Excersize 3, Summer 2017 | ~~Atom~~

- Construction of Fock matrix. As a first step "no updates"

  Fock matrix = $h_{\alpha\beta}$

  - Initialization of $h_{\alpha\beta}$, allocation in fortran, C
  - C-users: double h[NBE][NBE], indexed from "0"!

- Construction of the overlap matrix $S_{\alpha\beta}$, allocation.

- Zero'th HF iteration: $hC = SC\varepsilon$

  - allocate coefficients C and the array of orbital energies ε.
  - Explain LAPACK, BLAS1, BLAS2, BLAS3 libraries
  - Explain DSYGV( ) from LAPACK

DSYGV(ITYPE, JOBZ, UPLO, N, A, LDA, B, LDB, W, WORK, LWORK, INFO)

- ITYPE = 1. $Ax = \lambda Bx$ ($hC = SC\varepsilon$)
  2. $ABx = \lambda x$ ($S^{-1}hC = C\varepsilon$)
  3. $BAx = \lambda x$ (the same)

- JOBZ = 'N' ... eigenvalues only
  'V' ... eigenvectors + eigenvalues

- UPLO = 'U' ...
  'L' ... which part (triangle) of A, B are read

- N = order of the problem (integer)
- A = real(8) :: A(LDA, N) ... destroyed during the diagonalization gives eigenvectors on exit
- LDA = integer, leading array of A. In our case, LDA = N. Explain use of the LDA

- B = real(8) :: B(LDA,N) ... overlap matrix, destroyed during the diagonalization
- LDB = integer(4), same as LDA
- W = real(8) :: W(N) .. ~~eigenvalues~~ eigenvalues in ascending order
- WORK = real(8) :: WORK(LWORK) ... auxiliary memory allocation needed by dsygv()

  LWORK = integer(4) ... length of WORK() array

  Method of 2 calls:

  dry run to determine the allocation size of WORK() array → call dsygv(ITYPE, JOBZ, UPLO, N, A, LDA, B, LDB, tmp, -1, info)

  lwork = tmp ... ! conversion real(8) → integer(4)

  allocate(work(LWORK))

  diagonalization → call dsygv(ITYPE, JOBZ, UPLO, N, A, LDA, B, LDB, WORK, LWORK, info)

- INFO = integer(4), output, if INFO = 0 successfull exit

- Do not forget to perform 2 copies before the diagonalization:

  1) $h_{\alpha\beta} \rightarrow C_{\alpha\beta}$

  2) $S_{\alpha\beta} \rightarrow St_{\alpha\beta}$ .. temporary overlap

- In zero-th iteration the orbital energy for RHF = -2.0 Hartree ($E_n = -\frac{Z^2}{2n^2}$)

Helium He with RHF

1) First, create tables of 2-electron integrals, allocate DAOI2(NBR, NBR, NBR, NBR)

~~i4=0~~
~~do l4=0,LMAX~~
~~do m4=-l4,l4~~

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do i4 = 1, NBR
do i3 = 1, NBR
do i2 = 1, NBR
do i1 = 1, NBR
    DAOI2(i1,i2,i3,i4) = dint2(i1,0,0, i2,0,0, i3,0,0, i4,0,0)
end do
end do
end do
end do
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continued

2.) Updates of J and K matrices

First, update J:

$$J_{\alpha\beta} = \sum_{i=1}^{\bar{N}} \sum_{\gamma,\delta} DADI2(\alpha,\beta,\gamma,\delta) \times C(\gamma,i) \times C(\delta,i)$$

second, update K:

$$K_{\alpha\beta} = \sum_{i=1}^{\bar{N}} \sum_{\gamma,\delta} DAOI2(\alpha,\delta,\gamma,\beta) \times C(\gamma,i) \times C(\delta,i)$$

3.) For RHF (singlet) we have $\bar{N} = N/2 = 1$ and $H_{\alpha\beta} = h_{\alpha\beta} + 2 * J_{\alpha\beta} - K_{\alpha\beta}$

For UHF (triplet) we have $\bar{N} = N = 2$ and $H_{\alpha\beta} = h_{\alpha\beta} + J_{\alpha\beta} - K_{\alpha\beta}$

4.) Calculate Singlet energy each iteration:

1 spatial orbital, with 2 spins: ↑ ↓

$$E = \sum_{i=1}^{N} \langle i|h|i\rangle + \frac{1}{2} \sum_{i,j}^{N} \{ [ii|jj] - [ij|ji]\, \delta_{s_i s_j} \}$$

Case of singlet:

4 terms → $[ii|jj] = \sum_{\alpha\beta\gamma\delta} C_{\alpha i} C_{\beta i} C_{\gamma j} C_{\delta j} [\alpha\beta|\gamma\delta]$

$= \sum_{\alpha\beta} C_{\alpha i} C_{\beta i} J_{\alpha\beta} = C_i^T J C_i$

2 terms (cancel to $\delta_{s_i s_j}$) → $[ij|ji] = C_i^T K C$

Singlet energy (variational):

$$E^S = 2 C^T h C + 2 C^T J C - C^T K C$$

5) Calculate triplet energy each iteration

2 spatial orbitals with identical spin: ↑ ↑

$$E^t = \sum_{i=1}^{2} \langle i|h|i\rangle + \frac{1}{2} \sum_{i=1}^{2} \left(J_{\alpha\beta} C_{\alpha i} C_{\beta i} - K_{\alpha\beta} C_{\alpha i} C_{\beta i} \right)$$

Sum $\sum_{j=1}^{2}$ is already in construction of $J_{\alpha\beta}$ and $K_{\alpha\beta}$

$$E^t = C_1^T h C_1 + C_2^T h C_2 + \frac{1}{2} \left(C_1^T J C_1 + C_2^T J C_2 - C_1^T K C_1 - C_2^T K C_2 \right)$$

Variational triplet energy