

**REPO LINK:** <https://github.com/neal-p/CHEM279>

## HW5

### Compilation Instructions

1. Go to the top level repo directory `CHEM279/`
2. `mkdir -p build`
3. `cd build`
4. `cmake ..`
5. `make hw5`

### Run Instructions

Once you have compiled, there will be one executable: - `CHEM279/HW5/hw5`

There is a script `run_samples.sh` that will build and run the code on all `sample_input` files putting output in a corresponding `my_outputs` folder.  
NOTE! I was only successful for H2 in this problem set :(

### Main `hw5` program

This executable takes in an xyz file in the specification of our class and a basis set file in Gaussian format. It gets the initial energy and computes the gradient. An exmaple output is shown below for HF: `./hw5 sample_input/H2.txt basis/basis_set.txt`

```
Nuclear Repulsion Energy=19.4587
Electron Energy=-60.0338
Total Energy=-40.5751
```

```
Suv_RA
    0  0.346262 -0.346262      0
    0          0          0      0
    0          0          0      0
```

```
coef Xuv
-18 -18
-18 -18
```

```
gradient (gamma part)
    0  5.41613 -5.41613      0
    0          0          0      0
    0          0          0      0
```

```
Yab
```

```

-1.5 -1.5
-1.5 -1.5

e term 1
-6.23272  6.23272
      0      0
      0      0

e term 2
-8.12419  8.12419
      0      0
      0      0

e grad total
-14.3569  14.3569
      0      0
      0      0

gradient (Nuclear part)
13.915 -13.915
      0      0
      0      0

TOTAL GRAD
-0.441958  0.441958
      0      0
      0      0

```

The derivations and figuring out all the indexing took me a long time, and I got some support from the other students, so the code is especially messy, but it does give output that matches the sample output for H2. I'll discuss how I got to the outcomes below and attach the pages of hand-written math at the end!

I found that the coefficient to the overlap derivative  $X_{uv}$  is  $P_{tot\_uv} * (B_a + B_b)$  which ended up not being too hard to figure out since only terms where the AOs are on different atoms are non-zero and these are the only terms that multiply  $S_{uv}$ .

The derivative of the overlap wrt coordinates was much harder to understand for me until I realized that the integrals shown in the lab slides are the exact same form as our overlap integral. Once this clicked, it was just a matter of doing all the book-keeping correct to make sure I was indexing the right AOs, primitives, and atoms. My math is pretty weak and I am much more comfortable thinking in code, so once I made the connection that I just needed to call my `__inner_overlap` function twice with different `la` values that make things a lot simpler.

The gamma terms were much more complex. Most of my time was spent on the gamma derivative. With the help of the lab slides, I came to a solution for the derivative and implemented it (though my implementation is laughably inefficient... and the code is all tossed in the main function unfortunately). I found the  $\text{Yab}$  matrix coefficient to gamma derivative  $\text{Paa}*\text{Pbb} - \text{ZB}*\text{Paa} - \text{ZA}*\text{Pbb} - \text{SUM}(\text{p}_a^2 + \text{p}_b^2)$  over all pairs  $uv$ . The final summation term I got right away, but the other terms required some guess and check.

My output for  $\text{H2}$  is fully correct, but I couldn't get all of my terms for  $\text{HF}$  or  $\text{HO}$ . My nuclear gradient is always correct, as is my gamma derivative matrix. I suspect my  $\text{Yab}$  and  $\text{Xuv}$  matrices are also correct, but my overlap derivative matrix is not correct.

For example, here is my overlap derivative for  $\text{HF}$ . My output:

`Suv_RA`

0	0.357071	0	0.710104	0.710104	-0.357071	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0

Correct output:

`Suv_RA (A is the center of u)`

0	0.3571	-0.1807	0	0	-0.3571	0	0	0
0	0	0	0.2044	0	0	0	0	0
0	0	0	0	0.2044	0	0	0	0

The element at  $(0,1)$  and  $(0, 5)$  are fine (I'm pretty sure its because they are just  $\text{H}$  related elements). But clearly I'm not treating the  $p$  orbitals fully correctly since I'm missing/incorrect with the other matrix elements.

Here is my full output for  $\text{HF}$ :

Nuclear Repulsion Energy=110.742

Electron Energy=-873.141

Total Energy=-762.399

`Suv_RA`

0	0.357071	0	0.710104	0.710104	-0.357071	0	0	0
0	0	-0.710104	0	0	0	0	-0.710104	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0

`coef Xuv`

-13.9636	-19.4684	42.5338	-0	-0
-19.4684	-145.519	-22.8986	-0	-0
42.5338	-22.8986	-105.972	-0	-0
-0	-0	-0	-156	-0

-0 -0 -0 -0 -156

gradient (gamma part)

