

Different Programs to Perform Ab-initio Calculations within Highly Localized Orbitals — version for molecules

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Description of the series of programs to perform calculations on molecules, based on the initial periodic project. (TeXed on July 17, 2015)

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INTRODUCTION

The programs described were implemented as a rapid adaptation from the ring systems, by dropping in the source code all dependence on the cell indices, but have been modified subsequently for more specific needs. For the cases of interest — smaller molecules — the correlation programs seem still be efficient enough, despite the much more elaborate programs existing on the market. The intention of the special branch for molecules lies in the preparation of wavefunctions for QMC calculations, and in the generation of starting vectors for the dimer series or the periodic systems. Especially for the latter, efficiency of the molecular programs are not the most important aspect.

However, the electrostatic part, and the MP3 calculations are only implemented here, neither in the dimer nor in the programs for periodic systems.

I. GENERAL OVERVIEW

The programs are on hydrogene in the directory /home/reinh/bin as executables and the sources may be found in /home/reinh/programs/package/molecules.

A general flow chart of the package is the following (new branch):

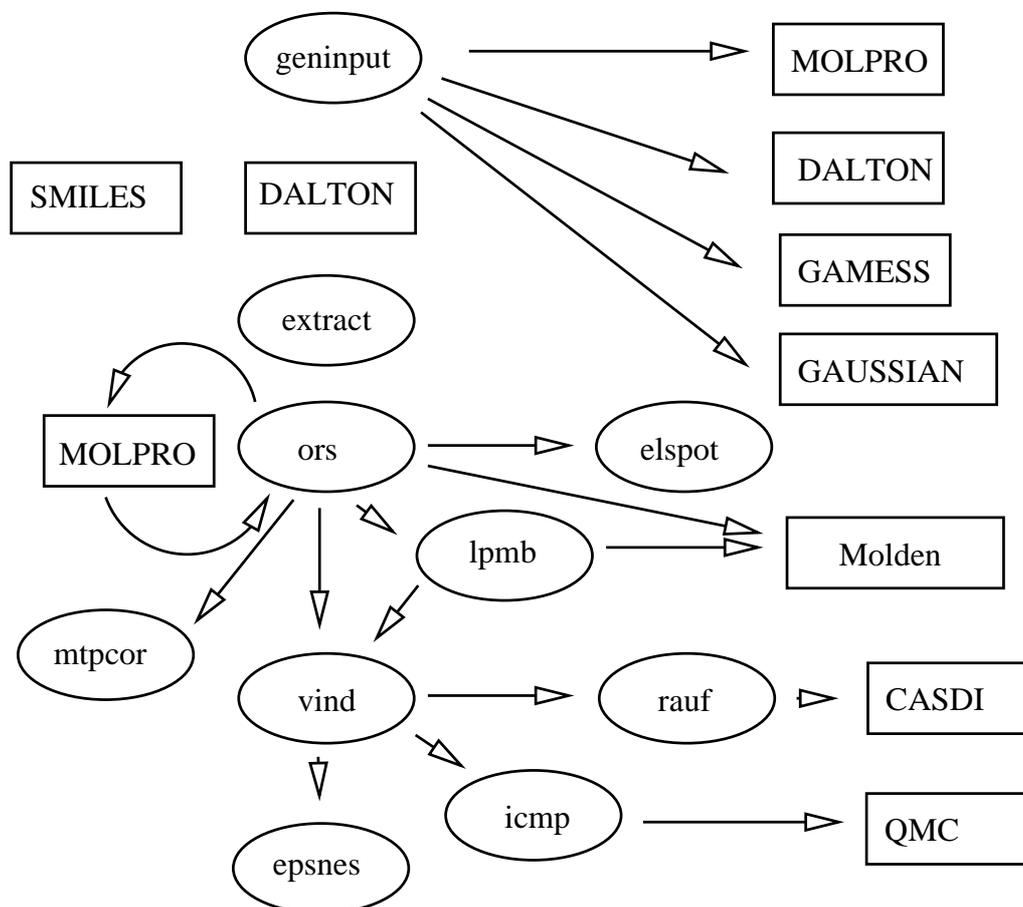


FIG. 1. Flow chart

II. THE PROGRAM GENINPUT

This program generates the input for the several SCF branches, for the moment the ORTHO series of programs, the DALTON SCF and the GAMESS package. An interface to MOLPRO and GAUSSIAN is as well implemented.

One file is absolutely necessary to run the input generator: the description of the system. This can be in any file, e.g. `system`, which is then used as input like

```
geninput_mol < system
```

A. Description of the System

The structure of the file (lines in free format) is the following:

- 1) NATOM: number of atoms in the molecule

For each atom a set of cards has to be given

2) NAT, NSHL, POS: atomic number, number of shells and position with respect to the center of the reference cell

For each shell:

3) ISTYPE, NPRIM: shell type (0,1,2 for *s*, *p*, *d*) and number of primitives for this shell.

For each primitive:

4) EXX, COEFF: Exponent and coefficient

As example might serve the input for NH₃ in a small basis

```
4                                     4 atoms in this molecule
7 6  -2.481795969  -0.023514305  0.000006953  the N
0 5
4177.5687      0.001829476
627.23610     0.013995972
142.77926     0.06836863
40.271825     0.23023378
12.893158     0.46369183
0 1
4.4175095     1.000000
0 1
.76130776     1.000000
0 1
.22402545     1.000000
1 3
14.089373     0.037761819
3.0322858     0.20922098
.82469052     0.50670505
1 1
.22435351     1.0000000
1 2  -2.865352733  1.859673616  -0.000029210  the first H
0 3
13.361500     0.01906000
2.0133000     0.13424000
.45375700     0.47449000
0 1
.12331700     1.0
1 2  -3.312917613  -0.792592254  1.552599025  the second H
0 3
13.361500     0.01906000
2.0133000     0.13424000
.45375700     0.47449000
0 1
.12331700     1.0
1 2  -3.312654127  -0.792598221  -1.552723180  the third H
0 3
13.361500     0.01906000
2.0133000     0.13424000
.45375700     0.47449000
0 1
.12331700     1.0
```

It is necessary to include for every atom a separate basis set, even if the basis sets are the same for several atoms. No pseudopotentials are supported.

B. Program directives

With an additional file INPUT.GEN the various features of the program can be addressed. If this file is not present, a default will be assumed, in this case the ORTHO sequence of programs with a neutral molecule.

The file `INPUT.GEN` is scanned until a line starting with `*INP` is found. The lines between this line and a line `*END` are considered as relevant input for the program `geninput_mol`.

Several keywords are possible:

- GAMESS: produces input for the GAMESS package.
- MOLPRO: produces input for the MOLPRO package.
- GAUSSIAN: produces input for a Gaussian RHF input.
- DALTON produces input for the DALTON SCF
- ORTHO produces input for the ORTHO series of programs (default)
- Two further keywords may be relevant:
 - 5 D asks for a run with spherical basis functions, i.e. 5 d functions, 7 f functions etc.
 - 6 D asks for a run with cartesian basis functions, i.e. xx , xy , xz , yy , yz and zz for the d functions, xxx etc. for f and so on.
- CHARGE plus a next line containing an integer puts a charge on the molecule. The programs, however, does not like open-shell systems, thus an uneven number of electrons.
- ATOMIC specifies that positions are to be taken in atomic units (1 a.u. = 0.529177249 Å). This is assumed by default.
- ANGSTR specifies that units are Ångströms.
- EXTDFIT assumes the option ORTHO to be set and creates an additional input to MOLPRO in order to let MOLPRO perform the DFT part of the calculation.
- SLATER produces the input files for the SMILES program of the group in Madrid. One additional integer number is needed as the expansion of a Slater into STO-nG for some three- and all four-center integrals.

C. Files created

- Having specified GAMESS a file `GAMESS.inp` and a file `gamess_script` are created. GAMESS can be invoked with the command `sh gamess_script`. It may be necessary to specify the environment variable `$TMPDIR` pointing to the scratch space. In the directory containing the files `gamess_script` and `GAMESS.inp` the GAMESS output is found in a file `gamess.output` and files `GAMESS.dat`, `GAMESS.PUNCH`, and `GAMESS.DICTNRY` are saved.
- With the option DALTON the DALTON input files `DALTON.INP` and `MOLECULE.INP`, as well as a script `script_dalton` are put on disk. Typing `sh script_dalton` launches the SCF calculation with the DALTON program.
- With the option GAUSSIAN an input file `GAUSSIAN.inp` is created as input file. The atomic coordinates are stored as cartesian coordinates, and for every atom a separate basis set is defined. A script `gaussian_script` contains two lines for launching Gaussian.
- With the option MOLPRO a file `MOLPRO.inp` and as well a two-line script `molpro_script` is put on disk. The atomic coordinates are stored in XYZ format, and for every atom a separate basis set is defined. For every atom a separate basis set is specified.
- The ORTHO series of programs needs the DALTON for the calculation of integrals, thus having specified ORTHO as SCF package, the files `SYSTEM.ORTHO`, `Startvektor`, `MOLECULE.INP`, `DALTON.INP`, and `script_ortho` are created. The file `Startvektor` (well, I know, it is german ...) contains the default starting vector for the SCF iterations, that is the unit matrix as coefficients, specified by `E` in the first line, and two more lines specifying occupation numbers.

The script launches the series of programs like in the flow chart until the completion of `ors_can_mol`.

D. Using pseudopotentials

Pseudopotentials allow for the use of heavy elements, and even scalar relativistic effects. They have to be given explicitly in the definition of the molecule.

A pseudopotential at the origin has the general semi-local form

$$V_{\text{PP}}(r) = \underbrace{-\frac{Z - Z_{\text{core}}}{r}}_{\text{Coulomb term}} + \underbrace{\sum_i d_i r^{n_i} e^{-a_i r^2}}_{\text{local term}} + \underbrace{\sum_{\ell} \left(\sum_i d_{i,\ell} r^{n_{i,\ell}} e^{-a_{i,\ell} r^2} \right) |P_{\ell}\rangle \langle P_{\ell}|}_{\text{semi-local term}} \quad (1)$$

The nuclear charge is reduced thus by Z_{core} , and for each angular momentum a different projector $|P_{\ell}\rangle \langle P_{\ell}|$ is defined. We have to specify thus the parameters Z_{core} , d_i , n_i , a_i , and $d_{i,\ell}$, $n_{i,\ell}$, $a_{i,\ell}$.

In the input a flag for pseudopotentials is given by the atomic number : if it is negative, the definition of the pseudopotential has to follow immediately, before giving the basis set.

- first card: Z_{core} and the number of projectors ($\ell_{\text{max}} + 1$).
- number of terms in the local potential
- for each term: n_i , a_i and d_i
- for each ℓ from 0 up to ℓ_{max} the same structure:
 - number of terms in the local potential
 - for each term: $n_{i,\ell}$, $a_{i,\ell}$ and $d_{i,\ell}$

Example :

```
-6 5 0.000000 0.000000 0.000000 Carbon atom with PP and and 5 basis functions
 2 3   pseudopotential, Z=2 and 3 projectors (s, p, d)
 1
 2 1.00000000 0.00000000   no local potential
 1
 2 6.40105200 33.12163800   s potential, n, a, d
 1
 2 7.30774700 -1.98625700   p potential
 1
 2 5.96179600 -9.45431800   d potential
0 3                               basis set
 2.263101 0.496548
 1.773186 -0.422391
 0.408619 -0.599356
0 1
 0.139175 1.0
 1 3
 8.383025 -0.038544
 1.993132 -0.203185
 0.559543 -0.498176
 1 1
 0.156126 1.0
 2 1
 0.6260000 1.0000000
 1 3 -0.943102 -0.544500 0.000000 Hydrogen atom without PP
 0 3
 18.7311370 0.03349460
 2.8253937 0.23472695
 0.6401217 0.81375733
 0 1
 0.1612778 1.0000000
```

As DALTON can not handle general pseudopotentials, we write an input for MOLPRO for just calculating one-electron integrals, and extracting thus the full Hamilton integrals from this calculation, replacing the DALTON one-electron integrals.

If the MOLPRO-generated file is present, the EXTRACT program will use this and will not extract the integrals from the DALTON-generated AOPROPER file.

III. THE PROGRAM EXTRACT

Possible options in an (optional) input file INPUT.EXT are between the keywords *EXT and *END. They are

- **FORMAT**: the bielectronic integrals file AOTWO_FORMATTED contains the integrals in simple ASCII format. The default is unformatted output to the file AOTWO.
- **NOTWO**: no bielectronic integrals are written.
- **NOONE**: no monoelectronic integrals are written.
- **KINETI**: kinetic energy integrals are written to the file KINETIC.
- **HAMILT**: all monoelectronic integrals are written to the file HAMILTO.
- **THRESH**: bielectronic integrals are stored if they are larger than the threshold. Next input is an integer I , from which the threshold is calculated as 10^{-I} .
- **NOMULT**: the integrals stored are NOT premultiplied with weight factors for the subsequent SCF cycles.
- **NONORM**: the integrals are NOT renormalized by means of the diagonal of the overlap matrix.

Without any options the program reads the DALTON output files AOONEINT, AOPROPER, and AOTWOINT. It produces the files OVERLAP, KINETIC, HAMILTO and AOTWO. For simplifying the construction of the Fock matrix

$$\sum_{\alpha\beta} \Pi_{\alpha\beta} \sum_{\gamma\delta} \Pi_{\gamma\delta} [2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta)]$$

the bielectronic integrals are premultiplied for that any integral $(\alpha\beta|\gamma\delta)$ is used as its 8 permutations of indices, without checking for same indices. The weights are 1 for integrals $(\alpha\beta|\gamma\delta)$ or $(\alpha\beta|\alpha\gamma)$, 1/2 for $(\alpha\alpha|\gamma\delta)$ or $(\alpha\beta|\alpha\beta)$ or $(\alpha\alpha|\alpha\beta)$, 1/4 for $(\alpha\alpha|\beta\beta)$, and 1/8 for the double-diagonal $(\alpha\alpha|\alpha\alpha)$.

The integral $(\alpha\beta|\gamma\delta)$ contributes to the bielectronic integral $(ii|jj)$ and $(ij|ji)$ as

| integral | $(ii jj)$ | $(ij ji)$ |
|------------------------------|--|--|
| $(\alpha\beta \gamma\delta)$ | $c_{\alpha} i c_{\beta} i c_{\gamma} j c_{\delta} j$ | $c_{\alpha} i c_{\beta} j c_{\gamma} j c_{\delta} i$ |
| $(\beta\alpha \gamma\delta)$ | $c_{\alpha} i c_{\beta} i c_{\gamma} j c_{\delta} j$ | $c_{\beta} i c_{\alpha} j c_{\gamma} j c_{\delta} i$ |
| $(\beta\alpha \delta\gamma)$ | $c_{\alpha} i c_{\beta} i c_{\gamma} j c_{\delta} j$ | $c_{\beta} i c_{\alpha} j c_{\gamma} j c_{\delta} i$ |
| $(\alpha\beta \delta\gamma)$ | $c_{\alpha} i c_{\beta} i c_{\gamma} j c_{\delta} j$ | $c_{\beta} i c_{\alpha} j c_{\gamma} j c_{\delta} i$ |
| $(\gamma\delta \alpha\beta)$ | $c_{\alpha} i c_{\beta} i c_{\gamma} j c_{\delta} j$ | $c_{\beta} i c_{\alpha} j c_{\gamma} j c_{\delta} i$ |
| $(\gamma\delta \beta\alpha)$ | $c_{\alpha} i c_{\beta} i c_{\gamma} j c_{\delta} j$ | $c_{\beta} i c_{\alpha} j c_{\gamma} j c_{\delta} i$ |
| $(\delta\gamma \beta\alpha)$ | $c_{\alpha} i c_{\beta} i c_{\gamma} j c_{\delta} j$ | $c_{\beta} i c_{\alpha} j c_{\gamma} j c_{\delta} i$ |
| $(\delta\gamma \alpha\beta)$ | $c_{\alpha} i c_{\beta} i c_{\gamma} j c_{\delta} j$ | $c_{\beta} i c_{\alpha} j c_{\gamma} j c_{\delta} i$ |

A given integrals $(\alpha\beta|\gamma\delta)$ will thus be premultiplied by $4 \times \Pi_{\alpha\beta}$ and $4 \times \Pi_{\gamma\delta}$ for the Coulomb term of the Fock matrix, and by $2 \times \Pi_{\alpha\beta}$, $2 \times \Pi_{\alpha\gamma}$, $2 \times \Pi_{\beta\gamma}$ and $2 \times \Pi_{\alpha\delta}$ for the exchange sum.

If the file AOPROPER is present, the program tries to extract the dipole integrals $\langle \chi_{\alpha} | \vec{r} | \chi_{\beta} \rangle$ onto files DIPOL_X, DIPOL_Y, and DIPOL_Z, for being used in a possible Boys localization. Traceless quadrupole moment integrals

$$\langle \chi_{\alpha} | \frac{1}{2} (3\vec{r} \otimes \vec{r} - r^2 \mathbf{1}) | \chi_{\beta} \rangle$$

are as well extracted, onto files QUAD_XX etc. .

IV. THE CLOSED-SHELL SCF PROGRAM ORS

I will not describe in detail the input for the older version of ORS, coming directly from the ring programs. Instead the new program, nearly completely rewritten from the base of the new dimer ORS, is discussed.

As input data files `OVERLAP`, `HAMILTON`, `KINETIC` and `AOTWO` are needed apart from the system definition file `SYSTEM.ORTHO`, and the program stops if any of these files is missing. The main differences between the old and the new version are that bielectronic integrals are not stored in complete blocks but are given as the four indices and the value of the integral for each integral. The multiplicity of each integral through index permutations is taken into account, and expected from the integral file prepared by `EXTRACT`.

Options for the program `ORS_MOL` have to be in a file `INPUT.ORS` between labels `*ORS` and `*END`, and are the following:

- `ECONVE`: convergency criterion is the change of the total energy between two SCF iteration.
- `FCONVE`: the convergency criterion is the mean size of the Fock-matrix elements coupling occupied and virtual orbitals, which has to be zero for a Hartree-Fock solution.
- `TEST`: read options, files, and stop.
- `CANONI`: do the canonical SCF iterations, that is diagonalizing the Fock matrix in every cycle. The default SCF algorithm is the Singles-CI, producing localized orbitals.
- `COREHA`: start the canonical SCF iteration with the Core Hamiltonian, that is without the bielectronic integrals in the Fock matrix. This is equivalent to setting the density matrix to zero for the first iteration. Default is the density matrix created from the starting orbitals found on the file `GUESS`.

An interesting (?) observation: if we start the iterations with zero on the diagonal of the very first Fock matrix, the first iteration seems better than when starting with the correct diagonal. The exemple is NH_3 in a decent basis.

```
FOR THE FIRST ITERATION WE DIAGONALIZE THE CORE HAMILTONIAN
ITER   0: E_TOT=      0.000000000000 EDIFF=0.00E+00 SFN=0.15E+00
ITER   1: E_TOT=     -53.720905227971 EDIFF=-.54E+02 SFN=0.14E-01
ITER   2: E_TOT=     -56.139489019534 EDIFF=-.24E+01 SFN=0.12E-02
...
ITER  17: E_TOT=     -56.214440407480 EDIFF=-.40E-10 SFN=0.19E-07
CONVERGENCE AFTER 17 ITERATIONS
```

And for the correct core hamiltonian:

```
FOR THE FIRST ITERATION WE DIAGONALIZE THE CORE HAMILTONIAN
ITER   0: E_TOT=      0.000000000000 EDIFF=0.00E+00 SFN=0.25E-01
ITER   1: E_TOT=     -42.017875167738 EDIFF=-.42E+02 SFN=0.18E-01
ITER   2: E_TOT=     -50.482177592857 EDIFF=-.85E+01 SFN=0.56E-02
ITER   3: E_TOT=     -55.565873455021 EDIFF=-.51E+01 SFN=0.38E-02
ITER   4: E_TOT=     -56.009582907291 EDIFF=-.44E+00 SFN=0.20E-02
...
ITER  20: E_TOT=     -56.214440407489 EDIFF=-.19E-10 SFN=0.13E-07
CONVERGENCE AFTER 20 ITERATIONS
```

- `MAXITE`: maximal number of SCF iterations.
- `LAMBDA`: premultiply the bielectronic term by a factor λ for tuning electron-electron interaction. $\lambda = 0$ are non-interacting electrons, thus the Bohr model for atoms.
- `FMIXIN`: Fock matrix mixing as convergency accelerator, the value or the percentage can be given: 0.30 or 30%.
- `PIPEKLM`: localize the Hartree-Fock solution by the Pipek-Mezey localization scheme, a posteriori.
- `BOYS`: localize the orbitals by the Boys localization.

