TDDFT pushing the limits of and going beyond the adiabatic approximation:
“Real” TDDFT meets “real” photochemistry

oxirane,
ethylene oxide,
epoxyethane,
dimethylene oxide

Mark E. Casida
Laboratoire de Chimie Théorique (LCT)
Département de Chimie Moléculaire (DCM, UMR 5250)
Institut de Chimie Moléculaire de Grenoble (ICMG, FR 2607)
Université Joseph Fourier (Grenoble I)
F-38041 Grenoble
France
e-mail: Mark.Casida@UJF-Grenoble.FR
http://dcm.ujf-grenoble.fr/PERSONNEL/CT/casida/

TDDFT 08
Benasque
50 min.
Thurs. 11 Sept. 2008
I. From Ideas to Applications

II. Objective: Better Photochemistry through TDDFT

III. Brief Review of LR-TDDFT (Casida's equations)

IV. Using the TDA to Reduce Bond-Breaking Problems

V. The Dilemma of Conical Intersections

VI. Many-Body DFT Corrections to Conventional DFT

VII. Conclusions and Perspectives
Abstract Greek mathematics helped Romans build amazing aqueducts.
Before the 1990's “DFT” was a “four letter word” in Quantum Chemistry. Now Hartree-Fock is rarely done unless followed by post-Hartree-Fock correlated methods (MP, CI, CC.)

GW/BSE people: Why start with Hartree-Fock at all?
Linear response TDDFT has become the most popular single-determinant method for modeling the excited states of medium and large molecules.
TDDFT IS THE MAIN SINGLE-DETERMINANT THEORY FOR EXCITED STATES

web of science search:
time dependent density functional theory
configuration interaction singles
CASPT2

As of June 2008
LIMITATIONS OF CONVENTIONAL TDDFT

When it works:
- For (dressed) 1-electron excitations
- Low energies
- Little or no density relaxation
- Not too delocalized

Main problems:
- Under estimation of charge density-transfer excitations
- No explicit treatment of excitations with 2- or higher-electron character

Today's talk focuses mainly on the second issue!
Some other problems may emerge as well.
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PHOTOCHEMISTRY: A NECESSARY TOOL FOR ORGANIC SYNTHESIS


\[ \text{NBS} \rightarrow \text{I} \rightarrow \text{II} \rightarrow \text{III} \rightarrow \text{IV} \rightarrow \text{V} \rightarrow \text{VI}, \text{R=H} \rightarrow \text{VII}, \text{R=CH}_3 \text{cubane} \]

pharmaceuticals
polymers
explosives
PHOTOCHEMISTRY: EXPERIMENTAL CHEMICAL PHYSICS

PHOTOCHEMISTRY: PROPOSED MECHANISM

[E. Gomer et W.A. Noyes, Jr., J. Am. Chem. Soc. 72, 101 (1950)]
MODERN PICTURE BASED UPON POTENTIAL ENERGY SURFACES

- Competing processes!
- React fast or loose your chance!

**TYPICAL TIME SCALES**

Femtosecond (fs) – picosecond (ps) :
   - electron motion
high fs – low ps :
   - vibrational motion, **breaking weak bonds**
picosecond (ps) – nanosecond (ns) :
   - small molecule rotations and translations, **breaking strong bonds**, spin-orbit coupling, **fluorescence**
nanosecond (ns) – microsecond (µs) :
   - large molecule rotations and translations, hyperfine coupling, **ultrafast chemical reactions**, **fluorescence**
microsecond (µs) – seconds (s) :
   - fast chemical reactions, **phosphorescence**

*Primary photochemical events occur on high fs to mid ps time-scales!*
THE DISTINCTION BETWEEN CHEMISTRY AND PHYSICS IS WELL DEFINED HERE
A conical intersection (CX) is the analogue in N dimensions of avoided crossings in diatomics.

Ever since the 1990's we believe that many (most?) photochemical reactions proceed through CX rather than intersurface jumps at avoided crossings.
A molecule with \( N \) internal degrees of freedom has an \( N \)-dimensional potential energy surface (PES) in an \((N+1)\)-dimensional space.

\[
E_I = E_I(Q_1, Q_2, \ldots, Q_N)
\]

In the absence of coupling 2 PESs cross in an \((N-1)\)-dimensional intersection.

\[
E_I(Q_1, Q_2, \ldots, Q_N) = E_J(Q_1, Q_2, \ldots, Q_N)
\]

A conical intersection is \((N-2)\)-dimensional.

\[
0 = H_{I,J}(Q_1, Q_2, \ldots, Q_N)
\]
PATHWAY APPROACH

- Trace out minimum energy pathways
- Look for funnels (avoided crossings, conical intersections)

Conical Intersection Branching Coordinates

derivative coupling (DG) vector

\[ h_{m,n}^{(q_i)} = C_m^+ \frac{\partial H}{\partial Q_I} C_n \]

unscaled gradient difference (UGD) vector

\[ g_{m,n}^{(q_i)} = C_m^+ \frac{\partial H}{\partial Q_I} C_n - C_n^+ \frac{\partial H}{\partial Q_I} C_n \]
Fig. 1. Scheme of the main photophysical and photochemical molecular events.

