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Representation of a molecular-electronic transition Reduced-density-matrix theory meets matrix perturbation theory

Thibaud Etienne
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Laboratoire
Physique et Chimie
Théoriques

I. HYPOTHESES

I. Hypotheses

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We consider a finite set of M molecular electronic excited states

$$S = \{|\psi_1\rangle, \ldots, |\psi_M\rangle\}$$

I. Hypotheses

Definition I.1. *Let* $\mathbf{A}$ *and* $\mathbf{B}$ *be* $m \times m$ *and* $n \times n$ *complex-valued matrices, respectively. The direct sum of* $\mathbf{A}$ *and* $\mathbf{B}$ *reads*

$$\mathbf{A} \oplus \mathbf{B} = \begin{pmatrix} \mathbf{A} & \mathbf{0}_{m\times n} \\ \mathbf{0}_{n\times m} & \mathbf{B} \end{pmatrix}.$$

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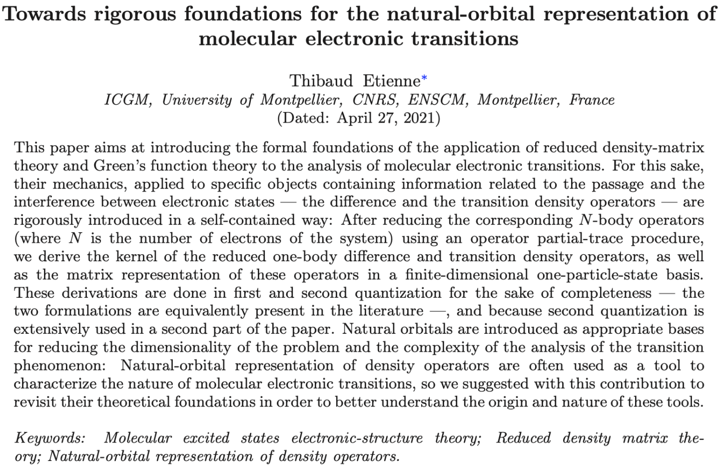
II. QUALITATIVE ANALYSIS

II.1 Natural orbitals – Generalities



Towards rigorous foundations for the natural-orbital representation of molecular electronic transitions

Thibaud Etienne*
ICGM, University of Montpellier, CNRS, ENSCM, Montpellier, France

(Dated: April 27, 2021)

This paper aims at introducing the formal foundations of the application of reduced density-matrix theory and Green's function theory to the analysis of molecular electronic transitions. For this sake, their mechanics, applied to specific objects containing information related to the passage and the interference between electronic states — the difference and the transition density operators — are rigorously introduced in a self-contained way: After reducing the corresponding N-body operators (where N is the number of electrons of the system) using an operator partial-trace procedure, we derive the kernel of the reduced one-body difference and transition density operators, as well as the matrix representation of these operators in a finite-dimensional one-particle-state basis. These derivations are done in first and second quantization for the sake of completeness — the two formulations are equivalently present in the literature —, and because second quantization is extensively used in a second part of the paper. Natural orbitals are introduced as appropriate bases for reducing the dimensionality of the problem and the complexity of the analysis of the transition phenomenon: Natural-orbital representation of density operators are often used as a tool to characterize the nature of molecular electronic transitions, so we suggested with this contribution to revisit their theoretical foundations in order to better understand the origin and nature of these tools.

Keywords: Molecular excited states electronic-structure theory; Reduced density matrix theory; Natural-orbital representation of density operators.

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arxiv.org/abs/2104.11947

II.1 Natural orbitals – Generalities

We set the one-electron reduced *difference* ($\hat{\Delta}$) and *transition* ($\hat{\mathrm{T}}$) density operators:

$$\forall m \in [\![1, M]\!],\ \hat{\Delta}_1^{0\to m} := \sum_{i=1}^{N} \mathrm{tr}_{[\![1,N]\!]\setminus\{i\}} \left(|\psi_m\rangle \langle\psi_m| - |\psi_0\rangle \langle\psi_0| \right),$$

$$\hat{\mathrm{T}}_1^{0\to m} := \sum_{i=1}^{N} \mathrm{tr}_{[\![1,N]\!]\setminus\{i\}} \left(|\psi_m\rangle \langle\psi_0| \right).$$

$\mathcal{C} = \mathrm{span}\left(\mathbf{C}\right)$, where **C** stands for the L–dimensional "**C**anonical" basis

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Their restriction on $\mathcal{C}$ has a $\mathcal{M}$atrix representation in the **C** basis:

$$\mathbf{C}_{\hat{\Delta}_1^{0\to m}} := \mathcal{M}\left(\hat{\Delta}_1^{0\to m}\Big|_{\mathcal{C}}, \mathbf{C} \right) \in \mathbb{S}_L,$$

$$\mathbf{C}_{\hat{\mathrm{T}}_1^{0\to m}} := \mathcal{M}\left(\hat{\mathrm{T}}_1^{0\to m}\Big|_{\mathcal{C}}, \mathbf{C} \right) \in \mathbb{R}^{L\times L},$$

where $\mathbb{S}_L$ is the set of $L \times L$ real symmetric matrices.

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Again:

$$\begin{aligned}\mathbf{C}_{\hat{\Delta}_1^{0\to m}} &\coloneqq \mathcal{M}\left(\left.\hat{\Delta}_1^{0\to m}\right|_{\mathcal{C}}, \mathbf{C}\right) \in \mathbb{S}_L,\\ \mathbf{C}_{\hat{\mathrm{T}}_1^{0\to m}} &\coloneqq \mathcal{M}\left(\left.\hat{\mathrm{T}}_1^{0\to m}\right|_{\mathcal{C}}, \mathbf{C}\right) \in \mathbb{R}^{L\times L}.\end{aligned}$$

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In what follows,

$\hat{\gamma}_\Delta$ will stand for **any** $\hat{\Delta}_1^{0\to m}\Big|_{\mathcal{C}}$, with

$$\boldsymbol{\gamma}_\Delta := \mathcal{M}\left(\hat{\gamma}_\Delta, \mathbf{C}\right),$$

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Any $\boldsymbol{\gamma}_\Delta$ is an $L \times L$ real symmetric matrix. Let

$$\mathbf{U} \coloneqq (\mathbf{u}_r)_{r \in [\![1, L]\!]}$$

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We then build the so-called detachment

$$\boldsymbol{\gamma}_d \coloneqq -\mathbf{U}\,\mathrm{diag}\left(\min\left(u_r, 0\right)\right)_{r \in [\![1,L]\!]}\,\mathbf{U}^\top$$

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$$\boldsymbol{\gamma}_d \coloneqq -\mathbf{U}\, \mathrm{diag}\left(\min\left(u_r, 0\right)\right)_{r \in [\![1,L]\!]} \mathbf{U}^\top$$

and attachment

$$\boldsymbol{\gamma}_a \coloneqq \mathbf{U}\, \mathrm{diag}\left(\max\left(u_r, 0\right)\right)_{r \in [\![1,L]\!]} \mathbf{U}^\top$$

1–RDM's.

$\boldsymbol{\gamma}_\Delta$ stands for any one-electron *difference* density matrix in the L–dimensional $\mathbf{C}$ basis

II.1 Natural orbitals – Generalities

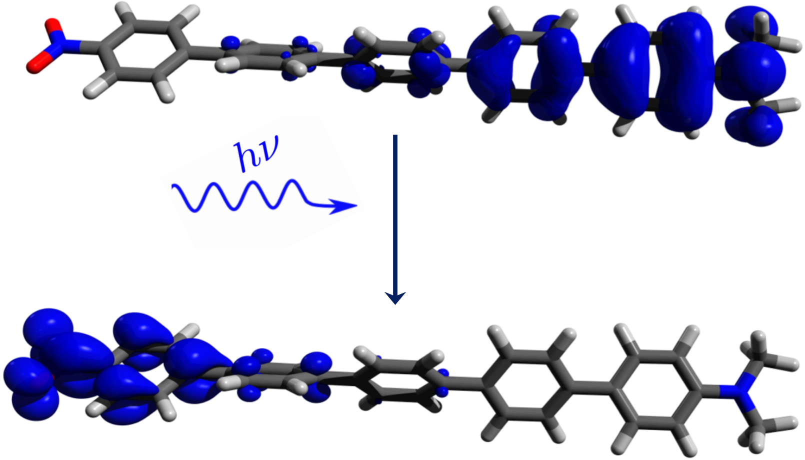

Figure – Detachment (top) and attachment (bottom) densities.

II.1 Natural orbitals – Generalities

$\boldsymbol{\gamma}_{\mathrm{T}}$ is an $L \times L$ real matrix. Let

$$\mathbf{L} \coloneqq (\boldsymbol{\ell}_r)_{r \in [\![1,L]\!]}$$

be the L–tuple of its **left**-singular vectors, the so-called "**left** natural *transition* orbitals" in the **C** basis.

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The left and right singular vectors are paired (each pair shares a singular value).

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II.1 Natural orbitals – Generalities

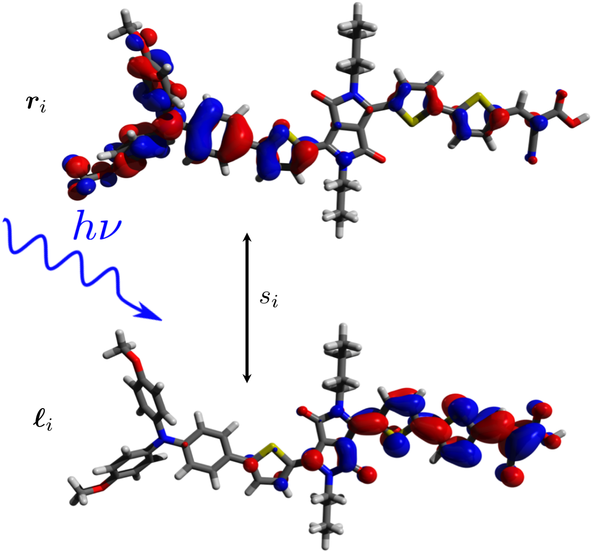

Figure – One pair of natural transition orbitals.