- FREEZE: freeze some orbitals for the localization process. Two lines are needed as additional input: the number of orbitals to be frozen, and their index in the list of all orbitals.
- REMOVE: the number and indices of atomic orbitals to be eliminated from the list of atomic orbitals when creating the virtual space. Default is the overlap of the atomic orbitals with the occupied space for selection of orbitals to be deleted.
- WFN: print a Gaussian WFN file; not yet operative.
- MOLDEN: put a MOLDEN input file on disk.
- QMC: generate input for M.Caffarel's quantum Monte Carlo program.
- COMPLETE: do a complete 4-index transformation in the SCI step.
- EXTERN: the SCF cycles will be done by MOLPRO (good for DFT calculations).
- MULTIP: a file containing multipole definition will be read; the created electrostatic field will be added to the Fock operator as external field.
- ODA: we will employ the Optimal Damping Algorithm of E.Cancès (see next section).
- DIPOL: dipole and quadrupole moments of the molecule will be calculated. Results are the same as Dalton, slightly different from Gaussian.
- ORIGIN: for the calculation of the non-invariant multipole moments (dipole, quadrupole) we can set an origin position.
- 6 D: calculation expects integrals in cartesian Gaussians and writes an output vector to the file VECTOR.???.6D.

A. Some words concerning the Singles CI

In order to obtain localized orbitals, the default option for the SCF is to pass via a Singles CI step. The loop consists of i) orthogonalization, ii) construction of the Fock matrix and calculation of the total energy, iii) construction of the CI matrix, iv) diagonalization of the CI matrix, v) generation of new molecular orbitals. In step ii) we test whether the Fock-matrix elements coupling occupied and virtual orbitals are on average small — convergence is reached for vanishing coupling elements due to Brillouin's theorem $\langle \Phi_0 | \mathbf{H} | \Phi_i^a \rangle = F_{ia} \rightarrow 0$.

The Singles CI matrix is reduced to its Fock-matrix contributions, neglecting pure bielectronic interactions like $\langle \Phi_i^a | \mathbf{H} | \Phi_j^b \rangle = (ia|jb) - (ib|ja)\delta_{\sigma_i\sigma_j}$. We take as well the spin-adapted combination $(\Phi_i^a + \Phi_i^{\bar{a}})/\sqrt{2}$. This leads to

$$\begin{aligned}
 \langle \Phi_0 | \mathbf{H} | \Phi_i^a \rangle &= \frac{1}{\sqrt{2}} \langle \Phi_0 | \mathbf{H} | (\Phi_i^a + \Phi_i^{\bar{a}}) \rangle = \sqrt{2} F_{ia} \\
 a \neq b : \langle \Phi_i^a | \mathbf{H} | \Phi_i^b \rangle &= h_{ab} + (ab|ii) + \underbrace{(ai|ib)}_{= \langle \Phi_i^a | \mathbf{H} | \Phi_i^{\bar{b}} \rangle} + \sum_{j \in occ, j \neq i} (2(ab|jj) - (aj|jb)) = F_{ab} - (ab|ii) + 2(ai|ib) \\
 \rightarrow \langle \Phi_i^a | \mathbf{H} - E_0 \mathbf{1} | \Phi_j^b \rangle &= F_{ab}\delta_{ij} - F_{ij}\delta_{ab}
 \end{aligned} \tag{2}$$

Diagonalization of the CI matrix leads to coefficients c_i^a which are used to update the molecular orbitals:

$$\phi_i \leftarrow \phi_i + \sum_{a \in virt.} c_i^a \phi_a; \quad \phi_a \leftarrow \phi_a - \sum_{i \in occ.} c_i^a \phi_i$$

This ensures that if occupied and virtual orbitals were orthonormal, the spaces remain orthogonal:

$$\begin{aligned}
 \langle \phi_i^{new} | \phi_a^{new} \rangle &= \left\langle \phi_i + \sum_{b \in virt} c_i^b \phi_b \left| \phi_a + \sum_{j \in occ} c_j^a \phi_j \right. \right\rangle \\
 &= \langle \phi_i | \phi_a \rangle + \sum_{b \in virt} c_i^b \langle \phi_b | \phi_a \rangle + \sum_{j \in occ} c_j^a \langle \phi_i | \phi_j \rangle + \sum_{b \in virt} \sum_{j \in occ} c_i^b c_j^a \langle \phi_b | \phi_j \rangle \\
 &= c_i^a (\langle \phi_a | \phi_a \rangle - \langle \phi_i | \phi_i \rangle) = 0.
 \end{aligned} \tag{3}$$

Within the block of occupied orbitals, and within the block of virtual orbitals, we have to reorthogonalize the new orbitals, preferably by $\mathbf{S}^{-1/2}$, in order to maintain the initial properties of the starting orbitals as best as possible.

The obtained Hartree-Fock orbitals resemble the most the initial orbitals, however we have no criterion to maximize or minimize any localization functional, as the Boys or the Pipek-Mezey measure. The advantage lies in the fact that we never have to deal with the diagonalization of the Fock matrix, thus we never delocalize explicitly. Instead we try to keep localized what was initially localized. Of course, for small molecules this seems not very interesting. But for longer chains, rings etc, where building blocks can be defined, final Hartree-Fock orbitals can be qualified through their difference to the starting orbitals, without the obligation to resort to a localization scheme with an arbitrary functional to be optimized, giving different results for fragments and the supermolecule.

B. The optimal damping algorithm of E.Cancès

With the keyword ODA the Optimal Damping Algorithm of Eric Cancès and Claude Le Bris is addressed. The idea is to look for a mixture of the old and a new density matrix for evaluating the Hartree-Fock energy and for constructing a new Fock matrix to be handled. The optimal density matrix should lie somewhere between the old and the new one

$$\tilde{P}(\lambda) = (1 - \lambda)P^{old} + \lambda P^{new} \quad \text{with } \lambda \in [0, 1] \quad .$$

We may express the Hartree-Fock energy through the parametrized density matrix

$$E(\lambda) = E_N + \sum_{\mu\nu} \tilde{P}_{\mu\nu}(\lambda) h_{\mu\nu} + \frac{1}{2} \sum_{\mu\nu} \tilde{P}_{\mu\nu}(\lambda) \sum_{\rho\sigma} \tilde{P}_{\rho\sigma}(\lambda) [2(\mu\nu|\rho\sigma) - (\mu\sigma|\rho\nu)]$$

and look for the minimum with respect to λ . If it is beyond 1 we restrict the step to one.

With the quantities

$$\begin{aligned} A_1 &= \sum_{\mu\nu} P_{\mu\nu}^{old} h_{\mu\nu} = E_1^{old} \\ A_2 &= \sum_{\mu\nu} P_{\mu\nu}^{new} h_{\mu\nu} = E_1^{new} \\ X_{\rho\sigma}^{old} &= \sum_{\mu\nu} P_{\mu\nu}^{old} [2(\mu\nu|\rho\sigma) - (\mu\sigma|\rho\nu)] \\ X_{\rho\sigma}^{new} &= \sum_{\mu\nu} P_{\mu\nu}^{new} [2(\mu\nu|\rho\sigma) - (\mu\sigma|\rho\nu)] \\ B_1 &= \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu}^{old} X_{\mu\nu}^{old} = E_2^{old-old} \\ B_2 &= \sum_{\mu\nu} P_{\mu\nu}^{new} X_{\mu\nu}^{old} = 2 E_2^{new-old} \\ B_3 &= \frac{1}{2} \sum_{\mu\nu} P_{\mu\nu}^{new} X_{\mu\nu}^{new} = E_2^{new-new} \end{aligned} \quad (4)$$

and the symmetry $E_2^{new-old} = E_2^{old-new}$ we have then

$$E^{old} = E_N + E_1^{old} + E_2^{old-old} = E_N + A_1 + B_1; \quad E^{new} = E_N + E_1^{new} + E_2^{new-new} = E_N + A_2 + B_3$$

$$\begin{aligned} E(\lambda) &= E_N + (1 - \lambda) A_1 + \lambda A_2 + (1 - \lambda)^2 B_1 + (1 - \lambda)\lambda B_2 + \lambda^2 B_3 \\ &= \lambda^2 (B_1 - B_2 + B_3) + \lambda (A_2 - A_1 + B_2 - 2 B_1) + (A_1 + B_1 + E_N) \end{aligned} \quad (5)$$

as quadratic expression in λ , the minimum of which is at

$$\lambda = -\frac{1}{2} \frac{A_2 - A_1 + B_2 - 2 B_1}{B_1 - B_2 + B_3} \quad .$$

With this λ we may construct now the Fock matrix for the next iteration as

$$F_{\mu\nu} = h_{\mu\nu} + (1 - \lambda) X_{\mu\nu}^{old} + \lambda X_{\mu\nu}^{new} \quad .$$

To implement this algorithm we have to save the first density matrix $P_{\mu\nu}^{old}$ and the first half-contraction $X_{\mu\nu}^{old}$ somewhere. The first construction of the total energy gives us as well A_1 and B_1 . In the subsequent iterations A_2 , B_2 and B_3 are calculated, a λ is determined, and A_1 and B_1 are updated from the optimal mixture of old and new quantities as

$$\begin{aligned} A_1 &:= (1 - \lambda) A_1 + \lambda A_2 \\ B_1 &:= (1 - \lambda)^2 B_1 + (1 - \lambda) \lambda B_2 + \lambda^2 B_3 \end{aligned} \quad . \quad (6)$$

Between the lecture of the bielectronic integrals and the construction of the new Fock matrix we may easily determine the optimal λ and construct the matrix with the modified density matrix.

For the CRYSTAL programs there is a little difference, since the density matrix enters the expression of the total energy as well via the infinite summation of multipoles. This summation is only partly included in the mono-electronic part of the Fock matrix.

The Fock matrix is constructed from the pure bielectronic integrals and pure monoelectronic integrals and the infinite summation of multipoles

$$F_{\mu\nu} = T_{\mu\nu} + Z_{\mu\nu} + \sum_{rho\sigma} P_{\rho\sigma} \cdot I_{\mu\nu\rho\sigma} + C J J_{\mu\nu}$$

The total energy in CRYSTAL, on the other hand, includes a spheropole, multipoles, electron-electron, electron-nucleus, nucleus-nucleus and kinetic energy terms, which are all added together.

```
+++ ENERGIES IN A.U. +++
::: EXT EL-POLE : L = 0          -2.270671816404E+03
::: EXT EL-POLE : L = 1          4.457494198476E-03
::: EXT EL-POLE : L = 2         -2.707232206735E-02
::: EXT EL-POLE : L = 3         -6.601530543733E-04
::: EXT EL-POLE : L = 4         -2.383032540856E-03
::: EXT EL-SPHEROPOLE           1.750330131406E+01
::: BIELET ZONE E-E             2.677259647194E+03
::: TOTAL E-E                   4.240654740909E+02
::: TOTAL E-N + N-E            -4.063795306747E+03
::: TOTAL N-N                   -3.570413799528E+02
::: KINETIC ENERGY             2.000113440719E+03
::: TOTAL ENERGY              -1.996657771890E+03
::: VIRIAL COEFFICIENT           1.000864615122E+00
```

We have to find out, in which way the density matrix enters these terms (linear, quadratic or not at all) for determining which of the terms have to be added to A_1 or A_2 , and which of the terms become part of B_1 , B_2 and B_3 .

The spheropole is, as kinetic and e-n interaction, a contraction of monoelectronic integrals and the density matrix. But it is not added to the Fock matrix. The external EL-POLE terms are a product of e-n integrals (TZ), effective multipoles for each atom (QVRS) and precontracted integrals (CJ). The formulæ for the calculation of these integrals should be in the article of V.R.Saunders and R.Dovesi, Mol.Phys, 1992. The effective multipoles themselves depend directly on the density matrix. QVRS can be printed via the print option 68, it seems to be the multipoles per shell.

C. Calculating multipole moments of a molecule

Multipole moments may be calculated directly from the AO integrals. However, some care has to be taken for the choice of the origin. Dalton puts the origin in the center of mass for the calculation of moments, but integrals are calculated in the original frame, without displacements.

We may define the electronic multipole moments as expectation values

$$\begin{aligned}
 q &= \langle \Psi | \left(\sum_i \mathbf{1}_i \right) | \Psi \rangle = \sum_i \langle \phi_i | \mathbf{1} | \phi_i \rangle \\
 \vec{\mu} &= \langle \Psi | \left(\sum_i \vec{r}_i \right) | \Psi \rangle = \sum_i \langle \phi_i | \vec{r} | \phi_i \rangle \\
 Q &= \langle \Psi | \left(\sum_i \frac{1}{2} (3\vec{r}_i \otimes \vec{r}_i - r_i^2 \mathbf{1}) \right) | \Psi \rangle = \sum_i \langle \phi_i | \frac{1}{2} (3\vec{r} \otimes \vec{r} - r^2 \mathbf{1}) | \phi_i \rangle
 \end{aligned} \tag{7}$$

The charge is the double trace of overlap and density matrix :

$$q_{tot} = \sum_i Z_i + \sum_{\alpha\beta} P_{\alpha\beta} S_{\alpha\beta} \quad .$$

No coordinates enter, so the result is unique. For a non-zero total charge the dipole moment depends on the coordinate system, and we have to calculate it according to

$$\begin{aligned}
 \vec{\mu}_{tot} &= \sum_i Z_i (\vec{r}_i - \vec{R}) + \sum_{\alpha\beta} P_{\alpha\beta} \langle \chi_\alpha | (\vec{r} - \vec{R}) | \chi_\beta \rangle \\
 &= \sum_i Z_i (\vec{r}_i - \vec{R}) + \sum_{\alpha\beta} P_{\alpha\beta} \left(\underbrace{\langle \chi_\alpha | \vec{r} | \chi_\beta \rangle}_{\text{dipole integrals}} - \vec{R} \underbrace{\langle \chi_\alpha | \chi_\beta \rangle}_{S_{\alpha\beta}} \right)
 \end{aligned} \tag{8}$$

Similar is the calculation of the quadrupole moment: the operator $\frac{1}{2} (3\vec{r} \otimes \vec{r} - r^2 \mathbf{1})$ has to be shifted correctly. That is (for xx and xy , the other components being similar)

$$\begin{aligned}
 (Q_{tot,nucl})_{xx} &= \sum_i Z_i \left((x_i - X)^2 - \frac{1}{2}(y_i - Y)^2 - \frac{1}{2}(z_i - Z)^2 \right) \\
 (Q_{tot,elec})_{xx} &= \sum_{\alpha\beta} P_{\alpha\beta} \langle \chi_\alpha | \left((x_i - X)^2 - \frac{1}{2}(y_i - Y)^2 - \frac{1}{2}(z_i - Z)^2 \right) | \chi_\beta \rangle \\
 &= \sum_{\alpha\beta} P_{\alpha\beta} \left(\underbrace{\langle \chi_\alpha | (x^2 - \frac{1}{2}y^2 - \frac{1}{2}z^2) | \chi_\beta \rangle}_{\text{quadrupole integrals}} - \underbrace{2X \langle \chi_\alpha | x | \chi_\beta \rangle + Y \langle \chi_\alpha | y | \chi_\beta \rangle + Z \langle \chi_\alpha | z | \chi_\beta \rangle}_{\text{dipole integrals}} \right. \\
 &\quad \left. + (X^2 - \frac{1}{2}Y^2 - \frac{1}{2}Z^2) \underbrace{\langle \chi_\alpha | \chi_\beta \rangle}_{S_{\alpha\beta}} \right)
 \end{aligned} \tag{9}$$

$$\begin{aligned}
 (Q_{tot,nucl})_{xy} &= \frac{3}{2} \sum_i Z_i (x_i - X)(y_i - Y) \\
 (Q_{tot,elec})_{xy} &= \frac{3}{2} \sum_{\alpha\beta} P_{\alpha\beta} \langle \chi_\alpha | (x_i - X)(y_i - Y) | \chi_\beta \rangle \\
 &= \frac{3}{2} \sum_{\alpha\beta} P_{\alpha\beta} \left(\underbrace{\langle \chi_\alpha | xy | \chi_\beta \rangle}_{\text{quadrupole integrals}} - \underbrace{(X \langle \chi_\alpha | y | \chi_\beta \rangle + Y \langle \chi_\alpha | x | \chi_\beta \rangle)}_{\text{dipole integrals}} + XY \underbrace{\langle \chi_\alpha | \chi_\beta \rangle}_{S_{\alpha\beta}} \right)
 \end{aligned} \tag{10}$$

D. The half-electron approximation

Michael Dewar et al. published a proposition to treat open-shell systems the so-called half-electron method,¹ by using a closed-shell SCF program with occupation numbers n_i which can be 2, 1, or zero. The density matrix becomes thus

$$P_{\alpha\beta} = \sum_i n_i c_{\alpha i} c_{\beta i}$$

and the total energy

$$E_{tot} = \sum_{\alpha\beta} P_{\alpha\beta} h_{\alpha\beta} + \frac{1}{4} \sum_{\alpha\beta} P_{\alpha\beta} \left(\sum_{\gamma\delta} P_{\gamma\delta} (2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta)) \right) \quad (11)$$

$$= 2 \sum_{i \in c} h_{ii} + \sum_{i \in o} h_{ii} + \sum_{ij \in c} (2J_{ij} - K_{ij}) + \sum_{i \in c} \sum_{k \in o} (2J_{ij} - K_{ij}) + \frac{1}{4} \sum_{k, \ell \in o} (2J_{k\ell} - K_{k\ell}) \quad (12)$$

In contrast to the high-spin ROHF energy expression of Roothaan

$$E_{tot}(ROHF) = 2 \sum_{i \in c} h_{ii} + \sum_{i \in o} h_{ii} + \sum_{ij \in c} (2J_{ij} - K_{ij}) + \sum_{i \in c} \sum_{k \in o} (2J_{ij} - K_{ij}) + \frac{1}{2} \sum_{k, \ell \in o} (J_{k\ell} - K_{k\ell})$$

we have a term of

$$\frac{1}{4} \sum_{k, \ell \in o} (2J_{k\ell} - K_{k\ell}) - \frac{1}{2} \sum_{k, \ell \in o} (J_{k\ell} - K_{k\ell}) = \frac{1}{4} \sum_{k, \ell \in o} K_{k\ell}$$

which we have to subtract from our energy in order to have the same result for the total energy (if the orbitals were identical). Thus we use the Fock matrix

$$F_{\alpha\beta} = h_{\alpha\beta} + \sum_{\gamma\delta} P_{\gamma\delta} (2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta))$$

as before, and we modify at the end the total energy by the additional term $\frac{1}{4} \sum_{k, \ell \in o} K_{k\ell}$. This has been discussed in *N.C. Baird, R.F. Barr, Theor.Chim.Acta, 36 (1974) 125* and *F.O. Ellison, F.M. Matheu, Chem.Phys.Lett., 10 (1971) 322*.

