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**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  $p$   $\alpha$  electrons and  $q$   $\beta$  electrons, we define:

$$p_{\mu\nu}^{\alpha} = \sum_i^p c_{\mu i}^{\alpha} c_{\nu i}^{\alpha} \quad (1.1)$$

$$p_{\mu\nu}^{\beta} = \sum_i^q c_{\mu i}^{\beta} c_{\nu i}^{\beta} \quad (1.2)$$

$$p_{\mu\nu}^{\text{tot}} = p_{\mu\nu}^{\alpha} + p_{\mu\nu}^{\beta} \quad (1.3)$$

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

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

The off-diagonal elements are given by:

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

quantity	H	C	N	O	F
$\frac{1}{2}(I_s + A_s)$	7.176	14.051	19.316	25.390	32.272
$\frac{1}{2}(I_p + A_p)$		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  $\mu, \nu$  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  $I_\mu$  and  $A_\mu$  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  $A$ :

$$p_{AA} = \sum_{\mu \in A} p_{\mu\mu}^{\text{tot}} \quad (1.6)$$

$Z_A$  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.  $\beta_A$  are atomic bonding parameters, and are also tabulated in Table 1.

The only thing not yet defined are the quantities  $\gamma_{AB}$ . *You will develop code to evaluate  $\gamma_{AB}$  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  $\text{H}_2$  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  $\text{HO}^\bullet$  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:

$$\mathbf{f}^\alpha \mathbf{c}^\alpha = \mathbf{c}^\alpha \epsilon^\alpha \quad (2.1)$$

$$\mathbf{f}^\beta \mathbf{c}^\beta = \mathbf{c}^\beta \epsilon^\beta \quad (2.2)$$

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

$$\sum_{\nu} f_{\mu\nu}^{\alpha} c_{\nu i}^{\alpha} = c_{\mu i}^{\alpha} \epsilon_i^{\alpha} \quad (2.3)$$

$$\sum_{\nu} f_{\mu\nu}^{\beta} c_{\nu i}^{\beta} = c_{\mu i}^{\beta} \epsilon_i^{\beta} \quad (2.4)$$

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,  $\epsilon^{\alpha}$  and  $\epsilon^{\beta}$
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  $\alpha$  MOs and the  $q$  lowest energy  $\beta$  MOs and using Eqs. 1.1, 1.2 and 1.3
6. If the maximum magnitude of the change in the  $\alpha$  and  $\beta$  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:

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

The last term is the nuclear repulsion energy (be careful about its units also!). In the energy expression,  $h_{\mu\nu}$  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:

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

$$h_{\mu\nu} = \frac{1}{2} (\beta_A + \beta_B) s_{\mu\nu} \quad (2.7)$$

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  $\text{H}_2$  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;  $R_{NN} = 1.098\text{\AA}$ ), 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  $R_{NN} = 1.098\text{\AA}$ . And/or you could do an open shell diatomic such as  $O_2$  ( $p = 7, q = 5$ ; triplet multiplicity;  $R_{OO} = 1.208\text{\AA}$ ) vs O atom ( $p = 4, q = 2$ ), and optimize its bondlength to compare against the experimental value of  $R_{OO} = 1.208\text{\AA}$ . 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 $\gamma_{AB}$

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

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

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

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

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

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

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):

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

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

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

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

The quantities  $T, U, V$  are given by:

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

$$U = U_A U_B \quad (3.8)$$

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

And the remaining quantities  $U_A$  and  $\sigma_A$  are:

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

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

with analogous expressions for  $U_B$  and  $\sigma_B$ .

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:

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

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

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

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 erf( $\sqrt{T}$ ):

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

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

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  $\gamma_{AA}$ ) then the denominator of Eq. 3.14 goes to zero, and since erf(0) = 0, your code will blow up! The correct result can be evaluated from Eq. 3.6:

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

## 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 web-site, 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).