Numerical Algorithms Applied to Computational Quantum Chemistry
Homework 4: Build your own SCF program

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1 BUILD THE CNDO/2 FOCK MATRIX

In class, we have discussed semi-empirical Hartree-Fock methods in some detail. They have advantages over ab initio Hartree-Fock in speed and in simplicity of implementation. With the latter in mind, in this homework, you will implement your own version of the CNDO/2 method, which is a huge leap forwards from the extended Huckel method.

In this problem, you will build code to assemble the matrix elements of the CNDO/2 Fock operator, $\mathbf{f}$ (in the AO basis) given the AO basis total density matrix, $\mathbf{p}$, where, for an open shell molecule with p α electrons and q β electrons, we define:

$$p_{\mu\nu}^{\alpha} = \sum_{i}^{p} c_{\mu i}^{\alpha} c_{\nu i}^{\alpha} \tag{1.1}$$

$$p_{\mu\nu}^{\beta} = \sum_{i}^{q} c_{\mu i}^{\beta} c_{\nu i}^{\beta} \tag{1.2}$$

$$p_{\mu\nu}^{\text{tot}} = p_{\mu\nu}^{\alpha} + p_{\mu\nu}^{\beta} \tag{1.3}$$

The diagonal Fock matrix elements are given by (here we are going to do the unrestricted equations):

$$f_{\mu\mu}^{\alpha} = -\frac{1}{2}\left(I_\mu + A_\mu\right) + \left[\left(p_{AA}^{\text{tot}} - Z_A\right) - \left(p_{\mu\mu}^{\alpha} - \frac{1}{2}\right)\right]\gamma_{AA} + \sum_{B \neq A}\left(p_{BB}^{\text{tot}} - Z_B\right)\gamma_{AB} \tag{1.4}$$

The off-diagonal elements are given by:

$$f_{\mu\nu}^{\alpha} = \frac{1}{2}\left(\beta_A + \beta_B\right)s_{\mu\nu} - p_{\mu\nu}^{\alpha}\gamma_{AB} \tag{1.5}$$

quantity	H	C	N	O	F
$\frac{1}{2}\left(I_s + A_s\right)$	7.176	14.051	19.316	25.390	32.272
$\frac{1}{2}\left(I_p + A_p\right)$		5.572	7.275	9.111	11.080
$-\beta$	9	21	25	31	39

Table 1.1: Semi-empirical parameters that define the CNDO/2 model (units: eV)

Here, as usual μ, ν are atomic orbital indexes, and A, B are atom indexes such that atomic orbital $\omega_\mu(\mathbf{r})$ is centered on atom A at position $\mathbf{R}_A$, and atomic orbital $\omega_\nu(\mathbf{r})$ is centered on atom B at position $\mathbf{R}_B$.

The parameters I_μ and A_μ correspond to ionization energies and electron affinities and are fixed values tabulated below for the first row atoms in Table 1. The quantity p_{AA} is the total density on atom A:

$$p_{AA} = \sum_{\mu \in A} p_{\mu\mu}^{\text{tot}} \tag{1.6}$$

Z_A is the valence atomic number of atom A. $s_{\mu\nu}$ are elements of the AO basis overlap matrix, $\mathbf{s}$, which is familiar to you from building your extended Huckel program. β_A are atomic bonding parameters, and are also tabulated in Table 1.

The only thing not yet defined are the quantities γ_{AB}. *You will develop code to evaluate γ_{AB} in your compute lab this coming week, so this will be available to help you finish assembly of your Fock matrices.* We will provide the basic details as an appendix to this homework as a summary. After compute lab, you know that you have the capability to form them!

- Build your code to assemble $f_{\mu\nu}^\alpha$ (and of course $f_{\mu\nu}^\beta$ with exactly the same code).

- Be careful with units! The parameters given in Table 1 are in eV, so you will then need to make sure that your two-electron integrals are in the same units! Working in "atomic units", the conversion factor is 27.211 eV/a.u.

- Test first on the simple H_2 example that your GSI will provide reference data for (here we know $\mathbf{p}^\alpha$ and $\mathbf{p}^\beta$ so your GSI does not have to provide those!).

- Then test on the more challenging $HO^\bullet$ example, with $N = 5$, $p = 4$ and $q = 3$ where your GSI will provide inputs and outputs.

2 EVALUATE THE OPEN SHELL CNDO/2 SELF-CONSISTENT FIELD EQUATIONS

With your Fock matrix assembly code for $\mathbf{f}^\alpha$ and $\mathbf{f}^\beta$ from the previous question working, you are ready to implement your own SCF code for CNDO/2. In the AO basis, in matrix form, the SCF equations are:

$$\mathbf{f}^\alpha \mathbf{c}^\alpha = \mathbf{c}^\alpha \boldsymbol{\varepsilon}^\alpha \tag{2.1}$$

$$\mathbf{f}^\beta \mathbf{c}^\beta = \mathbf{c}^\beta \boldsymbol{\varepsilon}^\beta \tag{2.2}$$

