UNIVERSITY OF CALIFORNIA BERKELEY

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

Dr. Mayank Agrawal, with Yao Shen (CHEM279)

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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:

$$E^{\mathbf{R}_A}_{\mathrm{CNDO/2}} = \sum_{\mu \neq \nu} x_{\mu\nu} s^{\mathbf{R}_A}_{\mu\nu} + \sum_{B \neq A} y_{AB} \gamma^{\mathbf{R}_A}_{AB} + V^{\mathbf{R}_A}_{\mathrm{nuc}} \tag{1.1}$$

Here $s_{\mu\nu}$ and γ_{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:

$$E_{\mathrm{CNDO/2}} = \frac{1}{2} \sum_{\mu\nu} p^{\alpha}_{\mu\nu} \left(h_{\mu\nu} + f^{\alpha}_{\mu\nu} \right) + \frac{1}{2} \sum_{\mu\nu} p^{\beta}_{\mu\nu} \left(h_{\mu\nu} + f^{\beta}_{\mu\nu} \right) + \sum_{A} \sum_{B<A} \frac{Z_A Z_B}{R_{AB}} \tag{1.2}$$

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 γ_{AB} (and of course V_{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 γ_{AB}, find the terms that multiply γ_{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.

Your code will naturally include your answers to this part of the problem set. Since you cannot develop your code without having working expressions for these matrices, please start on this as soon as you can so that you have enough time to concentrate on the implementation. Some important hints will be provided in this week's compute lab. Please reach out to us if you run into troubles with your derivation. You may consult with each other also, but do not copy your class-mates' notes – instead get the help you need to do it yourself!

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, $E^{\mathbf{R}_A}_{\text{CNDO/2}}$. 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 γ_{AB} derivatives, which has no more than $6N^2_{\text{atoms}}$ 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_{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 your GSI 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_2O and NH_3) against the values reported in Table 4.1b, 4.2, and 4.3 of Pople and Beveridge's book.