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 November 21, 2024)

Contents

INTRODUCTION

Programs used in a school in Fès in Morokko, in 2008. English version of the manual.

I. GENERAL OVERVIEW

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

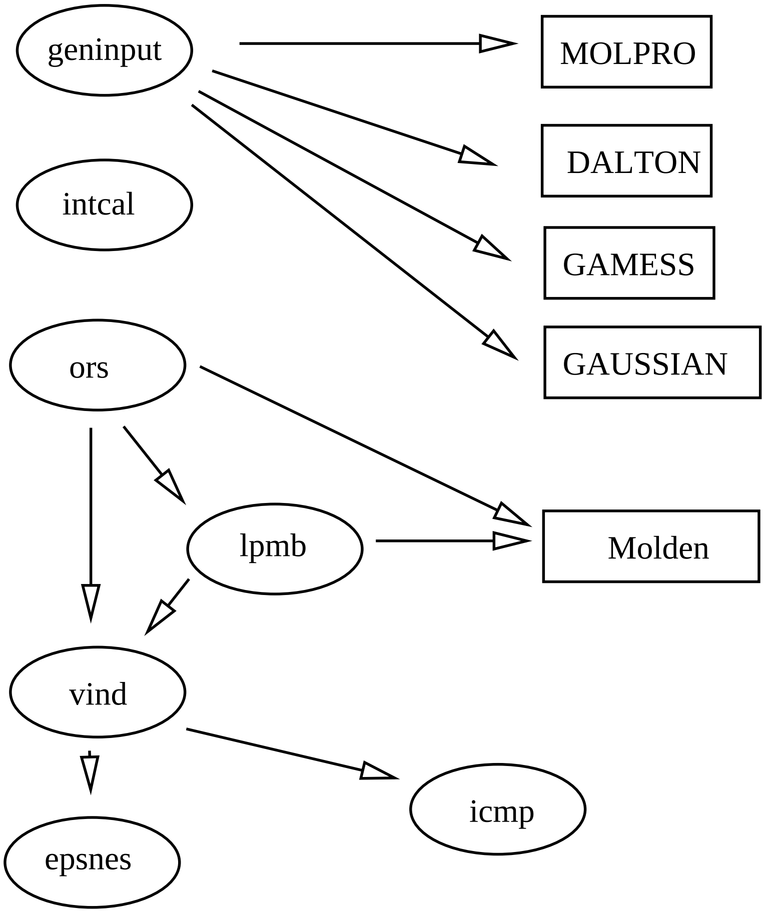

FIG. 1. Flow chart

II. THE PROGRAM GENINPUT

This programs 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 NH_3 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 Ångstrøms.

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`.

III. CALCULATION OF INTEGRALS INTCAL

In order to calculate integrals a program called INTCAL is available, based on the McMurchie-Davidson algorithm. The program can understand the following options, in a file `INIPUT.INT` between keywords `*INT` and `*END`:

- NOMONO: no mono-electronic integrals are calculated.
- NOBIEL: no-bielectronic integrals are calculated.
- THRESH: integrals smaller in abolute value than the threshold in the next line are not stored on file.
- FORMAT: bielectronic integrals are written out formatted instead of a binary output.
- CARTES: integrals are calculated in cartesion Gaussians (i.e. 6D, corresponding to the option 6D for GENINPUT and ORS).

Upon completion there should be the following files

- `KINETIC` contains kinetic energy integrals $-\frac{1}{2}\langle\chi_\alpha|\Delta|\chi_\beta\rangle$
- `HAMILTO` are the mono-electronic integrals (kinetic energy and electron-nuclei attraction $-\langle\chi_\alpha|\sum_I(1/|\vec{\mathrm{r}}-\vec{\mathrm{R}}_I)|\chi_\beta\rangle$).
- `DIPOL_X`, `DIPOL_Y`, `DIPOL_Z` contain integrals over the components of the dipole operator $\vec{\mu}_{\alpha\beta}=\langle\chi_\alpha|\vec{\mathrm{r}}|\chi_\beta\rangle$, used for Boys localization.
- `OVERLAP` are the overlap integrals $S_{\alpha\beta} = \langle\chi_\alpha|\chi_\beta\rangle$
- `FILE04` contains all bielectronic integrals $(\chi_\alpha\chi_\beta|\chi_\gamma\chi_\delta)$ in a binary file.
- `AOTWOINT_FORMATTED` are the bielectronic integrals on a formatted file. $(\chi_\alpha\chi_\beta|\chi_\gamma\chi_\delta)$ together with indices.