FIRST OF 3 DIFFERENT USES OF THE WORD “ADIABATIC”

TECHNICAL REQUIREMENTS FOR PHOTOCHEMICAL MODELING

- Ground and excited state gradients
- Routines to find conical intersections and determine branching coordinates
- Must be able to break bonds
- When symmetry is present would like to avoid symmetry breaking (spectroscopic assignments)
- Would like to be able to calculate nonadiabatic coupling elements for diabatizations and surface hopping dynamics
PHOTOCHEMICAL MODELERS' TOOLBOX

- DFT and TDDFT for and near Frank-Condon region
- CASSCF (sometimes CASPT2) for conical intersections (CXs)
- Tully surface hopping (rarely Ehrenfest) dynamics

See Ivano Tavernelli's talk
Take a linear combination of all possible configurations that can be constructed by placing $n$ electrons in $m$ orbitals.

Problems:
- The calculations get very expensive as $n$ and $m$ grow
- The choice of active space is often difficult to automate, requiring much human time.

But TDDFT calculations are often found useful as a guide to choosing CAS active spaces!
Error bars represent « TM accuracy »

$\Delta E$

- Experiment / ab initio
- OLYP
- V5XC
- B3LYP*

$\text{[Fe(bpy)$_3$]}^{2+}$

$\text{[Fe(H}_2\text{O)}_6]^{2+}$

$\text{[Fe(NH}_3$)$_6$]^{2+}$

$\text{[Fe(H}_2\text{O)}_6]^{2+}$

Pierloot and Vancoillie 2006
TDDFT IS NICE TO MAP OUT INITIAL REACTION PATHWAYS; CAS IS NECESSARY TO HANDLE CONICAL INTERSECTIONS

Example from Ahmed Zewail's group:


How close can (TD)DFT bring us to the main photochemical reaction (CX) region?
GOAL: PHOTOCHEMISTRY FROM DFT

Target: Help photochemical modelers by further developing DFT-based methods for photochemical modeling.
A WONDERFUL COLLABORATION

Claudia Filippi
Leiden
QMC

Enrico Tapavicza
Ivano Tavernelli
Ursula Röthlisberger
Lausanne
AIMD

Felipe Cordova
Loïc Joubert Doriol
Andrei Ipatov
Mark E. Casida
Grenoble (TD)DFT

Alberto Vela, Mexico City

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Response theory assumes that perturbations are switched on adiabatically slowly, so that there are no transient “wiggles” in time.
PROPAGATORS (GREEN'S FUNCTIONS)

\[ \langle A(t); B \rangle = \pm i \theta(t) \langle \Psi_0 | A_H(t) B | \Psi_0 \rangle + i \theta(\mp t) \langle \Psi_0 | B A_H(t) | \Psi_0 \rangle \]

\[ A_H(t) = e^{iHt} A e^{-iHt} \]

The upper sign is the usual (i.e. causal) propagator.
The lower sign is the response function (retarded propagator).

\[ \omega \langle A; B \rangle = \int_{-\infty}^{+\infty} e^{i\omega t} \langle A(t); B \rangle \]

\[ = \pm \sum_I \frac{\langle \Psi_0 | A | \Psi_I \rangle \langle \Psi_I | B | \Psi_0 \rangle}{\omega - \omega_I + i \eta} \pm \sum_I \frac{\langle \Psi_0 | B | \Psi_I \rangle \langle \Psi_I | A | \Psi_0 \rangle}{\omega + \omega_I + i \eta} \]
\( \chi(1,2;3,4;\omega) \)

(Here \( i=(x_i, y_i, z_i, \sigma_i) \) does not include include \( t_i \))

\[
\sum_I \frac{\left| \Psi_1 \right| \hat{\psi}^+(2) \hat{\psi}(1) \left| \Psi_0 \right| \hat{\psi}^+(3) \hat{\psi}(4) \left| \Psi_I \right|}{\omega + E_0 - E_I} \\
+ \sum_I \frac{\left| \Psi_0 \right| \hat{\psi}^+(2) \hat{\psi}(1) \left| \Psi_I \right| \hat{\psi}^+(3) \hat{\psi}(4) \left| \Psi_0 \right|}{E_0 - E_I - \omega}
\]

This has poles at the excitation energies!
### ZOOLOGY OF DIAGRAMIC CONVENTIONS

<table>
<thead>
<tr>
<th>Not time ordered</th>
<th>Time ordered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feynman</td>
<td>Goldstone</td>
</tr>
<tr>
<td>Abrikosov</td>
<td>Hugenholtz</td>
</tr>
</tbody>
</table>

**Richard Feynman had synesthesia:** “When I see equations, I see the letters in colors...” (Feynman, 1988)
\[ \chi(1, 2; 3, 4; \omega) = \sum \chi_{rs, tu}(\omega) \psi_r(1) \psi_s^*(2) \psi_t^*(3) \psi_u(4) \]

\[ \chi_{rs, tu}(\omega) = -\left\langle s^+ r \right| t^+ u \right\rangle \]

\[ = \sum_I \frac{\left\langle \Psi_I \right| s^+ r \Psi_0 \left| \Psi_0 \right| t^+ u \Psi_I \right\rangle}{\omega + E_I - E_0} \]

\[ + \sum_I \frac{\left\langle \Psi_0 \right| s^+ r \Psi_I \left| \Psi_I \right| t^+ u \Psi_0 \right\rangle}{E_0 - E_I - \omega} \]
\[ \chi_s(1,2;3,4;\omega) = \sum \frac{\psi_i(1) \psi_a^*(2) \psi_i^*(3) \psi_a(4)}{\omega + \epsilon_i - \epsilon_a} \]