For cumulating the correction, we have to do a partial four-index transformation while constructing the Fockmatrix:

$$K_{ij} = \sum_{\alpha\beta\gamma\delta} c_{\alpha i} c_{\beta j} c_{\gamma i} c_{\delta j} (\alpha\beta|\gamma\delta)$$

If we have an integral $(\alpha\beta|\gamma\delta)$ and look at its 8 permutations, we see that it contributes as

$$2 \times (c_{\alpha i} c_{\beta j} + c_{\alpha j} c_{\beta i}) \times (c_{\gamma i} c_{\delta j} + c_{\gamma j} c_{\delta i}) \times (\alpha\beta|\gamma\delta)$$

which is a priori a N^6 transformation, however reduced as i and j run only over the few open shells, and the bielectronic integrals over atomic orbitals are limited as N^2 for large systems.

The methods seems completely unused in ab-initio quantum chemistry, probably due to the rapid development of ROHF, UHF and MCSCF methods for the treatment of open-shell systems. Once the Fock matrix diagonalized one may indeed wonder how to attribute the electrons to the orbitals, especially to high-spin d-electron transition-metal systems, where the d orbitals do not have the highest orbital energies.

Second detail is the implementation of the Singles-CI scheme with the open shell.

¹*M.J.S. Dewar, J.A. Hashmall, C.G. Venier, JACS, 90 (1968) 1953*

V. THE UNRESTRICTED OPEN-SHELL SCF PROGRAM ORS_UHF

In UHF a separate Fock matrix is constructed for α and β spins.² From the two orbital sets ϕ^α and ϕ^β we construct two density matrices

$$\begin{aligned} P_{\gamma\delta}^\alpha &= \sum_{i \in \alpha} c_{\gamma i} c_{\delta i} \\ P_{\gamma\delta}^\beta &= \sum_{i \in \beta} c_{\gamma i} c_{\delta i} \end{aligned} \quad (13)$$

The two Fock matrices are coupled through the electrostatic interaction, leading to

$$\begin{aligned} F_{\rho\sigma}^\alpha &= h_{\rho\sigma} + \sum_{k \in \alpha} ((\rho\sigma|kk) - (\rho k|k\sigma)) + \sum_{k \in \beta} (\rho k|k\sigma) \\ &= h_{\rho\sigma} + \underbrace{\sum_{\gamma\delta} P_{\gamma\delta}^\alpha ((\rho\sigma|\gamma\delta) - (\rho\gamma|\delta\sigma)) + \sum_{\gamma\delta} P_{\gamma\delta}^\beta (\rho\sigma|\gamma\delta)}_{= \Xi_{\rho\sigma}^\alpha} \\ F_{\rho\sigma}^\beta &= h_{\rho\sigma} + \sum_{k \in \beta} ((\rho\sigma|kk) - (\rho k|k\sigma)) + \sum_{k \in \alpha} (\rho k|k\sigma) \\ &= h_{\rho\sigma} + \underbrace{\sum_{\gamma\delta} P_{\gamma\delta}^\beta ((\rho\sigma|\gamma\delta) - (\rho\gamma|\delta\sigma)) + \sum_{\gamma\delta} P_{\gamma\delta}^\alpha (\rho\sigma|\gamma\delta)}_{= \Xi_{\rho\sigma}^\beta} \\ F \phi_i &= \epsilon_i \phi_i \end{aligned} \quad (14)$$

The total energy is again composed of kinetic, Coulomb and exchange energy, as before:

$$\begin{aligned} E^{UHF} &= \sum_i h_{ii} + \frac{1}{2} \sum_{ij} (x_i x_i | x_j x_j) - \delta_{\sigma_i \sigma_j} (x_i x_j | x_j x_i) \\ &= \sum_i h_{ii} + \frac{1}{2} \sum_{ij \in \alpha} (ii|jj) - (ij|ji) + \frac{1}{2} \sum_{ij \in \beta} (ii|jj) - (ij|ji) + \sum_{i \in \alpha} \sum_{j \in \beta} (ii|jj) \\ &= \sum_{\rho\sigma} (P_{\rho\sigma}^\alpha + P_{\rho\sigma}^\beta) h_{\rho\sigma} + \frac{1}{2} \left(\sum_{\rho\sigma} [P_{\rho\sigma}^\alpha \Xi_{\rho\sigma}^\alpha + P_{\rho\sigma}^\beta \Xi_{\rho\sigma}^\beta] \right) \end{aligned} \quad (15)$$

where the sums run over spin orbitals and not only over spatial orbitals.

Instead of one set of spatial orbitals we have now one set for each spin. As well we have corresponding orbital energies for the two sets of orbitals.

The options are nearly the same as for the closed-shell case:

- ECONVE: convergency criterion is the change of the total energy between two SCF iteration.
- FCONVE: the convergency criterion is the mean size of the Fock-matrix elements coupling occupied and virtual orbitals, which has to be zero for a Hartree-Fock solution.
- TEST: read options, files, and stop.
- CANONI: do the canonical SCF iterations, that is diagonalizing the Fock matrix in every cycle. The default SCF algorithm is the Singles-CI, producing localized orbitals.
- COREHA: start the canonical SCF iteration with the Core Hamiltonian, that is without the bielectronic integrals in the Fock matrix.
- MAXITE: maximal number of SCF iterations.

²Pople-Nesbet-Berthier equations *G. Berthier*, *Comptes Rendus Acad. Sci.*, **238** (1954) 91

- LAMBDA: premultiply the bielectronic term by a factor λ for tuning electron-electron interaction. $\lambda = 0$ are non-interacting electrons, thus the Bohr model for atoms.
- FMIXIN: Fock matrix mixing as convergence accelerator, the value or the percentage can be given: 0.30 or 30%.
- FREEZE: freeze some orbitals for the localization process. Two lines are needed as additional input: the number of orbitals to be frozen, and their index in the list of all orbitals.
- EXTERN: the SCF cycles will be done by MOLPRO (good for DFT calculations).
- ODA: we will employ the Optimal Damping Algorithm of E.Cancès.
- 6 D: calculation expects integrals in cartesian Gaussians and writes an output vector to the file VECTOR.???.6D.

As α and β spin-orbitals are obtained separately, two files will be created at the end (VECTOR_ALPHA.XXX and VECTOR_BETA.XXX), and two starting vectors (GUESS_ALPHA and GUESS_BETA) will be needed to define orbitals (or a unit matrix), and the occupations.

VI. THE SINGLES-CI STEP IN THE UHF CASE

Again, we have to look for spin orbitals instead for the spatial part only. The wavefunction may be considered as a product of two determinants, one of spin α and one of spin β , $\Psi = D^\alpha D^\beta$. We may encounter three different types of matrix elements in the Singles CI procedure, same-spin or different-spin combinations, or interactions with the reference:

$$\begin{aligned}\langle \Phi_i^a | \hat{H} - E_{HF} | \Phi_j^b \rangle &\approx F_{ab}^\alpha \delta_{ij} - F_{ij}^\alpha \delta_{ab} \\ \langle \Phi_i^a | \hat{H} - E_{HF} | \Phi_j^b \rangle &= F_{ia}^\alpha + F_{jb}^\beta \\ \langle \Phi_i^a | \hat{H} - E_{HF} | \Phi_0 \rangle &= F_{ib}^\alpha\end{aligned}\quad (16)$$

There is no spin flip allowed, as the number of α and β spins should be invariant. The dimension of the CI matrix is twice that of the closed-shell case, and the elements coupling different spin settings are non-zero, in contrast to the Fock or density matrices for each spin.

A. Spin contamination

Szabo and Ostlund (page 107, equation 2.271) give, a formula to calculate the expectation value of the spin operator \hat{S}^2 from the mutual overlap-matrix elements between the two (occupied) orbital sets:

$$\langle \Phi_{UHF} | \hat{S}^2 | \Phi_{UHF} \rangle = \left(\frac{n_\alpha - n_\beta}{2} \right) \left(\frac{n_\alpha - n_\beta}{2} + 1 \right) + n_\beta - \sum_{i \in \alpha, occ} \sum_{j \in \beta, occ} |S_{ij}|^2 \quad (17)$$

The formula is symmetric in n_α and n_β due to

$$\left(\frac{n_\alpha - n_\beta}{2} \right) \left(\frac{n_\alpha - n_\beta}{2} + 1 \right) + n_\beta = \frac{1}{4} ((n_\alpha - n_\beta)^2 + 2(n_\alpha - n_\beta)) = S_z^2 + S_z$$

The underlying relation is the expression of S^2 in terms of S_+ , S_- , and S_z as

$$S^2 = S_+ S_- + S_z^2 - \hbar S_z = S_- S_+ + S_z^2 + \hbar S_z \quad (18)$$

The application of $S_- S_+$ permutes an α spin with a β spin, while S_z counts the difference in α and β spins.

For a high-spin ROHF determinant only the part $\left(\frac{n_\alpha - n_\beta}{2} \right) \left(\frac{n_\alpha - n_\beta}{2} + 1 \right)$ survives as all overlaps are either zero or one, leading to $S(S+1)$. Thus, for a closed-shell case this formula produces exactly zero.

The broken-symmetry UHF solution for H_2 with $S_z = 0$ yields thus about a singlet for the equilibrium distance, and a pure triplet for large distances, as $S_{ij} \rightarrow 0$, and $n_\beta = 1$.

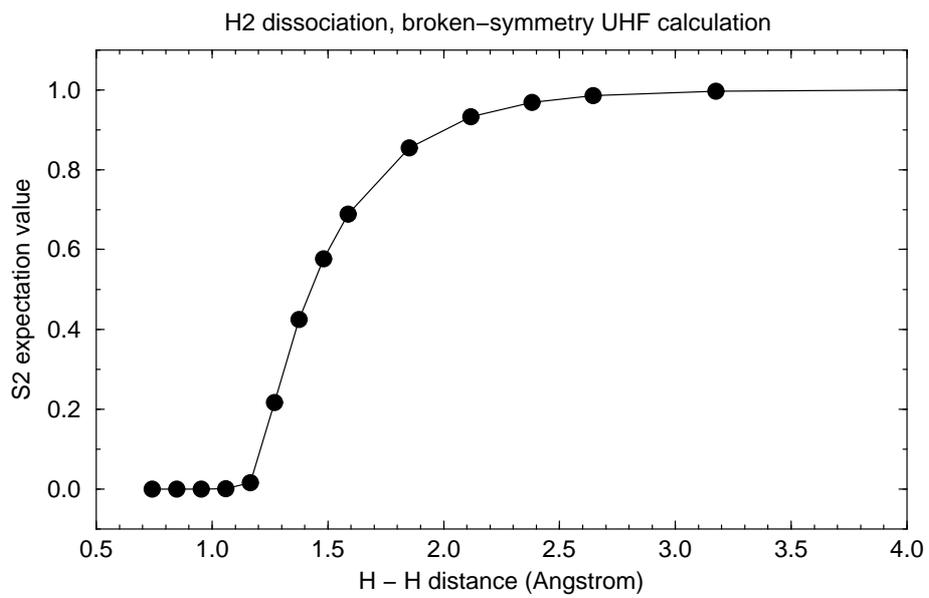


FIG. 2. The spin expectations value for a broken-symmetry UHF wavefunction.

VII. THE ROHF PROGRAM ORS_OPEN

This should be the version for a ROHF calculation. We give here a summary of what we intended to implement, following McWeeny's book (Methods of Molecular Quantum Mechanics).

A. Total energy expression

McWeeny starts with the density matrices for the open and the closed shells:

$$P_{\alpha\beta}^c = \sum_{i \in \text{closed}} c_{\alpha i} c_{\beta i} \quad , \quad P_{\alpha\beta}^o = \sum_{i \in \text{open}} c_{\alpha i} c_{\beta i} \quad . \quad (19)$$

Operators $\mathbf{J}(\mathbf{P})$ and $\mathbf{K}(\mathbf{P})$ are defined through the bielectronic integrals as

$$J(P)_{\alpha\beta} = \sum_{\gamma\delta} P_{\gamma\delta} \cdot (\alpha\beta|\gamma\delta) \quad , \quad K(P)_{\alpha\beta} = \sum_{\gamma\delta} P_{\gamma\delta} \cdot (\alpha\delta|\gamma\beta) \quad . \quad (20)$$

From an integral $(\alpha\beta|\gamma\delta)$ and the density matrix elements we update

$$4(\alpha\beta|\gamma\delta) P_{\gamma\delta} \rightarrow J_{\alpha\beta} \quad \text{and} \quad 4(\alpha\beta|\gamma\delta) P_{\alpha\beta} \rightarrow J_{\gamma\delta} \quad ,$$

due to the symmetry relations of the integral, and $J_{\alpha\beta} = J_{\beta\alpha}$ and $P_{\alpha\beta} = P_{\beta\alpha}$. For the (symmetric) exchange matrix K we have similar relations

$$2(\alpha\beta|\gamma\delta) P_{\beta\gamma} \rightarrow K_{\alpha\delta}, \quad 2(\alpha\beta|\gamma\delta) P_{\alpha\delta} \rightarrow K_{\beta\gamma}, \quad 2(\alpha\beta|\gamma\delta) P_{\alpha\gamma} \rightarrow K_{\beta\delta}, \quad 2(\alpha\beta|\gamma\delta) P_{\beta\delta} \rightarrow K_{\alpha\gamma} \quad .$$

With these two matrices \mathbf{G} and \mathbf{G}' are defined as

$$G(P) = J(P) - \frac{1}{2}K(P) \quad , \quad G'(P) = J(P) - K(P) \quad , \quad (21)$$

which serve for constructing the closed-shell and the open-shell bielectronic part

$$G_1 = 2G(P^c) + G(P^o) \quad , \quad G_2 = 2G(P^c) + G'(P^o) \quad , \quad (22)$$

of two effective Fock matrices

$$h_1 = h + G_1 \quad , \quad h_2 = h + G_2 \quad . \quad (23)$$

The total energy is obtained from these definitions as

$$E = 2 \sum_{\alpha\beta} P_{\alpha\beta}^c \left(h_{\alpha\beta} + \frac{1}{2}(G_1)_{\alpha\beta} \right) + \sum_{\alpha\beta} P_{\alpha\beta}^o \left(h_{\alpha\beta} + \frac{1}{2}(G_2)_{\alpha\beta} \right) \quad (24)$$

which we may write as in the closed-shell case from one-electron quantities

$$E = \sum_{\alpha\beta} P_{\alpha\beta}^c (h_{\alpha\beta} + F_{\alpha\beta}^c) + \frac{1}{2} \sum_{\alpha\beta} P_{\alpha\beta}^o (h_{\alpha\beta} + F_{\alpha\beta}^o) = \sum_{i \in \text{occ}} (h_{ii} + F_{ii}^c) + \frac{1}{2} \sum_{r \in \text{open}} (h_{rr} + F_{rr}^o) \quad (25)$$

We may write h_1 and h_2 explicitly with molecular orbitals:

$$\begin{aligned} (h_1)_{\alpha\beta} &= F_{\alpha\beta}^c = h_{\alpha\beta} + \sum_{i \in \text{occ}} 2(\alpha\beta|ii) - (i\beta|\alpha i) + \sum_{r \in \text{open}} (\alpha\beta|rr) - \frac{1}{2}(r\beta|\alpha r) \\ (h_2)_{\alpha\beta} &= F_{\alpha\beta}^o = h_{\alpha\beta} + \sum_{i \in \text{occ}} 2(\alpha\beta|ii) - (i\beta|\alpha i) + \sum_{r \in \text{open}} (\alpha\beta|rr) - (r\beta|\alpha r) \\ (h_1 - h_2)_{\alpha\beta} &= F_{\alpha\beta}^c - F_{\alpha\beta}^o = \frac{1}{2} \sum_{r \in \text{open}} (\alpha r|r\beta) \\ (2h_1 - h_2)_{\alpha\beta} &= 2F_{\alpha\beta}^c - F_{\alpha\beta}^o = h_{\alpha\beta} + \sum_{i \in \text{occ}} 2(\alpha\beta|ii) - (i\beta|\alpha i) + \sum_{r \in \text{open}} (\alpha\beta|rr) \end{aligned} \quad (26)$$

B. Something about projectors

The density matrices P^c and P^o are in fact projection operators on non-overlapping orbital spaces as

$$P^c S P^c = P^c \quad , \quad P^o S P^o = P^o \quad \text{and} \quad P^o S P^c = 0 \quad .$$

The purification scheme of McWeeny is, by the way, $P = 3 P S P - 2 P S P S P = P (3 - 2 S P) S P$. The idempotency can be proven easily:

$$(PSP)_{\alpha\beta} = \sum_{\gamma\delta} \sum_{k,l \in occ} c_{\alpha k} c_{\gamma k} S_{\gamma\delta} c_{\delta l} c_{\beta l} = \sum_{k,l \in occ} c_{\alpha k} c_{\beta l} S_{kl} = \sum_{k \in occ} c_{\alpha k} c_{\beta k} = P_{\alpha\beta}$$

We may prove as well that the matrix SPS , transformed onto molecular orbitals, is diagonal and has the occupation numbers on its diagonal:

$$(SPS)_{ij} = \sum_{\alpha\beta} c_{\alpha i} c_{\beta j} (SPS)_{\alpha\beta} = \sum_{\alpha\beta} \sum_{\gamma\delta} \sum_{k \in occ} c_{\alpha i} c_{\beta j} c_{\gamma k} c_{\delta k} S_{\alpha\gamma} S_{\delta\beta} = \sum_{k \in occ} S_{ik} S_{kj} = \delta_{ij} \Theta(i \in occ) \quad . \quad (27)$$

Thus

$$(S(P+Q)S)_{ij} = (SPS)_{ij} + (SQS)_{ij} = \delta_{ij} \quad \text{or} \quad S(P+Q)S = \mathbf{1} \quad (28)$$

We have as well $(SP)(SP) = S(PSP) = SP$, however, the matrix SP is not hermitian.

C. The equations to be solved

After this interlude concerning density matrices we continue with the open-shell matrices. In fact, we do not need the projectors in detail as we can start off by transforming h_1 and h_2 on molecular orbitals. In this basis the different projectors are all diagonal, with 1 as nonzero entries.

McWeeny proposes an effective Fock operator

$$\bar{h} = Q^o h_1 Q^o + Q^c h_2 Q^c + Q^v (2h_1 - h_2) Q^v \quad \text{or} \quad (29)$$

$$\begin{pmatrix} \bar{h}_{cc} & \bar{h}_{co} & \bar{h}_{cv} \\ \bar{h}_{oc} & \bar{h}_{oo} & \bar{h}_{ov} \\ \bar{h}_{vc} & \bar{h}_{vo} & \bar{h}_{vv} \end{pmatrix} = \begin{pmatrix} 3h_1 - h_2 & 2h_1 - h_2 & h_1 \\ 2h_1 - h_2 & 2h_1 - 2h_2 & h_2 \\ h_1 & h_2 & h_1 + h_2 \end{pmatrix}$$

the eigenvectors of which give the new orbitals in an SCF scheme. However, orbital energies have no significance here. The projectors Q are the complements to the projectors P^o (on open shells), P^c (on closed shells) and P^v (on virtual orbitals). For the closed-shell case we see that G_1 and G_2 become identical and thus h_1 and h_2 . Equation 29 leads then to

$$\bar{h} = h + Q^c h Q^c + Q^v h Q^v = \begin{pmatrix} 2h & h \\ h & 2h \end{pmatrix} \quad (30)$$

At the end of the SCF iterations we have the common Fock matrix, since the blocks coupling occupied and virtual orbitals disappear (Brillouin's theorem). Since it makes no difference whether \mathbf{F} or $1/2 \mathbf{F}$ are diagonalized, we may take half of the matrix in molecular orbitals. As well, multiplying only the blocks \bar{h}_{cc} , \bar{h}_{oo} and \bar{h}_{vv} with $1/2$, for the closed-shell case the common Fock matrix is obtained, and for the open-shell case the limit of a converged diagonal matrix is as well preserved. The convergence is significantly accelerated.

