DFT calculations using Exact Exchange Formalism (EXX)

Session E6

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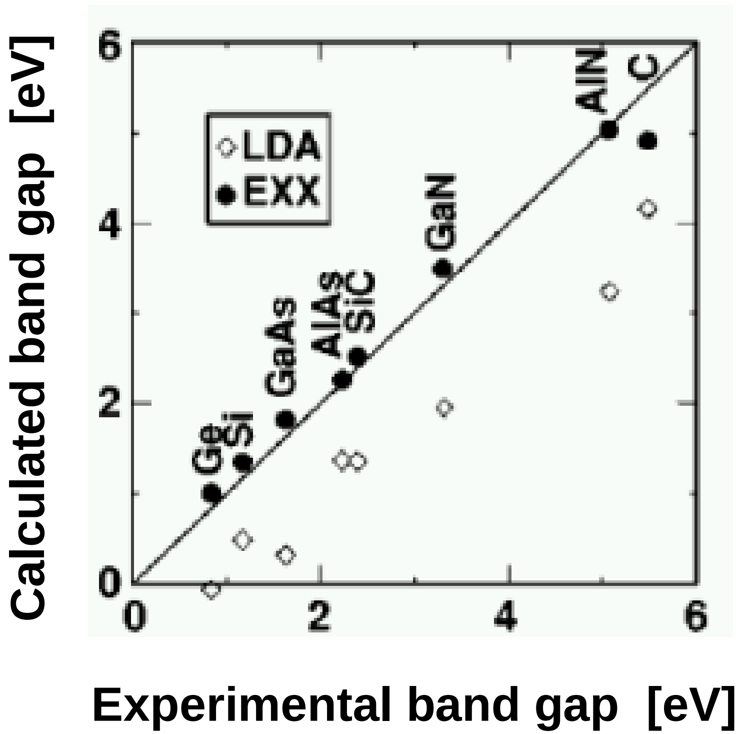
Why EXX formalism?



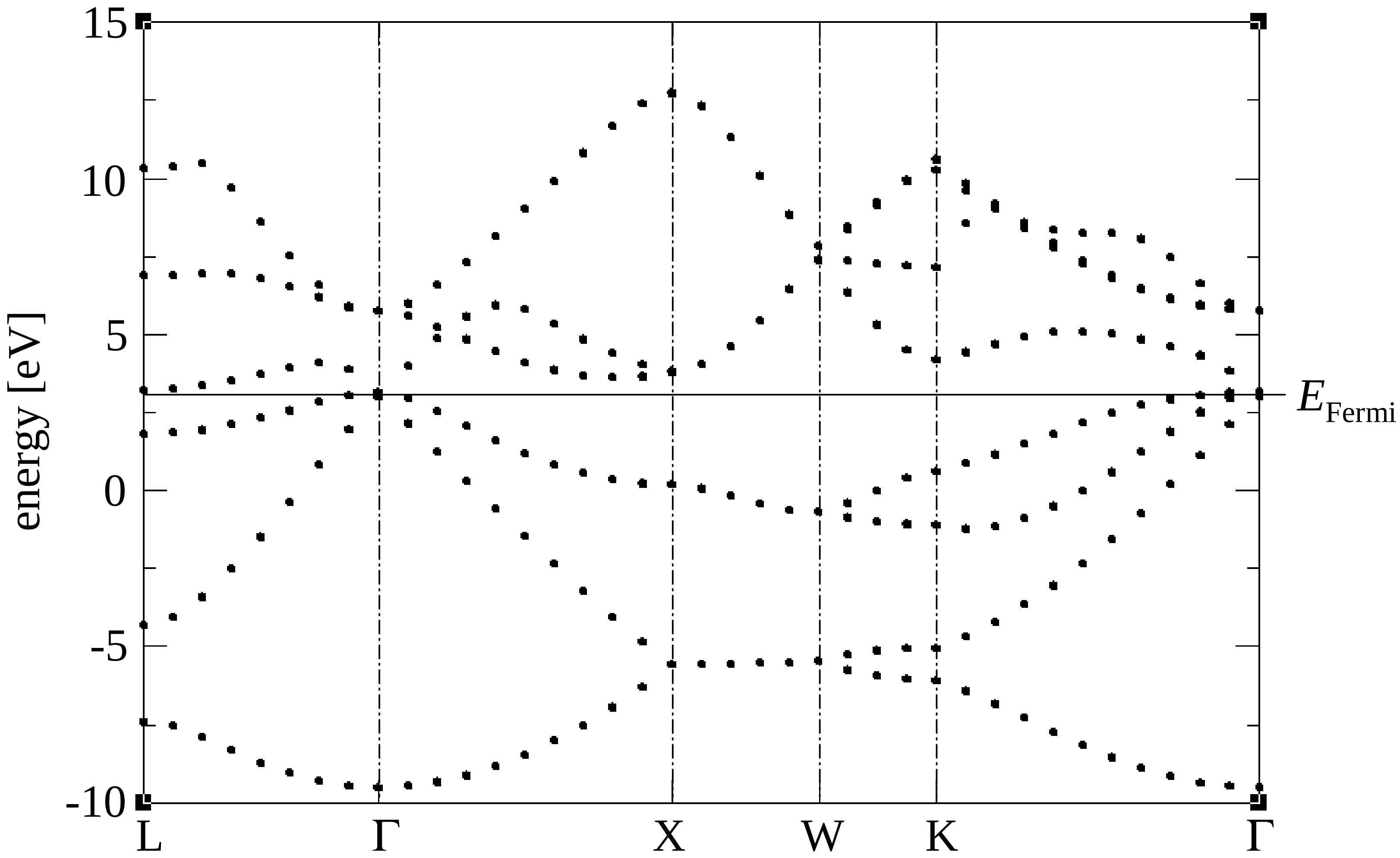
Source: M. Städele, M. Moukara, J.A. Majewski, P. Vogl, and A. Görling, *Phys. Rev. B* **59**, 10031 (1999)

Deficiencies of LDA / GGA:

- band gaps of semiconductors systematically underestimated
- wrong long range behaviour of the one-electron potential of finite systems ($\sim e^{-\alpha r}$ instead $\sim -1/r$)
- Experimentally stable negative ions are predicted to be unstable (e.g. H^-, O^-, F^-).