\[ + \sum \frac{\psi_a(1) \psi_i^*(2) \psi_a^*(3) \psi_i(4)}{\epsilon_i - \epsilon_a - \omega} \]
\[ \chi_{rs, tu}^s(\omega) = \frac{\delta_{r,i} \delta_{t,i} \delta_{s,a} \delta_{u,a}}{\omega + \epsilon_i - \epsilon_a} \]

\[ + \frac{\delta_{r,a} \delta_{s,i} \delta_{t,a} \delta_{u,i}}{\epsilon_i - \epsilon_a - \omega} \]
Rather than 

\[ \chi(1,2,t;3,4,t') = \frac{\delta \gamma(1,2,t)}{\delta v_{appl}(3,4,t')} \]

TDDFT uses 

\[ \chi(1,1,t;3,3,t') = (\gamma \chi \gamma^+) (1,t;3,t') = \frac{\delta \rho(1,t)}{\delta v_{appl}(3,t')} \]

Obtain the 2-point equation, 

\[ \gamma \chi \gamma^+ = \gamma \chi_s \gamma^+ + (\gamma \chi_s \gamma^+) f_{Hxc}(\gamma \chi \gamma^+) \]
HARRIMAN'S OPERATORS

Collapse operator: \[ \hat{\gamma} f(1,2) = f(1,1) \]

Expansion operator: \[ \hat{\gamma}^+ f(1) = f(1) \delta(1-2) \]

Why is this neat?

Expect \[ v_{xc}(1) \sim \Sigma_{xc}(1,1) \] So \[ v_{xc} \sim \hat{\gamma} \Sigma_{xc} \quad \text{Works in finite basis sets!} \]

\[ \Sigma_{xc}(1,2;\omega) = \sum \psi_r(1) \psi_s^*(2) \Sigma_{r,s}^{xc}(\omega) \]

\[ v_{xc}(1;\omega) = \sum g_I(1) v_{I}^{xc}(\omega) \]

\[ Y_{I,rs} = \langle g_I | \psi_r \psi_s^* \rangle \quad \text{and} \quad v_{I}^{xc}(\omega) \sim \sum Y_{I,rs} \Sigma_{r,s}^{xc}(\omega) \]
\[ Y \chi(\omega)Y^+ = Y \chi_s(\omega)Y^+ + (Y \chi_s(\omega)Y^+) f_{Hxc}(\omega)(Y \chi(\omega)Y^+) \]

Excitations are at the poles of \( Y \chi(\omega)Y^+ \)

Found by solving

\[ 0 = (Y \chi(\omega_I)Y^+)^{-1} G_I = [(Y \chi_s(\omega_I)Y^+)^{-1} - f_{xc}] G_I \]

Which is made to resemble LR-TDDFT

\[
\begin{bmatrix}
  A(\omega_I) & B(\omega_I) \\
  B(\omega_I) & A(\omega_I)
\end{bmatrix}
\begin{bmatrix}
  \vec{X}_I \\
  \vec{Y}_I
\end{bmatrix}
= \omega_I
\begin{bmatrix}
  1 & 0 \\
  0 & -1
\end{bmatrix}
\begin{bmatrix}
  \vec{X}_I \\
  \vec{Y}_I
\end{bmatrix}
\]

Except that

\[ A_{ia,jb}(\omega) = \delta_{i,j} \delta_a b (\epsilon_a - \epsilon_i) + (ia | f_H + f_{xc}(\omega) |jb) \]

\[ B_{ia,jb}(\omega) = (ia | f_H + f_{xc}(\omega) |jb) \]
EXCITATION ENERGIES

\[ \mu_i(t) = \mu_i + \sum_j \alpha_{i,j}(\omega) \varepsilon_j \cos \omega t + \cdots \]

\[ \alpha_{r_i,r_j}(\omega) = \sum_{I \neq 0} \frac{2 \omega_I \langle \Psi_0 | r_i | \Psi_I \rangle \langle \Psi_I | r_j | \Psi_0 \rangle}{\omega_I^2 - \omega^2} \]

Sum-over-states (SOS) theorem

\[ \alpha(\omega) = \sum_{I \neq 0} \frac{f_I}{\omega_I^2 - \omega^2} \]

\[ f_I = \frac{2}{3} \omega_I \left( |\langle \Psi_0 | x | \Psi_I \rangle|^2 + |\langle \Psi_0 | y | \Psi_I \rangle|^2 + |\langle \Psi_0 | z | \Psi_I \rangle|^2 \right) \]

LINEAR RESPONSE FORMULATION OF TDDFT (LR-TDDFT)