D. Two spin-dependent Fock operators

From the molecular orbitals we may construct two separate Fock matrices

$$F_{ij}^\sigma = h_{ij} + \sum_k \sum_\tau (ij|k\tau) - \delta_{\sigma\tau} (ik|kj) \quad (31)$$

We may try to write these two matrices from the density matrices, bearing in mind that all open-shell orbitals are of α occupation, leading to the high-spin ROHF solution. Thus

$$\begin{aligned} F_{ij}^\beta &= h_{ij} + \sum_{kl} P_{kl}^c (2(ij|kl) - (il|kj)) + P_{kl}^o (ij|kl) \\ F_{ij}^\alpha &= h_{ij} + \sum_{kl} P_{kl}^c (2(ij|kl) - (il|kj)) + P_{kl}^o (ij|kl) - P_{kl}^o (il|kj) = F_{ij}^\beta - \sum_{kl} P_{kl}^o (il|kj) \end{aligned} \quad (32)$$

The P matrices are trivially 1 on the diagonal for occupied orbital, and 0 elsewhere.

$$\begin{aligned} F_{ij}^\beta &= h_{ij} + \sum_{k \in \text{closed}} (2(ij|kk) - (ik|kj)) + \sum_{k \in \text{open}} (ij|kk) \\ F_{ij}^\alpha &= h_{ij} + \sum_{k \in \text{closed}} (2(ij|kk) - (ik|kj)) + \sum_{k \in \text{open}} (ij|kk) - (ik|kj) = F_{ij}^\beta - \sum_{k \in \text{open}} (ik|kj) \end{aligned} \quad (33)$$

The total energy reads explicitly

$$\begin{aligned} E_{HF} &= \sum_k n_k h_{kk} + \sum_k \frac{n_k(n_k - 1)}{2} J_{kk} + \sum_{k < l} n_k n_l J_{kl} - \sum_{k < l} \min(n_k, n_l) K_{kl} \\ &= 2 \sum_{k \in \text{closed}} h_{kk} + \sum_{k \in \text{open}} h_{kk} + \sum_{k \in \text{closed}} J_{kk} + 2 \sum_{k > l, \text{closed}} (2J_{kl} - K_{kl}) \\ &\quad + \sum_{k \in \text{closed}, l \in \text{open}} (2J_{kl} - K_{kl}) + \sum_{k < l, \text{open}} (J_{kl} - K_{kl}) \end{aligned} \quad (34)$$

E. Localized orbitals via the Singles CI

The Singles CI should work as for the closed-shell case, we have to consider just a third class of orbitals. But, perhaps it is not that easy ... Let i, j, \dots be closed shells, r, s, \dots open (spin up) shells, and a, b, \dots virtual orbitals. As one-electron excitations we have to calculate thus matrix elements

$$\left\langle \begin{array}{c} \Phi_0 \\ \Phi_i^a \\ \Phi_r^r \\ \Phi_r^t \\ \Phi_r^a \end{array} \middle| \mathbf{H} \middle| \begin{array}{c} \Phi_i^a \\ \Phi_r^r \\ \Phi_r^t \\ \Phi_r^a \end{array} \right\rangle$$

where we have to pay attention as well to spin settings. The element $\langle \Phi_0 | \mathbf{H} | \Phi_i^a \rangle$ is not the same as $\langle \Phi_0 | \mathbf{H} | \Phi_i^{\bar{a}} \rangle$:

$$\begin{aligned} \langle \bar{i}\bar{j}\bar{r}s | \mathbf{H} | \bar{a}\bar{i}\bar{j}\bar{r}s \rangle &= h_{ia} + (i\bar{i}|a\bar{i}) + 2(i\bar{a}|j\bar{j}) - (i\bar{j}|a\bar{j}) + (i\bar{a}|r\bar{r}) - (i\bar{r}|r\bar{a}) + (i\bar{a}|s\bar{s}) - (i\bar{s}|s\bar{a}) = F_{ia}^o \\ \langle \bar{i}\bar{i}\bar{j}\bar{r}s | \mathbf{H} | \bar{a}\bar{i}\bar{j}\bar{r}s \rangle &= h_{ia} + (i\bar{i}|a\bar{i}) + 2(i\bar{a}|j\bar{j}) + (i\bar{a}|r\bar{r}) + (i\bar{a}|s\bar{s}) - (i\bar{j}|a\bar{j}) = 2F_{ia}^c - F_{ia}^o \end{aligned} \quad (35)$$

For the excitation $\langle \Phi_0 | \mathbf{H} | \Phi_r^a \rangle$ and its spin counterpart $\langle \Phi_0 | \mathbf{H} | \Phi_r^{\bar{a}} \rangle$ we have exactly the same expressions: F_{ia}^o and $2F_{ra}^c - F_{ra}^o$. Since we would like to construct a restricted open-shell determinant, we need one single update for the orbitals i and a from the two spin possibilities; we may choose the average F_{ia}^c and F_{ra}^c to enter the Singles CI matrix for obtaining the expansion coefficients c_i^a and c_r^a .

For the diagonal element $\langle \Phi_r^a | \mathbf{H} | \Phi_r^a \rangle$ we have the expression $E_0 + F_{aa}^o - F_{ii}^o$. For its equivalent $\langle \Phi_r^{\bar{a}} | \mathbf{H} | \Phi_r^{\bar{a}} \rangle$ we find (again) $E_0 + (2F_{aa}^c - F_{aa}^o) - (2F_{ii}^c - F_{ii}^o)$. May we deduce from these examples that we might keep the elements from the closed-shell case by replacing F by F^c in case of closed shells involved ($ij \rightarrow ab, ij \rightarrow rs$) and F^o when it comes to excitations $rs \rightarrow ab$? What about the mixed case $ir \rightarrow aa$? We have $-F_{ir}^o$ in this case, and $-(2F_{ir}^c - F_{ir}^o)$ for the other spin setting. Thus $-F_{ir}^c$ on average. For the case $ii \rightarrow ra$ we can choose only \bar{r} as open-shell, since r is occupied. Thus we have $2F_{ra}^c - F_{ra}^o$. There remains the type $\langle \Phi_r^t | \mathbf{H} | \Phi_r^a \rangle$. The only common index may be r (we neglect again purely bielectronic interactions), but since we have to respect spin again, $|\Phi_r^t\rangle$ can only be $|\Phi_r^{\bar{t}}\rangle$, and thus the matrix element is zero.

Our CI matrix has now the following form:

$$\begin{array}{ccccc} & \Phi_0 & \Phi_i^r & \Phi_i^a & \Phi_r^a \\ \Phi_0 & 0 & 2F_{ir}^c - F_{ir}^o & F_{ia}^c & F_{ra}^o \\ \Phi_j^s & 2F_{js}^c - F_{js}^o & F_{rs}^c \delta_{ij} - F_{ij}^c \delta_{rs} & (2F_{sa}^c - F_{sa}^o) \delta_{ij} & 0 \\ \Phi_j^b & F_{jb}^c & (2F_{rb}^c - F_{rb}^o) \delta_{ij} & F_{ab}^c \delta_{ij} - F_{ij}^c \delta_{ab} & -F_{jr}^c \delta_{ab} \\ \Phi_s^b & F_{sb}^o & 0 & -F_{is}^c & F_{ab}^o \delta_{rs} - F_{rs}^o \delta_{ab} \end{array} \quad (36)$$

F. The optimal damping algorithm, again

For the open-shell case the same ODA may be implemented as for the closed-shell case. We just have to take into account that we have two density matrices, P^c and P^o , and two bielectronic interaction matrices, G_1 and G_2 .

We construct again

$$\begin{aligned}
E_1^{\text{old}} &= \sum_{\mu\nu} (2 P_{\mu\nu}^{c,\text{old}} + P_{\mu\nu}^{o,\text{old}}) h_{\mu\nu} = A_1 \\
E_1^{\text{new}} &= \sum_{\mu\nu} (2 P_{\mu\nu}^{c,\text{new}} + P_{\mu\nu}^{o,\text{new}}) h_{\mu\nu} = A_2 \\
(G_1^{\text{old}})_{\rho\sigma} &= \sum_{\mu\nu} (2 P_{\mu\nu}^{c,\text{old}} + P_{\mu\nu}^{o,\text{old}}) \left[(\mu\nu|\rho\sigma) - \frac{1}{2}(\mu\sigma|\rho\nu) \right] \\
(G_2^{\text{old}})_{\rho\sigma} &= \sum_{\mu\nu} (2 P_{\mu\nu}^{c,\text{old}} + P_{\mu\nu}^{o,\text{old}}) (\mu\nu|\rho\sigma) - (P_{\mu\nu}^{c,\text{old}} + P_{\mu\nu}^{o,\text{old}}) (\mu\sigma|\rho\nu) \\
(G_1^{\text{new}})_{\rho\sigma} &= \sum_{\mu\nu} (2 P_{\mu\nu}^{c,\text{new}} + P_{\mu\nu}^{o,\text{new}}) \left[(\mu\nu|\rho\sigma) - \frac{1}{2}(\mu\sigma|\rho\nu) \right] \\
(G_2^{\text{new}})_{\rho\sigma} &= \sum_{\mu\nu} (2 P_{\mu\nu}^{c,\text{new}} + P_{\mu\nu}^{o,\text{new}}) (\mu\nu|\rho\sigma) - (P_{\mu\nu}^{c,\text{new}} + P_{\mu\nu}^{o,\text{new}}) (\mu\sigma|\rho\nu) \\
E_2^{\text{old-old}} &= \sum_{\mu\nu} P_{\mu\nu}^{c,\text{old}} (G_1^{\text{old}})_{\mu\nu} + \frac{1}{2} P_{\mu\nu}^{o,\text{old}} (G_2^{\text{old}})_{\mu\nu} = B_1 \\
E_2^{\text{old-new}} &= \sum_{\mu\nu} P_{\mu\nu}^{c,\text{old}} (G_1^{\text{new}})_{\mu\nu} + \frac{1}{2} P_{\mu\nu}^{o,\text{old}} (G_2^{\text{new}})_{\mu\nu} = \frac{1}{2} B_2 \\
E_2^{\text{new-new}} &= \sum_{\mu\nu} P_{\mu\nu}^{c,\text{new}} (G_1^{\text{new}})_{\mu\nu} + \frac{1}{2} P_{\mu\nu}^{o,\text{new}} (G_2^{\text{new}})_{\mu\nu} = B_3
\end{aligned} \tag{37}$$

The optimum is again determined through

$$\lambda = -\frac{1}{2} \frac{A_2 - A_1 + B_2 - 2B_1}{B_1 - B_2 + B_3} \quad ,$$

and we obtain optimum quantities P and G to be used to construct a new effective Fock matrix \bar{h} by equation 23 and equation 30.

VIII. A PROGRAM TO CALCULATE $\nabla\rho(\vec{r})$, THE KATO CONDITION, AND DATA TO PLOT: GRADRH0

With the orbitals at hand on the file `VECTOR`, we may plot orbitals, densities, and in particular the gradient of the density over the density, in order to test the Kato condition. The data may be for Slater orbitals or Gaussian orbitals. Recently, the NCI index has been proposed, based on the evaluation of $(\nabla\rho)/\rho^{(4/3)}$.

A. Input options

For this program we may use an input block `*RHO ... *END` with the options

- `STARTPoint` : the starting point of the line, on that ρ and $\vec{\nabla}\rho$ are evaluated. Default is (0,0,0).
- `ENDPOINT` : the endpoint of the line. Default is (0,0,5).
- `NPOINT` : number of points on the line, default is 200.
- `DETAIL` : print details on the basis and the values on the points.
- `KATO` : spherical average of $1/2(\vec{\nabla}\rho(\vec{r}))/\rho(\vec{r})$ around the atoms.
- `BUCKMINSTER-FULLER` : refinement level of the basic icosahedron around each atom. Default is 0, and maximum value is 6, generating 1907 centers around the atom.
- `RADIUS` : radius of the polyhedron around the atoms. For Gaussians very small radii result in a near-zero gradient of the density.
- `PLANE` : requires the definition of 3 points to define the plane in which the data is plotted.
- `CUBE` : a cube file is produced, to be visualized with VMC or other graphics software. Two vectors are needed as additional input, designing two opposite corners of the cube (x_0, y_0, z_0) and (x_1, y_1, z_1) .
- `SHORT` : only the density is stored on the file `density.data`.
- `NCI` : the data for the NCI expression $(\nabla\rho)/\rho^{(4/3)}$ is evaluated and stored on the file `nci.data`. This may be combined with `PLANE` or `CUBE`.
- `BERLIN` : generate the force index of Berlin for a diatomic molecule.
- `ORBITAL` : orbital data is stored. Without additional input, for each occupied orbital one column in the file `orb.data` is stored.
- `PPM` : generate image files for orbitals, in a plane.
- `SLATER` : we assume that the calculation was done in Slater orbitals.

In a file `grad.data` all relevant data are concentrated and may be treated directly with a graphical program. If the options `NCI` or `BERLIN` are given, files `nci.data` or `Berlin.data` are produced, respectively.

B. Some aspects of the calculation of $1/2(\vec{\nabla}\rho(\vec{r}))/\rho(\vec{r})$

The theorem of T. Kato states that

$$Z = -\frac{1}{2} \left. \frac{\vec{\nabla}\rho(\vec{r})}{\rho(\vec{r})} \right|_{sph.av} .$$

For calculating this quantity we need the orbitals, basis functions and their derivatives. For a Hartree-Fock wavefunction the density $\rho(\vec{r})$ is the sum over the square of the orbitals :

$$\rho(\vec{r}) = \sum_{i \in occ.} \phi(\vec{r})^2$$

and thus the gradient is nothing else than

$$\vec{\nabla}\rho(\vec{r}) = \sum_{i \in occ.} 2\phi(\vec{r})\vec{\nabla}\phi(\vec{r})$$

The crucial points in the calculation of this quantity are the correct normalization of the basis functions (polynomials, exponentials) and the right order of the basis functions: Dalton and all other Gaussian-based quantum chemistry programs order the p functions as p_x , p_y and p_z , whereas SMILES takes the correct solid harmonics p_y , p_z , p_x . The program has been tested with the atomic program of Clementi.

C. The Berlin index

In 1951 Theodore Berlin publishes³ an remarkable article on the electrostatic notion of the interatomic force in chemical theory, in which he decomposes the force on the nuclei of a diatomic molecule into an integral over the density multiplied with a function depending only on geometrical parameters and nuclear charges.

The force on the nuclei is composed of the internuclear repulsion $Z_A Z_B / R^2$ and the attraction of each electron to both of the nuclei

$$-\sum_{i=1}^N \int \left(\frac{Z_A}{r_{i,A}^2} \frac{\partial r_{i,A}}{\partial R} + \frac{Z_B}{r_{i,B}^2} \frac{\partial r_{i,B}}{\partial R} \right) d^3 r_i$$

for N electrons. This gives, with the cylindrical symmetry of the problem a total force of

$$F = \frac{Z_A Z_B}{R^2} - \frac{1}{2} \int \rho(\vec{r}) \left(\frac{Z_A}{r_A^2} \cos \alpha + \frac{Z_B}{r_B^2} \cos \beta \right) d^3 r = \frac{Z_A Z_B}{R^2} - \frac{1}{2} \int \rho(\vec{r}) f(\vec{r}) d^3 r \quad (38)$$

employing the notation of Figure 3 and the Berlin function $f(\vec{r})$

$$f(\vec{r}) = \left(\frac{Z_A}{r_A^2} \cos \alpha + \frac{Z_B}{r_B^2} \cos \beta \right) \quad . \quad (39)$$

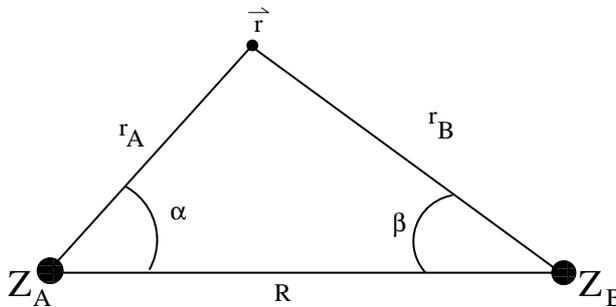


FIG. 3. Definition of the quantities used in the text.

Knowing the density we can immediately obtain the force on the nuclei by multiplying with the geometrical function $f(\vec{r})$ and by integrating over all space.

In order to be able to compare different situations we may normalize the force through a multiplication with $R^2/(Z_A Z_B)$ which reduces the first term exactly to one. By dividing all distances by R , the whole calculation is carried out with a normalized interatomic axis going from 0 to 1. Normalizing the electron density to one single electron by dividing by the total number of electrons leads now to identical “weight” functions f for homonuclear molecules. As a summary:

³Th. Berlin, J.Chem.Phys., **19** (1951) 208

$$\frac{R^2}{Z_A Z_B} F = 1 - \frac{1}{2} \frac{R^2}{Z_A Z_B} \int \frac{\rho(\vec{r}/R)}{N} \left(\frac{N Z_A}{(r_A/R)^2} \cos \alpha + \frac{N Z_B}{(r_B/R)^2} \cos \beta \right) d^3(r/R) \quad (40)$$

$$= 1 - \frac{1}{2} \frac{N R^2}{Z_A Z_B} \int \frac{\rho(\vec{r}/R)}{N} f(\vec{r}/R) d^3(r/R) \quad (41)$$

IX. THE FOUR-INDEX TRANSFORMATION VIND

This program implements the four-index transformation

$$(\alpha\beta|\gamma\delta) \rightarrow (ij|\gamma\delta) \rightarrow (ij|kl)$$

with the special feature of sorting and splitting of the integral file in many little files. The idea was pointed out by Christof Hättig and Thomas Neuheuser of the university of Bonn, and is the following: for sorting a large file of bielectronic integrals, every pair $(\alpha\beta|)$ of indices may be stored on a separate file, and subsequently transformed to $(ij|)$, without the need for fixed-record-length or direct-access files. In particular, when dealing with localized orbitals, where the number of significant bielectronic integrals is variable with the indices, direct-access files with fixed record lengths should be avoided. So the integral file `AOTWO` is read, and stored in about 20 files, each file holding a subset of all possible $(\alpha\beta|)$. After the first lecture and (coarse) sorting, every file is split again for smaller subsets, and the procedure of reading and sorting is repeated, until after several decompositions every file holds only one single pair $(\alpha\beta|)$. Every integral $(\alpha\beta|\gamma\delta)$ is stored on two files: one for $(\alpha\beta|)$ with $\alpha \leq \beta$ and one for $(\gamma\delta|)$ with $\gamma \leq \delta$.

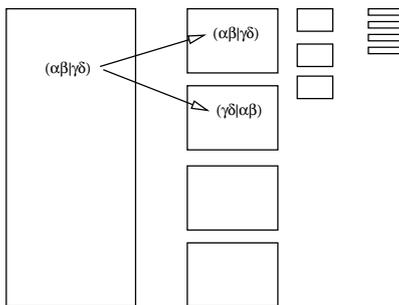


FIG. 4. The subsequent splitting of the integral file.

After the first sorting (and doubling) of integrals the first half-transformation is carried out, and the produced halftransformed integrals are again stored in several files, this time sorted by the indices $|\gamma\delta$.

Up to now, intermediate files `AOSRT.TMP` and `HALFTR.TMP` are created, which may become quite large, since the symmetry of pure AO or MO integrals $(\alpha\beta|\gamma\delta)$ or $(ij|kl)$ is broken for the halftransformed integrals $(ij|\gamma\delta)$. In these two files the integrals are stored in lexical order, for verifying or reinitialization of the decomposition. In principle the algorithm may be written up without large intermediate files, reading the smallest units while sorting and transforming on the fly, and storing in the first decomposition of the next level. However, the internal logic of the program becomes more complicated, and at a given time, several AO, AO/MO and MO files may be open simultaneously. But it may be implemented.

At the moment (4/2007) the first half-transformation is done from the sorted AO integrals file, and the second half-transformation takes the block of lowest-decomposed indices (only one pair on a file) and transforms them to the final bi-electronic integral. Doing so permits to have never more than 22 files open simultaneously (one for reading and 20 for writing the smaller units, and the file for the fully-transformed integrals). The file `HALFTRF.TMP` is not any more needed.

