UNIVERSITY OF CALIFORNIA BERKELEY

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

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:

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

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

This expression can be derived the expression for CNDO/2 energy:

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

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, this assignment will be structured differently. You will perform the derivations in the first week and submit them the first monday. Then solutions to derivations will be released. Your implementations will be due at the end of the two weeks. 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, $E^{\mathbf{R}_D}_{\text{CNDO}/2}$. 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 $S^{\mathbf{R}_A}_{uv}$, where u is in A, 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 derivative of V_{nuc} with respect to nuclear coordinates.

Develop a code to assemble the contributions of these pieces via Equation 1.1. 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).

GOING FURTHER

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.

APPENDIX: NOTES ON EVALUATING $S_{\mu\nu}$

Recall the definition of $S_{\mu\nu}$

$$S_{\mu\nu} = \sum_{k}^{3}\sum_{l}^{3} d_{k\mu} d_{l\nu} N_{k\mu} N_{l\nu} S_{kl} \tag{2.1}$$

Applying the chain rule yields:

$$S^{\mathbf{R}_A}_{\mu\nu} = \sum_{k}^{3}\sum_{l}^{3} d_{k\mu} d_{l\nu} N_{k\mu} N_{l\nu} \frac{\partial S^{kl}}{\partial \mathbf{R}_A} \tag{2.2}$$

Recalling the definition of S^{kl} :

$$S^{kl} = \int_x \int_y \int_z \omega_k(\mathbf{r}) \omega_k(\mathbf{r}) \tag{2.3}$$

$$= S^{kl}_x S^{kl}_y S^{kl}_z \tag{2.4}$$

And applying the chain rule yields:

$$\frac{\partial S^{kl}}{\partial \mathbf{R}_A} = \begin{bmatrix} \frac{\partial S^{kl}_x}{\partial \mathbf{R}_{A_x}} S^{kl}_y S^{kl}_z \\ S^{kl}_x \frac{\partial S^{kl}_y}{\partial \mathbf{R}_{A_y}} S^{kl}_z \\ S^{kl}_x S^{kl}_y \frac{\partial S^{kl}_z}{\partial \mathbf{R}_{A_z}} \end{bmatrix} \tag{2.5}$$

During this stage of the assignment, you are responsible for deriving the derivative of the 1-dimensional overlap.

APPENDIX: NOTES ON EVALUATING $\gamma_{AB}^{\mathbf{R}_A}$

Recall the definition of γ_{AB}:

$$\gamma_{AB} = \sum_{k}^{3}\sum_{k'}^{3}\sum_{l}^{3}\sum_{l'}^{3} d'_{ks_A} d'_{k's_A} d'_{ls_B} d'_{l's_B} [0]^{(0)} \tag{2.6}$$

The derivative of gamma can be derived from this definition and the chain rule. We will take the derivative with respect to the position atom A.

$$\gamma_{AB}^{\mathbf{R}_A} = \sum_{k=1}^{3}\sum_{k'=1}^{3}\sum_{l=1}^{3}\sum_{l'=1}^{3} d'_{ks_A} d'_{k's_A} d'_{ls_B} d'_{l's_B} \frac{\partial [0]^{(0)}}{\partial \mathbf{R}_A} \tag{2.7}$$

Recall the definition of $[0]^{(0)}$:

$$[0]^{(0)} = U_A U_B \sqrt{\frac{1}{(\mathbf{R}_A - \mathbf{R}_B)^2}} \operatorname{erf}\left(\sqrt{T}\right) \tag{2.8}$$

Application of the chain rule yields:

$$\frac{\partial [0]^{(0)}}{\partial \mathbf{R}_A} = U_A U_B \left[\frac{\partial}{\partial \mathbf{R}_A} \frac{1}{\sqrt{(\mathbf{R}_A - \mathbf{R}_B)^2}} \operatorname{erf}(\sqrt{T}) + \frac{1}{\sqrt{(\mathbf{R}_A - \mathbf{R}_B)^2}} \frac{\partial \operatorname{erf}(\sqrt{T})}{\partial \mathbf{R}_A} \right] \tag{2.9}$$

$$= U_A U_B \left[-\frac{\mathbf{R}_A - \mathbf{R}_B}{|\mathbf{R}_A - \mathbf{R}_B|^3} \operatorname{erf}(\sqrt{T}) + \frac{1}{\sqrt{(\mathbf{R}_A - \mathbf{R}_B)^2}} \frac{2V}{\sqrt{\pi}} e^{-T} \cdot \frac{\mathbf{R}_A - \mathbf{R}_B}{|\mathbf{R}_A - \mathbf{R}_B|} \right] \tag{2.10}$$

$$= \frac{U_A U_B (\mathbf{R}_A - \mathbf{R}_B)}{|\mathbf{R}_A - \mathbf{R}_B|^2} \left[-\frac{\operatorname{erf}(\sqrt{T})}{|\mathbf{R}_A - \mathbf{R}_B|} + \frac{2V}{\sqrt{\pi}} e^{-T} \right] \tag{2.11}$$

APPENDIX: NOTES ON EVALUATING $V_{\text{nuc}}^{\mathbf{R}_A}$

Recall the definition of V_{nuc}:

$$V_{\text{nuc}} = \sum_A \sum_{B<A} \frac{Z_A^* Z_B^*}{R_{AB}} \tag{2.12}$$

Applying the chain rule yields:

$$V_{\text{nuc}}^{\mathbf{R}_A} = \frac{\partial \sum_B \sum_{C<B} \frac{Z_B Z_C}{\sqrt{(\mathbf{R}_B - \mathbf{R}_C)^2}}}{\partial \mathbf{R}_A} \tag{2.13}$$

$$= \frac{\partial \sum_{B \neq A} \frac{Z_A Z_B}{\sqrt{(|\mathbf{R}_A - \mathbf{R}_B|^2)}}}{\partial \mathbf{R}_A} \tag{2.14}$$

$$= \sum_{B \neq A} Z_A Z_B \frac{\partial}{\partial \mathbf{R}_A} \left(\frac{1}{\sqrt{(\mathbf{R}_A - \mathbf{R}_B)^2}} \right) \tag{2.15}$$

$$= -\sum_{B \neq A} Z_A Z_B \frac{\mathbf{R}_A - \mathbf{R}_B}{|\mathbf{R}_A - \mathbf{R}_B|^3} \tag{2.16}$$