"Time-dependent density-functional response theory for molecules"

\[
\begin{bmatrix}
A(\omega_I) & B(\omega_I) \\
B(\omega_I) & A(\omega_I)
\end{bmatrix}
\begin{bmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{bmatrix}
= \omega_I
\begin{bmatrix}
1 & 0 \\
0 & -1
\end{bmatrix}
\begin{bmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{bmatrix}
\]
THE TIME-DEPENDENT KOHN-SHAM EQUATION

\[
\left[-\frac{1}{2} \nabla^2 + v_{\text{ext}}(\vec{r} \, t) + \int \frac{\rho(\vec{r} \,' t)}{|\vec{r} - \vec{r} \,'|} d \vec{r} \,' + v_{xc}[\rho](\vec{r} \, t) \right] \psi_r(\vec{r} \, t) = i \frac{\partial}{\partial t} \psi_r(\vec{r} \, t)
\]

\[
v_{xc}(\vec{r} \, t) = \frac{\delta A_{xc} [\rho]}{\delta \rho (\vec{r} \, t)} \quad \text{Adiabatic approximation} \quad v_{xc}(\vec{r} \, t) = \frac{\delta E_{xc} [\rho_t]}{\delta \rho_t (\vec{r})}
\]

(on the Keldysh contour)

\[
\rho_t (\vec{r}) = \rho (\vec{r} \, t)
\]

This defines “conventional TDDFT.”
This defines “conventional TDDFT.”
TWO POPULAR APPROXIMATIONS

Adiabatic approximation

\[
\begin{bmatrix}
A & B \\
B & A
\end{bmatrix}
\begin{pmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{pmatrix}
= \omega_I
\begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{pmatrix}
\]

Tamm-Dancoff approximation (TDA)

\[
A \vec{X}_I = \omega_I \vec{X}_I
\]
Theorem: The adiabatic approximation limits LR-TDDFT to 1e excitations.

Reasoning: Counting argument.

\[ f_{xc}(\omega) = f_{xc} \]

independent of frequency means that the eigenvalue problem has exactly the same number of solutions as the number of single excitations.

Alternatively: The "Casida equation" includes TDHF. Make the Tamm-Dancoff approximation, B=0. The "Casida equation" then reduces to CIS.

Note however that adiabatic TDDFT 1e excitations include some correlation effects (they are "dressed").
Theorem: The adiabatic approximation limits the poles of the nonlinear response to 1e excitations.

Proof: Complicated, but basically it is related to the idempotency of the KS density matrix. Tretiak et Chernyak have shown that singularities of the adiabatic TDDFT 2nd hyperpolarizability occur only at double excitations which are 1e excitations*.

For example,

\[ \gamma(\omega) = \frac{1}{3!} \left[ \gamma^{(I)}(\omega) + \gamma^{(II)}(\omega) + \cdots + \gamma^{(VIII)}(\omega) \right] \]

\[ \gamma^{(I)}(\omega) = \sum_{\alpha,\beta,\gamma} \frac{\mu_{-\alpha\beta} \mu_{-\beta\gamma} \mu_{\alpha} \mu_{-\gamma} S_{\alpha} S_{\beta} S_{\gamma}}{[\Omega_{\alpha} - 3\omega][\Omega_{\beta} - 2\omega][\Omega_{\gamma} - \omega]} \]

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THE SINGLET NONADIABATIC MECHANISM

Sudden polarization occurs at the avoided crossing of $S_1$ and $S_2$.

Notice the absence of $T_1$ !!!

Special thanks to the John H. Frederick Research Group from whose web site I "stole" these pictures.
SO WE SHOULD EXPECT A PROBLEM IN THE TDDFT DESCRIPTION OF GEOMETRIES OF TWISTED EXCITED STATES OF ETHYLENE

« Photodynamics of ethylene: ab initio studies of conical intersections »
OXIRANE I
“Troubleshooting time-dependent density-functional theory for photochemical applications: Oxirane”

OXIRANE II
Enrico Tapavicza, Ivano Tavernelli, Ursula Röthlisberger, Claudia Filippi, and Mark E. Casida, J. Chem. Phys. in press
“Mixed TDDFT TDA/Classical Photodynamics Study of Oxirane Photochemistry”
C$_{2v}$ RING OPENING WITH RELAXATION B3LYP/6-311++G**(2p,2d)

Mirror planes

Does Mother Nature love symmetry?  
or  
Do we find symmetry in nature because we look for it?

*Symmetry is imposed here to make our analysis easier!*
Important MOs for the classsic Woodward-Hoffman model

---

CAS(4,6) over \((a_1\ a_1\ b_1\ b_1\ b_2\ b_2)\)

Important MOs for the UV spectrum

Orbital 15: \(3b_1(3p_x)\)
Orbital 16: \(8a_1(3p_z)\)
Orbital 12 (HOMO): \(2b_1(n)\)
Orbital 13 (LUMO): \(7a_1(3s)\)
- Some curves are very different.
- Many curves are qualitatively similar but quantitatively different (i.e. energies are shifted).
3 TYPES OF EXCITED STATES

- States where double excitations are likely to be important: $1^1A_1$, $2^1A_1$, and $1^3A_1$
- States with triplet or near singlet instabilities: $1^3B_2$ and $1^1B_2$
- Rydberg states: $1^1B_1$, $1^3B_1$, $1^1A_2$, and $1^3A_2$
A PROBLEM WITH GROUND STATE DFT

- KS equations of conventional ground state DFT resemble HF equations.
- But DFT is exact when $E_{xc}$ is exact and HF is always an approximation.
- However practical applied DFT uses approximate functionals.
- $\Rightarrow$ “inherits” some of the problems of HF!
- Behaves like an (improved) single-determinantal theory
AB INITIO PICTURE FOR 1 \(^1\text{A}_1\) AND 2 \(^1\text{A}_1\)