The program `VIND` has as well several input options, form a file `INPUT.VIN` between keywords `*VIN` and `*END`:

- `INFORM`: input of bielectronic integrals is formatted.
- `OUTFOR`: the produced output file is formatted
- `THRE1`: a threshold for reading bielectronic AO integrals.
- `THRE2`: a threshold for storing half-transformed integrals.
- `THRE3`: a threshold for writing bielectronic MO integrals.
- `THRESH`: a global threshold for the bielectronic integrals; `THRE1`, `THRE2` and `THRE3` will be set to that value.

- **DIRECT**: a direct algorithm: we read the AO integrals file several times; on each scan we pick just all pairs ($\alpha\beta$) for a number of subsets ($\gamma\delta$), so that all these fit in the main buffer. After the scan the buffer is dumped onto records of a Direct Access file. Thus several pieces ($\gamma\delta$) are on several records. The records are read in for the second half-transformation and assembled to the final file. The advantage is that there are only two files open at a time: for reading the DA file and the AO file, and for writing the DA file and the MO file. But: the algorithm is NOT really integral driven, since ALL intermediate integrals are stored, zero or not zero.

A. Performance on a H₂O cluster

We try the four-index transformation on different clusters of H₂O in a helix structure. For these structures, from 1 to 9 water molecules, we have RHF wavefunctions from canonical monomer orbitals, relaxed toward the cluster wavefunction through the singles-CI procedure. The molecular orbitals are thus degenerate and as localized as possible on the monomers. So we can trace the evolution of the algorithm with the cluster size.

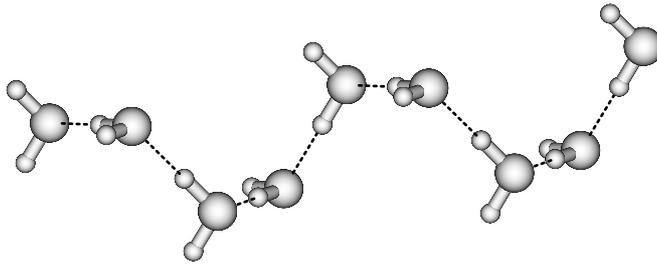


FIG. 5. The helix of water molecules

We can look at the CPU time, needed disk space, and the evolution of the disk occupation with time. The table gives the first data :

TABLE I. Timing and file sizes for the 4-index transformation. The first file is the AO integral file as calculated by Dalton (precision 10^{-11}), the second one the AO file after scanning against 10^{-8} , and the third one the MO integral file with a precision of 10^{-7} . The Halftransformed integrals take about as many space as the fully transformed ones. The timing is for a recent Xeon 5100 2.33 GHz Intel processor with a 150-GByte SATA-II disk. The basis set is a van-Duijneveldt one with 47 basis functions per H₂O.

| n | basis functions | cpu time(min) | disk AO in GBytes | disk AO 10^{-8} | disk MO 10^{-7} |
|---|-----------------|---------------|-------------------|-------------------|-------------------|
| 2 | 94 | 1 | 0.10 | 0.18 | 0.24 |
| 3 | 141 | 7 | 0.52 | 0.79 | 1.20 |
| 4 | 188 | 20 | 1.51 | 2.02 | 3.78 |
| 5 | 235 | 47 | — | — | — |
| 6 | 282 | 96 | 7.78 | 6.21 | 18.91 |
| 7 | 329 | 194 | 12.33 | 9.10 | 34.85 |
| 8 | 376 | 319 | 17.91 | 12.48 | 50.90 |
| 9 | 423 | 548 | 24.44 | 16.30 | 94.26 |

From log-log plots of the data we see that

- CPU time goes as $n^{4.1}$;
- the DALTON AO integral file size goes as $n^{3.6}$;

- the integral file after the scan and reformatting goes as $n^{3.0}$;
- the final MO file size goes as $n^{3.9}$.

Even with the localization we are not yet in the region of linear scaling with 9 water molecules. And we see that the file with the fully transformed integrals becomes quite large, and will be the limiting factor as it is the file necessary for the subsequent correlation steps. The evolution of the disk space through the four-index transformation is on the following diagram:

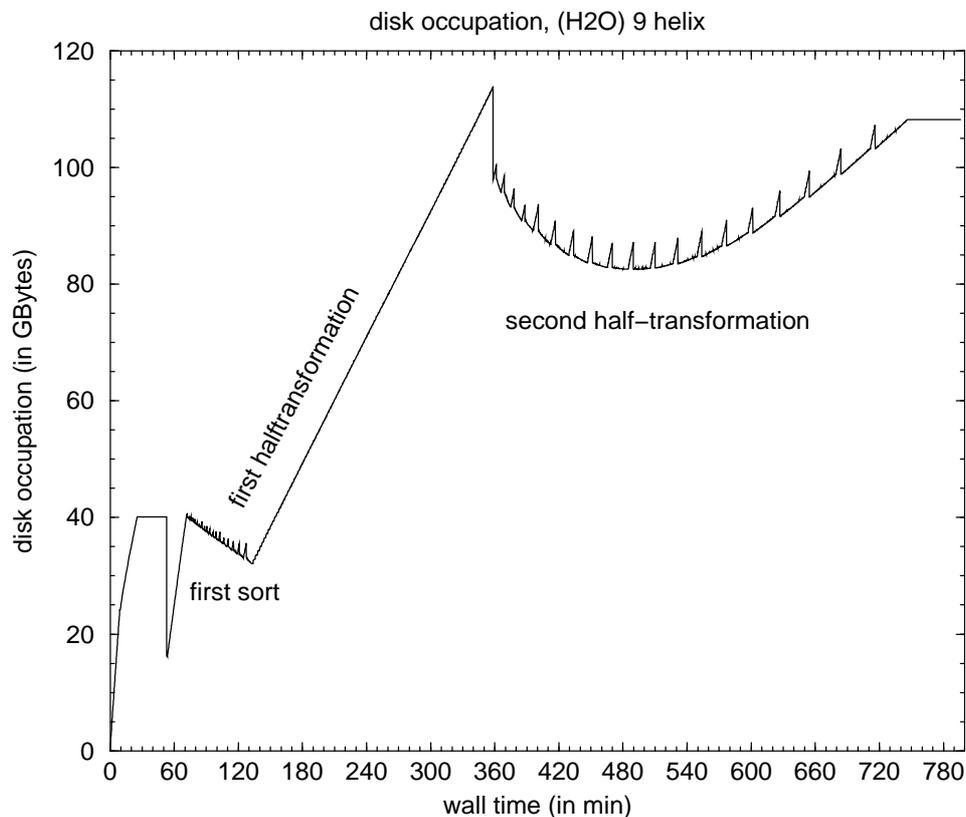


FIG. 6. The evolution of the disk occupation through the transformation, for the case of 9 water molecules. we see that the file splitting is not the most time-consuming step. for a CPU time of 548 minutes we have a wall time of 700 minutes, making it a ratio ≈ 1.3 for wall time/CPU time. The heavy file generation does not kill the disk.

The locality of the molecular orbitals may be inspected when looking to the gross Mulliken populations of the occupied orbitals, condensed to the individual molecules:

TABLE II. Orbital energies and Mulliken occupations for the occupied orbitals, for the cluster of 9 water molecules.

| n | Orb.energy | H ₂ O(1) | H ₂ O(2) | H ₂ O(3) | H ₂ O(4) | H ₂ O(5) | H ₂ O(6) | H ₂ O(7) | H ₂ O(8) | H ₂ O(9) |
|----|-------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 10 | -1.44445351 | 2.008 | -0.009 | — | — | — | — | — | — | — |
| 11 | -1.39335423 | 0.010 | 2.004 | -0.015 | — | — | — | — | — | — |
| 12 | -1.37398381 | — | 0.011 | 2.003 | -0.014 | — | — | — | — | — |
| 13 | -1.36025291 | — | — | 0.011 | 2.003 | -0.014 | — | — | — | — |
| 14 | -1.34745895 | — | — | — | 0.011 | 2.002 | -0.014 | — | — | — |
| 15 | -1.33484592 | — | — | — | — | 0.012 | 2.002 | -0.014 | — | — |
| 16 | -1.32170323 | — | — | — | — | — | 0.012 | 2.002 | -0.014 | — |
| 17 | -1.30328495 | — | — | — | — | — | — | 0.011 | 2.003 | -0.014 |
| 18 | -1.25505240 | — | — | — | — | — | — | — | 0.010 | 1.990 |
| 19 | -0.80745738 | 1.997 | 0.004 | — | — | — | — | — | — | — |
| 20 | -0.75925250 | 0.002 | 1.995 | 0.004 | -0.001 | — | — | — | — | — |
| 21 | -0.73977145 | — | — | 1.997 | 0.004 | -0.001 | — | — | — | — |
| 22 | -0.72610181 | — | — | 0.001 | 1.997 | 0.004 | -0.001 | — | — | — |
| 23 | -0.71337802 | — | — | — | 0.001 | 1.996 | 0.004 | -0.001 | — | — |
| 24 | -0.70078673 | — | — | — | — | 0.001 | 1.996 | 0.004 | -0.001 | — |
| 25 | -0.68867649 | 1.981 | 0.019 | -0.001 | — | — | — | — | — | — |
| 26 | -0.68764273 | — | — | — | — | — | — | 1.997 | 0.004 | -0.001 |
| 27 | -0.66940521 | — | — | — | — | — | — | — | 2.000 | 0.001 |
| 28 | -0.64289283 | -0.002 | 1.990 | 0.015 | -0.002 | — | — | — | — | — |
| 29 | -0.62426947 | — | -0.002 | 1.990 | 0.014 | -0.002 | — | — | — | — |
| 30 | -0.62361785 | — | — | — | — | — | — | — | -0.001 | 2.001 |
| 31 | -0.61290037 | 1.968 | 0.032 | -0.001 | — | — | — | — | — | — |
| 32 | -0.61078527 | — | — | -0.002 | 1.991 | 0.013 | -0.002 | — | — | — |
| 33 | -0.59801033 | — | — | — | -0.001 | 1.992 | 0.013 | -0.002 | — | — |
| 34 | -0.58516403 | — | — | — | — | -0.001 | 1.991 | 0.013 | -0.002 | — |
| 35 | -0.57169952 | — | — | — | — | — | -0.001 | 1.991 | 0.012 | -0.002 |
| 36 | -0.56324825 | — | 1.960 | 0.041 | 0.001 | — | — | — | — | — |
| 37 | -0.55265768 | — | — | — | — | — | — | — | 1.989 | 0.013 |
| 38 | -0.54432697 | — | 0.001 | 1.955 | 0.044 | 0.001 | — | — | — | — |
| 39 | -0.53076905 | — | — | 0.001 | 1.953 | 0.045 | 0.001 | — | — | — |
| 40 | -0.51805734 | — | — | — | — | 1.953 | 0.046 | 0.001 | — | — |
| 41 | -0.50543343 | — | — | — | — | — | 1.953 | 0.046 | 0.001 | — |
| 42 | -0.49389725 | — | — | — | — | — | — | — | 0.003 | 1.996 |
| 43 | -0.49218746 | — | — | — | — | — | 0.001 | 1.954 | 0.045 | 0.001 |
| 44 | -0.47318555 | — | — | — | — | — | — | 0.001 | 1.958 | 0.042 |
| 45 | -0.41341763 | — | — | — | — | — | — | 0.001 | 0.001 | 1.999 |

X. THE IMPLEMENTATION OF SECOND-ORDER PERTURBATION THEORY, EPSNES

The programs is taken nearly as is from the ring programs, with the options of calculating MP2 with 3rd and 4th order diagrams in \mathbf{F} , as well as Epstein-Nesbet perturbation in second order. This needs the Fock matrix elements and bielectronic integrals of the type $(ov|ov)$.

A new feature is the implementation of MP3.

A. MP3

The 12 diagrams to be summed up can be found explicitly with formulas in the book of Szabo and Ostlund. Rearranging indices results in a relatively compact expression, combining direct and exchange diagrams.

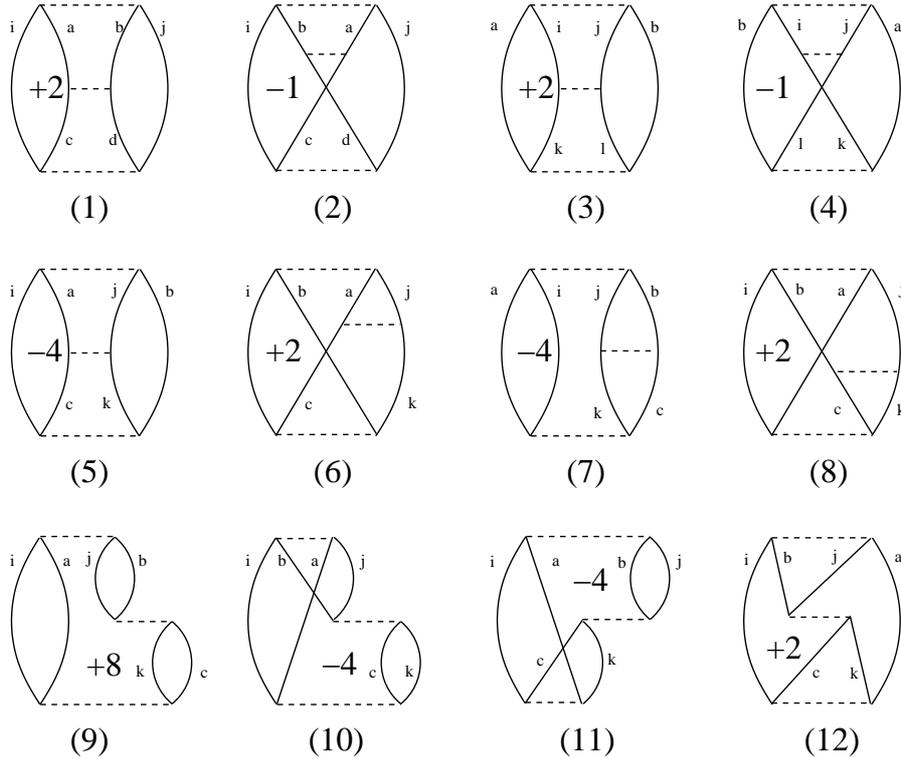


FIG. 7. The 12 diagrams appearing in MP3. For diagrams 1 and 2 we need additionally the integrals $(vv|vv)$, for 3 and 4 integrals $(oo|oo)$, and for diagrams 5, 6, 7, and 8 we need integrals $(oo|vv)$. Sign and weight of each diagram is included in the figure.

The diagrams have to be summed over all possible indices, not only for $i \leq j$ and $a \leq b$ — otherwise the details become too labourious. However, a common factor $[2(ia|jb) - (ib|ja)]/\Delta_{ij}^{ab}$ can be extracted for all pairs of diagrams. The remaining terms sum to

$$\sum_{cd} \underbrace{\frac{(ac|bd)(ic|jd)}{\Delta_{ij}^{cd}}}_{(1+2)} + \sum_{kl} \underbrace{\frac{(ik|jl)(ka|bl)}{\Delta_{kl}^{ab}}}_{(3+4)} + 2 \sum_{kc} \left[\underbrace{\frac{(jb|kc)}{\Delta_{ik}^{ac}} [2(kc|ia) - (ka|ic)]}_{(9+10+11+12)} - \underbrace{\frac{(ac|jk)(ic|kb)}{\Delta_{ik}^{bc}}}_{(5+6)} - \underbrace{\frac{(bc|jk)(ia|kc)}{\Delta_{ik}^{ac}}}_{(7+8)} \right]$$

The straight-forward implementation, i.e. having all integrals in memory and searching for every term the integrals and multiplying, seems to be quite unfavorable when dealing with larger molecules. One may observe that every term

multiplying three integrals needs two integrals of the type $(ov|ov)$ and one integral of the groups $(oo|oo)$, $(oo|vv)$, $(ov|ov)$ or $(vv|vv)$. Thus we may store only the integrals $(ov|ov)$ in memory, and read the others from disk. From the six indices of any term in the sums, four indices are fixed by the integral read, and the two others take every possible value. For diagrams 1+2 demanding integrals $(vv|vv)$ the virtual indices are fixed, and the loop runs over the two occupied orbitals. Diagrams 3+4 need $(oo|oo)$, diagrams 5–8 need $(oo|vv)$, and the diagrams 9–12 need integrals $(ov|ov)$.

Thus, when reading the bielectronic integrals file for the first time, the classes $(oo|oo)$, $(oo|vv)$, and $(vv|vv)$ can be extracted and stored on separate files, whereas the integrals $(ov|ov)$ are stored in core. As in the Hartree-Fock program, the integrals may be premultiplied before restoring them onto disk, in order to simplify the multiplication process: integral $(ij|ab)$ is as well $(ji|ab)$, $(ji|ba)$, $(ij|ba)$ for instance, but $(ii|aa)$ has no permutations.

It is even advantageous to loop over the list of $(ov|ov)$ integrals, premultiply the pure exchange integrals $(ia|ia)$ by a factor of 0.5, and sum diagrams 9–12 to

$$\sum_{ia \leq jb} \sum_{kc} \frac{4}{\Delta_{ik} \Delta_{jk}} \frac{(ia|jb)}{\Delta_{ac} \Delta_{bc}} [2(ia|kc) - (ic|ka)] [2(jb|kc) - (jc|kb)] \quad .$$

B. Third-order Epstein-Nesbet perturbation

From the general perturbation development we have for the third order

$$E^{(3)} = \sum_I \sum_J \frac{\langle 0|\mathbf{V}|I\rangle \langle I|\mathbf{V}|J\rangle \langle J|\mathbf{V}|0\rangle}{\langle I|\mathbf{H}_0 - E_0|I\rangle \langle J|\mathbf{H}_0 - E_0|J\rangle} - \langle 0|\mathbf{V}|0\rangle \sum_I \frac{\langle 0|\mathbf{V}|I\rangle \langle I|\mathbf{V}|0\rangle}{\langle I|\mathbf{H}_0 - E_0|I\rangle \langle I|\mathbf{H}_0 - E_0|I\rangle}$$

With the zeroth-order Hamiltonian

$$\mathbf{H}_0 = \sum_I |I\rangle \langle I|\mathbf{H}|I\rangle \langle I|$$

we can replace \mathbf{V} by \mathbf{H} in the numerators for $I \neq J$ and disregard the second sum since $\langle 0|\mathbf{V}|0\rangle$ is strictly zero for Epstein-Nesbet. I and J are running independently, so that we may use $I < J$ and a factor of 2.

In MP3 we may apply the same logic, but precalculate the simple sums over I , i.e. the diagonal term of the first sum

$$\sum_I \langle I|\mathbf{H} - \mathbf{H}_0|I\rangle \left(\frac{\langle 0|\mathbf{H}|I\rangle}{\langle I|\mathbf{H}_0 - E_0|I\rangle} \right)^2$$

and the renormalization term

$$-\langle 0|\mathbf{H} - \mathbf{H}_0|0\rangle \sum_I \left(\frac{\langle 0|\mathbf{H}|I\rangle}{\langle I|\mathbf{H}_0 - E_0|I\rangle} \right)^2 \quad .$$

These terms are quite large and of opposite sign as $\langle 0|\mathbf{V}|0\rangle$ and $\langle I|\mathbf{V}|I\rangle$ are both negative, but the renormalization term appears with a “–” sign. We may recall that the renormalization term has the quadratic dependency on the system size and has to be cancelled exactly by the other sum, leaving only the connected diagrams of the direct expansion.