II.1 Natural orbitals – Generalities

From what precedes, we get

$$\hat{\gamma}_\Delta = \overbrace{\sum_{r=1}^{L}\sum_{s=1}^{L}(\boldsymbol{\gamma}_\Delta)_{r,s}\left|\varphi_r\right\rangle\left\langle\varphi_s\right|}^{\mathbf{C}\text{ basis}} = \overbrace{\sum_{r=1}^{L}u_r\left|u_r\right\rangle\left\langle u_r\right|}^{\mathbf{U}\text{ basis}}$$

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and

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Finally, consider the transition “electron” operator and matrix representation

$$\hat{\gamma}_e = \sum_{p=1}^{L} s_p^2 \left|\ell_p\right\rangle \left\langle\ell_p\right| , \; \boldsymbol{\gamma}_e := \mathcal{M}\left(\hat{\gamma}_e, \mathbf{C}\right) = \boldsymbol{\gamma}_\mathrm{T}\boldsymbol{\gamma}_\mathrm{T}^\top ,$$

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and

$$\hat{\gamma}_\mathrm{T} = \underbrace{\sum_{r=1}^{L}\sum_{s=1}^{L} (\boldsymbol{\gamma}_\mathrm{T})_{r,s} \left|\varphi_r\right\rangle \left\langle\varphi_s\right|}_{\mathbf{C}\text{ basis}} = \underbrace{\sum_{p=1}^{L} s_p \left|\ell_p\right\rangle \left\langle r_p\right|}_{\mathbf{L}\text{ and }\mathbf{R}\text{ bases}} .$$

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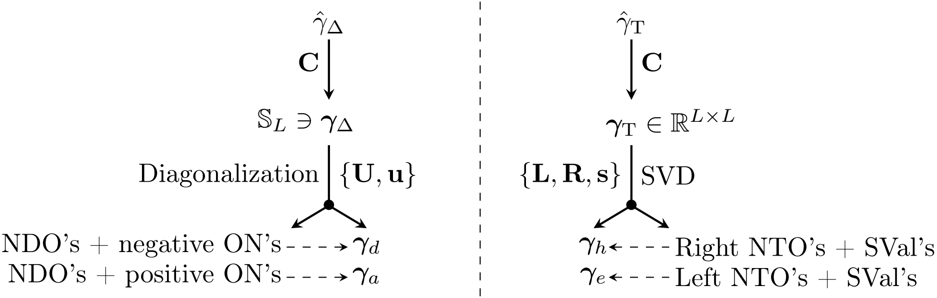
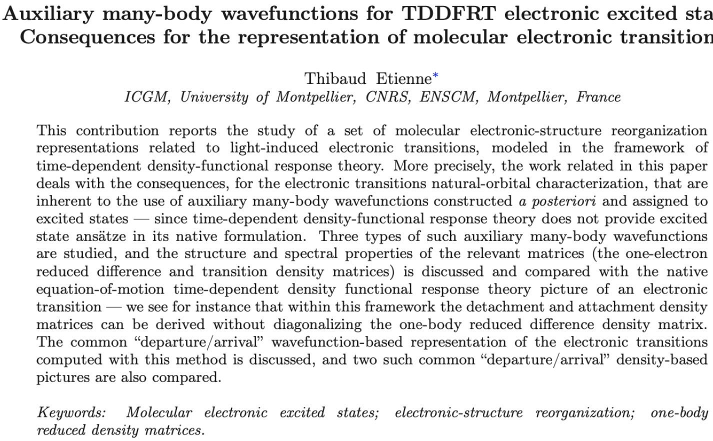
and the transition “hole” operator and matrix representation

$$\hat{\gamma}_h = \sum_{p=1}^{L} s_p^2 \left|r_p\right\rangle \left\langle r_p\right| , \ \boldsymbol{\gamma}_h := \mathcal{M}\left(\hat{\gamma}_h, \mathbf{C}\right) = \boldsymbol{\gamma}_\mathrm{T}^\top\boldsymbol{\gamma}_\mathrm{T} .$$

II.1 Natural orbitals – Generalities



II. Qualitative analysis



Auxiliary many-body wavefunctions for TDDFRT electronic excited states
Consequences for the representation of molecular electronic transitions

Thibaud Etienne*
ICGM, University of Montpellier, CNRS, ENSCM, Montpellier, France

This contribution reports the study of a set of molecular electronic-structure reorganization representations related to light-induced electronic transitions, modeled in the framework of time-dependent density-functional response theory. More precisely, the work related in this paper deals with the consequences, for the electronic transitions natural-orbital characterization, that are inherent to the use of auxiliary many-body wavefunctions constructed *a posteriori* and assigned to excited states — since time-dependent density-functional response theory does not provide excited state ansätze in its native formulation. Three types of such auxiliary many-body wavefunctions are studied, and the structure and spectral properties of the relevant matrices (the one-electron reduced difference and transition density matrices) is discussed and compared with the native equation-of-motion time-dependent density functional response theory picture of an electronic transition — we see for instance that within this framework the detachment and attachment density matrices can be derived without diagonalizing the one-body reduced difference density matrix. The common "departure/arrival" wavefunction-based representation of the electronic transitions computed with this method is discussed, and two such common "departure/arrival" density-based pictures are also compared.

Keywords: Molecular electronic excited states; electronic-structure reorganization; one-body reduced density matrices.

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arxiv.org/abs/2104.13616

Chapter II.2

NATURAL ORBITALS – THE CIS METHOD

II.2 Natural orbitals – The CIS method

THE CASE OF CIS

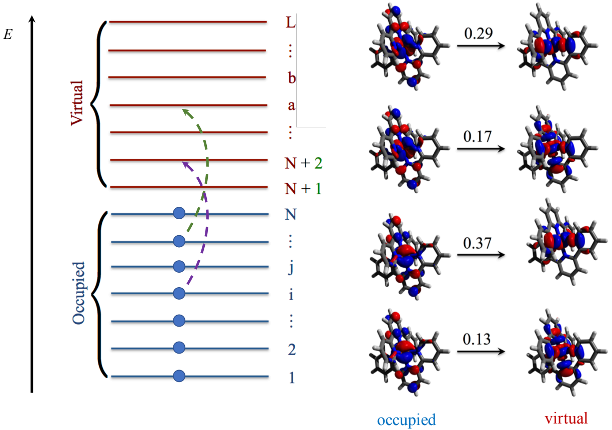

Figure – Canonical picture of an electronic transition with the CIS method.

II.2 Natural orbitals – The CIS method

With this method, the 1–TDM in the **C** basis is an $L \times L$ matrix partitioned as

$$\boldsymbol{\gamma}_{\mathrm{T}} = \begin{pmatrix} \mathbf{0}_o & \mathbf{0}_{ov} \\ \mathbf{X}^\top & \mathbf{0}_v \end{pmatrix} \qquad \text{with} \qquad \mathbf{X} \in \mathbb{R}^{N \times (L-N)}$$

1–TDM is the one-electron reduced transition density matrix

1–DDM is the one-electron reduced difference density matrix

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The CIS 1–DDM reads

$$\boldsymbol{\gamma}_\Delta = \color{red}{\boldsymbol{\gamma}_{\mathrm{T}}\boldsymbol{\gamma}_{\mathrm{T}}^\top} \color{black}{-} \color{blue}{\boldsymbol{\gamma}_{\mathrm{T}}^\top\boldsymbol{\gamma}_{\mathrm{T}}} \color{black}{=} \left(-\mathbf{X}\mathbf{X}^\top\right) \oplus \mathbf{X}^\top\mathbf{X}.$$

1–TDM is the one-electron reduced transition density matrix

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Lemma II.1. *The product of a real matrix by its transpose is positive semidefinite.*

1–TDM is the one-electron reduced transition density matrix

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Lemma II.1. *The product of a real matrix by its transpose is positive semidefinite.*

CIS NTO's and NDO's are identical in the **C** basis, and

$$\left(\boldsymbol{\gamma}_d = \boldsymbol{\gamma}_h = \mathbf{X}\mathbf{X}^\top \oplus \mathbf{0}_v \right) \implies n_d = n_h,$$
$$\left(\boldsymbol{\gamma}_a = \boldsymbol{\gamma}_e = \mathbf{0}_o \oplus \mathbf{X}^\top \mathbf{X} \right) \implies n_a = n_e.$$

1–TDM is the one-electron reduced transition density matrix
1–DDM is the one-electron reduced difference density matrix

II.2 Natural orbitals – The CIS method

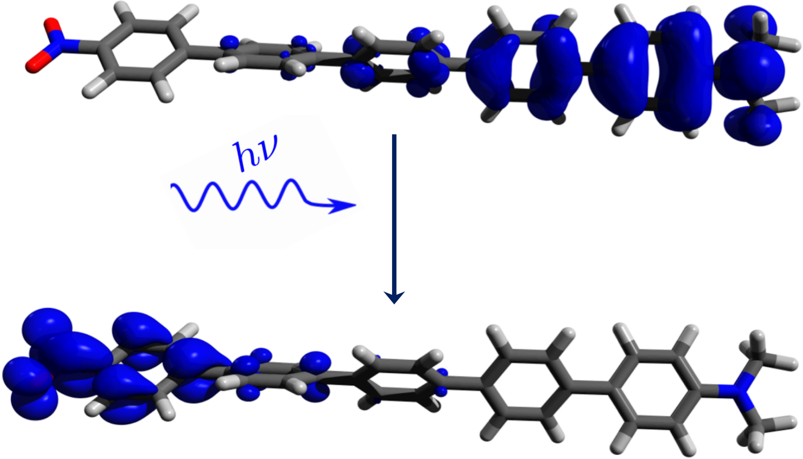


Figure – Detachment/attachment (or hole/electron) picture of a CIS transition.

