive Cartesian GTOs of the same angular-momentum quantum number l but of different Cartesian quantum numbers i, j and k , and of different exponent a .

1.2 Spherical-harmonic GTOs

The real-valued spherical-harmonic GTOs are defined as

$$G_{lm}(\mathbf{r}, a, \mathbf{A}) = S_{lm}(\mathbf{r}_A) \exp(-ar_A^2), \quad (7)$$

where $S_{lm}(\mathbf{r})$ is one of the real solid harmonics (see Table 1.2). Their explicit expression is:

$$S_{lm}(\mathbf{r}) = N_{lm} \sum_{t=0}^{\lfloor \frac{l-|m|}{2} \rfloor} \sum_{u=0}^t \sum_{v=v_m}^{v_m + \lfloor \frac{|m|}{2} - v_m \rfloor} C_{tuv}^{lm} x^{2t+|m|-2(u+v)} y^{2(u+v)} z^{l-2t-|m|} \quad (8)$$

where

$$N_{lm} = \frac{1}{2^{|m|}l!} \sqrt{\frac{2(l+|m|)!(l-|m|)!}{2^{\delta_{0m}}}} \quad (9)$$

$$C_{tuv}^{lm} = (-1)^{t+v-v_m} \left(\frac{1}{4}\right)^t \binom{l}{t} \binom{l-t}{|m|+t} \binom{t}{u} \binom{|m|}{2v} \quad (10)$$

$$v_m = \begin{cases} 0 & m \geq 0 \\ \frac{1}{2} & m < 0, \end{cases} \quad (11)$$

and where $\lfloor k \rfloor$ is the largest integer less than or equal to k . A shell of spherical-harmonic GTOs contains all GTOs of the same a and l but different $|m| \leq l$. The number of

Table 1: The real solid harmonics $S_{lm}(\mathbf{r})$ for $l \leq 2$

$m \backslash l$	0	1	2
2			$\frac{1}{2}\sqrt{3}(x^2 - y^2)$
1		x	$\sqrt{3}xz$
0	1	z	$\frac{1}{2}(3z^2 - r^2)$
-1		y	$\sqrt{3}yz$
-2			$\sqrt{3}(xy)$

spherical-harmonic GTOs in such a shell is given by

$$N_l^s = 2l + 1. \quad (12)$$

The relationship between the spherical-harmonic and Cartesian GTOs is given by the expression

$$G_{lm}(\mathbf{r}, a, \mathbf{A}) = N_{lm} \sum_{t=0}^{\lfloor \frac{l-|m|}{2} \rfloor} \sum_{u=0}^t \sum_{v=v_m}^{v_m + \lfloor \frac{|m|}{2} - v_m \rfloor} C_{tuv}^{lm} G_{2t+|m|-2(u+v), 2(u+v), l-2t-|m|}(\mathbf{r}, a, \mathbf{A}) \quad (13)$$

1.3 Contracted GTOs

The primitive Cartesian Gaussians are combined not only in their angular parts but also in their radial parts. The final contracted GTOs may be written as linear combinations of primitive spherical-harmonic GTOs of different exponents a_ν

$$G_{\mu lm}(\mathbf{r}, \mathbf{A}) = \sum_{\nu} G_{lm}(\mathbf{r}, a_\nu, \mathbf{A}) d_{\nu\mu} \quad (14)$$

where the contraction coefficients $d_{\gamma\mu}$ are the same for all the angular components. The number of contracted GTOs is often much smaller than the number of primitive GTOs.

2 Cartesian Gaussians

2.1 Normalisation

The primitive Cartesian GTOs are not normalized, it is therefore of interest to look at their self overlap. The self-overlap of the x component of the unnormalized GTO (Eq. 5) is given by

$$\langle G_i | G_i \rangle = \frac{(2i-1)!!}{4a^i} \sqrt{\frac{\pi}{2a}} \quad (15)$$

where the double factorial is given by

$$n!! = \begin{cases} 1 & n = 0 \\ n(n-2)(n-4) \cdots 2 & \text{even } n > 0 \\ n(n-2)(n-4) \cdots 1 & \text{odd } n > 0 \\ \frac{1}{(n+2)(n+4) \cdots 1} & \text{odd } n < 0 \end{cases} \quad (16)$$