XI. THE DETERMINANT-BASED SINGLE-REFERENCE, SINGLES-AND-DOUBLES CORRELATION PROGRAM, ICMP

- EPSTEIn-Nesbet: Epstein-Nesbet perturbation energy is calculated. This is not by default since the program EPSNES is originally designed for this.
- selection of the dressing of the CI matrix, several options may be given, which will be worked off one after another:
 - LCCD

- CEPA-0
 - CEPA-2
 - CEPA-3
 - SCSC
 - CISD
 - ACPF
 - LCCSD: equivalent to CEPA-0
 - AQCC
 - AQCC-V
 - CIS
 - CID
 - MP2EGO
 - MP2CAN
 - EN2CAN
- APPROX: not the real Hamilton matrix is diagonalized but its diagonal approximation (see section XI D). All flavours of dressing may be chosen to design the construction of the Hamilton matrix.
 - NITDAV: max. number of iterations in the Davidson scheme.
 - ITLCCD: max. number of iterations in the conjugated gradient iterations.
 - PRINTL: set a print level for the construction of the determinants.
 - NOPERT: ???
 - TOLCCD: convergence threshold for the CEPA (conjugated gradients).
 - TOLCI: convergence threshold for the CI (Davidson).
 - THRPRI: threshold for printing CI or CEPA amplitudes.
 - XGADEA: Xavier Gadea's speed-up of the Davidson iterations.
 - READCI: Starting vector of the CI from separate file.
 - READLC: Starting vector of the CEPA from separate file.
 - FORMAT: integrals are expected as formatted on file.
 - THRINT: threshold for maintaining bielectronic integrals.
 - QMC: generate output for the QMC program of M.Caffarel.
 - DETAIL: store additional details on the QMC output file.
 - SELECT: select excitations to be included in the CI through a threshold for MP2 amplitudes. All singles are included.
 - FREEZE: do not include orbitals in the CI.
 - DELETE: delete virtual orbitals from the CI.
 - NATORB: calculate and save natural orbitals (see section XI A)
 - CALPHP: calculate the real expectation value $\langle \Psi | \mathbf{H} | \Psi \rangle$, not only the variational energy
- $$E = \sum_I c_I \langle \Phi_0 | \mathbf{H} | \Phi_I \rangle \quad .$$
- BANDStructure: calculate correlated orbital energies through perturbation theory (see section XI B).
 - MP3: Møller-Plesset 3rd order perturbation calculation, based on determinants instead of diagrams.
 - EN3: Epstein-Nesbet 3rd-order perturbation.

A. Natural orbitals

As explained e.g. in the book of Szabo and Ostlund natural orbitals are derived from the one-particle density matrix

$$\gamma(\vec{x}, \vec{x}') = N \int d^3x_2 \dots d^3x_n \Psi(\vec{x}, \vec{x}_2, \dots, \vec{x}_n) \Psi(\vec{x}', \vec{x}_2, \dots, \vec{x}_n) \quad (42)$$

What is may be missing is the link between this one-particle density matrix and the known matrix $P_{\alpha\beta} = 2 \sum_{i \in occ} c_{\alpha i} c_{\beta i}$. If we assume that we have one single determinant and that the molecular orbitals are orthogonal, we have

$$\gamma(\vec{x}, \vec{x}') = 2 \sum_{i \in occ} \phi_i(\vec{x}) \phi_i(\vec{x}') \quad (43)$$

and thus for the matrix elements of the one-particle matrix

$$\begin{aligned} \gamma_{ij} &= \int d^3x d^3x' \phi_i(\vec{x}) \gamma(\vec{x}, \vec{x}') \phi_j(\vec{x}') \\ &= \sum_{\alpha\beta} c_{\alpha i} c_{\beta j} \int d^3x d^3x' \chi_{\alpha}(\vec{x}) \gamma(\vec{x}, \vec{x}') \chi_{\beta}(\vec{x}') \\ &= \sum_{\alpha\beta} \sum_{\beta\delta} \sum_{k \in occ} c_{\alpha i} c_{\beta j} c_{\gamma k} c_{\delta k} \left(\int d^3x \chi_{\alpha}(\vec{x}) \chi_{\gamma}(\vec{x}) \right) \left(\int d^3x' \chi_{\beta}(\vec{x}') \chi_{\delta}(\vec{x}') \right) \\ &= \sum_{\alpha\beta} c_{\alpha i} c_{\beta j} (S P S)_{\alpha\beta} \end{aligned} \quad (44)$$

Diagonalization of this matrix in molecular orbitals gives the natural orbitals as eigenvectors and occupation numbers as eigenvalues.

For a linear combination of determinants we may form a density matrix P_i for each determinant, multiply it with the expansion coefficient in the wavefunctions, and construct a one-particle density matrix in atomic orbitals as

$$\gamma_{\alpha\beta} = \left(S \left(\sum_i P^i \right) S \right)_{\alpha\beta} \quad (45)$$

This matrix is transformed to molecular orbitals and diagonalized.

B. Correlated orbital energies

As we calculate a correlated band structure for the ring case, we may calculate correlated orbital energies in the same way, by constructing and diagonalizing an effective Hamiltonian. For the molecular case we do not need to write a special program as we had for solids (`bandstr.r`), we can incorporate all into the CI program, as we have all necessary integrals present.

The Fock matrix represents the zeroth-order interaction matrix between $N + 1$ and N , and $N - 1$ and N electron determinants.

To include correlation corrections the first way to do so is using perturbation theory in order to construct an effective Hamiltonian to describe the interaction of the various positive or negative ions. For each pair of $N + 1$ or $N - 1$ electron determinants the following diagrams have to be evaluated to incorporate electron interaction up to second order.

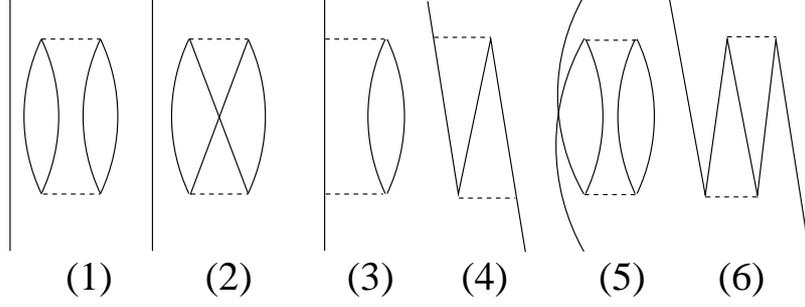


FIG. 8. Unique diagrams of the second order effective Hamiltonian.

The terms (1) and (2), (3) and (4), and (5) and (6) can be treated together since they form the Coulomb-like and Exchange-like diagram of the same involved indices. The sum of the first two diagrams is equal to the MP2 correlation energy of the neutral system minus the EPV terms, i.e., terms with one internal index equal to an incoming or outgoing line index. Indexing of the diagrams is straight forward, the incoming and outgoing line must have the same direction, and in each interaction point the line has to be followed. Let up-going lines (particles) be denoted by a, b, c, \dots , and down-going lines (holes) by i, j, k, \dots . The resulting formulae are symmetric with respect to treating hole states ($N - 1$ electrons) or particle states ($N + 1$ electrons), so we restrict ourselves here to hole states. Outer lines are thus a (above) and b (below), and inner lines c, d, r , and s will be summed. A denominator Δ_{abcd} will stand for $F_{aa} + F_{bb} - F_{cc} - F_{dd}$, involving the diagonal elements of the Fock operator.

The diagrams (1) and (2) will only occur on the diagonal of the effective Hamiltonian, whereas diagrams (5) and (6) appear only for off-diagonal elements since otherwise they would constitute EPV diagrams.

The following formulae apply

$$\begin{aligned}
 (1) + (2) &= E_{\text{MP2}} - \sum_{kab} \frac{(ia|kb)(2(ia|kb) - (ib|ka))}{\Delta_{ikab}} \quad \text{on diagonal element } i \\
 (3) + (4) &= \sum_{kla} \frac{(ik|al)(2(jk|al) - (jl|ak))}{\Delta_{klja}} \\
 (5) + (6) &= \sum_{kab \ k \neq i, k \neq j} \frac{(ia|kb)(2(ja|kb) - (jb|ka))}{\Delta_{ikab}} + \sum_{ab} \frac{(ia|jb)(ja|jb)}{\Delta_{jjab}} + \sum_{ab} \frac{(ja|ib)(ia|ib)}{\Delta_{iiab}}
 \end{aligned}$$

To write up the matrix of the Effective Hamiltonian we first look at the total energy of the neutral system (correlated up to MP2) which is given by

$$\mathbf{E}_{\text{MP2}}^{(N)} = \mathbf{E}_{\text{SCF}}^{(N)} + \text{diagram (1)} + \text{diagram (2)}$$

FIG. 9.

and the total energy of the positive ion, given by

$$\begin{aligned}
\mathbf{E}_{\text{MP2}}^{(N-1)}(i) &= \mathbf{E}_{\text{SCF}}^{(N)} - \mathbf{F}_{ii} + \left| \begin{array}{c} \text{Diagram 1} \\ \text{Diagram 2} \end{array} \right| + \left| \begin{array}{c} \text{Diagram 3} \\ \text{Diagram 4} \end{array} \right| + \left| \begin{array}{c} \text{Diagram 5} \\ \text{Diagram 6} \end{array} \right| \\
&= \mathbf{E}_{\text{MP2}}^{(N)} - \mathbf{F}_{ii} - \left| \begin{array}{c} \text{Diagram 1} \\ \text{EPV} \end{array} \right| - \left| \begin{array}{c} \text{Diagram 3} \\ \text{EPV} \end{array} \right| + \left| \begin{array}{c} \text{Diagram 5} \\ \text{Diagram 6} \end{array} \right|
\end{aligned}$$

FIG. 10.

EPV stands in this case for one index in the loops being identical to the index of the “ionisation hole”. Interactions between different positive ions are represented via

$$\mathbf{H}_{ij}^{(N-1)} = \mathbf{F}_{ij} + \left| \begin{array}{c} \text{Diagram 1} \\ \text{Diagram 2} \end{array} \right| + \left| \begin{array}{c} \text{Diagram 3} \\ \text{Diagram 4} \end{array} \right| + \left(\left| \begin{array}{c} \text{Diagram 5} \\ \text{Diagram 6} \end{array} \right| + \left| \begin{array}{c} \text{Diagram 7} \\ \text{Diagram 8} \end{array} \right| \right)$$

FIG. 11.

From these elements the effective Hamiltonian will be built, transformed to the individual \mathbf{k} -points, and diagonalized:

$$H_{\text{eff}}^{(N-1)} = \begin{pmatrix} E_{\text{MP2}}^{(N-1)}(i) - E_{\text{MP2}}^{(N)} & \dots & H_{ij}^{(N-1)} \\ \vdots & \ddots & \vdots \\ H_{ji}^{(N-1)} & \dots & E_{\text{MP2}}^{(N-1)}(j) - E_{\text{MP2}}^{(N)} \end{pmatrix}$$

This Effective Hamiltonian will be in general not hermitian. The simplest approach to overcome this unpleasant feature is to take the average

$$\frac{1}{2} \left(H_{ij}^{(N-1)} + H_{ji}^{(N-1)} \right)$$

of the off-diagonal matrix elements.

C. Dressed CI methods

The basic idea in this chapter is the fact that any CI eigenvalue problem can be written as system of linear equations, and vice versa. Kutzelnigg pointed this out for the LCCSD in *W.Kutzelnigg, Chem.Phys.Lett.*, **35** (1975) 283, and the equality “full CEPA” and “self-consistent size-consistent CI” was developed in *J.-P.Daudey, J.-L.Heully, J.-P.Malrieu, J.Chem.Phys.*, **99** (1993) 1240.

The CI eigenvalue problem

$$\begin{pmatrix} 0 & H_{0I} & H_{0J} \\ H_{0I} & H_{II} & H_{IJ} \\ H_{0J} & H_{IJ} & H_{JJ} \end{pmatrix} \begin{pmatrix} 1 \\ c_I \\ c_J \end{pmatrix} = E_{\text{corr}} \begin{pmatrix} 1 \\ c_I \\ c_J \end{pmatrix}$$

becomes

$$H_{0I} c_I + H_{0J} c_J = E_{\text{corr}}$$

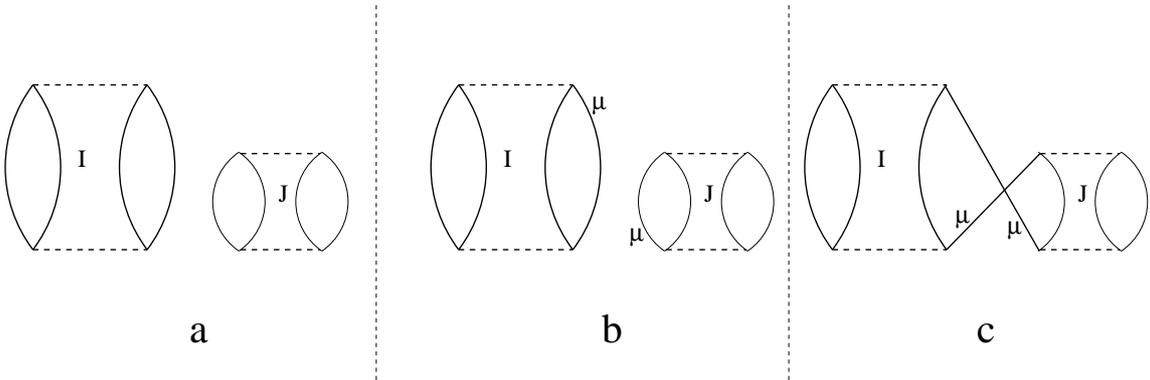
$$H_{0I} + \underbrace{(H_{II} - E_{corr})}_{+\Delta_I} c_I + \sum_{I \neq J} H_{IJ} c_J = 0$$

which is a system of linear equations with a diagonal dressing Δ_I for every determinant Ψ_I . We start from the CEPA-0, which is the infinite summation of all double excitations in the perturbation series, with $\Delta_I = 0$ for all determinants. All diagrams are perfectly linked, which assures the size consistency. Dressing through the correlation energy introduces unlinked diagrams, which destroy the size consistency for the CISD procedure, but adds as well unlinked EPV diagrams, which are present in e.g. fourth-order perturbation theory⁴, and which belong in fact to the linked diagrams. CEPA-2, CEPA-3, and the self-consistent size-consistent CI add more and more linked EPV diagrams to the dressing, without introducing any unlinked higher-order terms.

TABLE III. Different CEPA dressings Δ_{ij}^{ab} to address the variety of CEPA methods within the same algebra. For CEPA-2 the quadriexcited EPV determinants are explicitly written up and reference is made to the “e”-tables introduced in *M.-B.Lepetit, J.P.Malrieu, Chem.Phys.Lett., 208 (1993) 503*. CEPA-0bis, dressing with the same determinant becomes more meaningful in the diagonal approximation.

| | |
|----------------------|---|
| CEPA-0 | 0 |
| CEPA-0bis | $-\langle \Phi_{ij}^{ab} \mathbf{H} \Phi_{ijij}^{abab} \rangle c_{ij}^{ab} = -\langle \Phi_0 \mathbf{H} \Phi_{ij}^{ab} \rangle c_{ij}^{ab}$ |
| CEPA-2 | $-\sum_{cd} \langle \Phi_{ij}^{ab} \mathbf{H} \Phi_{ijij}^{abcd} \rangle c_{ij}^{cd} \approx -\sum_{cd} \langle \Phi_0 \mathbf{H} \Phi_{ij}^{cd} \rangle c_{ij}^{cd} = -e(i,j)$ |
| CEPA-3 | $-\sum_{kcd} \langle \Phi_0 \mathbf{H} \Phi_{ik}^{cd} \rangle c_{ik}^{cd} - \sum_{kcd} \langle \Phi_0 \mathbf{H} \Phi_{kj}^{cd} \rangle c_{kj}^{cd} + \sum_{cd} \langle \Phi_0 \mathbf{H} \Phi_{ij}^{cd} \rangle c_{ij}^{cd} = -e(i) - e(j) + e(i,j)$ |
| (SC) ² CI | $-\sum_{\text{EPV}(i,j,a,b)} \langle \Phi_0 \mathbf{H} \Phi_{kl}^{cd} \rangle c_{kl}^{cd}$ |
| CISD | $-E_{\text{Corr}} = - \underbrace{\sum_{\text{non-EPV}(i,j,a,b)} \langle \Phi_0 \mathbf{H} \Phi_{kl}^{cd} \rangle c_{kl}^{cd}}_{\text{unlinked diagrams}} - \sum_{\text{EPV}(i,j,a,b)} \langle \Phi_0 \mathbf{H} \Phi_{kl}^{cd} \rangle c_{kl}^{cd}$ |

Using the full Hamilton matrix elements \mathbf{H}_{IJ} in the CEPA/CI procedure corresponds in perturbation theory to the Epstein-Nesbet Hamiltonian or the infinite summation of diagonal elements in the Møller-Plesset series. Using $\mathbf{H}_{II} - E_{HF}$ instead of the MP2 denominators $\langle \Phi_0 | \mathbf{F} | \Phi_0 \rangle - \langle \Phi_I | \mathbf{F} | \Phi_I \rangle$ introduces just an infinite summation of these diagonal diagrams, and the EPV discussion applies equally well to the fundamental MP2 diagram.



⁴*M.Urban, I.Hubac, V.Kellö, J.Noga, J.Chem.Phys., 72 (1980) 3378*

FIG. 12. Unlinked diagrams: a) true unlinked diagram without any common index in excitation I and excitation J; b) unlinked diagram with common index μ ; c) the same, but drawn linked. The same level of the interaction line indicates the sum of two diagrams, one with I being the first excitation, and one with J being the first excitation.

The diagrams a) to c) lead with Møller-Plesset denominators to the formula

$$\langle 0 | \mathbf{H} \frac{|I\rangle\langle I|}{E_I - E_0} \mathbf{H} \frac{|I+J\rangle\langle I+J|}{E_{I+J} - E_0} \mathbf{H} \frac{|I\rangle\langle I|}{E_I - E_0} | \mathbf{H} | 0 \rangle + \langle 0 | \mathbf{H} \frac{|J\rangle\langle J|}{E_J - E_0} \mathbf{H} \frac{|I+J\rangle\langle I+J|}{E_{I+J} - E_0} \mathbf{H} \frac{|I\rangle\langle I|}{E_I - E_0} | \mathbf{H} | 0 \rangle$$

which simplifies with $\langle J | \mathbf{H} | I+J \rangle = \langle 0 | \mathbf{H} | I \rangle = H_{0I}$, $\langle I | \mathbf{H} | I+J \rangle = \langle 0 | \mathbf{H} | J \rangle = H_{0J}$, $E_{I+J} - E_0 = (E_I - E_0) + (E_J - E_0)$ and

$$\frac{1}{AB} = \frac{1}{A(A+B)} + \frac{1}{B(A+B)}$$

to

$$\frac{H_{0I} H_{0J} H_{0I}}{(E_I - E_0)(E_J - E_0)} = c_J c_I H_{0I}$$

independently of the EPV nature of the intermediate state $I+J$. To include only diagrams of type c) and not the unlinked diagrams with disjoint orbital sets, determinant J has to be dressed with the elements $c_I H_{0I}$ with I and J having at least one orbital index in common.

Averaging the effects of the EPV diagrams results in ACPF (Gdanitz, Ahlrichs) and the AQCC approaches of Szalay and Bartlett.

TABLE IV. Different averaged dressings leading to ACPF and AQCC

| | |
|---|---|
| ACPF | $-\frac{2}{n_e} E_{\text{Corr}}$ |
| AQCC | $-E_{\text{Corr}} \left(1 - \frac{(n_e-2)(n_e-3)}{n_e(n_e-1)} \right)$ |
| AQCC-v | $-E_{\text{Corr}} \left(1 - \frac{(n_e-2)(n_e-3)}{n_e(n_e-1)} \frac{(n_v-2)(n_v-3)}{n_v(n_v-1)} \right)$ |
| n_e : electrons; n_v : virtual orbitals | |

D. The diagonal approximation

If the CEPA matrix is approximated by only its diagonal, the computational effort is highly reduced, but the infinite summations of the EPV diagrams are still incorporated. In *M.-B.Lepetit, J.P.Malrieu, J.Chem.Phys., 87 (1987) 5937* the procedure is derived directly from the perturbation expansion and in *M.-B.Lepetit, J.P.Malrieu, Chem.Phys.Lett., 208 (1993) 503* the procedure is presented as 2×2 dressed CI submatrices and a eigenvalue problem. Here I will maintain the CEPA view.