1 & 2 \(^1\text{A}_1\)

**WARNING:**
Active space is too small
1 \(^1A_1\), 2 \(^1A_1\), and \(^3A_1\)

**Figure:**

- **DMC 1\(^1A_1\)**
- **DMC 2\(^1A_1\)**
- **DMC 1\(^3A_1\)**
- **B3LYP 1\(^1A_1\)**
- **TDB3LYP 2\(^1A_1\)**
- **LDA 1\(^1A_1\)**
- **TDLDA 2\(^1A_1\)**

**Graph Details:**

- **Energy (eV)**
- **Angle (degrees)**

**Cusp** indicated at specific energy and angle values for each curve.
ADIABATIC AND DIABATIC SURFACES : INFORMAL DEFINITION

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- Rydberg states: $1^1B_1$, $1^3B_1$, $1^1A_2$, and $1^3A_2$
AT **ALL** GEOMETRIES:

\[ 1 \sum_g^+ \Rightarrow \rho_\alpha = \rho_\beta \]

\[ \Rightarrow \nu_{xc}^\alpha = \nu_{xc}^\beta \]

\[ \Rightarrow \psi_{i\alpha} = \psi_{i\beta} \]

*Fails for virtually all approximate functionals! Coincidence?*

Depends upon the nondegeneracy of the noninteracting system.
Triplet Instability in $H_2$

Following

M.E. Casida, F. Gutierrez, J. Guan, F.-X. Gadea, D. Salahub and J.-P. Daudey, 

We can improve the approximation of the biradical by symmetry breaking,

$$
\Psi_\lambda = |\sqrt{1 - \lambda^2} \sigma + \lambda \sigma^*|, \sqrt{1 - \lambda^2} \bar{\sigma} - \lambda \bar{\sigma}^*| \rightarrow |s_A, \bar{s}_B|
$$

The corresponding energy,

$$
E_\lambda = E_0 + 2 \lambda^2 \left(\frac{\omega_{T}^{TDDFT}}{\epsilon_{\sigma^*} - \epsilon_\sigma}\right)^2 + O(\lambda^3),
$$

is lowered if there is an imaginary triplet excitation energy.

For a more general treatment, see

The LR-TDDFT and LR-TDHF can be put into the canonical form of a pseudo-eigenvalue problem,

\[
\begin{pmatrix}
A & B \\
B & A
\end{pmatrix}
\begin{pmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{pmatrix}
= \omega_I
\begin{pmatrix}
1 & 0 \\
0 & -1
\end{pmatrix}
\begin{pmatrix}
\vec{X}_I \\
\vec{Y}_I
\end{pmatrix}
\]

B=0 defines the Tamm-Dancoff approximation

\[ A \vec{X}_I = \omega_I \vec{X}_I \]

CIS = TDHF + TDA

Response theory depends upon having a good description of the ground state.

Less sensitive to the quality of the ground state (because “variational.”)

THE MOST SEVERE PROBLEM
(TRIPLET INSTABILITIES)
IS FIXED BY THE TDA

REMARKS:
→ “Well-known” for LR-TDHF, but why would anyone stop at CIS?
→ Formal justification of TDA is lacking in LR-TDDFT except by analogy with LR-TDHF. (Also unnecessary when $A_{xc}$ is exact!)
→ Only a few investigations of LR-TDDFT/TDA for photochemistry. All indicate that this is an essential modification of conventional LR-TDDFT.
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- States where double excitations are likely to be important: $1^1A_1$, $2^1A_1$, and $1^3A_1$
- States with triplet or near singlet instabilities: $1^3B_2$ and $1^1B_2$
- Rydberg states: $1^1B_1$, $1^3B_1$, $1^1A_2$, and $1^3A_2$

These are qualitatively correctly described by TDDFT.
TDLDA/TDA and QMC potential energy curves have typically the same overall form and are found at roughly similar energies. Some significant differences remain in the shapes of the $2^1A_1$ and $1^1B_2$ curves and in the detailed energy ordering of the different states.
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Collaboration began at TDDFT 2006 right here in Benasque!
Enrico Tapavicza, Ivano Tavernelli and Ursula Röthlisberger, École Polytechnique Fédérale de Lausanne, 2007

TDPBE/TDA with Landau-Zener surface hopping.

Hot reactions (~4000K):
$cyclic$-$\text{CH}_2\text{OCH}_2$ $\rightarrow$ $\text{CH}_2\text{CH}_2\text{O}$ $\rightarrow$ $\text{CH}_3 + \text{CHO}$ or $\text{CH}_4 + \text{CO}$
A molecule with N internal degrees of freedom has an N-dimensional potential energy surface (PES) in an (N+1)-dimensional space. In the absence of coupling 2 PESs cross in an (N-1)-dimensional intersection. A conical intersection is (N-2)-dimensional.