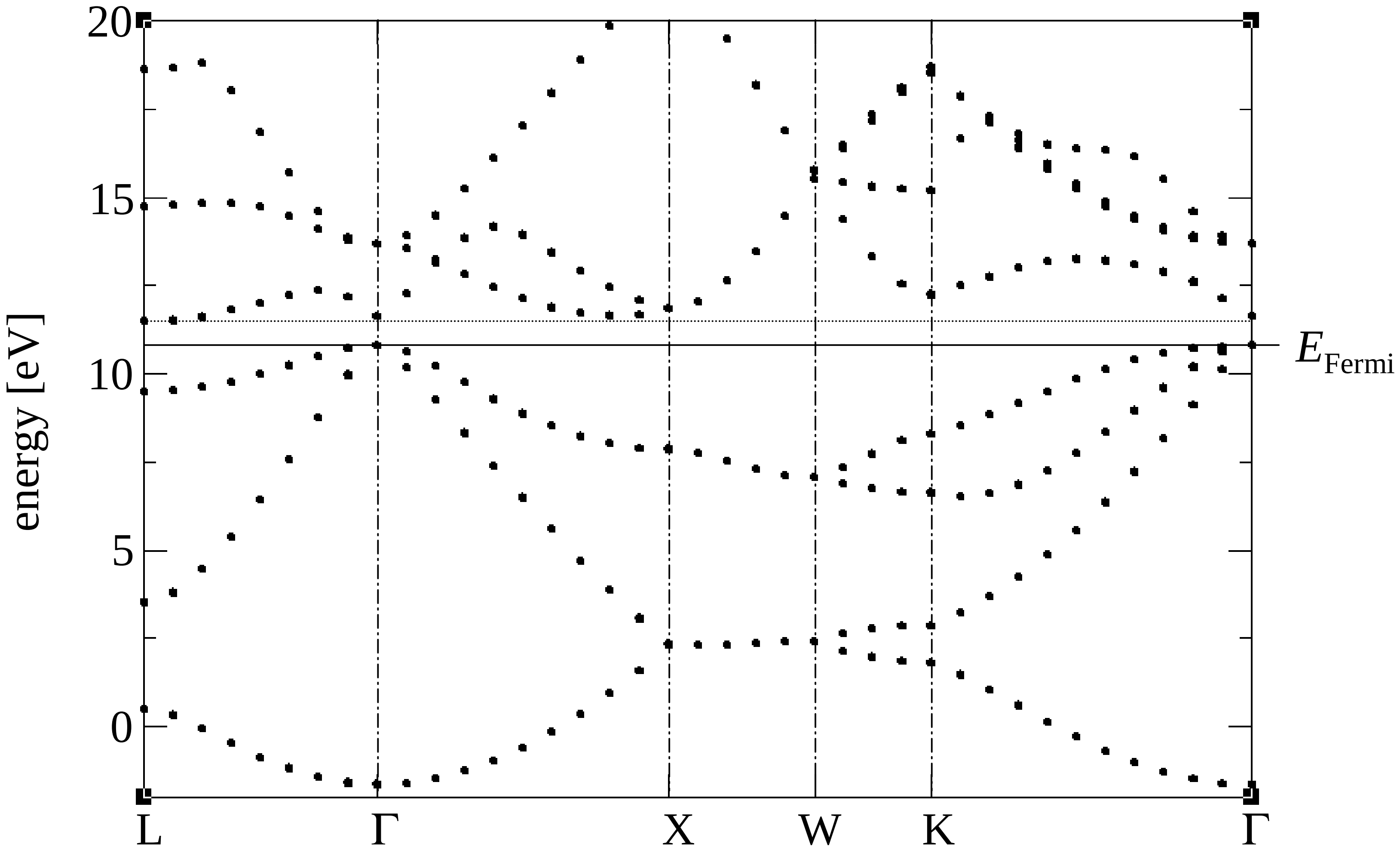
EXX formalism overcomes these deficiencies!

Ge : bandstructure in LDA



Ge: In LDA a bandgap of 0 eV is obtained!

Ge : bandstructure in EXX



Ge: In EXX one obtains a bandgap of 0.68 eV!
(Experimental gap: 0.66 eV)

Accessing the EXX potential

Problem of LDA / GGA: **contains unphysical electronic self-interaction**

Hartree-Fock (HF)-formalism $\rightarrow$ **complete cancellation of self-interaction:**

$$E^{\mathrm{x}}[\rho](\mathbf{r}) := -\frac{1}{2}\sum_{i,j}^{\mathrm{occ}} \delta_{\sigma_i \sigma_j} \int \frac{\phi_i^*(\mathbf{r})\phi_j^*(\mathbf{r}')\phi_i(\mathbf{r}')\phi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \mathrm{d}^3 r\, \mathrm{d}^3 r'$$

Applying the chain rule leads to the EXX-potential:

$$\mathrm{v}^{\mathrm{EXX}}[\rho](\mathbf{r}) := \frac{\delta E^{\mathrm{x}}[\rho]}{\delta\rho(\mathbf{r})} = \sum_i^{\mathrm{occ}} \int \mathrm{d}^3 r' \int \mathrm{d}^3 r'' \left(\frac{\delta E^{\mathrm{x}}[\{\phi_k\}]}{\delta\phi_i^*(\mathbf{r}')} \frac{\delta\phi_i^*(\mathbf{r}')}{\delta \mathrm{v}^{\mathrm{KS}}(\mathbf{r}'')} + \mathrm{c.c.} \right) \underbrace{\frac{\delta \mathrm{v}^{\mathrm{KS}}(\mathbf{r}'')}{\delta\rho(\mathbf{r})}}$$

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$$\frac{\delta \mathrm{v}^{\mathrm{KS}}(\mathbf{r})}{\delta\rho(\mathbf{r}')} = \chi^{-1}(\mathbf{r},\mathbf{r}') \quad \rightarrow$$ inverse of linear response:

$$\chi(\mathbf{G},\mathbf{G}') = \frac{4}{\Omega}\sum_i^{\mathrm{occ}}\sum_j^{\mathrm{unocc}}\sum_{\mathbf{k}} \frac{\langle i\mathbf{k}|e^{-\mathrm{i}\mathbf{G}\mathbf{r}}|j\mathbf{k}\rangle\langle j\mathbf{k}|e^{+\mathrm{i}\mathbf{G}'\mathbf{r}}|i\mathbf{k}\rangle}{\varepsilon_{i\mathbf{k}} - \varepsilon_{j\mathbf{k}}}$$

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$$\frac{\delta \mathrm{v}^{\mathrm{KS}}(\mathbf{r})}{\delta \rho(\mathbf{r}')} = \chi^{-1}(\mathbf{r},\mathbf{r}')$$ → inverse of linear response:

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⇒ parameter `chiEcut` in the `basis`{…} group of “`input.sx`”

DFT-EXX calculations:

Structure of the system under consideration

Self-consistent LDA / GGA run

→ initial charge density for EXX run

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Structure of the system under consideration