II.2 Natural orbitals – The CIS method

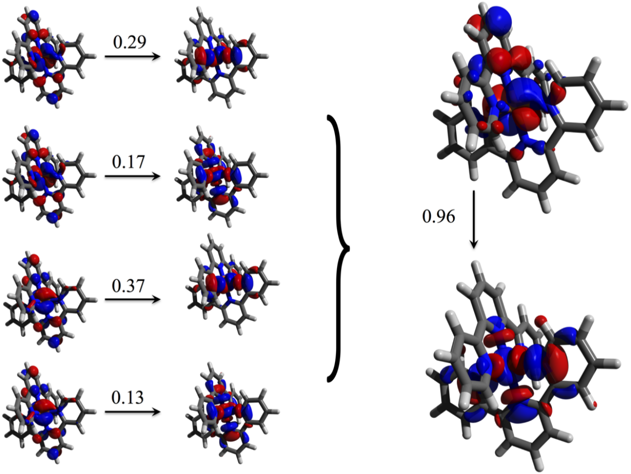
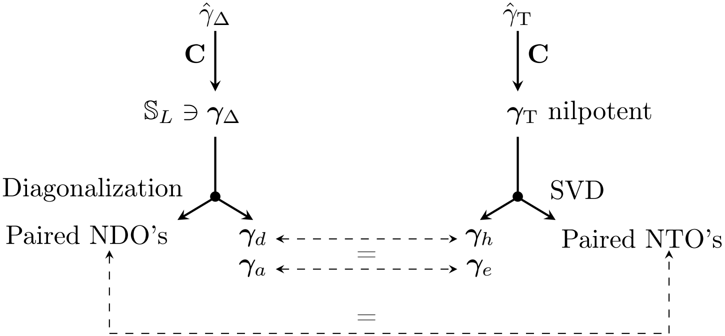


Figure – Canonical (left) and NTO/NDO (right) picture of a CIS transition.

II.2 Natural orbitals – The CIS method



$\hat{\gamma}_\Delta$ $\xrightarrow{\mathbf{C}}$ $\mathbb{S}_L \ni \boldsymbol{\gamma}_\Delta$

$\hat{\gamma}_\mathrm{T}$ $\xrightarrow{\mathbf{C}}$ $\boldsymbol{\gamma}_\mathrm{T}$ nilpotent

Diagonalization

Paired NDO's

$\boldsymbol{\gamma}_d$ $\overset{=}{\longleftrightarrow}$ $\boldsymbol{\gamma}_h$

$\boldsymbol{\gamma}_a$ $\longleftrightarrow$ $\boldsymbol{\gamma}_e$

SVD

Paired NTO's

$=$

Chapter II.3

NATURAL ORBITALS – BEYOND CIS

II.3 Natural orbitals – Beyond CIS

Let $\mathbf{x}$ and $\mathbf{y}$ be the vectors containing single-electron excitation and de-excitation amplitudes used for computing matrix elements

$$\hat{T} \coloneqq \sum_{i=1}^{N} \sum_{a=N+1}^{L} \left(\mathbf{x}_{ia}\, \hat{a}^\dagger \hat{i} - \mathbf{y}_{ia}\, \hat{i}^\dagger \hat{a} \right).$$

1–DDM is the one-electron reduced difference density matrix

1–TDM is the one-electron reduced transition density matrix

II.3 Natural orbitals – Beyond CIS

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1–DDM elements in the **C** basis have the following expression:

$$\forall (r,s) \in [\![1, L]\!]^2,\ (\boldsymbol{\gamma}_\Delta)_{r,s} = \left\langle \psi_0 \middle| \left[\hat{T}^\dagger, \left[\hat{r}^\dagger \hat{s}, \hat{T} \right] \right] \middle| \psi_0 \right\rangle.$$

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1–DDM is the one-electron reduced difference density matrix

1–TDM is the one-electron reduced transition density matrix

II.3 Natural orbitals – Beyond CIS

With this method, the 1–TDM in the **C** basis is an $L \times L$ matrix partitioned as

$$\boldsymbol{\gamma}_{\mathrm{T}} = \begin{pmatrix} \mathbf{0}_o & \mathbf{Y} \\ \mathbf{X}^\top & \mathbf{0}_v \end{pmatrix}$$

with the excitation and de-excitation amplitudes being stored in

$$\mathbf{X} \in \mathbb{R}^{N \times (L-N)},$$
$$\mathbf{Y} \in \mathbb{R}^{N \times (L-N)}.$$

II.3 Natural orbitals – Beyond CIS

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$$\mathbf{Y} \in \mathbb{R}^{N \times (L-N)}.$$

The 1–DDM in the **C** basis is again block-diagonal, and reads

$$\boldsymbol{\gamma}_{\Delta} = \left(-\mathbf{X}\mathbf{X}^\top - \mathbf{Y}\mathbf{Y}^\top\right) \oplus \left(\mathbf{X}^\top\mathbf{X} + \mathbf{Y}^\top\mathbf{Y}\right).$$

II.3 Natural orbitals – Beyond CIS

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Lemma II.2. *The sum of two positive semidefinite matrices is positive semi-definite.*

II.3 Natural orbitals – Beyond CIS

The EOM-TDDFT detachment/attachment 1–RDM's read

$$\begin{aligned}\boldsymbol{\gamma}_d &= \left(\mathbf{X}\mathbf{X}^\top + \mathbf{Y}\mathbf{Y}^\top\right) \oplus \mathbf{0}_v, \\ \boldsymbol{\gamma}_a &= \mathbf{0}_o \oplus \left(\mathbf{X}^\top\mathbf{X} + \mathbf{Y}^\top\mathbf{Y}\right).\end{aligned}$$

II.3 Natural orbitals – Beyond CIS

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II.3 Natural orbitals – Beyond CIS

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This implies that for EOM–TDDFT, the two pictures do not coincide:

$$\begin{aligned}\boldsymbol{\gamma}_d \neq \boldsymbol{\gamma}_h &\implies n_d \neq n_h, \\ \boldsymbol{\gamma}_a \neq \boldsymbol{\gamma}_e &\implies n_a \neq n_e.\end{aligned}$$

II.3 Natural orbitals – Beyond CIS

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For this method, NTO's and NDO's are, in general, NOT identical.

II.3 Natural orbitals – Beyond CIS

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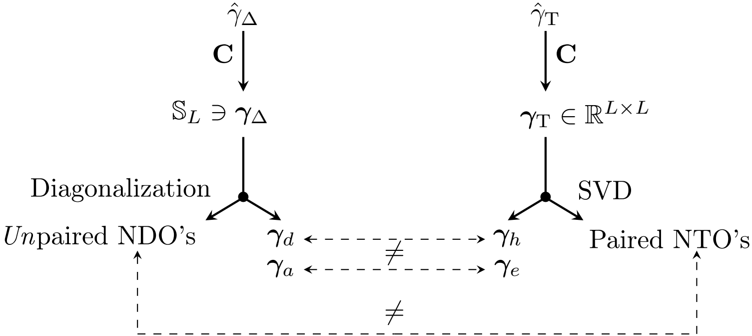
II.3 Natural orbitals – Beyond CIS



$\hat{\gamma}_\Delta$ $\xrightarrow{\mathbf{C}}$ $\mathbb{S}_L \ni \boldsymbol{\gamma}_\Delta$

Diagonalization

*Un*paired NDO's

$\boldsymbol{\gamma}_d$

$\boldsymbol{\gamma}_a$

$\neq$

$\hat{\gamma}_\mathrm{T}$ $\xrightarrow{\mathbf{C}}$ $\boldsymbol{\gamma}_\mathrm{T} \in \mathbb{R}^{L\times L}$

SVD

$\boldsymbol{\gamma}_h$

$\boldsymbol{\gamma}_e$

Paired NTO's

$\neq$

II.3 Natural orbitals – Beyond CIS

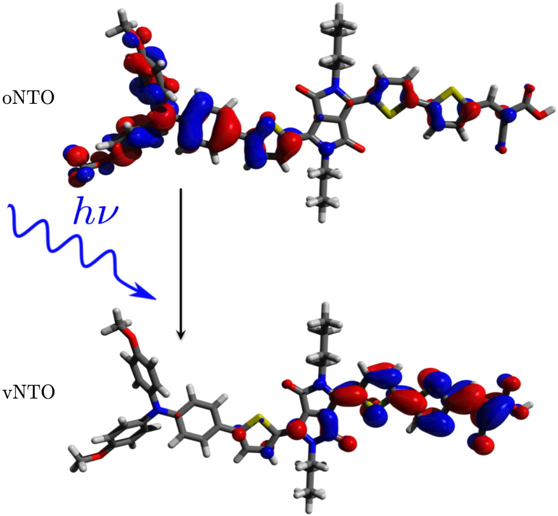


Figure – Widespread schematic interpretation of light-induced electronic transition.

II.3 Natural orbitals – Beyond CIS

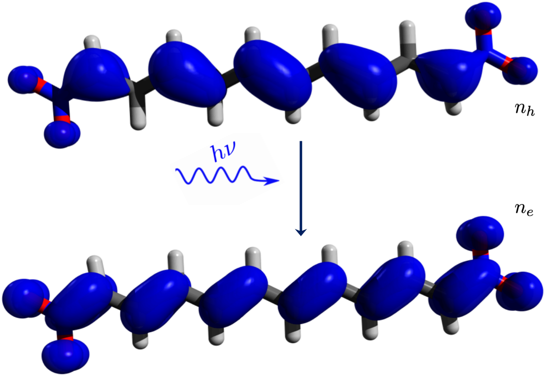


Figure – Widespread schematic interpretation of light-induced electronic transition.

II.3 Natural orbitals – Beyond CIS

The abovementioned transition picture in terms of a series of

$$\textit{transition-hole}\ \text{NTO} \longrightarrow \textit{transition-electron}\ \text{NTO}$$

maps

$\hat{\mathrm{T}}_1$ is the 1–TDM, i.e., the one-body reduced transition density matrix

II.3 Natural orbitals – Beyond CIS

The abovementioned transition picture in terms of a series of

transition-hole NTO ⟶ *transition-electron* NTO

maps, together with the

transition-hole density ⟶ *transition-electron* density

map

$\hat{\mathrm{T}}_1$ is the 1–TDM, i.e., the one-body reduced transition density matrix

II.3 Natural orbitals – Beyond CIS

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$$\textit{transition-hole}\ \text{NTO} \longrightarrow \textit{transition-electron}\ \text{NTO}$$

maps, together with the

$$\textit{transition-hole}\ \text{density} \longrightarrow \textit{transition-electron}\ \text{density}$$

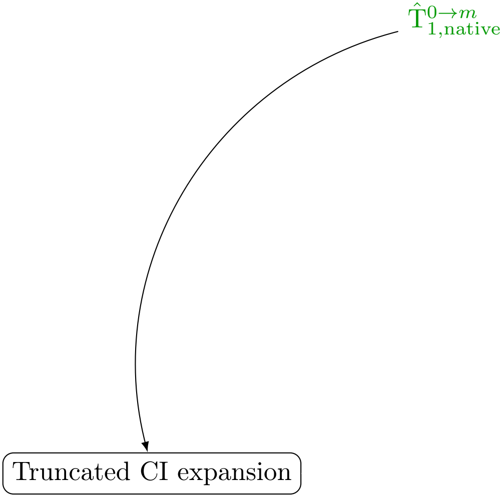
map is dangerous beyond CIS.