As given already as exercise in the book of Szabo and Ostlund, the CEPA-0 in the diagonal approximation

$$\sum_I H_{0I} c_I = \sum_I E_I = E_{\text{Corr}}$$

$$H_{0I} + (H_{II} - H_{00}) c_I = 0$$

leads directly to $c_I = -H_{0I}/(H_{II} - H_{00})$ and $E_I = -(H_{0I})^2/(H_{II} - H_{00})$, i.e. the Epstein-Nesbet second-order energy. Dressing by $-E_I$ is equivalent to the two-electron Full CI, thus not introducing any unlinked diagrams, but only the infinite series of same-index EPV diagrams. This egoistic CI is the CEPA-0bis in the previous section with

the minimal dressing through EPV diagrams, but not yet coupling any different determinants or indices. It can be solved in a closed form without any iterations:

$$E_I = \frac{1}{2} \left(H_{0I} - \sqrt{H_{0I}^2 - 4 H_{II}} \right)$$

and prevents the catastrophe for the Epstein-Nesbet 2nd-order energy for vanishing differences $H_{II} - H_{00} = H_{II} - E_{HF}$.

Of course, all the dressings presented in the last section may be added.

A 2×2 submatrix

$$\begin{pmatrix} H_{00} & H_{0I} \\ H_{0I} & H_{II} \end{pmatrix}$$

may be considered for each doubly excited determinant Φ_{ij}^{ab} . This matrix may either be diagonalized in an eigenvalue problem, or it may be considered as a system of linear equations, like before, with a possible dressing Δ_I , which we derived from the CEPA point of view, that is $\Delta_I = 0$ for CEPA-0:

$$\underbrace{\begin{pmatrix} H_{00} & H_{0I} \\ H_{0I} & E_I + H_{II} + \Delta_I \end{pmatrix} \begin{pmatrix} 1 \\ c_I \end{pmatrix} = E_I \begin{pmatrix} 1 \\ c_I \end{pmatrix}}_{\text{CI-like view}} \quad \text{or} \quad \underbrace{\begin{matrix} H_{00} & + & H_{0I} c_I & = & E_I \\ H_{0I} & + & (H_{II} + \Delta_I) c_I & = & 0 \end{matrix}}_{\text{CEPA-like view}}$$

The 2×2 development of the CEPA-0 matrix into submatrices yields exactly the Epstein-Nesbet perturbation energy in second order, since (SC)²CI dressing Δ_I proposed inleads to

$$\begin{matrix} H_{00} & + & H_{0I} c_I & = & E_I \\ H_{0I} & + & (H_{II} + \Delta_I) c_I & = & 0 \end{matrix} \quad \text{or} \quad \begin{pmatrix} H_{00} - E_I & H_{0I} \\ H_{0I} & H_{II} + \Delta_I \end{pmatrix} \begin{pmatrix} 1 \\ c_I \end{pmatrix} = E'_I \begin{pmatrix} 1 \\ c_I \end{pmatrix} .$$

With the equality $E_I = H_{0I} c_I$ the original equations of the paper are obtained. E'_I is not the correlation energy E_I , but some fictitious energy, thus the correlation energy is obtained from the coefficients and again $E_I = H_{0I} c_I$.

The 2×2 rotations or submatrices are computationally much less demanding than the full diagonalization of the CI matrix, only the diagonal elements of the Hamilton matrix and the first column are needed, H_{II} and H_{0I} . Couplings between different determinants are introduced via a dressing CEPA-2, CEPA-3 or (SC)²CI where the dressing contains other determinants.

Another class of approximations is obtained when taking only the diagonal and the first line/column of the CI matrix:

$$\begin{pmatrix} 0 & \cdots & H_{0I} & \cdots & H_{0J} & \cdots \\ \vdots & \ddots & 0 & 0 & 0 & 0 \\ H_{0I} & 0 & H_{II} & 0 & 0 & 0 \\ \vdots & 0 & 0 & \ddots & 0 & 0 \\ H_{0J} & 0 & 0 & 0 & H_{JJ} & 0 \\ \vdots & 0 & 0 & 0 & 0 & \ddots \end{pmatrix} \begin{pmatrix} 1 \\ \vdots \\ c_I \\ \vdots \\ c_J \\ \vdots \end{pmatrix} = E \begin{pmatrix} 1 \\ \vdots \\ c_I \\ \vdots \\ c_J \\ \vdots \end{pmatrix}$$

Into this matrix we can incorporate all the different dressing used for the complete CI matrix, from CEPA-0 to AQCC-V, and we see that for the CEPA-like dressings CEPA-0, CEPA-2, CEPA-3, and (SC)²CI, the same 2×2 submatrix equations $H_{0I} + (H_{II} + \Delta_I) c_I = 0$, $H_{0I} c_I = E_I$, and $E_{Corr} = \sum_I E_I$ are obtained as before. However ACPF dresses now the 2×2 CI matrices with a common, averaged $-E_I$ as $-(2/n) E_{Corr} = -2/n \sum_I E_I$. The same holds for CI with the complete $\Delta_I = -E_{Corr} = -\sum_I E_I$, AQCC and AQCC-V. Thus from the two forms of approximations, we obtain one for any of the eight dressings presented before, and one completely different one, by dressing every 2×2 matrix by its individual correlation energy E_I :

| method | CEPA dressing | approximation |
|----------|----------------|--------------------------|
| CI | $-E_{Corr}$ | diagonal approximation |
| ACPF | same as before | diagonal approximation |
| AQCC | | |
| AQCC - V | | |
| CEPA-0 | — | Epstein-Nesbet 2nd order |

| | | |
|--|-----------------|---------------|
| CEPA - 2 } CEPA - 3 } (SC) ² CI } | same as before | 2×2 rotations |
| IC égoïste | -E _I | 2×2 rotations |

TABLE V. The approximations with respect to CCSD(T), for Boys and Pipek–Mezey localized orbitals, and for canonical orbitals, in a standard TZP basis. CISD_1 is dressed with the whole correlation energy, whereas CISD_2 dresses each 2×2 matrix by its individual E_I .

| | C2H2 | CH4 | CO | H2O | HF | LiF | LiH | N2 | NH3 |
|--------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Boys localization | | | | | | | | | |
| ACPF | -0.2318914 | -0.1451624 | -0.2921584 | -0.1939744 | -0.2271164 | -0.2282484 | -0.0301344 | -0.2443344 | -0.1732534 |
| AQCC | -0.2304934 | -0.1444684 | -0.2900924 | -0.1930084 | -0.2257434 | -0.2271824 | -0.0300304 | -0.2431644 | -0.1723644 |
| AQCC-V | -0.2298954 | -0.1441804 | -0.2889384 | -0.1924784 | -0.2248194 | -0.2263864 | -0.0299234 | -0.2425054 | -0.1719484 |
| CEPA-2 | -0.2330084 | -0.1456164 | -0.2939354 | -0.1948124 | -0.2283374 | -0.2291654 | -0.0300944 | -0.2453244 | -0.1739704 |
| CEPA-3 | -0.2300614 | -0.1445384 | -0.2893144 | -0.1928704 | -0.2254204 | -0.2266074 | -0.0300824 | -0.2427814 | -0.1723164 |
| CISD_1 | -0.2234024 | -0.1421464 | -0.2797824 | -0.1897824 | -0.2212074 | -0.2226464 | -0.0299784 | -0.2371394 | -0.1694024 |
| CISD_2 | -0.2334254 | -0.1459244 | -0.2944354 | -0.1950714 | -0.2286754 | -0.2294384 | -0.0302774 | -0.2455954 | -0.1742524 |
| EN2 | -0.2334474 | -0.1459604 | -0.2944754 | -0.1950874 | -0.2287074 | -0.2294484 | -0.0302934 | -0.2456304 | -0.1742784 |
| SCSC | -0.2297564 | -0.1444814 | -0.2886344 | -0.1926754 | -0.2249754 | -0.2262694 | -0.0300784 | -0.2425264 | -0.1721884 |
| Pipek–Mezey localization | | | | | | | | | |
| ACPF | -0.2896754 | -0.1732534 | -0.2945354 | -0.2229144 | -0.2115124 | -0.2401234 | -0.0310954 | -0.3513434 | -0.2126624 |
| AQCC | -0.2861604 | -0.1719814 | -0.2923564 | -0.2214084 | -0.2103954 | -0.2388514 | -0.0309684 | -0.3469304 | -0.2108614 |
| AQCC-V | -0.2846914 | -0.1714574 | -0.2911414 | -0.2205874 | -0.2096424 | -0.2379044 | -0.0308384 | -0.3445164 | -0.2100264 |
| CEPA-2 | -0.2924214 | -0.1740574 | -0.2963744 | -0.2241794 | -0.2124734 | -0.2411964 | -0.0310384 | -0.3549914 | -0.2140964 |
| CEPA-3 | -0.2840744 | -0.1720814 | -0.2912074 | -0.2211204 | -0.2100354 | -0.2380934 | -0.0310264 | -0.3437944 | -0.2106984 |
| CISD_1 | -0.2698864 | -0.1678244 | -0.2815474 | -0.2164614 | -0.2066834 | -0.2334774 | -0.0309054 | -0.3264734 | -0.2050404 |
| CISD_2 | -0.2934964 | -0.1746644 | -0.2969464 | -0.2246094 | -0.2127744 | -0.2415354 | -0.0312604 | -0.3560244 | -0.2146984 |
| EN2 | -0.2937374 | -0.1747344 | -0.2969824 | -0.2246614 | -0.2128014 | -0.2415584 | -0.0312924 | -0.3564414 | -0.2147714 |
| SCSC | -0.2833364 | -0.1719594 | -0.2903724 | -0.2208464 | -0.2097194 | -0.2376984 | -0.0310234 | -0.3425134 | -0.2104624 |
| canonical Orbitals | | | | | | | | | |
| ACPF | -0.3784614 | -0.2289904 | -0.4265644 | -0.2867924 | -0.2899524 | -0.2990654 | -0.0348934 | -0.4672954 | -0.2649914 |
| AQCC | -0.3698114 | -0.2256894 | -0.4180064 | -0.2828534 | -0.2867314 | -0.2960354 | -0.0346754 | -0.4553054 | -0.2610284 |
| AQCC-V | -0.3663294 | -0.2243604 | -0.4134634 | -0.2807594 | -0.2846104 | -0.2938264 | -0.0344554 | -0.4490674 | -0.2592304 |
| CEPA-2 | -0.3858924 | -0.2319494 | -0.4340724 | -0.2904254 | -0.2928824 | -0.3016574 | -0.0347524 | -0.4776254 | -0.2686324 |
| CEPA-3 | -0.3635724 | -0.2248464 | -0.4124084 | -0.2813854 | -0.2854314 | -0.2937664 | -0.0347304 | -0.4454074 | -0.2597484 |
| CISD_1 | -0.3346044 | -0.2155844 | -0.3819744 | -0.2707574 | -0.2766204 | -0.2839624 | -0.0345694 | -0.4077784 | -0.2489694 |
| CISD_2 | -0.3888124 | -0.2329654 | -0.4365894 | -0.2914284 | -0.2937154 | -0.3024194 | -0.0351924 | -0.4808084 | -0.2697424 |
| EN2 | -0.3891114 | -0.2329804 | -0.4369084 | -0.2915434 | -0.2937884 | -0.3025764 | -0.0352324 | -0.4822624 | -0.2697964 |
| SCSC | -0.3615824 | -0.2241434 | -0.4093164 | -0.2808874 | -0.2846754 | -0.2933084 | -0.0347224 | -0.4415284 | -0.2591234 |
| CCSD(T) | -0.3331023 | -0.2152351 | -0.3645188 | -0.2503342 | -0.2490877 | -0.2546239 | -0.0364568 | -0.3791562 | -0.2380879 |

TABLE VI. The corrected approximations with respect to CCSD(T), for Boys and Pipek–Mezey localized orbitals, and for canonical orbitals, in a standard TZP basis. CISD–1 is dressed with the whole correlation energy, whereas CISD–2 dresses each 2×2 matrix by its individual E_I . The correction consists in taking the approximation and adding the difference MP2C–MP2L for adding the infinite series of Fock-matrix elements.

| | C ₂ H ₂ | CH ₄ | CO | H ₂ O | HF | LiF | LiH | N ₂ | NH ₃ |
|--------------------------|-------------------------------|-----------------|------------|------------------|------------|------------|-------------|----------------|-----------------|
| Boys localization | | | | | | | | | |
| MP2C–MP2L | –0.105067 | –0.0645846 | –0.0959558 | –0.0702148 | –0.0488701 | –0.0512268 | –0.00286735 | –0.152018 | –0.069444 |
| ACPF | –0.336958 | –0.209747 | –0.388114 | –0.264189 | –0.275986 | –0.279475 | –0.0330011 | –0.396352 | –0.242697 |
| AQCC | –0.335560 | –0.209053 | –0.386047 | –0.263222 | –0.274613 | –0.278409 | –0.0328970 | –0.395182 | –0.241808 |
| AQCC–V | –0.334962 | –0.208765 | –0.384893 | –0.262692 | –0.273689 | –0.277613 | –0.0327900 | –0.394523 | –0.241392 |
| CEPA–2 | –0.338075 | –0.210200 | –0.389891 | –0.265027 | –0.277207 | –0.280392 | –0.0329616 | –0.397342 | –0.243414 |
| CEPA–3 | –0.335128 | –0.209123 | –0.385270 | –0.263085 | –0.274290 | –0.277834 | –0.0329498 | –0.394799 | –0.241760 |
| CISD–1 | –0.328469 | –0.206730 | –0.375738 | –0.259997 | –0.270077 | –0.273873 | –0.0328456 | –0.389157 | –0.238846 |
| CISD–2 | –0.338492 | –0.210508 | –0.390390 | –0.265286 | –0.277545 | –0.280665 | –0.0331442 | –0.397613 | –0.243696 |
| EN2 | –0.338514 | –0.210545 | –0.390431 | –0.265302 | –0.277577 | –0.280675 | –0.0331604 | –0.397648 | –0.243722 |
| SCSC | –0.334823 | –0.209066 | –0.384589 | –0.262890 | –0.273845 | –0.277496 | –0.0329452 | –0.394544 | –0.241632 |
| Pipek–Mezey localization | | | | | | | | | |
| MP2C–MP2L | –0.0671939 | –0.0436725 | –0.0956769 | –0.0492822 | –0.0608943 | –0.0441598 | –0.0027801 | –0.0795367 | –0.0412634 |
| ACPF | –0.356869 | –0.216925 | –0.390212 | –0.272196 | –0.272406 | –0.284283 | –0.0338756 | –0.430880 | –0.253925 |
| AQCC | –0.353354 | –0.215653 | –0.388033 | –0.270690 | –0.271289 | –0.283011 | –0.0337482 | –0.426466 | –0.252125 |
| AQCC–V | –0.351885 | –0.215130 | –0.386818 | –0.269869 | –0.270537 | –0.282064 | –0.0336177 | –0.424052 | –0.251289 |
| CEPA–2 | –0.359615 | –0.217730 | –0.392051 | –0.273462 | –0.273367 | –0.285356 | –0.0338185 | –0.434528 | –0.255359 |
| CEPA–3 | –0.351268 | –0.215754 | –0.386884 | –0.270402 | –0.270930 | –0.282253 | –0.0338064 | –0.423331 | –0.251961 |
| CISD–1 | –0.337080 | –0.211496 | –0.377223 | –0.265743 | –0.267577 | –0.277637 | –0.0336854 | –0.406010 | –0.246303 |
| CISD–2 | –0.360690 | –0.218336 | –0.392623 | –0.273892 | –0.273668 | –0.285695 | –0.0340404 | –0.435561 | –0.255961 |
| EN2 | –0.360931 | –0.218406 | –0.392659 | –0.273944 | –0.273695 | –0.285718 | –0.0340717 | –0.435977 | –0.256034 |
| SCSC | –0.350530 | –0.215631 | –0.386049 | –0.270128 | –0.270613 | –0.281858 | –0.0338035 | –0.422050 | –0.251725 |
| canonical Orbitals | | | | | | | | | |
| ACPF | –0.378461 | –0.228990 | –0.426564 | –0.286792 | –0.289952 | –0.299065 | –0.0348925 | –0.467295 | –0.264991 |
| AQCC | –0.369811 | –0.225689 | –0.418006 | –0.282853 | –0.286731 | –0.296035 | –0.0346750 | –0.455305 | –0.261028 |
| AQCC–V | –0.366329 | –0.224360 | –0.413463 | –0.280759 | –0.284610 | –0.293826 | –0.0344547 | –0.449067 | –0.259230 |
| CEPA–2 | –0.385892 | –0.231949 | –0.434072 | –0.290425 | –0.292882 | –0.301657 | –0.0347525 | –0.477625 | –0.268632 |
| CEPA–3 | –0.363572 | –0.224846 | –0.412408 | –0.281385 | –0.285431 | –0.293766 | –0.0347304 | –0.445407 | –0.259748 |
| CISD–1 | –0.334604 | –0.215584 | –0.381974 | –0.270757 | –0.276620 | –0.283962 | –0.0345688 | –0.407778 | –0.248969 |
| CISD–2 | –0.388812 | –0.232965 | –0.436589 | –0.291428 | –0.293715 | –0.302419 | –0.0351921 | –0.480808 | –0.269742 |
| EN2 | –0.389111 | –0.232980 | –0.436908 | –0.291543 | –0.293788 | –0.302576 | –0.0352323 | –0.482262 | –0.269796 |
| SCSC | –0.361582 | –0.224143 | –0.409316 | –0.280887 | –0.284675 | –0.293308 | –0.0347222 | –0.441528 | –0.259123 |
| CCSD(T) | –0.3331023 | –0.2152351 | –0.3645188 | –0.2503342 | –0.2490877 | –0.2546239 | –0.0364568 | –0.3791562 | –0.2380879 |

E. Third-order Epstein-Nesbet and MP perturbation

From the general perturbation development we have for the third order

$$E^{(3)} = \sum_I \sum_J \frac{\langle 0 | \mathbf{V} | I \rangle \langle I | \mathbf{V} | J \rangle \langle J | \mathbf{V} | 0 \rangle}{\langle I | \mathbf{H}_0 - E_0 | I \rangle \langle J | \mathbf{H}_0 - E_0 | J \rangle} - \langle 0 | \mathbf{V} | 0 \rangle \sum_I \frac{\langle 0 | \mathbf{V} | I \rangle \langle I | \mathbf{V} | 0 \rangle}{\langle I | \mathbf{H}_0 - E_0 | I \rangle \langle I | \mathbf{H}_0 - E_0 | I \rangle} \quad (46)$$

These formulæ may be evaluated in a quite straight way, since we may use

$$\begin{aligned} \langle I | \mathbf{V} | I \rangle - \langle 0 | \mathbf{V} | 0 \rangle &= \langle I | \mathbf{H} - \mathbf{H}_0 | I \rangle - \langle 0 | \mathbf{H} - \mathbf{H}_0 | 0 \rangle \\ &= \langle I | \mathbf{H} - E_{HF} | I \rangle - \langle I | \mathbf{H}_0 - E_0 | I \rangle \end{aligned} \quad (47)$$

which allows us to rewrite eq. 46 with $\langle 0 | \mathbf{V} | I \rangle = \langle 0 | \mathbf{H} | I \rangle$ as

$$E^{(3)} = \sum_I \sum_J \frac{\langle 0 | \mathbf{H} | I \rangle \langle I | \mathbf{H} - E_{HF} | J \rangle \langle J | \mathbf{H} | 0 \rangle}{\langle I | \mathbf{H}_0 - E_0 | I \rangle \langle J | \mathbf{H}_0 - E_0 | J \rangle} - \sum_I \frac{\langle 0 | \mathbf{V} | I \rangle \langle I | \mathbf{V} | 0 \rangle}{\langle I | \mathbf{H}_0 - E_0 | I \rangle} \quad (48)$$

With the vector

$$\mathbf{x} = \sum_J |J\rangle \frac{\langle J | \mathbf{V} | 0 \rangle}{\langle J | \mathbf{H}_0 - E_0 | J \rangle}$$

the last equation reduces to

$$E^{(3)} = \mathbf{x} \cdot (\mathbf{H} \cdot \mathbf{x}) - \underbrace{\sum_I \frac{\langle 0 | \mathbf{H} | I \rangle \langle I | \mathbf{H} | 0 \rangle}{\langle I | \mathbf{H}_0 - E_0 | I \rangle}}_{-E^{(2)}}$$

The third-order energy consists thus of the sum of \mathbf{xHx} and the second-order energy and we have

$$E^{(2)} + E^{(3)} = \mathbf{x} \cdot (\mathbf{H} \cdot \mathbf{x}) + 2 E^{(2)} \quad .$$

All this holds both for Møller-Plesset and Epstein-Nesbet perturbation theory, the only difference being the definition of \mathbf{H}_0 .