Self-consistent LDA / GGA run

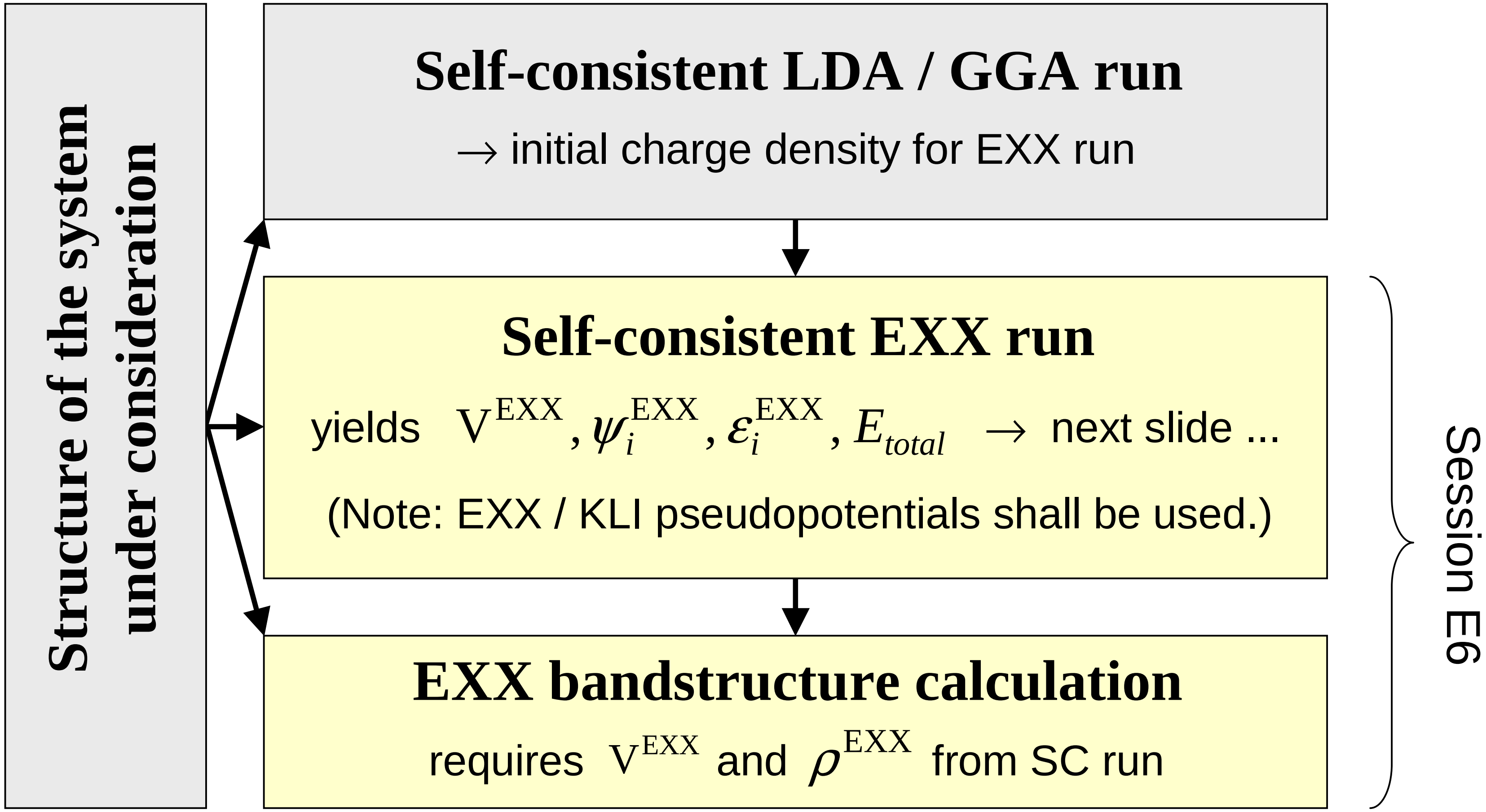
$\rightarrow$ initial charge density for EXX run

Self-consistent EXX run

yields $\mathrm{V}^{\mathrm{EXX}}, \psi_i^{\mathrm{EXX}}, \varepsilon_i^{\mathrm{EXX}}, E_{total}$ $\rightarrow$ next slide ...

(Note: EXX / KLI pseudopotentials shall be used.)

DFT-EXX calculations:



Self-consistent cycle of an EXX run

EXX_LOOP {...}

Self-consistent cycle of an EXX run

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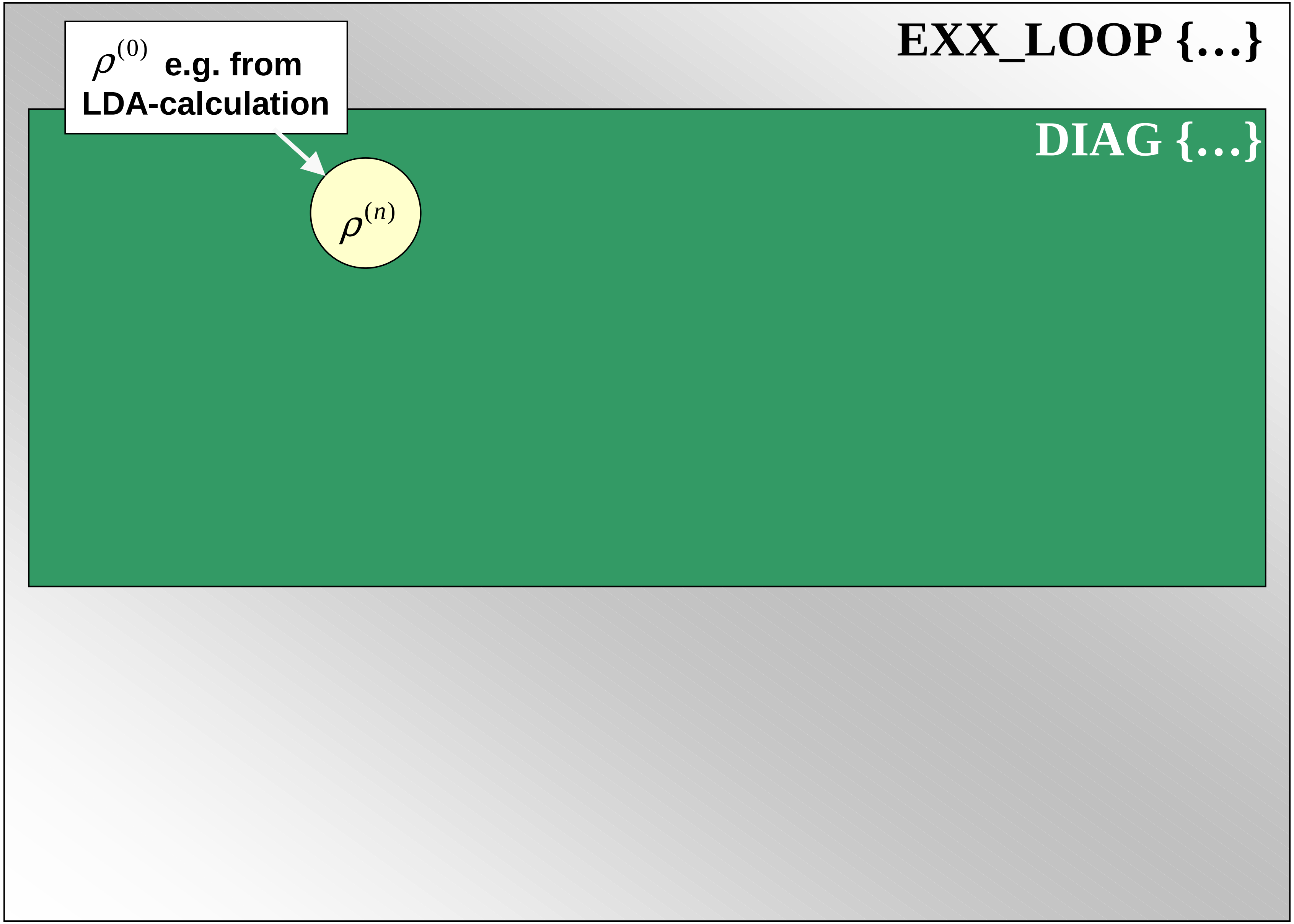