The problem with adiabatic TDDFT is that (you would think that) there is no coupling between the ground and excited states. *Hence there is no conical intersection!*

“The dynamics through a conical intersection is very very sensitive to the details of the structure and dimensionality of the intersection.”
- Lorenz Cederbaum, personal communication 3 August 2007

“The CI exists but has wrong topology. But this is to first order. If you did a finite difference computation I think you might see that the topology is in fact correct.”
- Mike Robb, personal communication 3 August 2007

“I believe we are in agreement that it is POSSIBLE for the physical picture to be similar in the two cases (N-1 D intersection space vs N-2 D intersection space) when the lifting of degeneracy is very slow along one direction and rather fast along another (in the N-2 D case). .... please note that this is known to occur in cases involving relatively long-range electron transfer.”
- Todd Martinez, personal communication 4 August 2007
H$_2$O Conical Intersection

![Figure 8](image1.png)

Figure 8. As in figure 7, but using SA3-CAS(6/4)/6-31G. The pronounced conical nature of the intersection is clear, in contrast to figure 7.

![Figure 9](image2.png)

Figure 9. As in figure 7, but using TD.B3LYP(6-31G). As in CIS, only one branching direction is observed instead of the two which should be present. Furthermore, note the change in scale of the energy axis compared to figures 7 and 8. (see figure 8) predict that this intersection is conical and therefore has two branching directions.

WHAT DOES THE CONICAL INTERSECTION LOOK LIKE IN OXIRANE?

biradicaloid

:O:

H C
H H

:O:

H C
H
H H

(zwitterion
(conventional literature structure))

C(+)
H H

CASSCF CX
COMPARISON OF “CONICAL INTERSECTIONS”

CASSCF

TDPBE TDA

CIS

Conical (or almost conical) intersection
COMPARISON OF “CONICAL INTERSECTIONS”

Conical (or almost conical) intersection
COMPARISON OF “CONICAL INTERSECTIONS”

- Holes below the Fermi level
- Interpenetrating double cone
SELF-INTERACTION ERROR PROBLEM

Hartree-Fock  \( \epsilon_L > \epsilon_H \)

Because the occupied orbitals see N-1 electrons and the unoccupied orbitals see N electrons ...

\[
\langle \psi_i | v_H | \psi_i \rangle = \int \int \frac{\rho_i(1) \rho(2)}{r_{12}} \, d1 \, d2 - n_i \int \int \frac{\rho_i(1) \rho_i(2)}{r_{12}} \, d1 \, d2 + \cdots
\]

DFT, sometimes  \( \epsilon_L < \epsilon_H \)

Because the occupied and unoccupied orbitals see the same number (N-\( \eta \)) of electrons, but only the unoccupied orbitals can avoid the occupied orbital density.

\[
\langle \psi_i | v_H | \psi_i \rangle = \int \int \frac{\rho_i(1) \rho(2)}{r_{12}} \, d1 \, d2 - \langle \psi_i | v_x | \psi_i \rangle
\]
The solution is to let the electrons follow the orbitals by restarting the SCF calculation for each new geometry with the density matrix from the previous geometry.  

*This is quite natural to do in the context of AIMD and even essential!*
THE ALLEGORY OF PLATO'S CAVE

Ideal TDDFT:
should produce CX

--> *but how!*? <--

Real DFT:
approximate CX

us
THE “ANSWER” THAT EMERGED AT THE
Workshop on Range-Separated Hybrids (RSH),
organized by Andreas Savin and Julien Toulouse,
9-13 May 2008, Université Pierre et Marie Curie (Paris VI),
Jussieu Campus, Paris, France.

Facts
- Integer occupation number + constrained search DFT => holes below the Fermi level.
- Holes below the Fermi level is a special type of singlet instability implying the need for complex orbitals.
- Long ago, Mel Levy showed that 2 complex orbitals is equivalent to fractional occupation numbers.

Conclude
Geometry-dependent fractional occupation numbers are the right answer.

Problem
Satisfactory algorithms for optimizing fractional occupation numbers and taking analytic geometric derivatives with fractional occupation numbers are very rare.
Around $\text{H}_3\text{C}_{3v}$ conical intersection

(MLR uses orbital occupation number averaged excitation energies)

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STRATEGIES TO INTRODUCE 2-ELECTRON CHARACTER

POLARIZATION PROPAGATOR CORRECTIONS


SPIN-FLIP THEORY

\[ |\bar{a} a| \quad |\bar{i} i| \quad |i \bar{a}| \quad |i \bar{i}| \]

H\textsubscript{2} deMon2k implementation
OUR INITIAL WORK


- Initial implementation in deMon2k by Andrei IPATOV: revealed some problems (probably from insufficient care about mixing orders of MBPT)

Desirable to go back and rederive equations at a more basic level (also permits to make additional connections with other work in the literature)

Begin with BSE
\[ (4) \chi(1, 2; 7, 8) = \chi_s(1, 2; 7, 8) + \int d(3, 4, 5, 6) \chi_s(1, 2; 3, 4) K_{Hxc}(3, 4; 5, 6) \chi(5, 6; 7, 8) \]

where \( i = (x_i, y_i, z_i, t_i) = (i, t_i) \)

This is a nasty equation because it is a 4-time equation.