$\hat{\mathrm{T}}_1$ is the 1–TDM, i.e., the one-body reduced transition density matrix

II.3 Natural orbitals – Beyond CIS

$$\hat{\mathrm{T}}^{0\to m}_{1,\mathrm{native}}$$

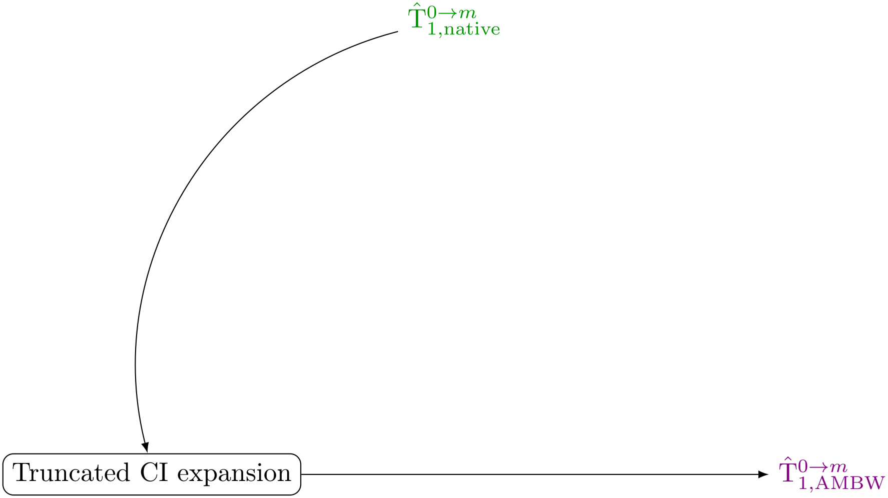
II.3 Natural orbitals – Beyond CIS



$\hat{\mathrm{T}}_{1,\mathrm{native}}^{0\to m}$

Truncated CI expansion

II.3 Natural orbitals – Beyond CIS

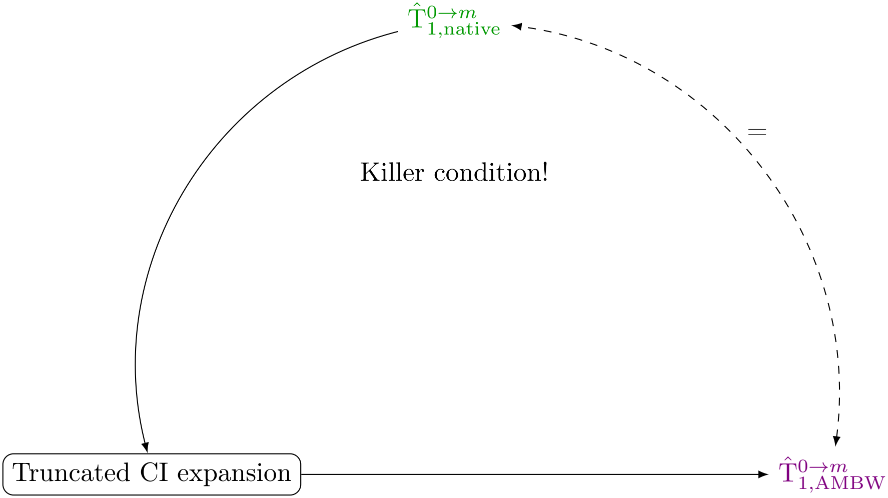


$\hat{\mathrm{T}}_{1,\mathrm{native}}^{0\to m}$

Truncated CI expansion

$\hat{\mathrm{T}}_{1,\mathrm{AMBW}}^{0\to m}$

II.3 Natural orbitals – Beyond CIS



$\hat{\mathrm{T}}^{0\to m}_{1,\mathrm{native}}$

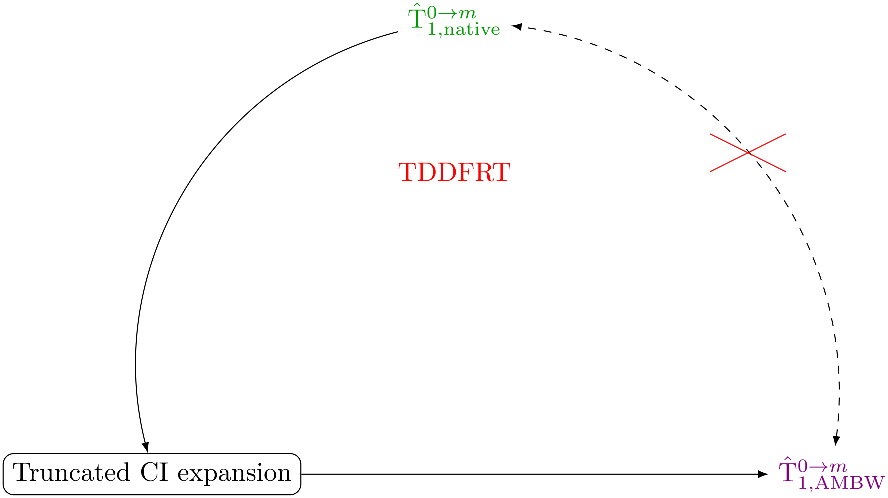
$=$

Killer condition!

Truncated CI expansion

$\hat{\mathrm{T}}^{0\to m}_{1,\mathrm{AMBW}}$

II.3 Natural orbitals – Beyond CIS



$\hat{\mathrm{T}}^{0\to m}_{1,\mathrm{native}}$

TDDFRT

Truncated CI expansion

$\hat{\mathrm{T}}^{0\to m}_{1,\mathrm{AMBW}}$

II.3 Natural orbitals – Beyond CIS

Reminder: the one-particle reduced *difference* ($\hat{\Delta}$) and *transition* ($\hat{\mathrm{T}}$) density operators

$$\forall m \in [\![1, M]\!], \quad \hat{\Delta}_1^{0\to m} := \sum_{i=1}^{N} \mathrm{tr}_{[\![1,N]\!]\setminus\{i\}} \left(|\psi_m\rangle \langle\psi_m| - |\psi_0\rangle \langle\psi_0| \right),$$

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INTERPRETATION

Difference density matrix: “Population difference”, “Departure/Arrival”,...

II.3 Natural orbitals – Beyond CIS

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INTERPRETATION

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Transition density matrix: “Coherence”, “Interference”, “Coupling”,...

II.3 Natural orbitals – Beyond CIS

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INTERPRETATION

Difference density matrix: “Population difference”, “Departure/Arrival”,...

Transition density matrix: “Coherence”, “Interference”, “Coupling”,...

+ The 1–TDM misses multiple excitations and orbital relaxation effects.

II.3 Natural orbitals – Beyond CIS

THE CASE OF EOM-TDDFT

II.3 Natural orbitals – Beyond CIS

THE CASE OF EOM-TDDFT

1. NDOs are, in general, unpaired.

II.3 Natural orbitals – Beyond CIS

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II.3 Natural orbitals – Beyond CIS

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3. TDDFRT transition pictures: *incomplete, equivocal, or arbitrary ?*

II.3 Natural orbitals – Beyond CIS

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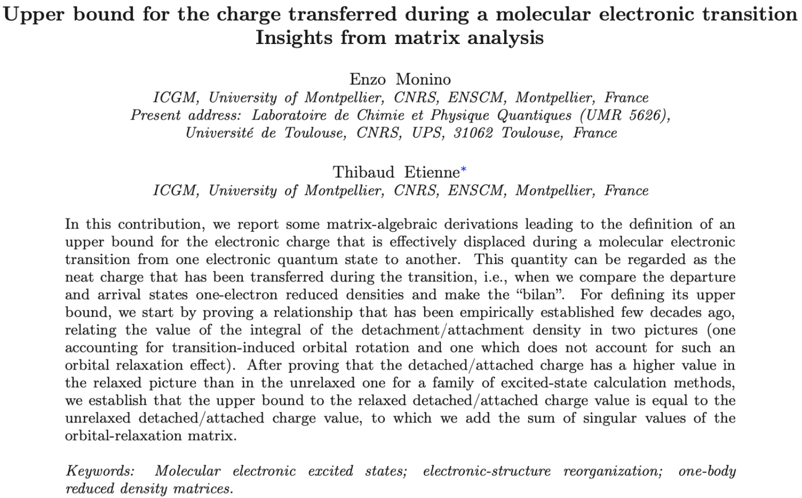
3. TDDFRT transition pictures: *incomplete, equivocal, or arbitrary ?*

CONCLUSION

To date, there is no universal "departure/arrival" natural-spinorbital representation of molecular-electronic transitions.

III. QUANTITATIVE ANALYSIS

III. Quantitative analysis



Upper bound for the charge transferred during a molecular electronic transition Insights from matrix analysis

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In this contribution, we report some matrix-algebraic derivations leading to the definition of an upper bound for the electronic charge that is effectively displaced during a molecular electronic transition from one electronic quantum state to another. This quantity can be regarded as the neat charge that has been transferred during the transition, i.e., when we compare the departure and arrival states one-electron reduced densities and make the "bilan". For defining its upper bound, we start by proving a relationship that has been empirically established few decades ago, relating the value of the integral of the detachment/attachment density in two pictures (one accounting for transition-induced orbital rotation and one which does not account for such an orbital relaxation effect). After proving that the detached/attached charge has a higher value in the relaxed picture than in the unrelaxed one for a family of excited-state calculation methods, we establish that the upper bound to the relaxed detached/attached charge value is equal to the unrelaxed detached/attached charge value, to which we add the sum of singular values of the orbital-relaxation matrix.