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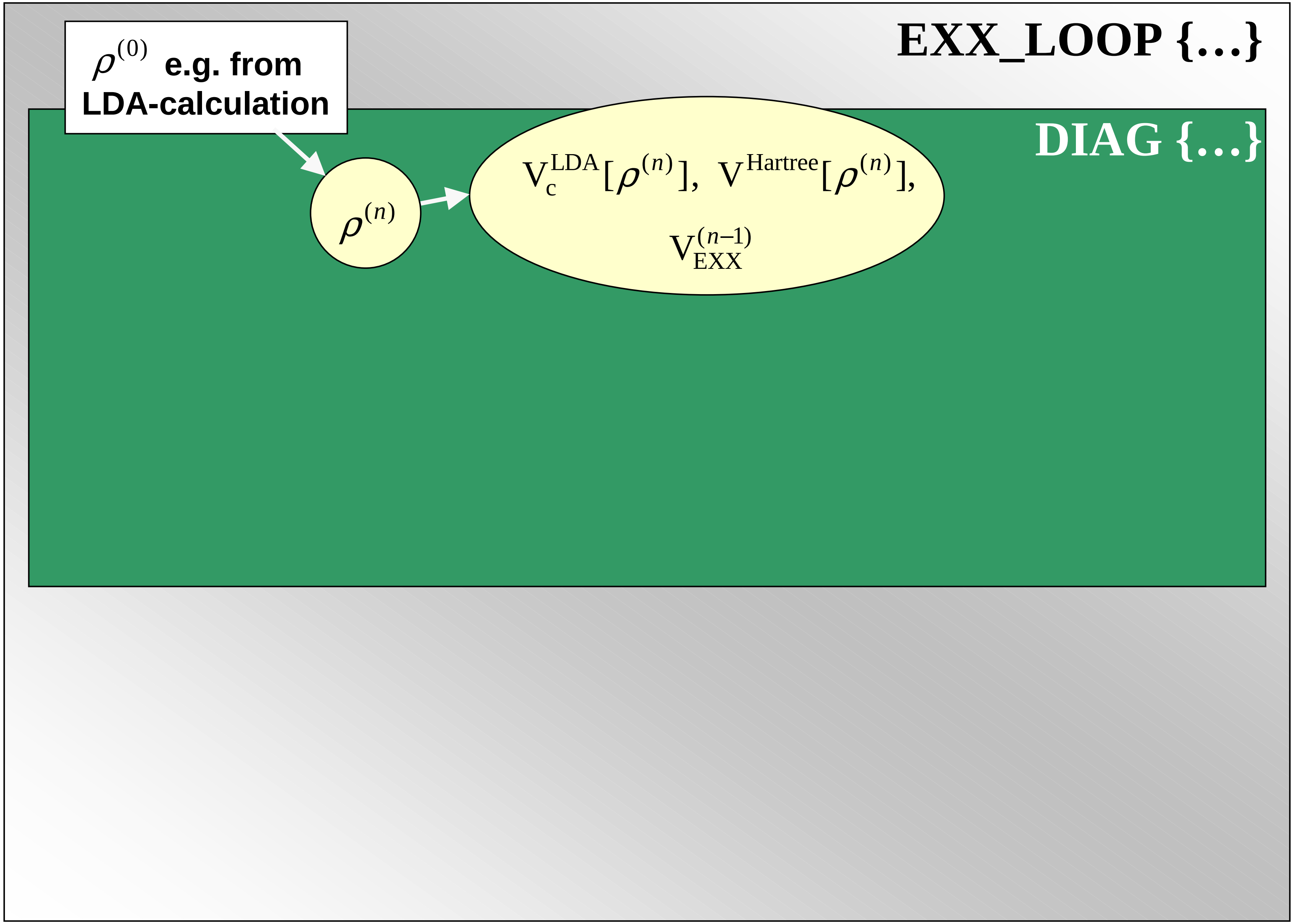

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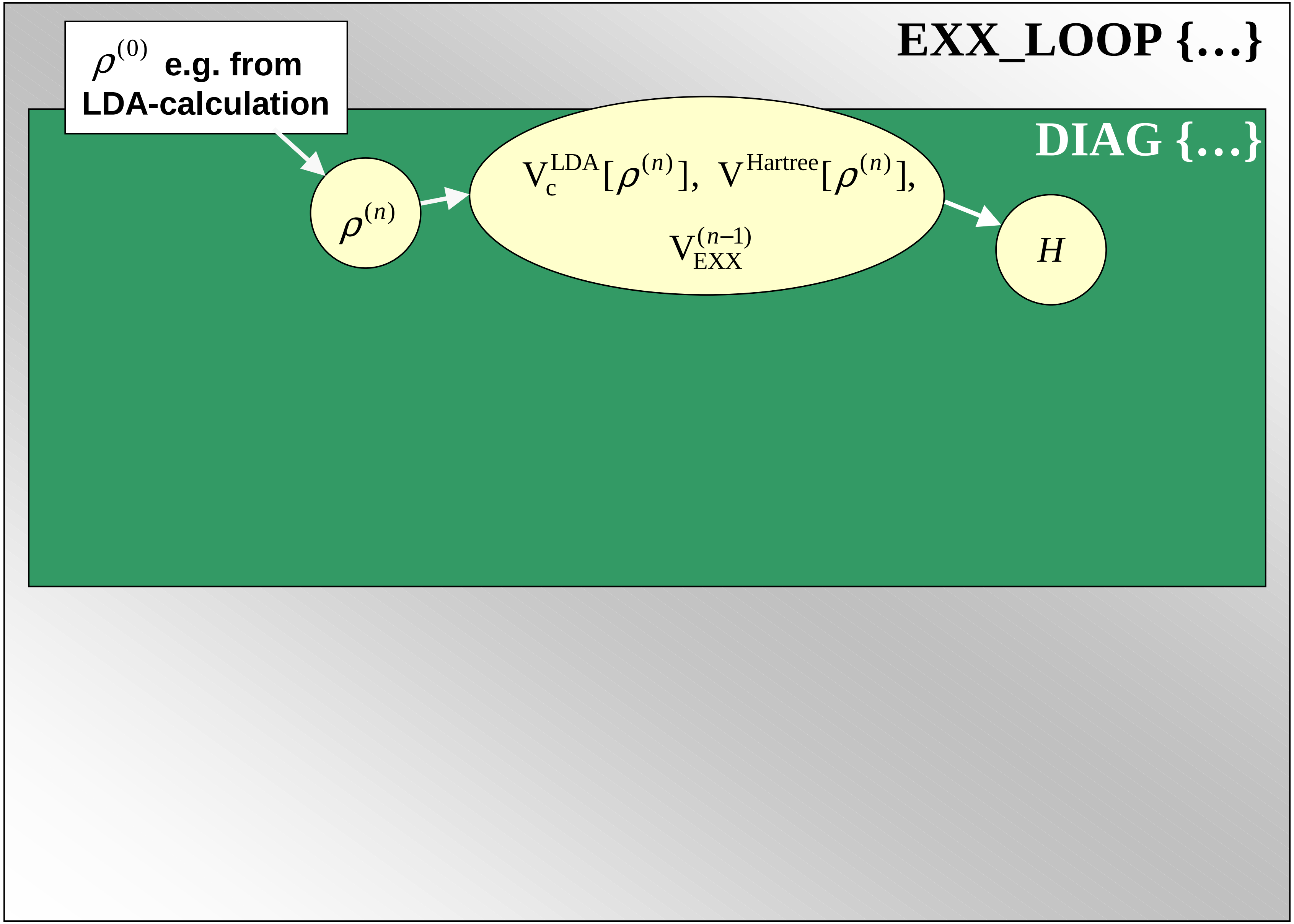