2.2 Gaussian product Rule

The product of two spherical Gaussians centred on \mathbf{A} and \mathbf{B} is given by

$$\exp(-ar_A^2) \exp(-br_B^2) = \exp(-\mu R_{AB}^2) \exp(-pr_P^2) \quad (17)$$

where the total exponent p and the reduced exponent μ are given by

$$p = a + b \quad \mu = \frac{ab}{a + b} \quad (18)$$

and the center of charge \mathbf{P} and Gaussian separation are defined as

$$\mathbf{P} = \frac{a\mathbf{A} + b\mathbf{B}}{p} \quad \mathbf{R}_{AB} = \mathbf{A} - \mathbf{B}. \quad (19)$$

The first factor $K_{ab} = \exp(-\mu R_{AB}^2)$ is constant and is referred to as the pre-exponential factor.

2.3 Gaussian Overlap Distributions

The overlap distribution of two Gaussians $G_a(\mathbf{r}) = G_{ikm}(\mathbf{r}, a, \mathbf{A})$ and $G_b(\mathbf{r}) = G_{jln}(\mathbf{r}, b, \mathbf{B})$ is defined as

$$\Omega_{ab}(\mathbf{r}) = G_a(\mathbf{r})G_b(\mathbf{r}), \quad (20)$$

which can be factorized along the three Cartesian directions. The x component would then be:

$$\Omega_{ij}^x(x, a, b, A_x, B_x) = K_{ab}^x x_A^i x_B^j \exp(-px_P^2) \quad (21)$$

according to the Gaussian product in Eq. 17. Using the relations

$$\begin{cases} x_A &= x_P - \frac{b}{p} X_{AB} \\ x_B &= x_P + \frac{p}{a} X_{AB} \end{cases} \quad (22)$$

and the binomial theorem

$$(x + y)^n = \sum_k \binom{n}{k} x^k y^{n-k}, \quad (23)$$

the overlap distribution can be expanded in Cartesian Gaussians of orders $0 \leq k \leq i + j$ centred at \mathbf{P}

$$\Omega_{ij}^x(x, a, b, A_x, B_x) = K_{ab}^x \sum_{k=0}^{i+j} C_k^{ij} x_P^k \exp(-p x_P^2) \quad (24)$$

where the coefficients C_k^{ij} can be determined using the binomial theorem.

2.4 Hermite Gaussians

The Hermite Gaussians of exponent p and centred on \mathbf{P} are defined by

$$\Lambda_{tuv}(\mathbf{r}, p, \mathbf{P}) = \left(\frac{\partial}{\partial P_x} \right)^t \left(\frac{\partial}{\partial P_y} \right)^u \left(\frac{\partial}{\partial P_z} \right)^v \exp(-p r_P^2). \quad (25)$$

Like the Cartesian Gaussians they are separable along the three Cartesian directions and the x component is then defined as

$$\Lambda_t(x, p, P_x) = \left(\frac{\partial}{\partial P_x} \right)^t \exp(-p x_P^2). \quad (26)$$

One advantage of the Hermite Gaussians is their straightforward integration relations. Indeed one can easily show that

$$\int_{-\infty}^{+\infty} \Lambda_t(x, p, P_x) dx = \delta_{t0} \sqrt{\frac{\pi}{p}}. \quad (27)$$

2.5 The MacMurchie-Davidson scheme for overlap integrals

The overlap distribution is a polynomial of degree $i + j$ in x_P , it may be expanded exactly in the Hermite polynomials of degree $t \leq i + j$

$$\Omega_{ij}^x = \sum_{t=0}^{i+j} E_t^{ij} \Lambda_t \quad (28)$$

where the coefficients E_t^{ij} can be determined by using recurrence relations. The MacMurchie-Davidson recurrence relation for the coefficients are given by

$$\begin{cases} E_t^{i+1,j} &= \frac{1}{2p} E_{t-1}^{ij} + X_{PA} E_t^{ij} + (t+1) E_{t+1}^{ij} \\ E_t^{i,j+1} &= \frac{1}{2p} E_{t-1}^{ij} + X_{PB} E_t^{ij} + (t+1) E_{t+1}^{ij} \end{cases} \quad (29)$$

where the starting coefficient for the recursion is

$$E_0^{00} = K_{ab}^x = \exp(-\mu R_{AB}^2) \quad (30)$$

and $E_t^{ij} = 0$, for $t < 0$ or $t > i + j$. The overlap integral is then obtained by integration over space

$$S_{ij} = \int_{-\infty}^{+\infty} \Omega_{ij}^x dx. \quad (31)$$

3 Exercises

3.1 Contracted to Spherical Transformation

Most atomic basis sets can be found on <https://www.basissetexchange.org/>, written in different software formats. In what follows, we will focus on the DALTON format, for the 6-31G basis set. For each atom in the basis file, the following format is used