Or if you prefer them written out explicitly, they are:

$$\sum_v f_{\mu v}^{\alpha} c_{vi}^{\alpha} = c_{\mu i}^{\alpha} \epsilon_i^{\alpha} \tag{2.3}$$

$$\sum_v f_{\mu v}^{\beta} c_{vi}^{\beta} = c_{\mu i}^{\beta} \epsilon_i^{\beta} \tag{2.4}$$

Your code should execute the classic SCF algorithm:

1. Guess $\mathbf{p}^{\alpha} = \mathbf{p}^{\beta} = \mathbf{0}$

2. Build $\mathbf{f}^{\alpha}$ and $\mathbf{f}^{\beta}$ using your code from above.

3. Solve the eigenvalue problems, Eqs. 2.3 and 2.4, to obtain new MO coefficients, $\mathbf{c}^{\alpha}$ and $\mathbf{c}^{\beta}$, and the corresponding eigenvalues, $\boldsymbol{\epsilon}^{\alpha}$ and $\boldsymbol{\epsilon}^{\beta}$

4. Copy the old density matrices to $\mathbf{p}_{\text{old}}^{\alpha}$ and $\mathbf{p}_{\text{old}}^{\beta}$

5. Assemble new density matrices by occupying the p lowest energy α MOs and the q lowest energy β MOs and using Eqs. 1.1, 1.2 and 1.3

6. If the maximum magnitude of the change in the α and β density matrices is less than a tolerance you specify (e.g. 10^{-6}), then you have converged. Otherwise return to step 2.

Make sure you extract the final prize from converging your SCF calculations, namely the total energy:

$$E_{\text{CNDO/2}} = \frac{1}{2} \sum_{\mu v} p_{\mu v}^{\alpha} \left(h_{\mu v} + f_{\mu v}^{\alpha} \right) + \frac{1}{2} \sum_{\mu v} p_{\mu v}^{\beta} \left(h_{\mu v} + f_{\mu v}^{\beta} \right) + \sum_A \sum_{B < A} \frac{Z_A Z_B}{R_{AB}} \tag{2.5}$$

The last term is the nuclear repulsion energy (be careful about its units also!). In the energy expression, $h_{\mu v}$ is the core hamiltonian matrix, which consists of the one-electron parts of the Fock matrices (i.e. those that are independent of the electron density). Specifically this means:

$$h_{\mu\mu} = -\frac{1}{2} \left(I_\mu + A_\mu \right) - \left(Z_A - \frac{1}{2} \right) \gamma_{AA} - \sum_{B \neq A} Z_B \gamma_{AB} \tag{2.6}$$

$$h_{\mu v} = \frac{1}{2} \left(\beta_A + \beta_B \right) s_{\mu v} \tag{2.7}$$

You can readily make code for this core hamiltonian as a stripped down version of your Fock matrix builder.

So, altogether, we want you to:

1. Write and debug the unrestricted CNDO/2 SCF algorithm above, using armadillo to handle the matrix operations. Use H_2 as your first debugging case (where there should only be 2 iterations). Then HF as a second case. Your GSI will provide reference data for you for these cases.

2. Explore a little bit of chemistry with your CNDO/2 code. For example, you could look at the molecular orbitals and the bond energy of a simple diatomic molecule, such as N_2 ($p = 5, q = 5$; singlet multiplicity; $R_{NN} = 1.098$Å), getting the bond energy by also evaluating the N atom ($p = 4, q = 1$; quartet multiplicity). It would also be maybe nice to go evaluate the equilibrium bondlength, by minimizing the total energy, and compare with the experimental value of $R_{NN} = 1.098$Å. And/or you could do an open shell diatomic such as O_2 ($p = 7, q = 5$; triplet multiplicity; $R_{OO} = 1.208$Å) vs O atom ($p = 4, q = 2$), and optimize its bondlength to compare against the experimental value of $R_{OO} = 1.208$Å. Or you could choose something yourself and surprise us! Your code can in principle do quite large molecules, if you just provide the structure.

3 APPENDIX: NOTES FOR COMPUTE LAB ON EVALUATING γ_{AB}

γ_{AB} are two-center 2-electron repulsion integrals evaluated over the square of the valence s orbital centered on atoms A and B:

$$\gamma_{AB} = \int_{\mathbf{r}_1} \int_{\mathbf{r}_2} s_A^2(\mathbf{r}_1) \frac{1}{r_{12}} s_B^2(\mathbf{r}_2) \tag{3.1}$$

While 6-dimensional integrals look intimidating, this one can be analytically reduced to a 1-dimensional integral. Remembering that

$$s_A(r) \equiv \sum_k^3 \left(d_{ks_A} N_k^s \right) \omega_k^s(\mathbf{r} - \mathbf{R}_A) = \sum_k^3 d'_{ks_A} \omega_k^s(\mathbf{r} - \mathbf{R}_A) \tag{3.2}$$

The integral then becomes a sum over two-electron integrals over primitive Gaussians:

$$\gamma_{AB} = \sum_k^3 \sum_{k'}^3 \sum_l^3 \sum_{l'}^3 d'_{ks_A} d'_{k's_A} d'_{ls_B} d'_{l's_B} [0]^{(0)} \tag{3.3}$$

