

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

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

- Initialization of $h_{\alpha\beta}$, allocation in fortran, C.

- C-users : double $h[\text{NBR}][\text{NBR}]$; indexed from "0"!

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

- Zero'th HF iteration : $hC = SCE$

- 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. $Ax = \lambda Bx$ ($hC = SCE$)
 2. $ABx = \lambda x$ ($S^{-1}hC = C\epsilon$)
 3. $Bx = \lambda x$ (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(B) :: $A(LDA, N)$... destroyed during the diagonalization gives eigenvectors on exit

- LDA = integer, leading array of A. In our case, $LDA = N$. Explain use of the LDA

- $B = \text{real}(8) :: B(LDA, N)$... overlap matrix, destroyed during the diagonalization

- $LDB = \text{integer}(4)$, same as LDA

- $W = \text{real}(8) :: W(N)$... ~~the~~ eigenvalues in ascending order

- $WORK = \text{real}(8) :: WORK(LWORK)$... auxiliary memory allocation needed by dsygv;

$LWORK = \text{integer}(4)$... length of $WORK()$ array.

Method of 2 calls :

```

try run to determine the allocation size of WORK() array } → call dsygv ( ITYPE, JOBZ, UPLD, N, A, LDA, B, LDB, tmp, -1, info )
                                |
                                | work = tmp ... ! conversion real(8) → integer(4)
                                | allocate( work(LWORK) )
diagonalization →           | call dsygv ( ITYPE, JOBZ, UPLD, N, A, LDA, B, LDB, WORK, LWORK, info )
                                |
                                |
                                |
    
```

- $INFO = \text{integer}(4)$, output, if $INFO=0$ successful 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 ($E_n = -\frac{2^2}{2n^2}$)

Helium He with RHF

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

```

i4 = 0
do i4 = 1, LMAX
do i3 = 1, LMAX
do i2 = 1, LMAX
do i1 = 1, LMAX
    
```

```

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
    
```

continued

2.) Updates of J and K matrices.

First, update J:

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

second, update K:

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

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

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

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
(due to $\delta_{s_i s_j}$)

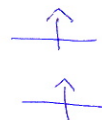
$$[ij | ji] = c_i^T K c_i$$

Singlet energy (variational):

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

5.) Calculate triplet energy each iteration

2 spatial orbitals with identical spin:



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

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

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

Variational triplet energy