The timing seems to be comparable to the diagrammatic approach in EPSNES – here we have a simple logic of the routine with a single call to the multiplication of \mathbf{H} and \mathbf{x} , whereas in the diagrammatic procedure the operations are simpler, but the external logic is more complicated with 12 classes of diagrams. However, in the diagrammatic approach we may loop over integrals and not determinants, searching in memory for the corresponding integrals. This more direct construction may explain a factor of about 2 for the two programs (H₂O in a medium basis, 58 basis functions, ca. 10000 spin determinants)

In order to apply the dressings discussed in the previous chapters, we may write the third-order energy as

$$E^{(3)} + E^{(2)} = \sum_{I,J} c_I c_J H_{IJ} + 2 \sum_I c_I H_{0I} \quad (49)$$

where the coefficients c_I are those of the dressed MP2 or Epstein-Nesbet calculation. Do we find here another expression of the $2n + 1$ rule, i.e. the first-order wavefunction determines the third-order energy?

All we have to do then after the calculation of the dressed c_I is the multiplication $c_I c_J H_{IJ}$

F. Spin-Scaled MP2

Stefan Grimme published a paper speaking of the Spin-Scaled MP2 or SCSMP2, as implemented from Molpro 2006.1 on. As in TURBOMOL the contributions from the pairs with parallel spin ij and $\bar{i}\bar{j}$ are attributed to triplet contributions and the unlike spin settings to singlet contributions. In MP2 the contributions are independent of the spin, thus the triplet combination from unlike spins $\frac{1}{\sqrt{2}}(\bar{i}\bar{j} - i\bar{j})$ is zero. So one might speak of Singlet correlation

and Triplet correlation, meaning correlated singlet pairs of occupied orbitals and correlated triplet pairs of occupied orbitals.

We may adopt another point of view: the expansion runs over determinants, and the perturbation adds a first-order wavefunction, which is composed of determinants with closed shells, two open shells or four open shells, giving rise to singlet, triplet and quintet contributions. In the Epstein-Nesbet case we constructed proper singlet wavefunctions, cutting out some interaction coming from the simple determinantal approach, but rendering the perturbation uniquely defined with respect to spin coupling. The same could be done for the MP2, leaving only the singlet spin-adapted configurations interact with the reference determinant. Thus the first-order wavefunction will necessarily be a pure singlet state.

In order to separate the different contributions properly (singlet, triplet and quintet) we may use a projection operator for the MP2 case.

Hey, but $\Psi^{(1)} = \sum_I \frac{|I\rangle\langle I|\mathbf{H}|0\rangle}{\langle I|\mathbf{H}_0-E_0|I\rangle}$ contains only singlet functions, since the denominator is independent of spin settings and the matrix element selects only the singlet components !!! That is the proof why MPn is correctly spin adapted.

For a determinant in occupation notation ($|i\bar{a}b\bar{j}\rangle$) with the same number of α and β spins the spin operator \mathbf{S}^2 becomes $\mathbf{S}^2 = \mathbf{S}_- \mathbf{S}_+$ as

$$\begin{aligned} \mathbf{S}^2|i\bar{a}b\bar{j}\rangle &= \mathbf{S}_- \mathbf{S}_+ |i\bar{a}b\bar{j}\rangle \\ &= \mathbf{S}_- (|i\bar{a}b\bar{j}\rangle + |i\bar{a}b\bar{j}\rangle) \\ &= |i\bar{a}b\bar{j}\rangle + |i\bar{a}b\bar{j}\rangle + |i\bar{a}b\bar{j}\rangle + |\bar{i}a\bar{b}j\rangle + |i\bar{a}b\bar{j}\rangle + |i\bar{a}b\bar{j}\rangle \\ &= -|a\bar{i}b\bar{j}\rangle + |i\bar{a}b\bar{j}\rangle - |i\bar{a}b\bar{j}\rangle - |b\bar{i}j\bar{a}\rangle - |i\bar{a}j\bar{b}\rangle + |i\bar{a}b\bar{j}\rangle \end{aligned}$$

From this we may construct the projectors

$$\begin{aligned} P^S &= +\frac{1}{12} (\mathbf{S}^2 - 2) (\mathbf{S}^2 - 6) \\ P^T &= -\frac{1}{8} \mathbf{S}^2 (\mathbf{S}^2 - 6) \\ P^Q &= +\frac{1}{24} \mathbf{S}^2 (\mathbf{S}^2 - 2) \end{aligned}$$

on the respective spin states and apply this on the combination of the different possibilities for the four orbitals i, j, a and b . For $i = j$ and $a = b$ we have only a singlet, for $i = j$ and $a \neq b$ or $a = b$ and $i \neq j$ we have singlet and triplet and for all indices different we may have singlet, triplet and quintet. The projectors have to be constructed once and are fixed, that is we have to find the constant matrices d^S, d^T and d^Q for the four different cases and

$$\begin{aligned} P^S \left(\sum_I c_I \Phi_I \right) &= \sum_J d_{IJ}^S c_I \Phi_J \\ P^T \left(\sum_I c_I \Phi_I \right) &= \sum_J d_{IJ}^T c_I \Phi_J \\ P^Q \left(\sum_I c_I \Phi_I \right) &= \sum_J d_{IJ}^Q c_I \Phi_J \quad . \end{aligned}$$

We have explicitly

$$\begin{aligned} P^S \Phi_{ii}^{a\bar{a}} &= \Phi_{ii}^{a\bar{a}} \\ P^S \left(c_{ii}^{a\bar{b}} \Phi_{ii}^{a\bar{b}} + c_{ii}^{\bar{a}b} \Phi_{ii}^{\bar{a}b} \right) &= \frac{1}{2} \left(c_{ii}^{a\bar{b}} + c_{ii}^{\bar{a}b} \right) \Phi_{ii}^{a\bar{b}} + \frac{1}{2} \left(c_{ii}^{a\bar{b}} + c_{ii}^{\bar{a}b} \right) \Phi_{ii}^{\bar{a}b} \\ P^T \left(c_{ii}^{a\bar{b}} \Phi_{ii}^{a\bar{b}} + c_{ii}^{\bar{a}b} \Phi_{ii}^{\bar{a}b} \right) &= \frac{1}{2} \left(c_{ii}^{a\bar{b}} - c_{ii}^{\bar{a}b} \right) \Phi_{ii}^{a\bar{b}} - \frac{1}{2} \left(c_{ii}^{a\bar{b}} - c_{ii}^{\bar{a}b} \right) \Phi_{ii}^{\bar{a}b} \\ &\text{the same for } \Phi_{ij}^{a\bar{a}} \end{aligned}$$

The action of $\mathbf{S}_- \mathbf{S}_+$ on the six different determinants for 4 different indices is

$$\begin{aligned} \mathbf{S}_- \mathbf{S}_+ |i\bar{a}j\bar{b}\rangle &= 2|i\bar{a}j\bar{b}\rangle + |\bar{i}a\bar{b}j\rangle - |i\bar{a}b\bar{j}\rangle - |a\bar{i}j\bar{b}\rangle + |b\bar{i}j\bar{a}\rangle \\ \mathbf{S}_- \mathbf{S}_+ |i\bar{a}j\bar{b}\rangle &= |i\bar{a}j\bar{b}\rangle + 2|\bar{i}a\bar{b}j\rangle - |i\bar{a}b\bar{j}\rangle - |a\bar{i}j\bar{b}\rangle + |a\bar{i}b\bar{j}\rangle \\ \mathbf{S}_- \mathbf{S}_+ |i\bar{a}j\bar{b}\rangle &= -|i\bar{a}j\bar{b}\rangle - |\bar{i}a\bar{b}j\rangle + 2|i\bar{a}b\bar{j}\rangle - |b\bar{i}j\bar{a}\rangle - |a\bar{i}b\bar{j}\rangle \end{aligned}$$

$$\begin{aligned}
\mathbf{S}_- \mathbf{S}_+ |\bar{a}\bar{i}\bar{j}\bar{b}\rangle &= -|\bar{i}\bar{a}\bar{j}\bar{b}\rangle - |\bar{i}\bar{b}\bar{a}\bar{j}\rangle + 2|\bar{a}\bar{i}\bar{j}\bar{b}\rangle - |\bar{b}\bar{i}\bar{j}\bar{a}\rangle - |\bar{a}\bar{i}\bar{b}\bar{j}\rangle \\
\mathbf{S}_- \mathbf{S}_+ |\bar{b}\bar{i}\bar{j}\bar{a}\rangle &= |\bar{i}\bar{a}\bar{j}\bar{b}\rangle - |\bar{i}\bar{a}\bar{b}\bar{j}\rangle - |\bar{a}\bar{i}\bar{j}\bar{b}\rangle + 2|\bar{b}\bar{i}\bar{j}\bar{a}\rangle + |\bar{a}\bar{i}\bar{b}\bar{j}\rangle \\
\mathbf{S}_- \mathbf{S}_+ |\bar{a}\bar{i}\bar{b}\bar{j}\rangle &= |\bar{i}\bar{b}\bar{a}\bar{j}\rangle - |\bar{i}\bar{a}\bar{b}\bar{j}\rangle - |\bar{a}\bar{i}\bar{j}\bar{b}\rangle + |\bar{b}\bar{i}\bar{j}\bar{a}\rangle + 2|\bar{a}\bar{i}\bar{b}\bar{j}\rangle
\end{aligned}$$

We may write this as a matrix

$$\mathbf{S}_- \mathbf{S}_+ \begin{pmatrix} |\bar{i}\bar{a}\bar{j}\bar{b}\rangle \\ |\bar{i}\bar{b}\bar{a}\bar{j}\rangle \\ |\bar{i}\bar{a}\bar{b}\bar{j}\rangle \\ |\bar{a}\bar{i}\bar{j}\bar{b}\rangle \\ |\bar{b}\bar{i}\bar{j}\bar{a}\rangle \\ |\bar{a}\bar{i}\bar{b}\bar{j}\rangle \end{pmatrix} = \begin{pmatrix} 2 & 1 & -1 & -1 & 1 & 0 \\ 1 & 2 & -1 & -1 & 0 & 1 \\ -1 & -1 & 2 & 0 & -1 & -1 \\ -1 & -1 & 0 & 2 & -1 & -1 \\ 1 & 0 & -1 & -1 & 2 & 1 \\ 0 & 1 & -1 & -1 & 1 & 2 \end{pmatrix} \begin{pmatrix} |\bar{i}\bar{a}\bar{j}\bar{b}\rangle \\ |\bar{i}\bar{b}\bar{a}\bar{j}\rangle \\ |\bar{i}\bar{a}\bar{b}\bar{j}\rangle \\ |\bar{a}\bar{i}\bar{j}\bar{b}\rangle \\ |\bar{b}\bar{i}\bar{j}\bar{a}\rangle \\ |\bar{a}\bar{i}\bar{b}\bar{j}\rangle \end{pmatrix} \quad (50)$$

to be diagonalized. This gives the eigenvalues 0, 0, 2, 2, 2 and 6. The unique linear combination for the quintet is

$$\Psi_Q = \frac{1}{\sqrt{6}} (|\bar{i}\bar{a}\bar{j}\bar{b}\rangle + |\bar{i}\bar{b}\bar{a}\bar{j}\rangle - |\bar{i}\bar{a}\bar{b}\bar{j}\rangle - |\bar{a}\bar{i}\bar{j}\bar{b}\rangle + |\bar{b}\bar{i}\bar{j}\bar{a}\rangle + |\bar{a}\bar{i}\bar{b}\bar{j}\rangle) \quad .$$

For the singlets we proposed the interaction-guided linear combination as

$$\Psi_S = \sum_I |I\rangle \langle I | \mathbf{H} | 0 \rangle \quad (51)$$

as the other singlet, orthogonal to the first, has no interaction with the reference since

$$\begin{aligned}
\Psi'_S &= \sum_I d_I |I\rangle \\
\langle \Psi'_S | \Psi_S \rangle &= 0 = \sum_I d_I \langle I | I \rangle \langle I | \mathbf{H} | 0 \rangle = \langle \Psi'_S | \mathbf{H} | 0 \rangle \quad . \quad (52)
\end{aligned}$$

Remains to show that we have indeed a singlet by the construction in eq. 51. From the six independent linear combinations only one single has an interaction with the reference, collecting all possible contributions — from singlets. Since this maximizes the interaction with the reference this must be a pure singlet state without non-interacting triplet or quintet components.

Thus we defined unique constructions for the singlet and the quintet states. For the triplets we have three independent states which we might wish to render unique.

For Epstein-Nesbet theory up to third order the construction of the singlets is sufficient to render the method unique. For the CI/CEPA based methods we might want to define projectors on the singlet, triplet and quintet space as we defined the methods for simple determinants. This as well does not need a further development of the separation of the three triplets.

As we have $E_{\text{corr}} = \sum_I c_I \langle 0 | \mathbf{H} | I \rangle$ we have again just the previously formed maximum-interaction singlets which count for the correlation energy. But, as for any variational energy, all determinants have to be considered for the coefficients and only as the second step we have the singlet interaction. For having a singlet *wavefunction* we have to project first and normalize afterwards.

G. A way to overcome the search problem

Most of the time of the CI program is spent on the search for determinants and integrals in memory. As we can not assume complete lists due to the localization, we are not able to loop just over all indices with finite range or step size. A possible strategy is to establish lists of domains, as it is done in the linear-scaling approaches of Schütz and Werner in Molpro.

Here we follow a different strategy, proposed from the informatics community. We may look for the possible interactions of determinants, and classify in advance these connections, like a graph: which pair of determinants needs which integral. The complete graph is impossible to handle due to the huge number of operations to be tabulated.

For the moment we assume no symmetry and no spatial restriction, which may eliminate matrix elements from the very beginning from the work list.

Nevertheless, a first indication can be gained concerning the most numerous interactions: double excitations with double excitations. A general matrix element $\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{kl}^{cd} \rangle$ is only non-zero if the determinants have at most two differences in their occupation pattern. If we classify the determinants in blocks of common indices ij for instance, we only have to look for the virtual indices a, b, c and d . In any case there will be a non-zero interaction. Next we can classify the determinants by common indices ab , so we have in any case an interaction through the holes i, j, k and l . In total we may construct 6 lists differently ordered: by ij, ia, ib, ja, jb and ab .

For two determinants taken from blocks with common indices and two differences, we have immediately the corresponding bielectronic integrals as interaction matrix elements (written here only for same-spin excitations, for the other spin combinations only one of the two integrals contribute to the matrix element):

$$\begin{aligned}
\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ij}^{cd} \rangle &= (ac|bd) - (ad|bc) \\
\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ik}^{ac} \rangle &= \langle \dots a \dots b \dots k \dots | \mathbf{H} | \dots a \dots j \dots c \dots \rangle = (bj|kc) - (bc|jk) \\
\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{kj}^{ac} \rangle &= \langle \dots a \dots k \dots b \dots | \mathbf{H} | \dots i \dots a \dots c \dots \rangle = -(ik|bc) + (ib|ck) \\
\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{kj}^{cb} \rangle &= \langle \dots a \dots k \dots b \dots | \mathbf{H} | \dots i \dots c \dots b \dots \rangle = (ia|kc) - (ac|ik) \\
\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ik}^{cb} \rangle &= \langle \dots a \dots b \dots k \dots | \mathbf{H} | \dots c \dots j \dots b \dots \rangle = -(ac|kj) + (aj|kc) \\
\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{kl}^{ab} \rangle &= (ik|jl) - (il|jk)
\end{aligned} \tag{53}$$

In any case the matrix elements are calculated using the general routine implementing Slater's rules for the evaluation of Hamilton matrix elements. Otherwise we would have to write for each class and each possibility of spin settings the individual matrix elements one by one.

The story becomes more complicated when dealing with one difference between the determinants in a class, as these matrix elements may occur in different classes: $\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ij}^{cb} \rangle$ has common pair indices ij, ib and jb , so it will occur 3 times in 3 different groups.

However, the element $\langle \Phi_{ij}^{ab} | \mathbf{H} | \Phi_{ij}^{bc} \rangle$ seems to have 2 differences, not one, as the common indices are i and j , and b is in a different position.

H. The interior of the CI program

The main steps are

1. Reading data
2. Reading bielectronic integrals, generating 12 classes, 6 with repeated indices (OOOO1, OOOV1, OOVV1, OVOV1, OVVV1, VVVV1) and 6 with four different indices (OOOO2, OOOV2, OOVV2, OVOV2, OVVV2, VVVV2).
3. Generating the determinant list, and calculating the diagonal elements $\langle \Phi_I | \hat{H} | \Phi_I \rangle$ and the couplings with the reference $\langle \Phi_I | \hat{H} | \Phi_0 \rangle$
4. Iterative solution of $\hat{H}\Psi = E\Psi$ via the Davidson algorithm (CI problem) or via Conjugate Gradients $H_{0I} + \sum_J c_J (H_{IJ} + \Delta_I \delta_{IJ}) = 0$ with the diagonal dressing Δ_I (system of linear equation in coefficients c_J). Both variants need to calculate

$$H|\Psi\rangle = \sum_J d_J |\Phi_J\rangle = \sum_I c_I H|\Phi_I\rangle = \sum_J |\Phi_J\rangle \left(\sum_I c_I \langle \Phi_J | H | \Phi_I \rangle \right)$$

from a given CI vector $\Psi = \sum_I c_I \Phi_I$

5. Calculation of the correlation energy from the converged solution vector c_I

1. Reading data

The program needs the general data from file `SYSTEM.ORTHO`, the Fock matrix in AOs, the bielectronic integrals in MOs, the molecular orbitals, and the overlap matrix of the molecular orbitals.

2. Finding integrals and determinants in memory

Integrals are in memory, in 2D arrays for the one-electron quantities, and as an indexed list for the bielectronic integrals (i, j, k, l and the value $(ij|kl)$). For finding a precise integrals, a search by bisection in the ordered list is implemented, needing much time. More rapidly, use of a hash table has been implemented, but results in huge and sparse index arrays, the dimension of which is from time to time not sufficient to avoid collisions.

3. Generating determinants with selection

List over occupied, occupied, virtual and virtual orbitals. First a list of all possible quadruplets is created. This list is then augmented by all possible spin settings (1 determinant for $iaaa$, 2 determinants for $ijaa$, $iiab$, and 6 possibilities for 4 different indices $ijab$). The number of the thus generated determinants is the di

4. Forming $H|\Psi\rangle$ from $|\Psi\rangle$

The determinants are classified by the positive integer quadruplets $iaaa$ (for the mono-excitation $|\Phi_i^a\rangle$ and its complex conjugate, and the di-excitation $|\Phi_{ii}^{aa}\rangle$), $iiab$, $ijaa$ and $ijab$. The latter needs 3 different coefficients for the six determinants.

As for forming $H\Psi$ we have the update of a coefficient c_I as

$$c_I = \sum_J c_J \langle \Phi_I | \hat{H} | \Phi_J \rangle$$

we have

$$c_I = \sum_J c_J (\langle \Phi_I | \hat{H} | \Phi_J \rangle + \langle \Phi_I | \hat{H} | \Phi_{\bar{J}} \rangle)$$

5. The Davidson algorithm

Part taken from the CASDI program in Toulouse.