**Simplification 1:**

\[ (2) \chi(1, 2^+; 7, 8^+) = \chi_s(1, 2^+; 7, 8^+) + \int d(3, 4, 5, 6) \chi_s(1, 2^+; 3, 4) K_{Hxc}(3, 4; 5, 6) \chi(5, 6; 7, 8^+) \]

**Simplification 2:**

\[ (4) K_{Hxc}(1, 2; 3, 4) \rightarrow (2) K_{Hxc}(1, 2^+; 3, 4^+) \]

Can be done exactly by redefining

\[ (2) K_{xc}(1, 2; 3, 4; \omega) = \chi_s^{-1}(1, 2; 3, 4; \omega) - \chi^{-1}(1, 2; 3, 4; \omega) \]

*This is a highly nontrivial process!*  

*Joachim SCHIRMER*
Then
\[ \chi(1, 2^+; 7, 8^+) = \chi_s(1, 2^+; 7, 8^+) + \int d(3, 4^+, 5, 6^+) \chi_s(1, 2^+; 3, 4^+) K_{Hxc}(3, 4^+; 5, 6^+) \chi(3, 4; 7, 8^+) \]

And
\[ \chi(1, 2; 5, 6; \omega) = \chi_s(1, 2; 5, 6; \omega) + \int d(3, 4, 5, 6) \chi_s(1, 2; 3, 4; \omega) K_{Hxc}(3, 4; 5, 6; \omega) \chi(3, 4; 5, 6; \omega) \]

Short hand
\[ \chi(\omega) = \chi_s(\omega) + \chi_s(\omega) K_{Hxc}(\omega) \chi(\omega) \]

so
\[ \mathcal{Y} \chi(\omega) \mathcal{Y}^+ = \mathcal{Y} \chi_s(\omega) \mathcal{Y}^+ + \mathcal{Y} \chi_s(\omega) K_{Hxc}(\omega) \chi(\omega) \mathcal{Y}^+ \]

To be compared with
\[ \mathcal{Y} \chi(\omega) \mathcal{Y}^+ = \mathcal{Y} \chi_s(\omega) \mathcal{Y}^+ + (\mathcal{Y} \chi_s(\omega) \mathcal{Y}^+) \mathcal{f}_{Hxc}(\omega) (\mathcal{Y} \chi(\omega) \mathcal{Y}^+) \]
Fundamental Equation (exact)

\[ f_{Hxc}(\omega) = \left( Y \chi_s(\omega) Y^+ \right)^{-1} - \left( Y \chi(\omega) Y^+ \right)^{-1} \]

First Approximation (expand \((A-B)^{-1} = A^{-1} + A^{-1}BA^{-1} + \ldots\))

\[ \left( Y \chi_s(\omega) Y^+ \right) f_{Hxc}(\omega) \left( Y \chi_s(\omega) Y^+ \right) = Y \left( \chi(\omega) - \chi_s(\omega) \right) Y^+ \]

Second Approximation (set \(\chi = \chi_s\))

\[ f_{xc}(\omega) = \Lambda_s(\omega) K_{xc}(\omega) \Lambda_s(\omega) \]

The localizer is

\[ \Lambda_s(\omega) = \left( Y \chi_s(\omega) Y^+ \right)^{-1} Y \chi_s(\omega) \]

* Basically Nanoquanta Approximation + Quasiparticle Corrections
PROPERTIES OF LOCALIZER

\[ \Lambda_s(\omega) = \left[ Y \chi_s(\omega) \right]^{-1} Y \chi_s(\omega) \]

1) \( \Lambda(\omega=0) \) appears in the linear response Sham-Schlüter equation

\[ \nu_{xc} = \Lambda(\omega=0) \Sigma_x \]

2) \( \Lambda(\omega) \) has no poles, so perhaps

\[ \Lambda(\omega) \approx \Lambda(\omega=0) \]

which means that KLI and LHF/CEDA (ELP) may be used.

3) \( \langle \psi_i \psi_a | f_{xc}(\epsilon_a - \epsilon_i) | \psi_i \psi_a \rangle = \langle \psi_i \psi_a | K_{xc}(\epsilon_a - \epsilon_i) | \psi_i \psi_a \rangle \)

exactly! (basically the Gonze-Scheffler equation)


\[ Y^+ f_{xc}(\omega) Y = K_{xc}(\omega) \]

roughly valid for a small number of linear independent product functions?
ILLUSTRATION OF SECOND APPROXIMATION FOR EXACT EXCHANGE {Görling, IJQC 69, 265 (1998)}
\[ \chi(\omega) - \chi_s(\omega) = \]

\[ A1 = \sum \frac{(j^b | f_2^b | 10)}{(\epsilon_i - \epsilon_a - \omega)(\epsilon_j - \epsilon_b - \omega)} \psi_b(1) \psi_j(2) \psi_a(3) \psi_i(4) \]

\[ A2 = \sum \frac{(j^b | f_2^b | 10)}{(\epsilon_i - \epsilon_a + \omega)(\epsilon_j + \epsilon_b - \omega)} \psi_b(1) \psi_j(2) \psi_a(3) \psi_i(4) \]
Terms left out of the Nanoquanta Approximation
“QUASIPARTICLE CORRECTIONS”
(Goldstone diagrams)

\[
\begin{align*}
B_1 &= \sum \frac{\langle a | M_{xc} | b \rangle}{(\epsilon_i - \epsilon_b - \omega)(\epsilon_i + \epsilon_a - \omega)} \psi_a(1) \psi_b(2) \psi_b(3) \psi_f(4) \\
B_2 &= \sum \frac{\langle i | M_{xc} | j \rangle}{(\epsilon_j - \epsilon_a + \omega)(\epsilon_j + \epsilon_a - \omega)} \psi_f(1) \psi_f(2) \psi_f(3) \psi_f(4)
\end{align*}
\]