Keywords: Molecular electronic excited states; electronic-structure reorganization; one-body reduced density matrices.

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arxiv.org/abs/2104.13465

Chapter III.1

TRANSITION NUMBERS

III.1 Transition numbers

We have, by construction, that

$$\sum_{\ell=1}^{L} \max\left(u_\ell, 0\right) = \mathrm{tr}\left(\boldsymbol{\gamma}_a\right).$$

$\mathbf{u} = \left(u_r\right)_{r\in[\![1,L]\!]}$ is the L–tuple of eigenvalues of the real symmetric $\boldsymbol{\gamma}_\Delta$.

[1] JCTC 2011, 7, 2498–2506.

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$$\sum_{\ell=1}^{L} \max\left(u_\ell, 0\right) = \mathrm{tr}\left(\boldsymbol{\gamma}_a\right).$$

Since no fraction of charge was gained or lost during the electronic transition,

$$\mathrm{tr}\left(\boldsymbol{\gamma}_d\right) = \mathrm{tr}\left(\boldsymbol{\gamma}_a\right)$$

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In 2011, Le Bahers and coworkers[1] defined a number, the transferred charge:

$$q_{\mathrm{CT}} := \frac{1}{2} \int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_1 \left| n_\Delta(\mathbf{r}_1) \right|.$$

$\mathbf{u} = (u_r)_{r \in [\![1,L]\!]}$ is the L–tuple of eigenvalues of the real symmetric $\boldsymbol{\gamma}_\Delta$.

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In 2015, we gave the proof [2] that:

$$\vartheta \geq q_{\mathrm{CT}} := \frac{1}{2}\int_{\mathbb{R}^3} \mathrm{d}\mathbf{r}_1 \left|n_\Delta(\mathbf{r}_1)\right|.$$

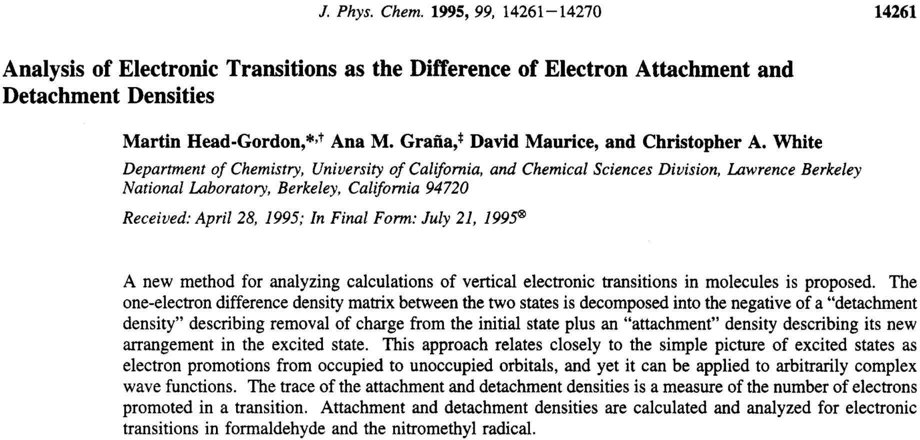
$\mathbf{u} = \left(u_r\right)_{r\in[\![1,L]\!]}$ is the L–tuple of eigenvalues of the real symmetric $\boldsymbol{\gamma}_\Delta$.

[2] JCTC 2015, 11, 1692–1699.

Chapter III.2

HG's CONJECTURE AND BEYOND

III.2 HG's conjecture and beyond



J. Phys. Chem. **1995,** *99,* 14261−14270 **14261**

Analysis of Electronic Transitions as the Difference of Electron Attachment and Detachment Densities

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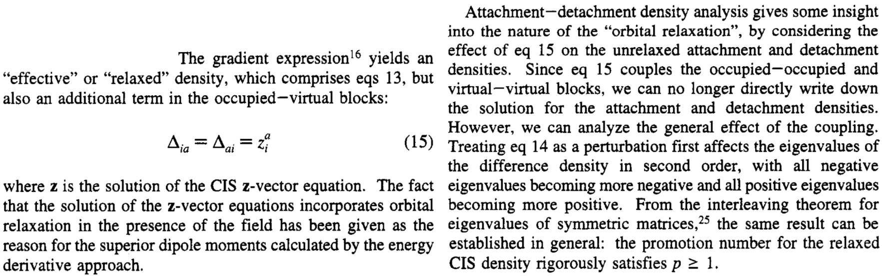
Department of Chemistry, University of California, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Received: April 28, 1995; In Final Form: July 21, 1995[⊗]

A new method for analyzing calculations of vertical electronic transitions in molecules is proposed. The one-electron difference density matrix between the two states is decomposed into the negative of a "detachment density" describing removal of charge from the initial state plus an "attachment" density describing its new arrangement in the excited state. This approach relates closely to the simple picture of excited states as electron promotions from occupied to unoccupied orbitals, and yet it can be applied to arbitrarily complex wave functions. The trace of the attachment and detachment densities is a measure of the number of electrons promoted in a transition. Attachment and detachment densities are calculated and analyzed for electronic transitions in formaldehyde and the nitromethyl radical.

III.2 HG's conjecture and beyond



The gradient expression[16] yields an "effective" or "relaxed" density, which comprises eqs 13, but also an additional term in the occupied−virtual blocks:

$$\Delta_{ia} = \Delta_{ai} = z_i^a \tag{15}$$

where **z** is the solution of the CIS **z**-vector equation. The fact that the solution of the **z**-vector equations incorporates orbital relaxation in the presence of the field has been given as the reason for the superior dipole moments calculated by the energy derivative approach.

Attachment−detachment density analysis gives some insight into the nature of the "orbital relaxation", by considering the effect of eq 15 on the unrelaxed attachment and detachment densities. Since eq 15 couples the occupied−occupied and virtual−virtual blocks, we can no longer directly write down the solution for the attachment and detachment densities. However, we can analyze the general effect of the coupling. Treating eq 14 as a perturbation first affects the eigenvalues of the difference density in second order, with all negative eigenvalues becoming more negative and all positive eigenvalues becoming more positive. From the interleaving theorem for eigenvalues of symmetric matrices,[25] the same result can be established in general: the promotion number for the relaxed CIS density rigorously satisfies $p \geq 1$.

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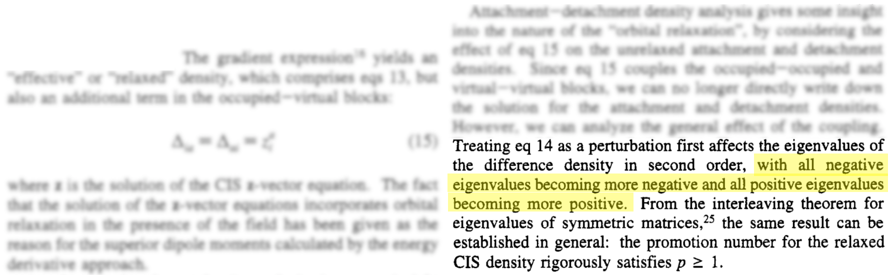
p is the trace of the detachment/attachment 1–RDM's.

III.2 HG's conjecture and beyond



Treating eq 14 as a perturbation first affects the eigenvalues of the difference density in second order, with all negative eigenvalues becoming more negative and all positive eigenvalues becoming more positive. From the interleaving theorem for eigenvalues of symmetric matrices,[25] the same result can be established in general: the promotion number for the relaxed CIS density rigorously satisfies $p \geq 1$.

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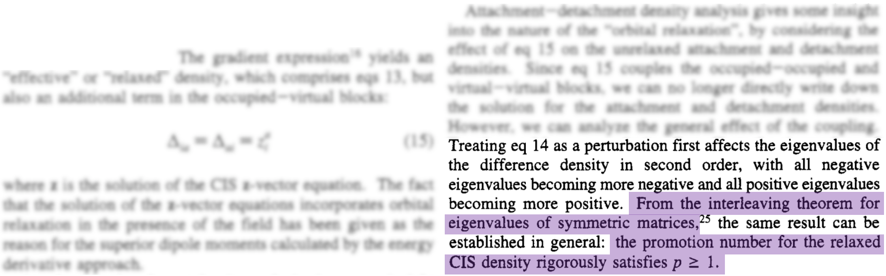
p is the trace of the detachment/attachment 1–RDM's.

III.2 HG's conjecture and beyond



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III.2 HG's conjecture and beyond

Let $\mathbf{x}$ be the vector containing single-electron excitation amplitudes used for computing matrix elements

$$\hat{T} := \sum_{i=1}^{N} \sum_{a=N+1}^{L} \mathbf{x}_{ia}\, \hat{a}^{\dagger} \hat{i}.$$

1–DDM is the one-electron reduced difference density matrix

1–TDM is the one-electron reduced transition density matrix

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$$\hat{T} := \sum_{i=1}^{N} \sum_{a=N+1}^{L} \mathbf{x}_{ia}\, \hat{a}^{\dagger} \hat{i}.$$

Relaxed 1–DDM elements in the **C** basis have the following expression:

$$\forall (r,s) \in [\![1, L]\!]^2,\ (\gamma_{\Delta}^{rlx})_{r,s} = \left\langle \psi_0 \middle| \left[\hat{T}^{\dagger}, \left[\hat{r}^{\dagger}\hat{s}, \hat{T}\right]\right] + \left[\hat{r}^{\dagger}\hat{s}, \hat{Z}\right] \middle| \psi_0 \right\rangle .$$

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with

$$\hat{Z} \coloneqq \sum_{i=1}^{N} \sum_{a=N+1}^{L} \left(\mathbf{z}_{ia}\, \hat{a}^\dagger \hat{i} - \mathbf{z}_{ai}\, \hat{i}^\dagger \hat{a} \right).$$

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III.2 HG's conjecture and beyond

The CIS unrelaxed 1–DDM is partitioned as

$$\gamma_\Delta := \begin{pmatrix} -\mathbf{X}\mathbf{X}^\top & \mathbf{0}_{ov} \\ \mathbf{0}_{vo} & \mathbf{X}^\top\mathbf{X} \end{pmatrix}.$$

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Theorem III.1. (Cauchy's interlacing) *Let* $\mathbf{A}$ *be a bordered* $n \times n$ *Hermitian matrix partitioned as*

$$\mathbf{A} = \begin{pmatrix} \mathbf{B} & \mathbf{y} \\ \mathbf{y}^* & a \end{pmatrix}$$

where a *is real,*

$$\mathbf{B} \in \mathbb{C}^{(n-1)\times(n-1)},$$

and

$$\mathbf{y} \in \mathbb{C}^{(n-1)\times 1}.$$

"*" stands for conjugate transpose in this context.