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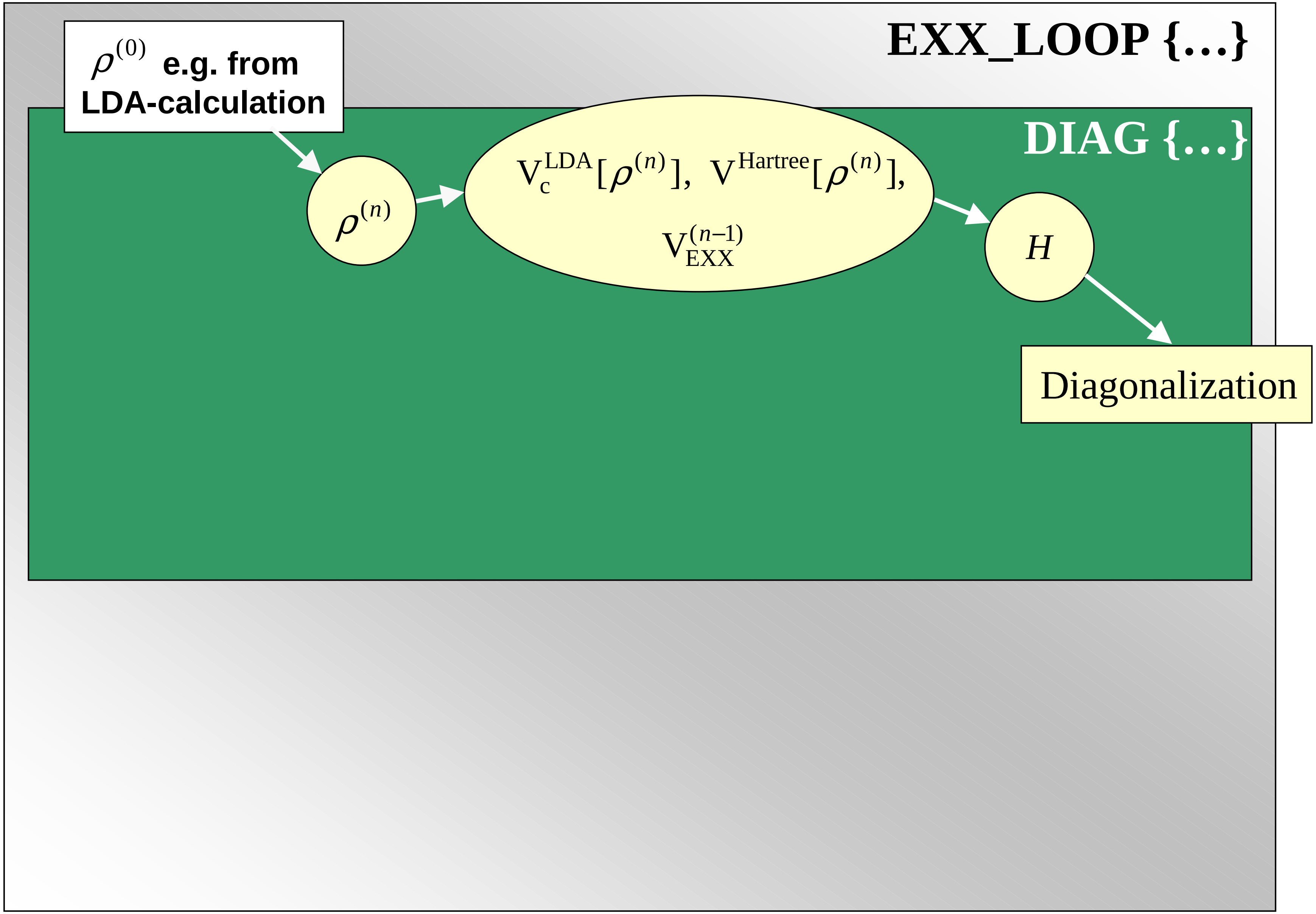

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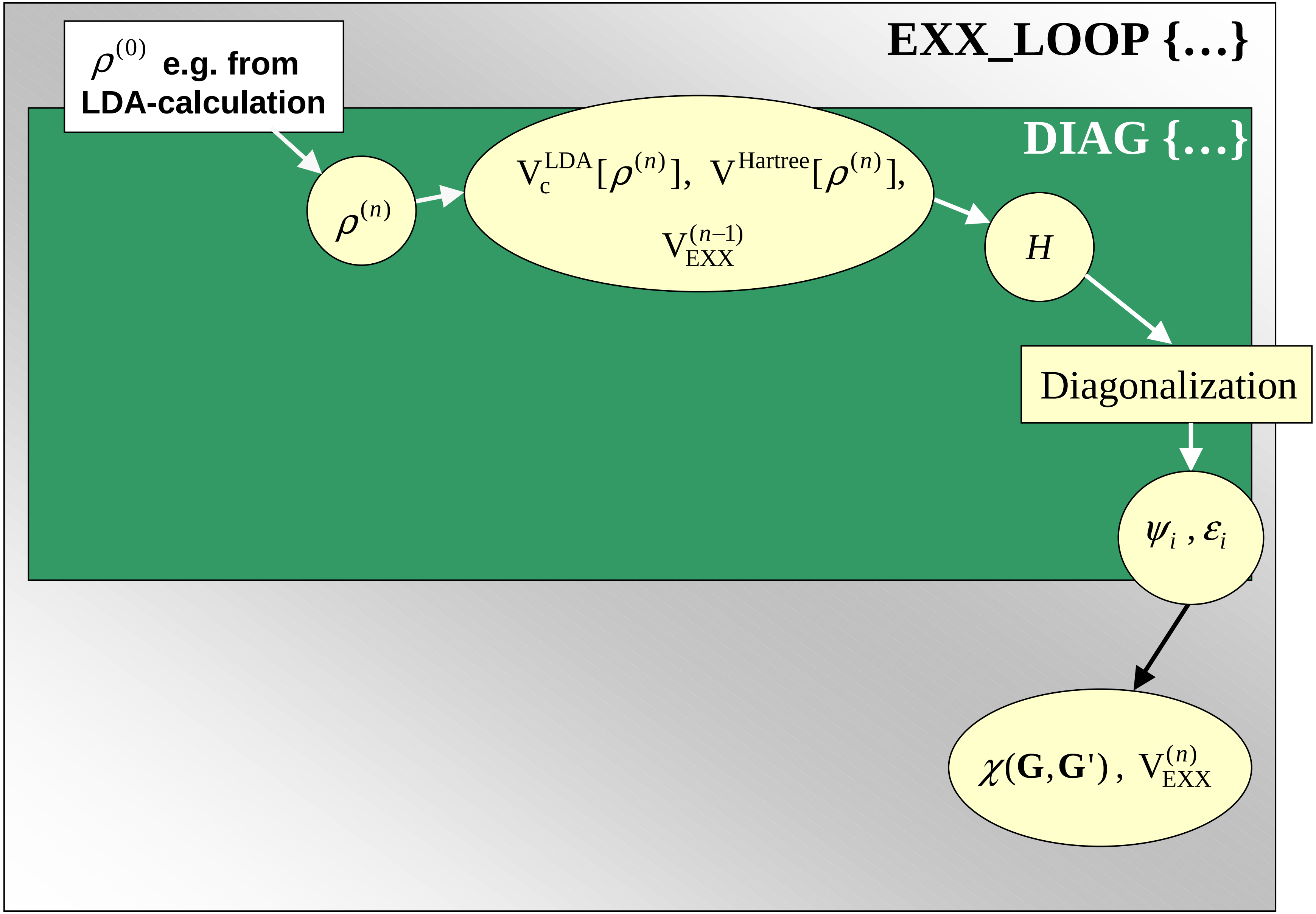