The 6-dimensional integral is hidden in $[0]^{(0)}$ (this is conventional notation for the integral over the product of 4 primitive Gaussian s functions):

$$[0]^{(0)} = \int_{\mathbf{r}_1} \int_{\mathbf{r}_2} \omega_k^s(\mathbf{r}_1 - \mathbf{R}_A) \omega_{k'}^s(\mathbf{r}_1 - \mathbf{R}_A) \frac{1}{r_{12}} \omega_l^s(\mathbf{r}_1 - \mathbf{R}_B) \omega_{l'}^s(\mathbf{r}_1 - \mathbf{R}_B) \tag{3.4}$$

$$\equiv \int_{\mathbf{r}_1} \int_{\mathbf{r}_2} \exp\left[-(\alpha_k + \alpha_{k'})(\mathbf{r}_1 - \mathbf{R}_A)^2 \right] \frac{1}{r_{12}} \exp\left[-(\beta_l + \beta_{l'})(\mathbf{r}_2 - \mathbf{R}_B)^2 \right] \tag{3.5}$$

It can be shown that (for original proof, see article by S.F. Boys, Proc. R. Soc. Lond. A200,542 (1950)):

$$[0]^{(0)} = U_A U_B \sqrt{2V^2} \sqrt{\frac{2}{\pi}} \int_0^1 \exp\left(-Tu^2 \right) du \tag{3.6}$$

The quantities T, U, V are given by:

$$T = V^2 (\mathbf{R}_A - \mathbf{R}_B)^2 \tag{3.7}$$

$$U = U_A U_B \tag{3.8}$$

$$V^2 = (\sigma_A + \sigma_B)^{-1} \tag{3.9}$$

And the remaining quantities U_A and σ_A are:

$$\sigma_A = (\alpha_k + \alpha_{k'})^{-1} \tag{3.10}$$

$$U_A = (\pi \sigma_A)^{3/2} \tag{3.11}$$

with analogous expressions for U_B and σ_B.

The 1-dimensional integral that remains is a specific case of the function known as the "Boys function", and for the special case we are interested in (s functions), $F_0(T)$ is given by:

$$F_0(T) = \int_0^1 \exp\left(-Tu^2\right) du = \frac{1}{2}\sqrt{\frac{\pi}{T}} \operatorname{erf}\left(\sqrt{T}\right) \tag{3.12}$$

Efficient evaluation of the error function is discussed in Numerical Recipes, in Sec. 6.2.2., and erf is defined as:

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp\left(-v^2\right) dv \tag{3.13}$$

The Boys function can also be related to other standard functions, such as the incomplete gamma function, discussed in Sec. 6.2 of Numerical Recipes.

A useful computable form of the fundamental 2-center integral over 4 primitive s-type Gaussians is given by rewriting Eqs. 3.6 in terms of $\operatorname{erf}\left(\sqrt{T}\right)$:

$$[0]^{(0)} = U_A U_B \sqrt{\frac{1}{(\mathbf{R}_A - \mathbf{R}_B)^2}} \operatorname{erf}\left(\sqrt{T}\right) \tag{3.14}$$

This result, Eq. 3.14, is then used in Eq. 3.3 to evaluate the not-that-tricky-after-all γ_{AB}!

Well, actually there is one tricky thing: note that if $\mathbf{R}_A = \mathbf{R}_B$ (i.e. a 1-center 2-electron integral like γ_{AA}) then the denominator of Eq. 3.14 goes to zero, and since $\operatorname{erf}(0) = 0$, your code will blow up! The correct result can be evaluated from Eq. 3.6:

$$[0]^{(0)}(T = 0) = U_A U_B \sqrt{2V^2} \sqrt{\frac{2}{\pi}} \tag{3.15}$$

4 APPENDIX: VALENCE STO-3G PARAMETERS FOR H, C, N, O, F

Given in Figure 4.1 are the exponents and contraction coefficients for the first row elements associated with most organic molecules (you should already have C and H from your adventures with extended Huckel theory). More are available in the paper posted on the class website, and, especially at the basis set exchange web site: `https://www.basissetexchange.org`

```
--------------------------------------------------------------
Atom      exponent        s contraction    p contraction
--------------------------------------------------------------
  H       3.42525091       0.15432897
          0.62391373       0.53532814
          0.16885540       0.44463454
--------------------------------------------------------------
  C       2.94124940      -0.09996723       0.15591627
          0.68348310       0.39951283       0.60768372
          0.22228990       0.70011547       0.39195739
--------------------------------------------------------------
  N       3.78045590      -0.09996723       0.15591627
          0.87849660       0.39951283       0.60768372
          0.28571440       0.70011547       0.39195739
--------------------------------------------------------------
  O       5.03315130      -0.09996723       0.15591627
          1.16959610       0.39951283       0.60768372
          0.38038900       0.70011547       0.39195739
--------------------------------------------------------------
  F       6.46480320      -0.09996723       0.15591627
          1.50228120       0.39951283       0.60768372
          0.48858850       0.70011547       0.39195739
--------------------------------------------------------------
```

Figure 4.1: Exponents and contraction coefficients for STO-3G for the standard light elements (in atomic units).