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Let $\boldsymbol{\alpha}^{\uparrow} = (\alpha_1^{\uparrow}, \ldots, \alpha_n^{\uparrow})$ *and* $\boldsymbol{\beta}^{\uparrow} = (\beta_1^{\uparrow}, \ldots, \beta_{n-1}^{\uparrow})$ *be the* n*–tuple of the eigenvalues of* $\mathbf{A}$ *sorted in the increasing order and the* $(n-1)$*–tuple of the eigenvalues of* $\mathbf{B}$ *sorted in increasing order, respectively.*

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$$\gamma_{\Delta} \coloneqq \begin{pmatrix} -\mathbf{X}\mathbf{X}^{\top} & \mathbf{0}_{ov} \\ \mathbf{0}_{vo} & \mathbf{X}^{\top}\mathbf{X} \end{pmatrix}.$$

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III.2 HG's conjecture and beyond

Theorem III.2. (Eigenvalue embedding I) *Let* $\mathbf{A}$ *be a* $n \times n$ *Hermitian matrix partitioned as*

$$\mathbf{A} = \begin{pmatrix} \mathbf{B} & \mathbf{D} \\ \mathbf{D}^* & \mathbf{C} \end{pmatrix}$$

with

$$\mathbf{B} \in \mathbb{C}^{m \times m} \qquad (m < n).$$

Let $\boldsymbol{\alpha}^{\uparrow} = (\alpha_1^{\uparrow}, \ldots, \alpha_n^{\uparrow})$ *and* $\boldsymbol{\beta}^{\uparrow} = (\beta_1^{\uparrow}, \ldots, \beta_m^{\uparrow})$ *be the* n*–tuple of the eigenvalues of* $\mathbf{A}$ *sorted in the increasing order and the* m*–tuple of the eigenvalues of* $\mathbf{B}$ *sorted in increasing order, respectively. Then,*

$$\forall i \in [\![1, m]\!],\ \alpha_i^{\uparrow} \leq \beta_i^{\uparrow} \leq \alpha_{i+n-m}^{\uparrow}.$$

III.2 HG's conjecture and beyond

Theorem III.3. (Eigenvalue embedding II) *Let* $\mathbf{A}$ *be a* $n \times n$ *Hermitian matrix partitioned as*

$$\mathbf{A} = \begin{pmatrix} \mathbf{B} & \mathbf{D} \\ \mathbf{D}^* & \mathbf{C} \end{pmatrix}$$

with

$$\mathbf{C} \in \mathbb{C}^{(n-m)\times(n-m)} \qquad (m < n).$$

Let $\boldsymbol{\alpha}^{\downarrow} = (\alpha_1^{\downarrow}, \ldots, \alpha_n^{\downarrow})$ *and* $\boldsymbol{\gamma}^{\downarrow} = (\gamma_1^{\downarrow}, \ldots, \gamma_m^{\downarrow})$ *be the* n*–tuple of the eigenvalues of* $\mathbf{A}$ *sorted in the increasing order and the* $(n-m)$*–tuple of the eigenvalues of* $\mathbf{C}$ *sorted in decreasing order, respectively. Then,*

$$\forall i \in [\![1, (n-m)]\!], \; \alpha_i^{\downarrow} \geq \gamma_i^{\downarrow} \geq \alpha_{i+m}^{\downarrow}.$$

III.2 HG's conjecture and beyond

We set the following four L–tuples of 1–DDM eigenvalues:

$$\mathbf{u}^{\uparrow} := (u_1^{\uparrow}, \ldots, u_L^{\uparrow}) \text{ and } \mathbf{u}^{\downarrow} := (u_1^{\downarrow}, \ldots, u_L^{\downarrow}),$$
$$\mathbf{r}^{\uparrow} := (r_1^{\uparrow}, \ldots, r_L^{\uparrow}) \text{ and } \mathbf{r}^{\downarrow} := (r_1^{\downarrow}, \ldots, r_L^{\downarrow}),$$

where "$\mathbf{u}$" and "u" stand for "unrelaxed", "$\mathbf{r}$" and "r" stand for "relaxed".

For both 1–DDM's, the NW (resp. SE) block is negative (resp. positive) semidefinite.

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where "**u**" and "u" stand for "unrelaxed", "**r**" and "r" stand for "relaxed".

From the eigenvalue embedding theorem I we find

$$\forall i \in [\![1, N]\!],\ r_i^{\uparrow} \leq u_i^{\uparrow} \leq 0.$$

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$$\forall i \in [\![1, (L-N)]\!],\ r_i^{\downarrow} \geq u_i^{\downarrow} \geq 0.$$

It is then straightforward to see that

$$\vartheta^{rlx} = \sum_{\ell=1}^{L} \max\left(r_\ell, 0\right) \geq \sum_{\ell=1}^{L} \max\left(u_\ell, 0\right) = \vartheta.$$

For both 1–DDM's, the NW (resp. SE) block is negative (resp. positive) semidefinite.

III.2 HG's conjecture and beyond

⇒ Can we prove that orbital relaxation increases the CIS $\boldsymbol{\gamma}_d/\boldsymbol{\gamma}_a$ traces ?

Answer: Yes, we can!

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CIS, TDHF, TDA, TDDFT, *and* BSE *methods share the necessary and sufficient condition that their unrelaxed* 1–DDM *is block-diagonal, with their* NW (*respectively,* SE) *block being negative (respectively, positive) semidefinite.*

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The relaxed–unrelaxed *difference* density matrix is partitioned as

$$\gamma_Z := \begin{pmatrix} \mathbf{0}_o & \mathbf{Z} \\ \mathbf{Z}^\top & \mathbf{0}_v \end{pmatrix}$$

with $\mathbf{Z}$ being a real $N \times (L - N)$ matrix.

ϑ is the trace of the unrelaxed detachment/attachment 1–RDM's.

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Let q be a positive integer defined as

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Let $\left(z_r\right)_{r \in [\![1,q]\!]}$ be the q–tuple of singular values of $\mathbf{Z}$. Then, the trace of the relaxation detachment/attachment 1–RDM's is

$$\vartheta^Z = \sum_{r=1}^{q} z_r.$$

ϑ is the trace of the unrelaxed detachment/attachment 1–RDM's.

III.2 HG’s conjecture and beyond

Theorem III.4. (Lidskii-Wielandt) *Let* **A** *and* **B** be two $n \times n$ *Hermitian matrices.*

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Theorem III.4. (Lidskii-Wielandt) *Let* **A** *and* **B** be two $n \times n$ *Hermitian matrices. Let* **C** *be their sum. Let*

$$\boldsymbol{\alpha}^{\downarrow} = (\alpha_1^{\downarrow}, \ldots, \alpha_n^{\downarrow}),$$
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$$\boldsymbol{\gamma}^{\downarrow} = (\gamma_1^{\downarrow}, \ldots, \gamma_n^{\downarrow}),$$

be the decreasing-order n*–tuples of the eigenvalues of* **A**, **B**, *and* **C** *respectively.*

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be the decreasing-order n*–tuples of the eigenvalues of* $\mathbf{A}$, $\mathbf{B}$, *and* $\mathbf{C}$ *respectively. Then, for any choice of* $1 \leq i_1 < \cdots < i_k \leq n$,

$$\sum_{j=1}^{k} \left(\gamma_{i_j}^{\downarrow} - \alpha_{i_j}^{\downarrow} \right) \leq \sum_{j=1}^{k} \beta_j^{\downarrow}.$$

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Corollary III.1. *Let* $\mathbf{A}$ *and* $\mathbf{B}$ be two $n \times n$ *Hermitian matrices. Let* $\mathbf{C}$ *be their sum. Let*

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$$\forall k \in [\![1, n]\!], \sum_{j=1}^{k} \gamma_j^{\downarrow} \leq \sum_{j=1}^{k} \left(\alpha_j^{\downarrow} + \beta_j^{\downarrow}\right) \quad \text{and} \quad \sum_{j=1}^{n} \gamma_j^{\downarrow} = \sum_{j=1}^{n} \left(\alpha_j^{\downarrow} + \beta_j^{\downarrow}\right).$$

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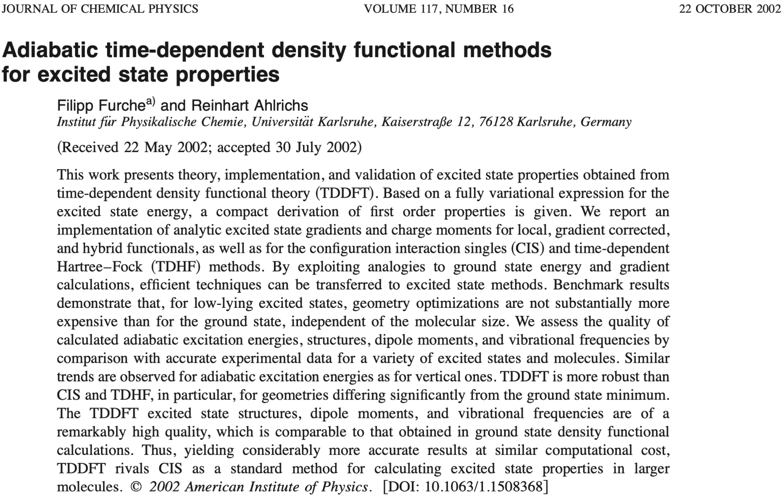
Chosing $\mathbf{A} = \boldsymbol{\gamma}_{\Delta}$, $\mathbf{B} = \boldsymbol{\gamma}_{Z}$, $\mathbf{C} = \boldsymbol{\gamma}_{\Delta}^{rlx}$, and $k = L - N$, we find

$$\left(\vartheta \leq \vartheta^{rlx} \leq \vartheta + \vartheta^{Z}\right) \text{ and } q_{\mathrm{CT}} \in \left[0, \left(\vartheta + \vartheta^{Z}\right)\right].$$