IV. THE CLOSED-SHELL SCF PROGRAM ORS

As input data files `OVERLAP`, `HAMILTON`, `KINETIC` and `AOTWO` are needed apart from the system definition file `SYSTEM.ORTHO`, and the programs stops if any of these files is missing. 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-martrix 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`.
- MAXITE: maximal number of SCF iterations.
- FMIXIN: Fock matrix mixing as convergency accelerator, the value or the percentage can be given: 0.30 or 30%.
- MOLDEN: put a MOLDEN input file on disk.
- 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.
- 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 $\langle\Phi_0|\mathbf{H}|\Phi_i^a\rangle = F_{ia} \to 0$.

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 $(\Phi_i^a + \Phi_{\bar{\imath}}^{\bar{a}})/\sqrt{2}$. This leads to

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

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

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

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

$$\begin{aligned}
\langle\phi_i^{new}|\phi_a^{new}\rangle &= \left\langle \phi_i + \sum_{b\in virt} c_i^b\phi_b \,\middle|\, \phi_a + \sum_{j\in occ} c_j^a\phi_j \right\rangle \\
&= \langle\phi_i|\phi_a\rangle + \sum_{b\in virt} c_i^b\langle\phi_b|\phi_a\rangle + \sum_{j\in occ} c_j^a\langle\phi_i|\phi_j\rangle + \sum_{b\in virt}\sum_{j\in occ} c_i^b\,c_j^a\langle\phi_b|\phi_j\rangle \\
&= c_i^a\left(\langle\phi_a|\phi_a\rangle - \langle\phi_i|\phi_i\rangle\right) \ = \ 0\ . \qquad (2)
\end{aligned}$$

Within the block of occupied orbitals, and within the block of virtual orbitals, we have to reorthogonlize 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 ressemble the most the initial orbitals, however we have no criterion to maximize or minimize any localization functional, as the Boys or the Pipek-Mezey mesure. The advantage lies in the fact that we never have to deal with the diagonalization of the Fock matrix, thus we never delocalize explicitely. 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

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

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

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

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

V. A POSTERIORI LOCALIZATION, LPMB

This program read a set of orbitals from a file `VECTOR`, and transformed them into a new set, localized or partially canonicalized. So there a principally two different ways to use the programs, either a group of orbitals is transformed to be localized, optimizing the Pipek-Mezey or the Boys localization criterion, or canonialc orbitals are generated, diagonalizing the Fock matrix on a set of orbitals.

Input keywords are

- GROUP
- CANONICal
- PIPEKMezey
- BOYS
- MOLDEN
- FRAGMEnt
- EXTREMely localized orbitals
- QMC: output for the QMC program. If the option EXTREME is given, the orbitals are not orthogonalized.

A. Extremely localized orbitals

Extremely localized orbitals are non-orthogonal, but span the same space as the original set. They are obtained via projection of the atomic orbitals onto the according space.

We read the given orbital set, and assure that it is composed of orthonormal functions. To obatin extremely localized occupied orbitals $\{\chi'_\alpha\}$ the virtual orbitals of the system are projected out of the atomic orbitals

$$\chi'_\alpha = \chi_\alpha - \sum_{i\in virt} \langle\phi_i|\chi_\alpha\rangle\ \phi_i \qquad .$$

From the set of projected basis functions, only the n_{occ} most localized functions are selected, with a localization criterion to be defined, and it has to checked whether these functions are linearly dependent. If this is the case, another projected AO has to be considered, until a set of n_{occ} is assembled. This new set is denoted ϕ_i^E.

We have for instance for the occupied projected orbitals

$$\begin{aligned} |\phi_\alpha^E\rangle &= |\chi_\alpha\rangle - \sum_{n\in virt.} |\phi_n\rangle\langle\phi_n|\chi_\alpha\rangle = |\chi_\alpha\rangle - \sum_{\beta\gamma} S_{\alpha\gamma} \underbrace{\left(\sum_n c_{\beta n} c_{\gamma n}\right)}_{P_{\beta\gamma}} |\chi_\beta\rangle \\ &= \sum_\beta \left(\delta_{\alpha\beta} - \sum_\gamma S_{\alpha\gamma} P_{\beta\gamma}\right) |\chi_\beta\rangle \end{aligned}$$

This should be, in a finite basis, the same as

$$|\phi_\alpha^E\rangle = \sum_{n\in occ.} |\phi_n\rangle\langle\phi_n|\chi_\alpha\rangle = \sum_{\beta\gamma} S_{\alpha\gamma} \underbrace{\left(\sum_n c_{\beta n} c_{\gamma n}\right)}_{P_{\beta\gamma}} |\chi_\beta\rangle$$

Two different ways to use these extremely localized orbitals may be employed: either for Quantum Monte-Carlo calculations, where the orthogonality of of no importance, but the value of the Slater determinant must be conserved, or as input for the correlation programs, where orthogonal orbitals are needed. In that second case the generated orbitals can orthogonalized hierarchially by $\mathbf{S}^{-1/2}$, preserving their character as good as possible. This is the default output of the EXTREME option.