0	5.76911	-5.76911	0
0	0	0	0
0	0	0	0

Yab

-1.25061	-7.52514
-7.52514	-55.6991

e term 1

-6.95159	6.95159
0	0
0	0

e term 2

-43.4133	43.4133
0	0
0	0

e grad total

-50.3649	50.3649
0	0
0	0

gradient (Nuclear part)

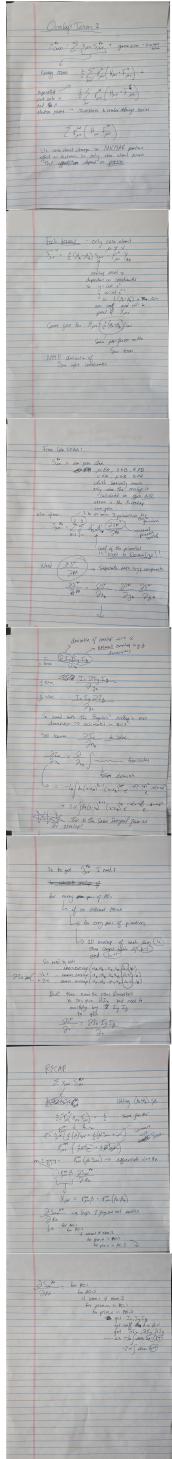
64.3851	-64.3851
0	0
0	0

TOTAL GRAD

14.0202	-14.0202
0	0
0	0

The missing terms in my overlap derivative make the electronic component of the gradient smaller than it should be (-50 instead of -58 for the (0,0) term).

## Derivations



### $\gamma_{AB}$ Matrix<sup>0</sup>

$$\frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\alpha} (H_{\mu\nu} + F_{\mu\nu}^{\alpha}) + \frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\beta} (H_{\mu\nu} + F_{\mu\nu}^{\beta}) + \text{Nuclear off } \gamma \text{ in drop terms}$$

for off diagonals  $H_{\mu\nu}$  don't have  $\gamma_{AB}$  component to drop out  $\rightarrow f = m - p_{\mu\nu}^{\alpha} \gamma_{AB}$

$$\frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\alpha} (f(-p_{\mu\nu}^{\alpha} \gamma_{AB})) + \frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\beta} (m - p_{\mu\nu}^{\beta} \gamma_{AB})$$

$$\sum_{\mu\nu} p_{\mu\nu}^{\alpha 2} \gamma_{AB} + \sum_{\mu\nu} p_{\mu\nu}^{\beta 2} \gamma_{AB} = \boxed{\sum_{\mu\nu} p_{\mu\nu}^{\alpha 2} + p_{\mu\nu}^{\beta 2}} \frac{\partial}{\partial \gamma_{AB}}$$

term #1 for  $\gamma_{AB}$

for on-diagonal terms

$$\frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\alpha} (H + F^{\alpha}) + \frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\beta} (H + F^{\beta})$$

now  $H$  and  $F$  have  $\gamma_{AB}$  terms

swapped  $f$  and  $H$  by accident!  
drop all  
M terms too

$$\left( \frac{1}{2} \sum_{\mu\nu} p_{\mu\nu}^{\alpha} \right) \left( f + \sum_{BFA} (P_{AB} - Z_B) \gamma_{AB} + \sum_{A} Z_A \gamma_{AB} \right) + \frac{1}{2} \left( \sum_{\mu\nu} p_{\mu\nu}^{\beta} \right) \left( m + \sum_{BFA} (P_{AB} - Z_B) \gamma_{AB} + \sum_{A} Z_A \gamma_{AB} \right)$$

Summing over  $\mu\nu$   $p_{\mu\nu}^{\alpha}$   
is equivalent to  $P_{AB}$  since it adds  
up using the total density of  
all  $N$

Sum  $L$  for  
 $\sum_{\mu\nu} p_{\mu\nu}^{\alpha} \rightarrow P_{AB}$

$$P_{AA} \left( \sum_{A+B} (P_{AB} - Z_B) \gamma_{AB} + \sum_{A+B} (Z_B \gamma_{AB}) \right) + P_{AB} \left( \sum_{A+B} (P_{AB} - Z_A) \gamma_{AB} + \sum_{A+B} (Z_A \gamma_{AB}) \right)$$

???  
I'm really  
not sure...  
guess and  
check  
from  
here.

$$\begin{aligned} & \frac{1}{2} - P_{AA} Z_B \\ & \frac{1}{2} P_{AB} = P_{AB} Z_B \\ & \frac{1}{2} P_{AB} = P_{AB} Z_A \\ & \frac{1}{2} P_{AB} = P_{AB} Z_B + P_{AB} Z_A \end{aligned}$$

Gamma Term 2

From lab notes:

$$Y_0 = \sum_{k=1}^3 \sum_{l=1}^3 \frac{U_k U_l}{(R_a - R_b)^3} \delta(r_a) \delta(r_b) \delta(\theta_a) \delta(\theta_b)$$