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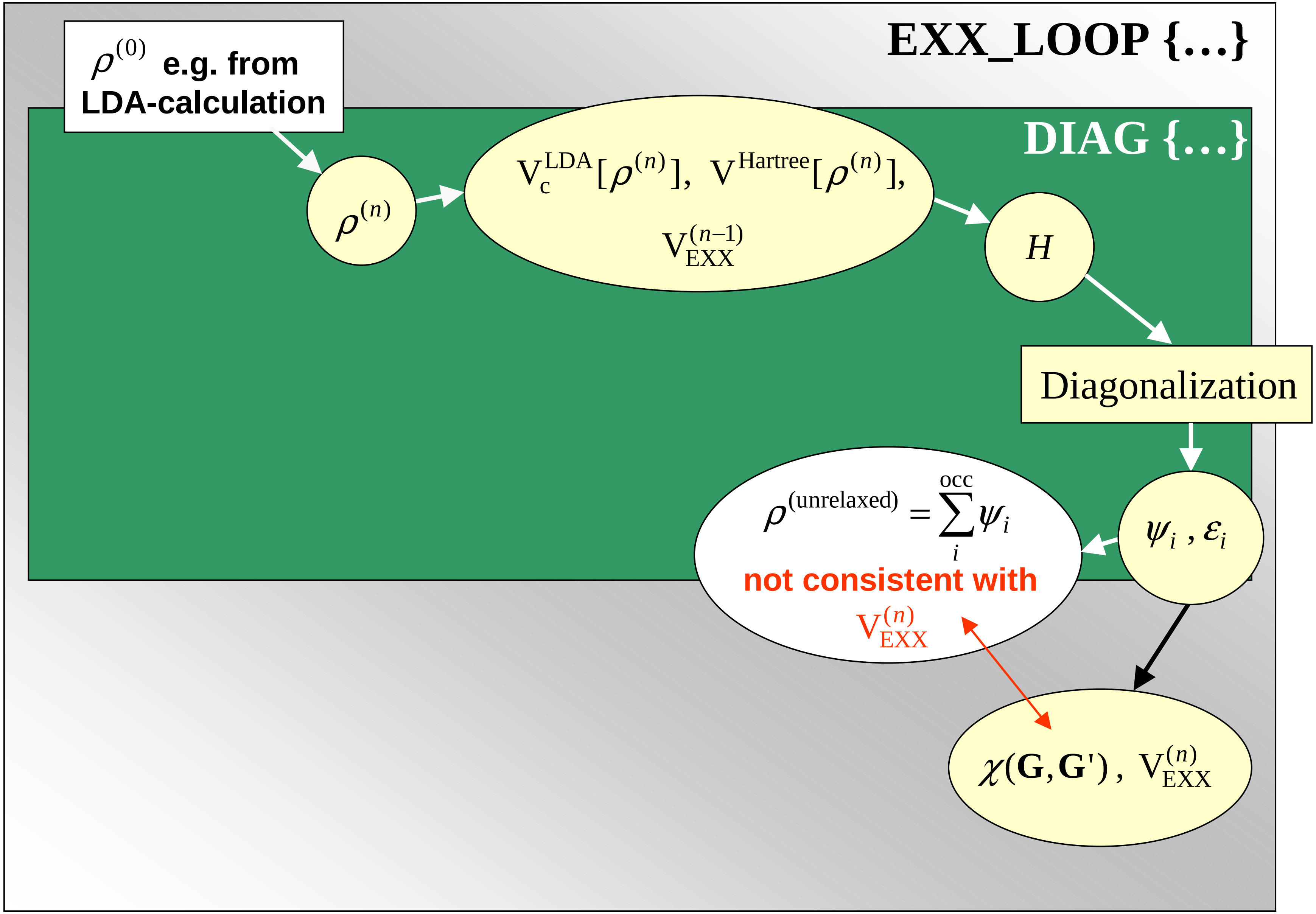

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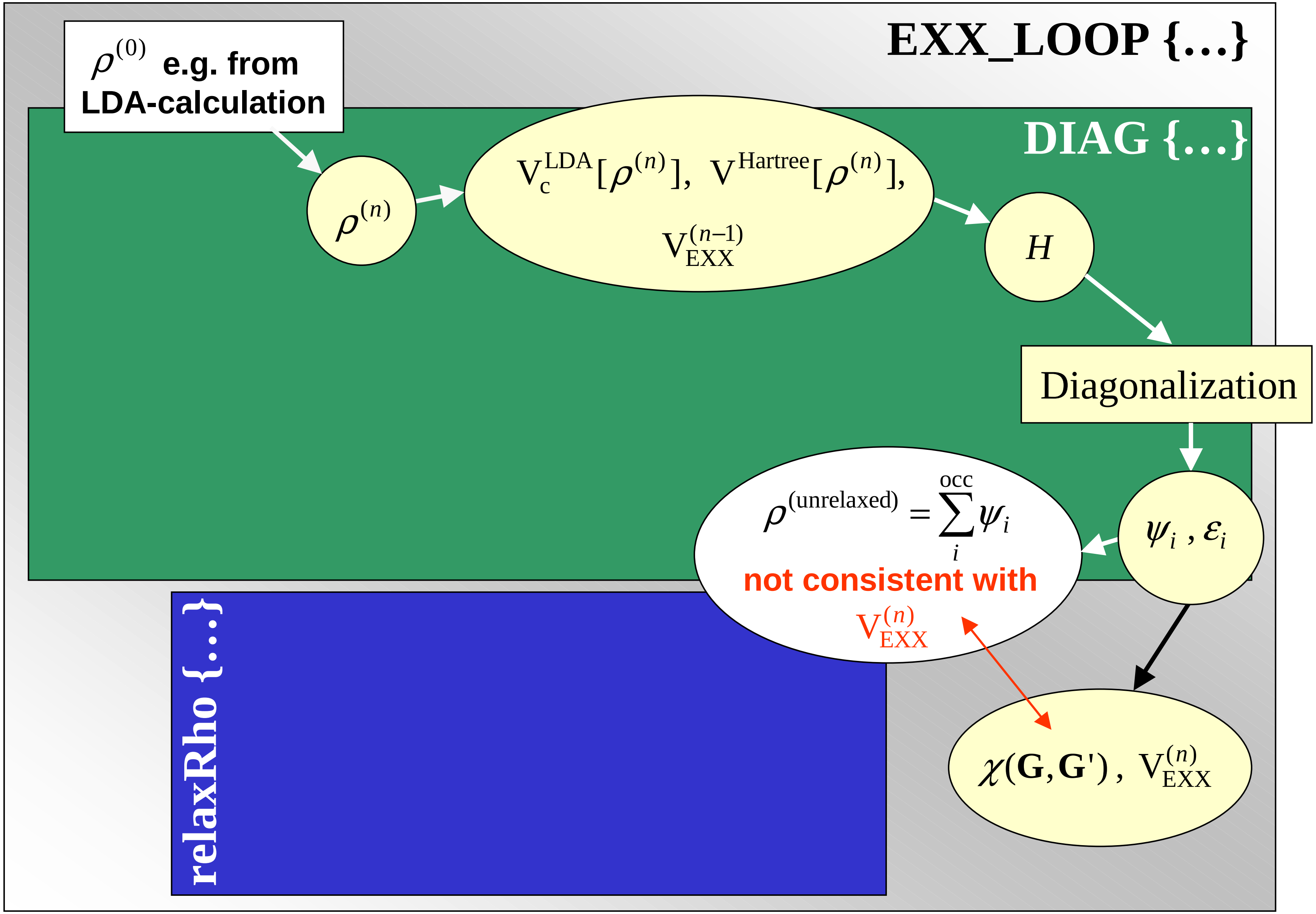