- a Z with Z the atomic number of the atom
- !ATOM, (Nprim list) -> [Ncont list] the name of the atom, the number of primitive (spherical-harmonic) and contracted basis functions for all l values
- Then for each value of l
 - H NPrim NCont Number of primitive and contracted functions for that value of l
 - Array of floats of size [NPrim, Ncont+1] where the first column is the exponent of each primitive a_ν and the remaining Ncont are the coefficients for each contracted function $d_{\nu\mu}$

! Basis = 6-31G

```
a 1
! HYDROGEN      (4 s) -> [2 s]
! s functions
H   4   2
    0.1873113696E+02      0.3349460434E-01      0.00000000
    0.2825394365E+01      0.2347269535E+00      0.00000000
    0.6401216923E+00      0.8137573261E+00      0.00000000
    0.1612777588E+00      0.00000000          1.00000000
```

1. The 6-31G basis file in Dalton format from the Basis set exchange website for all elements up to $Z = 36$ is given in the file 6-31g.1.dalton. Write a program which returns the AO basis centered at the origin, of the element of atomic number Z , in terms of the primitive spherical-harmonic GTOs. An example of a possible output for the carbon atom is given below

```
chi 1s=
    0.00183474 * exp( -3047.52488000 r^2)
    + 0.01403732 * exp( -457.36951800 r^2)
    + 0.06884262 * exp( -103.94868500 r^2)
    + 0.23218444 * exp( -29.21015530 r^2)
    + 0.46794135 * exp( -9.28666296 r^2)
    + 0.36231199 * exp( -3.16392696 r^2)
chi 2s=
    -0.11933242 * exp( -7.86827235 r^2)
    + -0.16085415 * exp( -1.88128854 r^2)
    + 1.14345644 * exp( -0.54424926 r^2)
chi 3s=
    1.00000000 * exp( -0.16871448 r^2)
chi 1p-1=
    0.06899907 * S1-1(r) * exp( -7.86827235 r^2)
    + 0.31642396 * S1-1(r) * exp( -1.88128854 r^2)
    + 0.74430829 * S1-1(r) * exp( -0.54424926 r^2)
chi 1p0=
    0.06899907 * S10(r) * exp( -7.86827235 r^2)
    + 0.31642396 * S10(r) * exp( -1.88128854 r^2)
    + 0.74430829 * S10(r) * exp( -0.54424926 r^2)
chi 1p1=
    0.06899907 * S11(r) * exp( -7.86827235 r^2)
    + 0.31642396 * S11(r) * exp( -1.88128854 r^2)
    + 0.74430829 * S11(r) * exp( -0.54424926 r^2)
chi 2p-1=
    1.00000000 * S1-1(r) * exp( -0.16871448 r^2)
chi 2p0=
    1.00000000 * S10(r) * exp( -0.16871448 r^2)
chi 2p1=
    1.00000000 * S11(r) * exp( -0.16871448 r^2)
```

3.2 Spherical-harmonic to Cartesian GTOs

1. Write two subroutines which, for a given l , compute the transformation matrix from the spherical-harmonic to Cartesian GTO basis using either the results of Table 1.2 for $l = 0, 1, 2$ (that would typically be the result of a code generator) or Eq. 8 (in the general case).
2. Using the relation 15, write a subroutine which computes the self overlap of each of the Cartesian GTOs $\langle G_{ijk} | G_{ijk} \rangle$
3. Using the general expression

$$\int_0^\infty x^{2n} \exp(-\alpha x^2) dx = \frac{(2n-1)!!}{2^{n+1}} \sqrt{\pi} \alpha^{2n+1} n \geq 0, \alpha > 0 \quad (32)$$

write a subroutine which computes the self-overlap of the spherical-harmonic GTOs $\langle G_{lm} | G_{lm} \rangle$

3.3 MacMurchie Davidson for a diatomic

1. Write a function which computes all MacMurchie-coefficients up to a given order.

2. Build a diatomic molecule of your choice and compute the overlap matrix in between the AO basis function using the MacMurchie-Davidson scheme