If, however, the keyword QMC is given, the generated orbitals are assigned to the original ϕ_is and normalized for having $|\phi_i^E\rangle = |\phi_i\rangle + \sum_{j\neq i} c_j|\phi_j\rangle$ for that:

$$\begin{vmatrix} \phi_1^E(1) & \cdots & \phi_1^E(n) \\ \vdots & \ddots & \vdots \\ \phi_n^E(1) & \cdots & \phi_n^E(n) \end{vmatrix} = \begin{vmatrix} \phi_1(1) + \sum_{j\neq 1} c_j\phi_j(1) & \cdots & \phi_1(n) + \sum_{j\neq 1} c_j\phi_j(n) \\ \vdots & \ddots & \vdots \\ \phi_n(1) + \sum_{j\neq n} c_j\phi_j(1) & \cdots & \phi_n(n) + \sum_{j\neq n} c_j\phi_j(n) \end{vmatrix} = \begin{vmatrix} \phi_1(1) & \cdots & \phi_1(n) \\ \vdots & \ddots & \vdots \\ \phi_n(1) & \cdots & \phi_n(n) \end{vmatrix}$$

This is easily achieved by dividing each ϕ_i^E by the diagonal of the overlap matrix $\langle\phi_i^E|\phi_i\rangle$.

VI. 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 $\gamma \leq \delta$.

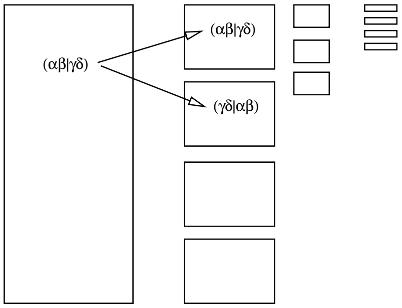

FIG. 2. The subsequent splitting of the integral file.

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 halftransfored 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 transformes 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.

VII. 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 desingned 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 VII C). All flavours of dressing may be chosen to designe 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: convengence 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 VII A
- CALPHP: calculate the real expectation value $\langle\Psi|\mathbf{H}|\Psi\rangle$, not only the variational energy

$$E = \sum_I c_I \langle\Phi_0|\mathbf{H}|\Phi_I\rangle \qquad .$$

- BANDSTructure: calculate correlated orbital energies through perturbation theory (see section **??**).
- 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

$$\gamma(\vec{\mathrm{x}},\vec{\mathrm{x}}') \;=\; N\int d^3x_2\ldots d^3x_n\,\Psi(\vec{\mathrm{x}},\vec{\mathrm{x}}_2,\ldots,\vec{\mathrm{x}}_n)\Psi(\vec{\mathrm{x}}',\vec{\mathrm{x}}_2,\ldots,\vec{\mathrm{x}}_n) \tag{3}$$

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

$$\gamma(\vec{\mathrm{x}},\vec{\mathrm{x}}') \;=\; 2\sum_{i\in occ}\phi_i(\vec{\mathrm{x}})\phi_i(\vec{\mathrm{x}}') \tag{4}$$

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

$$\begin{aligned}
\gamma_{ij} &= \int d^3x\,d^3x'\,\phi_i(\vec{\mathrm{x}})\gamma(\vec{\mathrm{x}},\vec{\mathrm{x}}')\phi_j(\vec{\mathrm{x}}') \\
&= \sum_{\alpha\beta} c_{\alpha\,i}c_{\beta\,j}\int d^3x\,d^3x'\,\chi_\alpha(\vec{\mathrm{x}})\gamma(\vec{\mathrm{x}},\vec{\mathrm{x}}')\chi_\beta(\vec{\mathrm{x}}') \\
&= \sum_{\alpha\beta}\sum_{\beta\delta}\sum_{k\in occ} c_{\alpha\,i}c_{\beta\,j}c_{\gamma\,k}c_{\delta\,k}\left(\int d^3x\chi_\alpha(\vec{\mathrm{x}})\chi_\gamma(\vec{\mathrm{x}})\right)\left(\int d^3x'\chi_\beta(\vec{\mathrm{x}}')\chi_\delta(\vec{\mathrm{x}}')\right) \\
&= \sum_{\alpha\beta} c_{\alpha\,i}c_{\beta\,j}(S\,P\,S)_{\alpha\beta}
\end{aligned} \tag{5}$$

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

$$\gamma_{\alpha\beta} \;=\; \left(S\left(\sum_i P^i\right)S\right)_{\alpha\beta} \tag{6}$$

This matrix is transformed to molecular orbitals and diagonalized.

