The Root of All Good: Molecular Integrals

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The goal of this Project is to carry out a complete *ab initio* computation on a molecular system without using any external data other than the molecular geometry, and basis set. The result of the calculation should be the equilibrium geometry and total energy of a homonuclear diatomic molecule. It is mandatory that you have completed the SCF programming project.

You are going to optimize H_2 molecule at the 3-21G(uc) RHF level. If you are willing to experiment further, you may want to make the code flexible enough to allow for other molecule, starting geometry, or basis set (of s-functions). However, most parameters (starting geometry, nuclear charges, basis set) can be simply hardwired for this particular case (this will save you some time if you are not familiar with `PSI 3` parsing):

- Start with a bond distance of 1.5 a.u.
- The 3-21G(uc) basis set for H:

  ```
  HYDROGEN:"321GUC" = (
      (S (    5.447178000          1.0000000000))
      (S (    0.824547240          1.0000000000))
      (S (    0.183191580          1.0000000000))
    )
  ```

  Thus, we have 3 s-functions here, all primitive Gaussians. It is a total of 6 basis functions per molecule.
- You should use C_1 symmetry. This simplifies the project somewhat and allows to generalize the program to heteronuclear diatomics if necessary.

Here is the recommended procedure:

1. Compute normalization constants for the basis functions. The normalization constant for a primitive s-Gaussian is

$$N = \left(\frac{2\alpha}{\pi}\right)^{3/4} \tag{1}$$

2. Implement a function to compute overlap integrals over unnormalized primitive Gaussians of arbitrary quantum numbers:

$$\int G_1(\alpha_1, \mathbf{A}, l_1, m_1, n_1) G_2(\alpha_2, \mathbf{B}, l_2, m_2, n_2) d\mathbf{r} = \exp[-\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma] I_x I_y I_z. \tag{2}$$

where

$$I_x = \sum_{i=0}^{(l_1+l_2)/2} f_{2i}(l_1, l_2, \overline{\mathbf{PA}}_x, PB_x) \frac{(2i-1)!!}{(2\gamma)^i} \left(\frac{\pi}{\gamma}\right)^{1/2}. \tag{3}$$

and

$$\gamma = \alpha_1 + \alpha_2 \tag{4}$$

$$\mathbf{P} = \frac{\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B}}{\gamma} \tag{5}$$

$$f_k(l_1, l_2, \overline{\mathbf{PA}}_x, \overline{\mathbf{PB}}_x) = \sum_{i=\max(0,k-l_2)}^{\min(l_1,k)} (\overline{\mathbf{PA}})_x^{l_1-i} \begin{pmatrix} l_1 \\ i \end{pmatrix} (\overline{\mathbf{PB}})_x^{l_2-k+i} \begin{pmatrix} l_2 \\ k-i \end{pmatrix} \tag{6}$$

3. Evaluate overlap integrals first. You may either use your general routine from the previous step or simply use

$$S_{12} = N_1 N_2 e^{-\alpha_1\alpha_2(\overline{\mathbf{AB}})^2/\gamma} \left(\frac{\pi}{\gamma}\right)^{3/2} \tag{7}$$

Remember that the matrix representations of Hermitian one-electron operators are symmetric, hence you need to evaluate only 21 integrals of each kind.

4. Using your general overlap routine and

$$T_{12} = -\frac{1}{2} N_1 N_2 \int e^{-\alpha_1 r_A^2} (\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) e^{-\alpha_2 r_B^2} d\mathbf{r} \tag{8}$$

$$= N_1 N_2 (I_x + I_y + I_z) \tag{9}$$

$$I_x = \alpha_2 \langle 0|0 \rangle - 2\alpha_2^2 \langle 0| + 2\rangle_x \tag{10}$$

where $\langle 0|0 \rangle$ and $\langle 0| + 2\rangle_x$ are overlap integrals over unnormalized Gaussians, evaluate the kinetic energy integrals.

5. Evaluate the nuclear attraction energy integrals

$$V_{12} = N_1 N_2 \sum_C \int e^{-\alpha_1 r_A^2} \Big(-\frac{Z_C}{r_C} \Big) e^{-\alpha_2 r_B^2} d\mathbf{r} \tag{11}$$

$$= -N_1 N_2 \frac{2\pi e^{-\alpha_1\alpha_2(\overline{\mathbf{AB}}^2)/\gamma}}{\gamma} \left(\sum_{C:\mathbf{P}\neq\mathbf{C}} Z_C \frac{\pi^{1/2}\mathrm{erf}(\gamma^{1/2}\overline{\mathbf{PC}})}{2\gamma^{1/2}\overline{\mathbf{PC}}} + \sum_{C:\mathbf{P}=\mathbf{C}} Z_C \right) \tag{12}$$

6. Evaluate the electron-repulsion integrals

$$(12|34) = N_1 N_2 N_3 N_4 \int e^{-\alpha_1 r_{1A}^2} e^{-\alpha_2 r_{1B}^2} \frac{1}{r_{12}} e^{-\alpha_3 r_{2C}^2} e^{-\alpha_4 r_{2D}^2} d\mathbf{r} \tag{13}$$

$$= N_1 N_2 N_3 N_4 \frac{2\pi^{5/2} K_{12} K_{34}}{\gamma_p \gamma_q (\gamma_p + \gamma_q)^{1/2}} F_0(\overline{\mathbf{PQ}}^2 \gamma_p \gamma_q / (\gamma_p + \gamma_q)) \tag{14}$$

where

$$\gamma_p = \alpha_1 + \alpha_2 \tag{15}$$

$$\gamma_q = \alpha_3 + \alpha_4 \tag{16}$$

$$\mathbf{P} = \frac{\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B}}{\gamma_p} \tag{17}$$

$$\mathbf{Q} = \frac{\alpha_3 \mathbf{C} + \alpha_4 \mathbf{D}}{\gamma_q} \tag{18}$$

$$K_{12} = e^{-[\alpha_1 \alpha_2 (\overline{\mathbf{AB}}^2)/\gamma_p]} \tag{19}$$

$$K_{34} = e^{-[\alpha_3 \alpha_4 (\overline{\mathbf{CD}}^2)/\gamma_q]} \tag{20}$$

$$F_0(T) = \frac{\pi^{1/2}}{2\sqrt{T}} \mathrm{erf}(\sqrt{T}) \ , \ T > 0 \tag{21}$$

$$F_0(0) = 1 \tag{22}$$

7. Evaluate RHF energy at this geometry

8. Evaluate RHF energy at two bond distances displaced by $+\delta r$ and $-\delta r$, where $\delta r = 0.010$ a.u.

9. Approximate the first and second derivative of the energy w.r.t. the bond distance by

$$\left.\frac{\partial E}{\partial r}\right|_{r=r_0} = \frac{E(r_0 + \delta r) - E(r_0 - \delta r)}{2 \ \delta r} \tag{23}$$

$$\left.\frac{\partial^2 E}{\partial r^2}\right|_{r=r_0} \approx \frac{E(r_0 + \delta r) + E(r_0 - \delta r) - 2E(r_0)}{\delta r^2} \tag{24}$$

10. If magnitude of $\left.\frac{\partial E}{\partial r}\right|_{r=r_0}$ is greater than 10^{-4} a.u., take a Newton-Raphson step:

$$r_0^{new} = r_0 - \frac{\left.\frac{\partial E}{\partial r}\right|_{r=r_0}}{\left.\frac{\partial^2 E}{\partial r^2}\right|_{r=r_0}} \tag{25}$$

and repeat all previous steps, otherwise report the bond distance and the electronic energy

11. Run `PSI 3` to verify your result.