III.2 HG's conjecture and beyond



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Adiabatic time-dependent density functional methods for excited state properties

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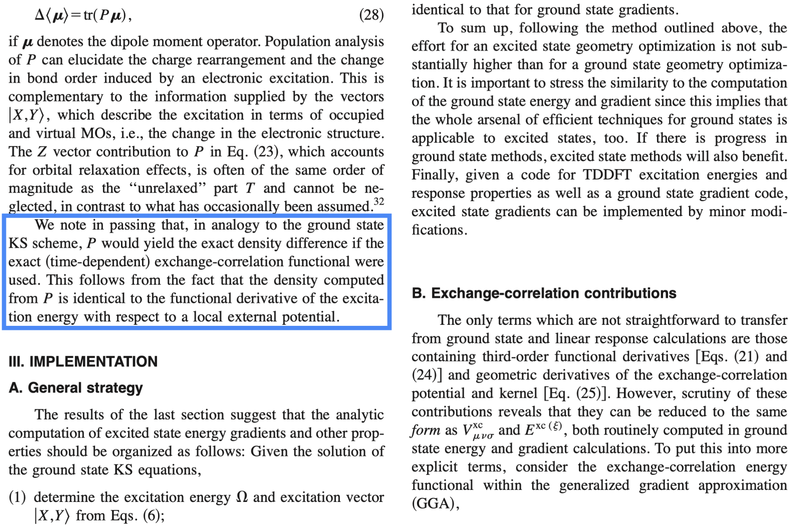
(Received 22 May 2002; accepted 30 July 2002)

This work presents theory, implementation, and validation of excited state properties obtained from time-dependent density functional theory (TDDFT). Based on a fully variational expression for the excited state energy, a compact derivation of first order properties is given. We report an implementation of analytic excited state gradients and charge moments for local, gradient corrected, and hybrid functionals, as well as for the configuration interaction singles (CIS) and time-dependent Hartree–Fock (TDHF) methods. By exploiting analogies to ground state energy and gradient calculations, efficient techniques can be transferred to excited state methods. Benchmark results demonstrate that, for low-lying excited states, geometry optimizations are not substantially more expensive than for the ground state, independent of the molecular size. We assess the quality of calculated adiabatic excitation energies, structures, dipole moments, and vibrational frequencies by comparison with accurate experimental data for a variety of excited states and molecules. Similar trends are observed for adiabatic excitation energies as for vertical ones. TDDFT is more robust than CIS and TDHF, in particular, for geometries differing significantly from the ground state minimum. The TDDFT excited state structures, dipole moments, and vibrational frequencies are of a remarkably high quality, which is comparable to that obtained in ground state density functional calculations. Thus, yielding considerably more accurate results at similar computational cost, TDDFT rivals CIS as a standard method for calculating excited state properties in larger molecules. © *2002 American Institute of Physics*. [DOI: 10.1063/1.1508368]

III.2 HG's conjecture and beyond



$$\Delta\langle\boldsymbol{\mu}\rangle = \mathrm{tr}(P\boldsymbol{\mu}), \tag{28}$$

if $\boldsymbol{\mu}$ denotes the dipole moment operator. Population analysis of P can elucidate the charge rearrangement and the change in bond order induced by an electronic excitation. This is complementary to the information supplied by the vectors $|X,Y\rangle$, which describe the excitation in terms of occupied and virtual MOs, i.e., the change in the electronic structure. The Z vector contribution to P in Eq. (23), which accounts for orbital relaxation effects, is often of the same order of magnitude as the "unrelaxed" part T and cannot be neglected, in contrast to what has occasionally been assumed.[32]

We note in passing that, in analogy to the ground state KS scheme, P would yield the exact density difference if the exact (time-dependent) exchange-correlation functional were used. This follows from the fact that the density computed from P is identical to the functional derivative of the excitation energy with respect to a local external potential.

III. IMPLEMENTATION

A. General strategy

The results of the last section suggest that the analytic computation of excited state energy gradients and other properties should be organized as follows: Given the solution of the ground state KS equations,

(1) determine the excitation energy Ω and excitation vector $|X,Y\rangle$ from Eqs. (6);

identical to that for ground state gradients.

To sum up, following the method outlined above, the effort for an excited state geometry optimization is not substantially higher than for a ground state geometry optimization. It is important to stress the similarity to the computation of the ground state energy and gradient since this implies that the whole arsenal of efficient techniques for ground states is applicable to excited states, too. If there is progress in ground state methods, excited state methods will also benefit. Finally, given a code for TDDFT excitation energies and response properties as well as a ground state gradient code, excited state gradients can be implemented by minor modifications.

B. Exchange-correlation contributions

The only terms which are not straightforward to transfer from ground state and linear response calculations are those containing third-order functional derivatives [Eqs. (21) and (24)] and geometric derivatives of the exchange-correlation potential and kernel [Eq. (25)]. However, scrutiny of these contributions reveals that they can be reduced to the same *form* as $V^{\mathrm{xc}}_{\mu\nu\sigma}$ and $E^{\mathrm{xc}\,(\xi)}$, both routinely computed in ground state energy and gradient calculations. To put this into more explicit terms, consider the exchange-correlation energy functional within the generalized gradient approximation (GGA),

---

P is $\boldsymbol{\gamma}^{rlx}_{\Delta}$.

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Answer: Yes, we can!

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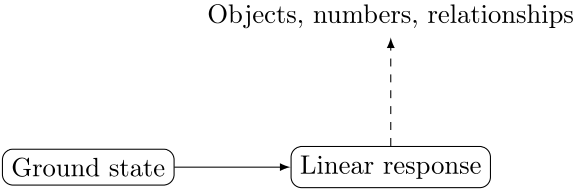
IV. CONCLUSION

IV. Conclusion – Map

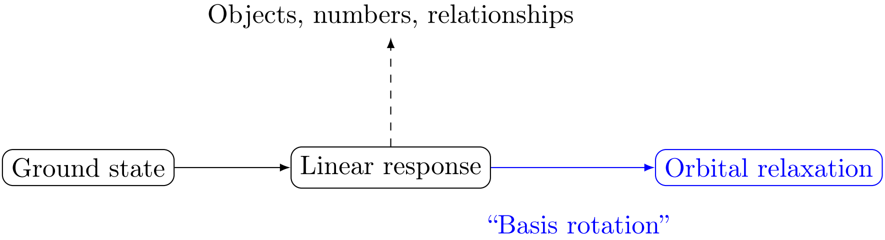


Objects, numbers, relationships

Ground state

Linear response

IV. Conclusion – Map



Objects, numbers, relationships

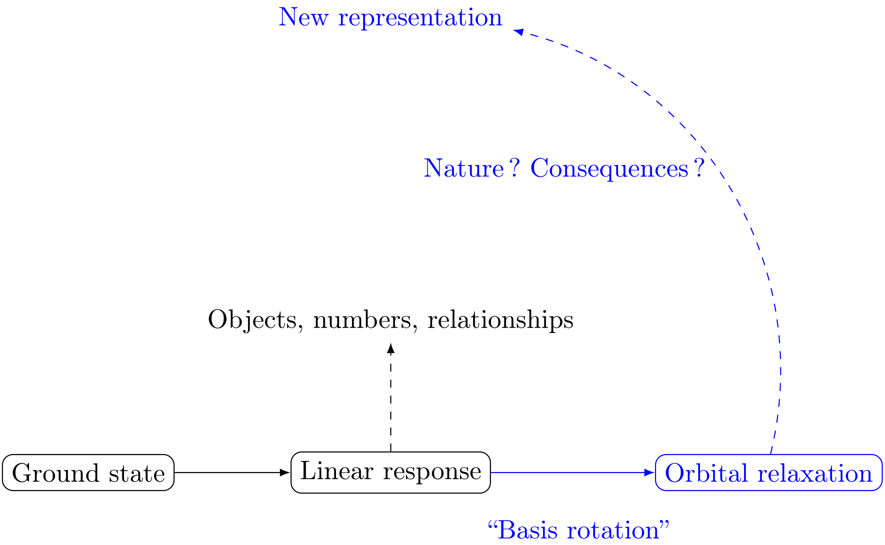
Ground state

Linear response

Orbital relaxation

“Basis rotation”

IV. Conclusion – Map



New representation

Nature ? Consequences ?

Objects, numbers, relationships

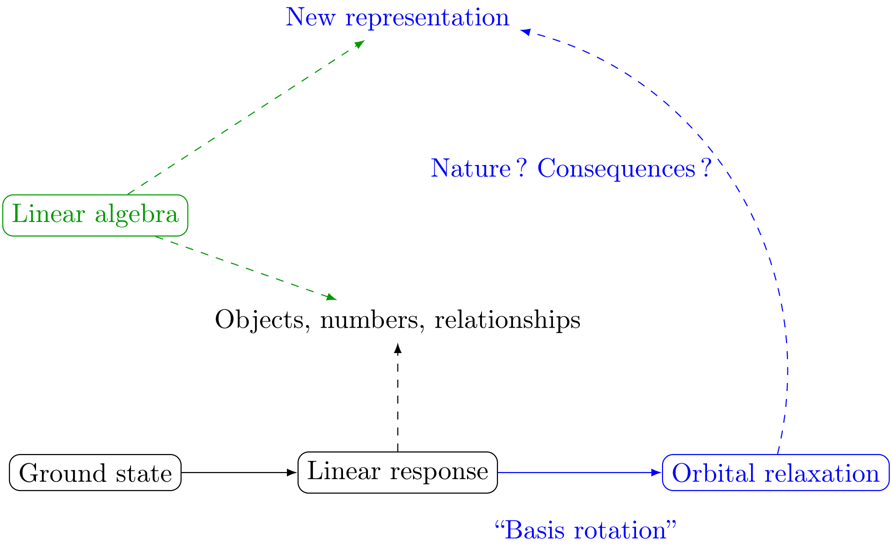
Ground state

Linear response

Orbital relaxation

“Basis rotation”

IV. Conclusion – Map



New representation

Nature ? Consequences ?

