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## Outline

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### i. *Preliminaries*

Full theoretical background has been concatenated in a presentation available [here](#) and summarized below with references. The link to this presentation will denoted by [\[P\]](#) from now on. Another reference that will be often cited below is section II of [\[15\]](#).

We strongly advise the future users of the MESRA software to consult this reference and check the presentation before reading this theoretical introduction. For any question, please use the e-mail address in the *Contact* section of this web site, and a quick answer will be sent to you.

### ii. *Introduction*

The code uses a theoretical approach valid for any single-reference excited-state calculation method promoting one electron in total. This covers CIS, TDA, TDHF, TDDFT, BSE methods, and any method for which an auxiliary many-body wave function (AMBW) for the excited states has been assigned (like LR-CC, ADC, TDDFT for instance - see Ref. [14]). In practice, we have interfaced our code with Gaussian 03, 09 and 16, and with the Quantum Package, so the case of BSE, LR-CC, and ADC methods has not been directly addressed.

The outcome of the abovementioned excited-state calculation methods is an ensemble of objects and data. Among the objects, we are particularly interested in the so-called *one-particle difference density matrix* (1-DDM) and the *one-particle transition density matrix* (1-TDM). Their complete derivation is explained in a comprehensive fashion in Ref. [13].

Once these two matrices have been obtained, one can perform both qualitative and quantitative analyses of the electronic-structure reorganization induced by the transition. These analyses are divided in two parts: density-based strategies, and wave function-based strategies.

### iii. *Qualitative, density-based strategies*

For a qualitative picture of the transition, one has the possibility to produce a pair of one-particle functions, the so-called detachment and attachment (D/A) densities, respectively depicting the hole and the electron in the one-particle/one-hole model. The corresponding density matrices are obtained by diagonalizing the 1-DDM in the canonical space, according to the general scheme (*dau* keyword in MESRA) introduced in Ref. [3]. However, we have demonstrated, according to the structure of the matrices produced by the methods mentioned above (see Ref. [13]), that one could also produce the D/A density matrices without diagonalizing the 1-DDM (*daxy* keyword in MESRA). This is summarized in chapters II.3 and III.3 of the presentation referred above [P], where one can also find details about the original derivation of the D/A density matrices in section II.1.B.

The passage from a one-body reduced density matrix to the corresponding one-body density function is recalled in section II.A of Ref. [15], together with the relation between canonical and atomic spaces in this context. In particular, the case of Löwdin's symmetrically orthogonalized basis of orbitals is mentioned there.

Taking the difference between the attachment and detachment densities returns the one-particle difference density, i.e., the difference between the excited- and ground-state one-particle density. Its positive contributions, and the absolute value of its negative contributions, are respectively denoted  $n^+$  and  $n^-$  in the code, as in Sections II.1.A of presentation [P].

### iv. *Quantitative, density-based approaches*

Any quantity described in section II.1.C of presentation [P] has its derivation and meaning fully detailed in section II.C of Ref. [15] and can be obtained by using the MESRA code. For any pair of density functions, the vectorial quantities depicted in section II.1.D of presentation [P] can also be evaluated.

### v. *Practical evaluation of the density-based descriptors*

The density-based descriptors from section II.1.C of presentation [P] (section II.C of Ref. [15]) can be obtained by numerical integration (*qmini* keywords in MESRA, see User's manual) of Cartesian grids of points (Gaussian cube files, see User's manual), or by performing a detachment/attachment Population Analysis (PA), see section II.1.G in [P], and section II.D in [15]. The whole **DS** ( $x = 0$ ) to **SD** ( $x = 1$ ) and **SA** to **AS** spectrum can be scanned using the *scanpa* option.

### vi. *Relaxing the hole/particle pair*

If the hole/particle pair, i.e., the detached/attached charges, are relaxed using Handy's Z-vector method [2], this relaxation can be studied using the MESRA software as in section II.1.E in [P], and II.E in [15]. The density-based descriptors from paragraph iv above have been adapted to include the relaxation, as in section II.1.F of [P]. Again, these density-based descriptors can be evaluated using a numerical integration using the *qmnirlx* keyword or through a population analysis procedure using the *rlxypa* keyword. Note that an adiabatic connection of the Z-vector is possible using the *adiabz* keyword.

It is important to note that, since the  $\zeta^Z$  descriptor in Ref. [15] (equation 36) and in [P] (section II.1.E) can be viewed as the  $\chi$  feature applied to the Z-vector instead of the unrelaxed 1-DDM, it will be named " $\chi$ " in the MESRA output when using the *daz* or any *qmni* keyword. This is also true for  $\phi^Z$  in section II.1.E of [P], which will be simply labelled  $\phi$  in MESRA. When analyzing the relaxed detachment/attachment, i.e., the one obtained by diagonalizing the relaxed 1-DDM with the *dar* keyword, for the same reasons, it is the qCT metric from Le Bahers *et. al.* recalled in section II.1.E of [P] that are actually printed under the  $\chi$  and  $\zeta(+/-)$  label.

#### vii. *Qualitative, wave function-based strategies*

An orbital picture of electronic transitions is possible using transition orbitals. However, according to the excited-state computation scheme used, the definition of the relevant transition matrix differs. The general and original idea is the Natural Transition Orbitals (NTOs) analysis [5]. Their derivation is detailed in section II.2.B of [P].

##### vii.A *Projected-NTOs*

In practice, for TDDFT calculations with hybrid and range-separated hybrid xc-functionals one can use the so-called *projected*-NTOs ([9] and section III.3.A in [P]). This feature is available using the *pntos* or the *orbsxy* keyword in MESRA.

##### vii.B *Auxiliary Many-Body Wave Function for the electronic excited state*

An auxiliary many-body wave function for GGA-TDDFT excited states can be constructed using eq. (4.48) in Ref. [4], and the characteristic transition orbitals are the *a*NTOs (section III.3.B in [P], where *a* stands for *auxiliary*). This procedure is depicted in Chapter III.2 of [P]. Note that in CIS and TDA, the *p*NTOs and *a*NTOs are identical, and simply correspond to the NTOs. The computation of *a*NTOs in MESRA can be done using the *antos* or the *orbsxy* keyword. Note that, though the construction of such an auxiliary wave function is permitted upon the invertibility of the  $(A - B)$  matrix in TDDFT, it is a common use to bypass this criterion and to construct the auxiliary wave function without knowledge of the invertibility of  $(A - B)$  with hybrid xc-functionals for instance.

##### vii.C *Canonical transition orbitals*

Finally, a last scheme was proposed in III.3.C of [P], which consists in the construction of a transition matrix based on the relative weight of the canonical couples of orbitals. The transition orbitals originating from the singular value decomposition of such a transition matrix are called *Canonical Transition Orbitals* (CTOs [9]) and are depicted in section III.3.C of [P]. Again, when the TDHF or TDDFT de-excitations are quenched, leading to CIS and TDA schemes, the CTOs are identical to the *p*NTOs and *a*NTOs, and one simply speaks in terms of

Natural Transition Orbitals. CTOs can be computed using MESRA with the *ctos* or the *orbsxy* keyword.

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*References - Any green color text below is a direct link to the document web page.*

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[P] Molecular electronic-structure reorganization: analysis

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