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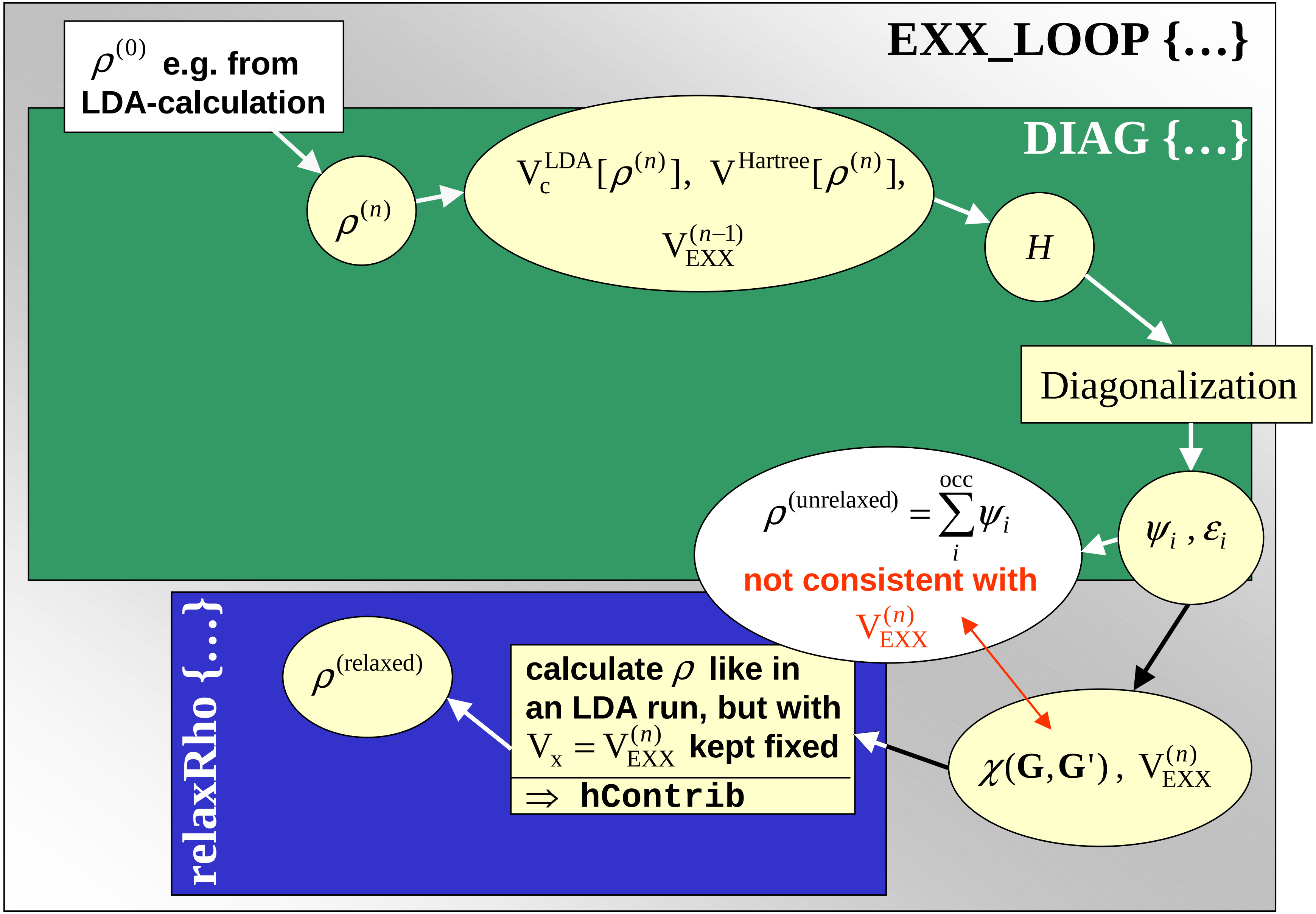

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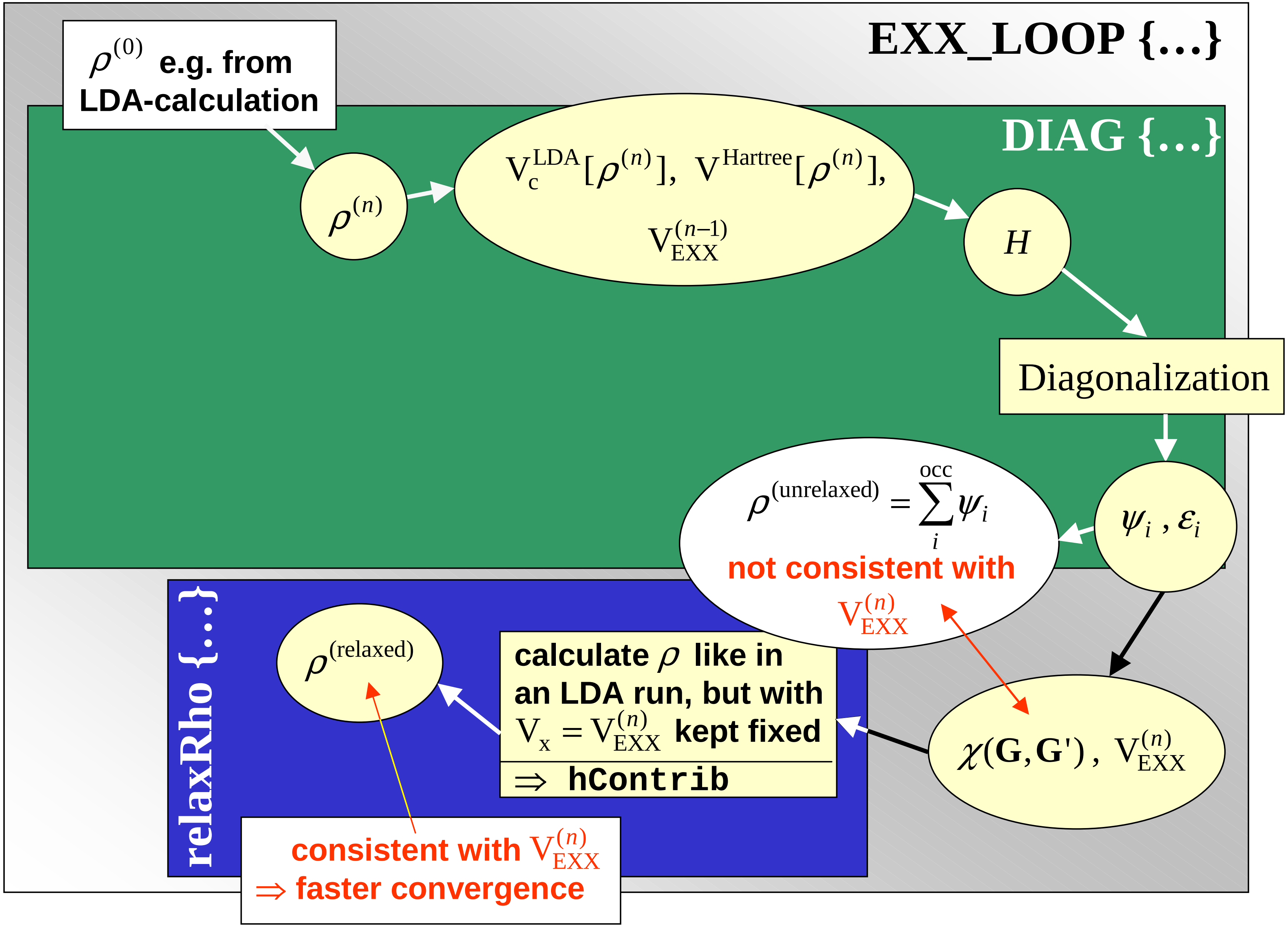

