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**Numerical Algorithms Applied to Computational Quantum Chemistry**  
**Homework 5: Evaluate the analytic gradient of your SCF energy**

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**Due Nov. 16, 2023**

## 1 DERIVING THE THEORY YOURSELF.

In class, we discussed the analytic gradient of the full ab initio SCF energy, as well as how to specialize it for the CNDO/2 method that you have implemented in the previous homework set. I presented reasons why the gradient can be written in the following general form:

$$E_{\text{CNDO}/2}^{\mathbf{R}_A} = \sum_{\mu\nu} x_{\mu\nu} s_{\mu\nu}^{\mathbf{R}_A} + \sum_{B \neq A} y_{AB} \gamma_{AB}^{\mathbf{R}_A} + V_{\text{nuc}}^{\mathbf{R}_A} \quad (1.1)$$

Here  $s_{\mu\nu}$  and  $\gamma_{AB}$  are as defined in the previous homework set to evaluate the CNDO/2 energy, and the superscript  $\mathbf{R}_A$  indicates differentiation with respect to  $\mathbf{R}_A$ : i.e.  $Z^{\mathbf{R}_A} = \frac{\partial Z}{\partial \mathbf{R}_A}$ .

This expression comes from your CNDO/2 energy:

$$E_{\text{CNDO}/2} = \frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\alpha} (h_{\mu\nu} + f_{\mu\nu}^{\alpha}) + \frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\beta} (h_{\mu\nu} + f_{\mu\nu}^{\beta}) + \sum_A \sum_{B < A} \frac{Z_A Z_B}{R_{AB}} \quad (1.2)$$

and the fact that the only quantities that depend on internuclear position in  $h_{\mu\mu}$ ,  $h_{\mu\nu}$ ,  $f_{\mu\mu}$ , and  $f_{\mu\nu}$  are  $s_{\mu\nu}$  and  $\gamma_{AB}$  (and of course  $V_{\text{nuc}}$  which is the last term of the energy expression). With this in mind:

1. Derive an expression for  $x_{\mu\nu}$  that is suitable for the unrestricted case that you coded. This result should depend only on quantities that are available at the end (or the beginning!) of a CNDO/2 SCF calculation. Suggestion: since the energy is linear in  $s_{\mu\nu}$ , find the terms that multiply  $s_{\mu\nu}$ , and you have found  $x_{\mu\nu}$ ..... the result should look pretty simple (one term). That's all there is to it because CNDO/2 theory takes the AOs as orthonormal in the SCF equations, so there is no additional overlap derivative coming from the orthonormality constraints (unlike the full SCF gradient).

2. Similarly, derive an expression for  $y_{AB}$ . Suggestion: since the energy is linear in  $\gamma_{AB}$ , find the terms that multiply  $\gamma_{AB}$ , and you have found  $y_{AB}$ ..... the result should just involve a few terms.
3. To see how to evaluate the overlap integral derivatives as an extension to your overlap integral code, write an expression for the derivative of a contracted gaussian s function with respect to its nuclear center. Repeat for a contracted gaussian p function noting that you will get a second term if the cartesian character of the p function matches the direction of the derivative.

Please send us your answers to this part of the problem set by **Thursday Nov. 10, 2022** so that you have enough time to concentrate on the implementation. Please send it to us earlier if you can!! We'll help fix any issues before you start coding.

## 2 IMPLEMENTING THE THEORY YOURSELF

The CNDO/2 analytic gradient is a vector of length  $G = 3 * N_{\text{atoms}}$ . Implement extensions to your CNDO/2 SCF code to evaluate the gradient once the SCF has converged.

Referring to Equation 1.1, it is evident that 5 quantities are necessary in order to evaluate the analytical CNDO/2 gradient,  $E_{\text{CNDO/2}}^{\text{RA}}$ . These are:

1. The matrix  $\mathbf{x}$ , which is  $N \times N$  where  $N$  is the number of AOs. Write code to assemble  $\mathbf{x}$  from your derivation.
2. The matrix  $\mathbf{y}$ , which is  $N_{\text{atoms}} \times N_{\text{atoms}}$ . Write code to assemble  $\mathbf{y}$  from your derivation.
3. The set of overlap matrix derivatives, which has no more than  $6N^2$  non-zero values (only half of which are independent by translational invariance). Write code to evaluate half of those non-zero values, based on your derivative above, and get the rest from translational invariance.
4. The set of  $\gamma_{AB}$  derivatives, which has no more than  $6N_{\text{atoms}}^2$  non-zero values (of which only half are needed; with the other half determined by translational invariance). Code to evaluate these will be the subject of the next computational lab
5. The (relatively) simple derivative of  $V_{\text{nuc}}$  with respect to nuclear coordinates.

Develop a gradient code to assemble the contributions of these pieces via Equation 1.1. Test using debug output that Rebecca will provide (i.e. examine the values of each of the 3 distinct terms of Eq. 1.1 for a diatomic molecule). Also note that each term, as well as the entire gradient should be translationally invariant (meaning the sum of the forces in each direction should be zero, because the energy of the molecule does not change when it is translated).

If you have time, we'd love you to try optimizing the geometry of a few molecules using the analytical gradient and the simple optimization method available from the first homework. Test one or two diatomics (e.g. CO and HF) and some simple triatomics (e.g. H<sub>2</sub>O and NH<sub>3</sub>) against the values reported in Table 4.1b, 4.2, and 4.3 of Pople and Beveridge's book.