Linear algebra

Objects, numbers, relationships

Ground state

Linear response

Orbital relaxation

“Basis rotation”

V. EPILOGUE

V. Epilogue – The MESRA software

MESRA

Molecular Electronic-Structure Reorganization: Analysis

Welcome!

The MESRA software is a free package mainly aiming at providing a qualitative and quantitative analysis of electronic transitions' nature. This is done using pairs of (relaxed) one-particle density or wave functions, constructed according to multiple variants (equation-of-motion/linear-response of the density, configuration interaction) of theories producing one-particle transitions from single-reference wave functions.

mesrasoftware.wordpress.com

V. Epilogue – Acknowledgements

I WOULD LIKE TO WARMLY THANK...

- Prof X. Assfeld & Drs E. Perpète, A. Monari and C. Michaux
- Drs F. De Angelis, E. Mosconi, and M. Pastore
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- Ms K. Shehu, Mr S. Pitié and Ms E. Lognon ; Mr G. Breuil
- Mr E. Monino, Mr M. Maréchal ; Dr Antoine Marion ; Dr ML Doublet
- Ms Sandrine Remy

... AND YOU FOR YOUR ATTENTION!

II. Qualitative analysis

Electronic transition: transition between two electronic states

$$\hat{\mathscr{H}} |\psi_i\rangle = \mathscr{E}_i |\psi_i\rangle \qquad (i \in [\![0, M]\!])$$

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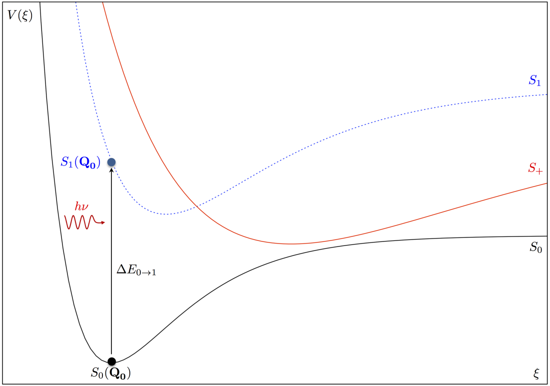
Black → "Ground" state ; Blue → First "Excited" state



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For each state $(i \in \llbracket 0, M \rrbracket)$ there corresponds a mathematical object called *wave function*

$$(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \ldots, \mathbf{r}_N, \sigma_N) \longmapsto \psi_i(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, \cdots, \mathbf{r}_N, \sigma_N).$$

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One can have a simple idea about the electronic spatial distribution by considering the state electron density

$$|\psi_i\rangle \;\longmapsto\; \psi_i \;\longmapsto\; [\mathbf{r}_1 \longmapsto n_i(\mathbf{r}_1)],$$

i.e., a very simple object with only three dimensions instead of $4N$.

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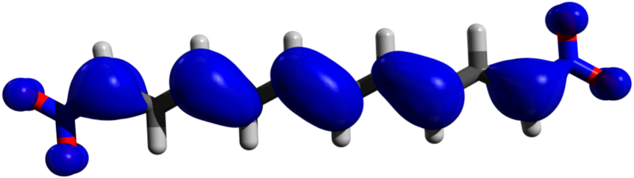

$\mathcal{D} := \mathbb{R}^3 \times \{\uparrow\downarrow\}$
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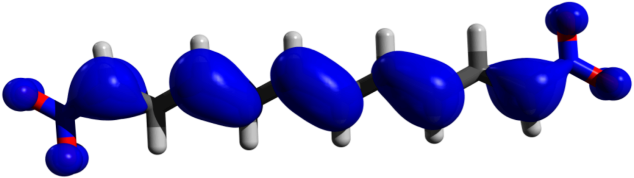

This distribution is unique for a given quantum electronic state, and reflects some of the properties of the molecule in this state. [2]

$$n_i(\mathbf{r}_1) = N \sum_{\sigma_1 \in \{\uparrow,\downarrow\}} \int_{\mathcal{D}} \mathrm{d}\mathbf{s}_1' \, \delta(\mathbf{s}_1 - \mathbf{s}_1') \int_{\mathcal{D}} \mathrm{d}\mathbf{s}_2 \cdots \int_{\mathcal{D}} \mathrm{d}\mathbf{s}_N \, \psi_i(\mathbf{s}_j)_{j \in [\![1,N]\!]} \psi_i(\mathbf{s}_j')_{j \in [\![1,N]\!]}$$

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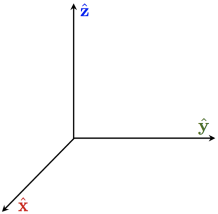
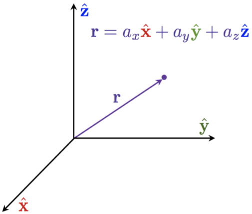
II. Qualitative analysis

In **C**, any n function reads [3]

$$\mathbf{r}_1 \longmapsto n(\mathbf{r}_1) = \sum_{\sigma_1 \in \{\uparrow,\downarrow\}} \int_{\mathcal{D}} \mathrm{d}\mathbf{s}_1'\, \delta(\mathbf{s}_1 - \mathbf{s}_1') \sum_{r=1}^{L} \sum_{s=1}^{L} (\boldsymbol{\gamma})_{r,s}\, \varphi_r(\mathbf{s}_1) \varphi_s(\mathbf{s}_1')$$

where the spinorbitals are treated similarly to x, y and z in the three-dimensional Cartesian basis





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where $\boldsymbol{\gamma}$ is called the *one-particle reduced density matrix* (1–RDM)

$$\boldsymbol{\gamma} = \begin{array}{ccccc} \varphi_1 & \varphi_2 & & \varphi_L & \\ \downarrow & \downarrow & & \downarrow & \\ \gamma_{11} & \gamma_{12} & \cdots & \gamma_{1L} & \longleftarrow \varphi_1 \\ \gamma_{21} & \gamma_{22} & \cdots & \gamma_{2L} & \longleftarrow \varphi_2 \\ \vdots & \vdots & \ddots & \vdots & \\ \gamma_{L1} & \gamma_{L2} & \cdots & \gamma_{LL} & \longleftarrow \varphi_L \end{array}$$

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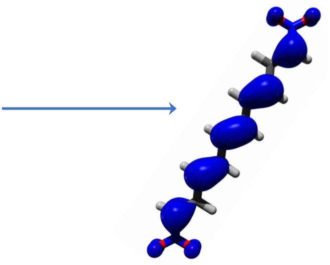

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The state-to-density matrix-to-electron density mapping in **C**, i.e.,

$$|\psi\rangle \longmapsto \hat{\gamma} \longmapsto \boldsymbol{\gamma} \longmapsto [\mathbf{r} \longmapsto n(\mathbf{r})]$$

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Addition of two 1–RDM's leads to the same operation on the density functions.

II.1 Natural orbitals – Generalities

Finding the appropriate $\mathbf{U}$ matrix so that $\mathbf{U}^{-1}\boldsymbol{\gamma}\mathbf{U}$ is diagonal:

$$\gamma = \begin{pmatrix} \gamma_{11} & \gamma_{12} & \dots & \gamma_{1L} \\ \gamma_{21} & \gamma_{22} & \dots & \gamma_{2L} \\ \vdots & \vdots & \ddots & \vdots \\ \gamma_{L1} & \gamma_{L2} & \dots & \gamma_{LL} \end{pmatrix} \xrightarrow{\mathbf{U}} \tilde{\gamma} = \begin{pmatrix} \tilde{\gamma}_{11} & 0 & \dots & 0 \\ 0 & \tilde{\gamma}_{22} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \tilde{\gamma}_{LL} \end{pmatrix}$$

produces **natural orbitals** $(\varphi'_i)_{i \in [\![1,L]\!]}$, i.e., columns of $\mathbf{U}$:

$$\mathbf{U} = \begin{array}{c} \begin{array}{cccc} \varphi'_1 & \varphi'_2 & & \varphi'_L \\ \downarrow & \downarrow & & \downarrow \end{array} \\ \begin{pmatrix} \mathbf{U}_{11} & \mathbf{U}_{12} & \dots & \mathbf{U}_{1L} \\ \mathbf{U}_{21} & \mathbf{U}_{22} & \dots & \mathbf{U}_{2L} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{U}_{L1} & \mathbf{U}_{L2} & \dots & \mathbf{U}_{LL} \end{pmatrix} \end{array}$$

The diagonal elements of $\tilde{\gamma}$ are called **natural occupation numbers**.

II.3 Natural orbitals – Beyond CIS

Reminder: the one-particle reduced *difference* ($\hat{\Delta}$) and *transition* ($\hat{\mathrm{T}}$) density operators

$$\forall m \in [\![1, M]\!], \quad \hat{\Delta}_1^{0\to m} := \sum_{i=1}^{N} \mathrm{tr}_{[\![1,N]\!]\setminus\{i\}} \left(|\psi_m\rangle \langle\psi_m| - |\psi_0\rangle \langle\psi_0| \right),$$

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Residues of the Fourier transform of

$$-L(1,2;1^+,2^+) = \mathrm{i}G_2(1,2;1^+,2^+) - \mathrm{i}G_1(1;1^+)G_1(2;2^+)$$

are, up to a partial trace, matrix elements in the **s**-representation of the

$$\hat{\mathrm{T}}_1^{0\to m}\hat{\mathrm{T}}_1^{m\to 0} \quad \text{and} \quad \hat{\mathrm{T}}_1^{m\to 0}\hat{\mathrm{T}}_1^{0\to m}$$

operators.

III.2 HG's conjecture and beyond

$\hat{\gamma}_\Delta$ and $\hat{\gamma}_\Delta^{rlx}$ are two $\mathcal{C} \longrightarrow \mathcal{C}$ maps.

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$$\begin{aligned} \hat{C}_v \ : \ (\mathcal{C} \longrightarrow \mathcal{C}) &\longrightarrow (\mathcal{C}_v \longrightarrow \mathcal{C}_v) \\ \hat{A} &\longmapsto \hat{R}_v^{\dagger} \hat{A} \hat{R}_v , \end{aligned}$$

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$$\mathbf{R}_v = \mathcal{M}\left(\hat{R}_v, \mathbf{C}, \mathbf{C}_v\right) = \begin{pmatrix} \mathbf{0}_{ov} \\ \mathbf{I}_v \end{pmatrix}$$

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