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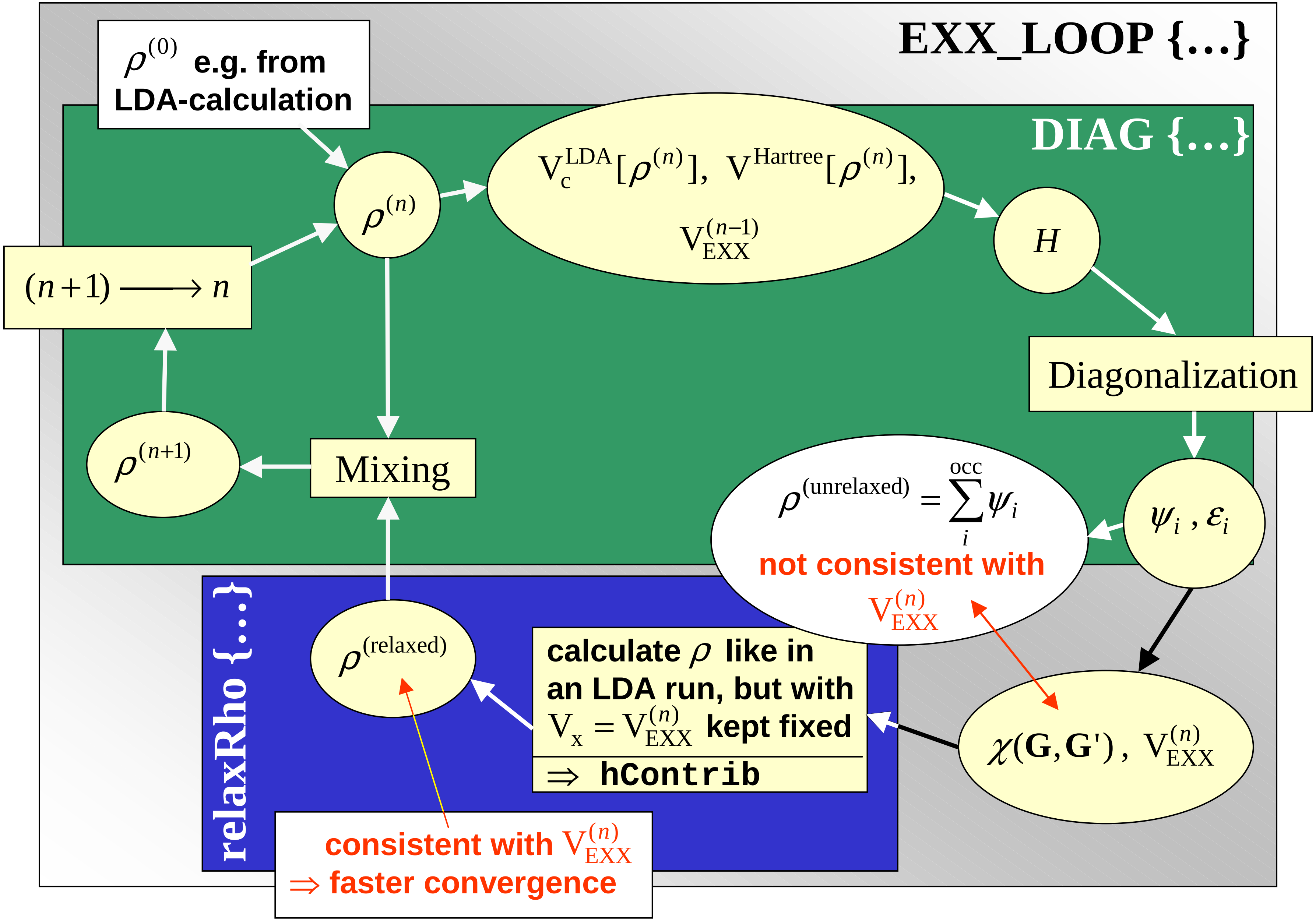

Input file for a self-consistent EXX run (1)

Don't forget to use KLI / EXX pseudopotentials!

```
...
species_1 = <species/ga-kli-ham.sx>;
...
...
basis {
   eCut    = 15;  //Ry
   chiEcut =  9;  //Ry
   ...
}

Hamiltonian {
   ...
   xc  =  EXX;
}

initialGuess {
   waves = { file =  "../LDA_or_GGA_run/waves.sxb"; }
   rho   = { fromWaves; }
}
...
```

input.sx

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Don't forget to use KLI / EXX pseudopotentials!

A further cut-off energy is required that controls how many elements will be regarded for inverting $\chi(\mathbf{G},\mathbf{G}')$.

input.sx

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```

Don't forget to use KLI / EXX pseudopotentials!

A further cut-off energy is required that controls how many elements will be regarded for inverting $\chi(\mathbf{G},\mathbf{G}')$.

Read in wavefunctions obtained from a previous LDA or GGA run to start with a good initial guess. The LDA / GGA run must have had the same cut-off energy `eCut`.

input.sx

Input file for a self-consistent EXX run (2)

```
...
main {
   EXX_LOOP {
      maxSteps          = 15;
      dEnergy           = 1e-5;
      writeControl      = EXX_WRITE_VXR + EXX_WRITE_VXG;
      DIAG {
         useFullBasis;
         maxSteps       = 1;
         printSteps     = 1;
         mixingMethod = LINEAR;
         rhoMixing      = 0.3;
      }
      relaxRho {
         DIIS_CCG {
            hContrib   = CALC_ALL - CALC_V_X;
            ...
         }
      }
   }
}
```

Writes EXX potential to output file (along (1,1,1)-direction).

Input file for a self-consistent EXX run (2)

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      }
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         DIIS_CCG {
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            ...
         }
      }
   }
}
```

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EXX formalism needs also the unoccupied states.

Input file for a self-consistent EXX run (2)

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Writes EXX potential to output file (along (1,1,1)-direction).

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Any minimization method is possible.

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            ...
         }
      }
   }
}
```

Writes EXX potential to output file (along (1,1,1)-direction).

EXX formalism needs also the unoccupied states.

Any minimization method is possible.

Keeps the exchange potential untouched, but updates all other components of the Hamiltonian (*important !!*).

Input file for an EXX bandstructure run

```
...
species_1 = <species/ga-kli-ham.sx>;
...
...
basis {
   eCut     = 15;  //Ry
   kPoints { ... }
}

Hamiltonian {
   nEmptyStates = 4;
   xc           = READ_VXX;
   ...
}
...
...
```

input.sx

Again: Use KLI / EXX pseudopotentials.

`chiEcut` is no longer required in the `basis{...}` group.

Except for reading in the EXX potential there is no difference to a "normal" bandstructure calculation.

Input file for an EXX bandstructure run

```
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...
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}

Hamiltonian {
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   xc           = READ_VXX;
   ...
}
...
...
```

input.sx

Again: Use KLI / EXX pseudopotentials.

`chiEcut` is no longer required in the **`basis{...}`** group.

This tells the code to read in the EXX-potential obtained from a previous self-consistent EXX run (performed in the same directory).

Except for reading in the EXX potential there is no difference to a "normal" bandstructure calculation.

“duties”

01 GaAs: Self-consistent run / bandstructure x-potential: LDA , pseudopotential: LDA
02 GaAs: Self-consistent run / bandstructure x-potential: LDA , pseudopotential: KLI
03 GaAs: Self-consistent run / bandstructure x-potential: EXX , pseudopotential: KLI
04 GaAs: Self-consistent run / bandstructure x-potential: EXX , pseudopotential: LDA *Compare band-gap with result of 01 - 03* *to see the influence of the pseudopotential.*
05 GaAs: EXX and LDA - the *deformation potential* (lattice-constant vs. bandgap)

all combinations of
LDA / EXX x-potentials
and LDA / KLI pseudopotentials

optional tasks / “homework”

06 Ge: Selfconsistent run / bandstructure x-potential: LDA , pseudopotential: LDA
07 Ge: Self-consistent run / bandstructure x-potential: EXX , pseudopotential: KLI
08 + 09 GaAs + Ge: Compare x-potential in LDA (“vxr-lda.dat”) with EXX potential (“vxr-?.dat” with ? = A, B, C, … denoting the updates of the EXX potential).

Compare the band-gaps!