Much simpler is to construct the density matrix directly in orthogonal molecular orbitals as we have to sum only occupation numbers multiplied with expansion coefficients, and overlap matrix elements are zero or one.

We transform the density matrix in AOs to occupation numbers and natural orbitals via

$$\begin{aligned} P_{ij} &= \sum_{k=1}^{N} n_k \delta_{ik}\delta_{jk} = \sum_{k=1}^{N} n_k S_{ik} S_{jk} \\ &= \sum_{k=1}^{N} n_k \sum_{\alpha\beta\gamma\delta} c_{\alpha i} c_{\beta j} c_{\gamma k} c_{\delta k} S_{\alpha\gamma} S_{\beta\delta} \\ &= \sum_{\alpha\beta}\left(\sum_\gamma S_{\alpha\gamma} c_{\alpha i}\right) P_{\gamma\delta}\left(\sum_\delta S_{\beta\delta} c_{\beta j}\right) \end{aligned} \tag{7}$$

Proof that the electron number is conserved:

$$\begin{aligned} N_{\text{el}} &= \sum_{i=1}^{N} n_i = \sum_{i,j=1}^{N} S_{ij} P_{ij} \\ &= \sum_{ij} \sum_{\alpha\beta\gamma\delta\mu\lambda} c_{\alpha i} c_{\beta j} c_{\gamma i} c_{\delta j} S_{\alpha\beta} S_{\gamma\lambda} S_{\delta\mu} S_{\alpha\beta} P_{\mu\lambda} \\ &= \sum_{\mu\lambda} P_{\mu\lambda} \sum_{ij} \sum_{\alpha\beta\gamma\delta} c_{\gamma i} S_{\gamma\lambda} \left(c_{\alpha i} S_{\alpha\beta} c_{\beta j}\right) S_{\delta\mu} c_{\delta j} \\ &= \sum_{\mu\lambda} P_{\mu\lambda} \left(\sum_{ij} S_{\lambda i} S_{ij} S_{j\mu}\right) = \sum_{\mu\lambda} P_{\mu\lambda} S_{\mu\lambda} \end{aligned} \tag{8}$$

B. 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

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

becomes

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

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 theory[1], 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 I. Different CEPA dressings $\Delta_{\rm ij}^{\rm ab}$ to address the variety of CEPA methods within the same algebra. For CEPA–2 the quadriexcited EPV determinants are explicitely 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	$-\langle\Phi_{\rm ij}^{\rm ab}\vert\mathbf{H}\vert\Phi_{\rm ijij}^{\rm abab}\rangle\, c_{\rm ij}^{\rm ab} \;= -\langle\Phi_0\vert\mathbf{H}\vert\Phi_{\rm ij}^{\rm ab}\rangle\, c_{\rm ij}^{\rm ab}$
CEPA-2	$-\sum_{\rm cd}\langle\Phi_{\rm ij}^{\rm ab}\vert\mathbf{H}\vert\Phi_{\rm ijij}^{\rm abcd}\rangle\, c_{\rm ij}^{\rm cd} \;\approx -\sum_{\rm cd}\langle\Phi_0\vert\mathbf{H}\vert\Phi_{\rm ij}^{\rm cd}\rangle\, c_{\rm ij}^{\rm cd} \;=\; -{\rm e(i,j)}$
CEPA-3	$-\sum_{\rm kcd}\langle\Phi_0\vert\mathbf{H}\vert\Phi_{\rm ik}^{\rm cd}\rangle\, c_{\rm ik}^{\rm cd} - \sum_{\rm kcd}\langle\Phi_0\vert\mathbf{H}\vert\Phi_{\rm kj}^{\rm cd}\rangle\, c_{\rm kj}^{\rm cd} + \sum_{\rm cd}\langle\Phi_0\vert\mathbf{H}\vert\Phi_{\rm ij}^{\rm cd}\rangle\, c_{\rm ij}^{\rm cd}$ $= \; -{\rm e(i)}-{\rm e(j)}+{\rm e(i,j)}$
(SC)^{2}CI	$-\sum_{\rm EPV(i,j,a,b)}\langle\Phi_0\vert\mathbf{H}\vert\Phi_{\rm kl}^{\rm cd}\rangle\, c_{\rm kl}^{\rm cd}$
CISD	$-E_{\rm Corr} = \underbrace{-\sum_{\rm non-EPV(i,j,a,b)}\langle\Phi_0\vert\mathbf{H}\vert\Phi_{\rm kl}^{\rm cd}\rangle\, c_{\rm kl}^{\rm cd}}_{\rm unlinked\ diagrams} - \sum_{\rm EPV(i,j,a,b)}\langle\Phi_0\vert\mathbf{H}\vert\Phi_{\rm kl}^{\rm cd}\rangle\, c_{\rm kl}^{\rm cd}$