$\langle \sigma \rangle^{(0)} = \text{Value} \left[ \frac{1}{(R_a - R_b)^2} \right] \text{erf}(\sqrt{\tau})$

This is the term that we need to differentiate w.r.t.  $r_a$

QD QD

$\frac{\partial}{\partial r_a} \frac{1}{(R_a - R_b)^2} = \text{break into x,y,z components just like before. Now overlap down}$

$\text{diff. 1: } \frac{1}{(R_a - R_b)^3} = \frac{R_a - R_b}{R_a R_b}$

$\text{diff. 2: } \frac{2}{(R_a - R_b)^2} = \frac{2 \text{erf}(\sqrt{\tau})}{\sqrt{\pi}}$

$\frac{\partial}{\partial r_a} \exp(-r_a^2) = \frac{2r_a}{\sqrt{\pi}}$

$\frac{\partial}{\partial r_a} \int_0^{\infty} \exp(-x^2) dx = \frac{2}{\sqrt{\pi}} \int_0^{\infty} x \exp(-x^2) dx = \frac{1}{\sqrt{\pi}}$

$\frac{\partial}{\partial r_a} \int_0^{\infty} \exp(-x^2) dx = \frac{2}{\sqrt{\pi}} \int_0^{\infty} x \exp(-x^2) dx = \frac{1}{\sqrt{\pi}}$

QD Taking derivative w.r.t. same thing as integral!

$= \frac{2}{\sqrt{\pi}} \exp(-r_a^2) \frac{1}{(R_a - R_b)} \frac{\partial}{\partial r_a} \exp(-r_a^2) \frac{1}{(R_a - R_b)}$

$= \frac{2r_a}{\sqrt{\pi}} e^{-r_a^2} \cdot \frac{R_a - R_b}{(R_a - R_b)^2}$

RECAP

$\langle \sigma \rangle^{(0)} = \text{Value} \left[ \frac{1}{(R_a - R_b)^2} \right] \text{erf}(\sqrt{\tau})$

$\frac{\partial}{\partial r_a} \frac{1}{(R_a - R_b)^2} = \frac{R_a - R_b}{(R_a - R_b)^3}$

$\frac{\partial}{\partial r_a} \frac{1}{(R_a - R_b)^2} = \frac{2r_a}{(R_a - R_b)^3}$

Combine!

$\frac{\partial}{\partial r_a} \frac{1}{(R_a - R_b)^2} = \frac{R_a - R_b}{(R_a - R_b)^3} \text{erf}(\sqrt{\tau}) + \frac{1}{(R_a - R_b)^3} \left( \frac{2r_a}{\sqrt{\pi}} e^{-r_a^2} \frac{R_a - R_b}{(R_a - R_b)} \right)$

$\frac{\partial}{\partial r_a} \frac{1}{(R_a - R_b)^2} = \frac{R_a - R_b}{(R_a - R_b)^3} \text{erf}(\sqrt{\tau}) + \frac{2r_a}{(R_a - R_b)^3} \frac{R_a - R_b}{\sqrt{\pi}}$

$\frac{\partial}{\partial r_a} \frac{1}{(R_a - R_b)^2} = \frac{R_a - R_b}{(R_a - R_b)^3} \text{erf}(\sqrt{\tau}) + \frac{2r_a}{(R_a - R_b)^3} \frac{R_a - R_b}{\sqrt{\pi}}$

from A briefly...

out

-  $U_a U_b (R_a - R_b) \frac{2r_a}{(R_a - R_b)^3} \text{erf}(\sqrt{\tau}) + \frac{1}{(R_a - R_b)^3} \frac{2r_a^2}{\sqrt{\pi}} \frac{R_a - R_b}{(R_a - R_b)}$

Push out  $\frac{1}{(R_a - R_b)^3}$  from each term

$+ U_a U_b (R_a - R_b) \frac{2r_a}{(R_a - R_b)^3} \frac{R_a - R_b}{\sqrt{\pi}}$

$+ U_a U_b (R_a - R_b) \frac{2r_a}{(R_a - R_b)^3} \frac{R_a - R_b}{\sqrt{\pi}}$

$+ U_a U_b (R_a - R_b) \frac{2r_a}{(R_a - R_b)^3} \frac{R_a - R_b}{\sqrt{\pi}}$

$+ U_a U_b (R_a - R_b) \frac{2r_a}{(R_a - R_b)^3} \frac{R_a - R_b}{\sqrt{\pi}}$

Matches slide! Yay!

more clearly  $\frac{\partial}{\partial r_a} \langle \sigma \rangle^{(0)} = \frac{U_a U_b (R_a - R_b)}{(R_a - R_b)^3} \left( \frac{-\text{erf}(\sqrt{\tau})}{\sqrt{\pi}} + \frac{2r_a}{\sqrt{\pi}} e^{-r_a^2} \right)$

Multiply by all the prefactors  
NO MASTERSIDE copy!