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.

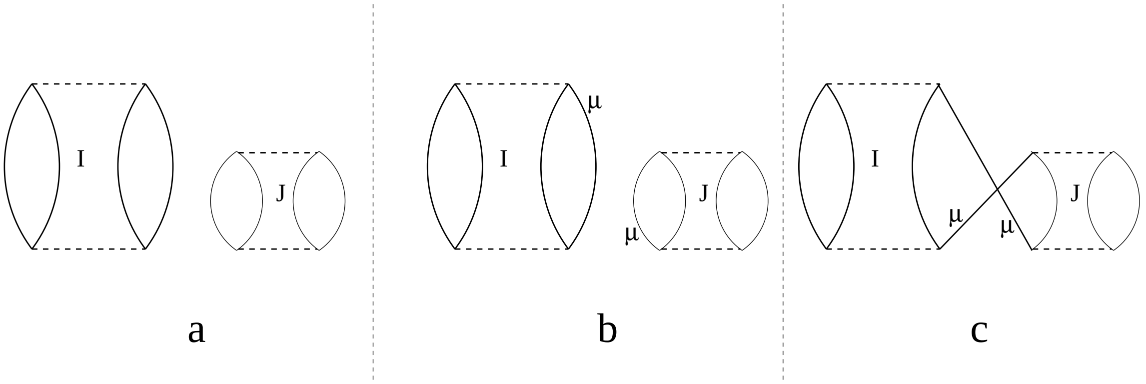

FIG. 3. Unlinked diagrams: a) true unlinked diagram without any common index in excitation I and excitation J; b) unlinked diagram with common index μ; c) the same, but drawn linked. The same level of the interaction line indicates the sum of two diagrams, one with I being the first excitation, and one with J being the first excitation.

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

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 $\langle J|\mathbf{H}|I+J\rangle = \langle 0|\mathbf{H}|I\rangle = H_{0I}, \quad \langle I|\mathbf{H}|I+J\rangle = \langle 0|\mathbf{H}|J\rangle = H_{0J},$ $E_{I+J} - E_0 = (E_I - E_0) + (E_J - E_0)$ 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 elemets $c_I\; H_{0I}$ 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 II. Different averaged dressings leading to ACPF and AQCC

ACPF	$-\frac{2}{n_\mathrm{e}}E_\mathrm{Corr}$
AQCC	$-E_\mathrm{Corr}\left(1 - \frac{(n_\mathrm{e}-2)(n_\mathrm{e}-3)}{n_\mathrm{e}(n_\mathrm{e}-1)}\right)$
AQCC-v	$-E_\mathrm{Corr}\left(1 - \frac{(n_\mathrm{e}-2)(n_\mathrm{e}-3)}{n_\mathrm{e}(n_\mathrm{e}-1)}\,\frac{(n_\mathrm{v}-2)(n_\mathrm{v}-3)}{n_\mathrm{v}(n_\mathrm{v}-1)}\right)$

n_e: electrons; n_v: virtual orbitals

C. 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

$$\begin{aligned} \sum_I H_{0I}\, c_I &= \sum_I E_I = E_{Corr} \\ H_{0I} + \;(H_{II} - H_{00})\, c_I &= 0 \end{aligned}$$

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 catastrophy 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 $\Phi_{\rm ij}^{\rm ab}$. This matrix may either be diagonalized in an eigenvalue problem, or it may be considered as as 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:

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

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

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

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)^{2}CI 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)^{2}CI, 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	same as before	2×2 rotations
CEPA − 3		
(SC)^{2}CI		
IC égoïste	$-E_I$	2×2 rotations

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

The program is integral-driven, based on the graphical approach to perturbation theory.