\[
\begin{align*}
C_1 &= -\sum \frac{\langle j | M_{xc} | i \rangle}{(\epsilon_j - \epsilon_a - \omega)(\epsilon_j + \epsilon_a - \omega)} \psi_a(1) \psi_j(2) \psi_a(3) \psi_f(4) \\
C_2 &= \sum \frac{\langle a | M_{xc} | b \rangle}{(\epsilon_i - \epsilon_b + \omega)(\epsilon_i + \epsilon_b + \omega)} \psi_f(1) \psi_f(2) \psi_f(3) \psi_f(4)
\end{align*}
\]

where \( M_{xc} = \sum_{xc} - \nu_{xc} \)
Mark E. Casida

A 3 seminar short course on TDDFT entitled: "Time-Dependent Density-Functional Theory for Molecular Excitations"

10 January 2007 "I. Foundations"

11 January 2007 "II. Conventional TDDFT"

12 January 2007 "III. Many-Electron Excitations"

Institute of High Performance Computing, Singapore.

LOCALIZATION

\[ f_{Hx}^{DFT(4)}(1;3)\delta(1-2)\delta(3-4) = f_{Hx}^{HF}(1,2;3,4) \]
\[ + \sum_{r,s} (n_r - n_s) \psi_r(1) \psi_s(2) \psi_r(3) \psi_s(4) \left| \epsilon_r^{DFT} - \epsilon_r^{HF} \right| - \left| \epsilon_s^{DFT} - \epsilon_s^{HF} \right| \]

\[ \int \int d2 d4 \gamma(1,2) \gamma(4,3) \times \]

\[ \Rightarrow \rho(1) f_{Hx}^{DFT}(1;3) \rho(3) = -\frac{|\gamma(1,3)|^2}{r_{13}} \quad \text{PGG approximation} \]

\[ - \sum_{a}^{\text{unocc}} \sum_{i}^{\text{occ}} \psi_a(1) \psi_i(1) \psi_a(3) \psi_i(3) \left[ \epsilon_a^{DFT} - \epsilon_a^{HF} \right] - \left[ \epsilon_i^{DFT} - \epsilon_i^{HF} \right] \quad \text{Derivative discontinuity correction} \]
Terms left out of the Second Approximation

\[ f_{xc}(\omega) = \Lambda_s(\omega) K_{xc}(\omega) \Lambda_s(\omega) \]
"DENSITY-SHIFT OPERATORS"
(Goldstone diagrams)

\[ D_1 = -\sum \frac{\langle a | M_{xc} | i \rangle}{(\epsilon_j - \epsilon_a - \omega)(\epsilon_i - \epsilon_a)} \psi_i(1)\psi_j(2)\psi_a(3)\psi_4(4) \]

\[ D_2 = \sum \frac{\langle a | M_{xc} | i \rangle}{(\epsilon_i - \epsilon_b + \omega)(\epsilon_i - \epsilon_a)} \psi_4(1)\psi_b(2)\psi_i(3)\psi_4(4) \]

\[ E_1 = -\sum \frac{\langle a | M_{xc} | i \rangle}{(\epsilon_j - \epsilon_a + \omega)(\epsilon_i - \epsilon_a)} \psi_j(1)\psi_4(2)\psi_i(3)\psi_4(4) \]

\[ E_2 = -\sum \frac{\langle a | M_{xc} | i \rangle}{(\epsilon_i - \epsilon_b - \omega)(\epsilon_i - \epsilon_a)} \psi_4(1)\psi_a(2)\psi_b(3)\psi_4(4) \]

where \[ M_{xc} = \sum_{xc} - \nu_{xc} \]
“DENSITY-SHIFT OPERATORS”

(Goldstone diagrams)

\[ P_1 = -\sum \frac{\langle i|M_{xc}|\alpha \rangle}{(\varepsilon_j - \varepsilon_\alpha - \omega)(\varepsilon_i - \varepsilon_\alpha)} \psi_\alpha(1)\psi_j(2)\psi_\alpha(3)\psi_j(4) \]

\[ P_2 = -\sum \frac{\langle i|M_{xc}|\alpha \rangle}{(\varepsilon_i - \varepsilon_j - \omega)(\varepsilon_i - \varepsilon_\alpha)} \psi_j(1)\psi_\alpha(2)\psi_\alpha(3)\psi_j(4) \]

\[ Q_1 = \sum \frac{\langle i|M_{xc}|\alpha \rangle}{(\varepsilon_i - \varepsilon_b - \omega)(\varepsilon_i - \varepsilon_\alpha)} \psi_\alpha(1)\psi_j(2)\psi_\alpha(3)\psi_j(4) \]

\[ Q_2 = \sum \frac{\langle i|M_{xc}|\alpha \rangle}{(\varepsilon_j - \varepsilon_\alpha + \omega)(\varepsilon_i - \varepsilon_\alpha)} \psi_\alpha(1)\psi_\alpha(2)\psi_j(3)\psi_j(4) \]

where \[ M_{xc} = \sum_{xc} \phi_{xc} \]
The density-shift terms arise from putting electron correlation into the physical vacuum.

They are the toughest things to include.

But they only affect amplitudes but not excitation energies.
SOME CONCLUSIONS

- The frequency dependence of $K_{xc}$ is expected to be more important than that in the localizer.
- My previous paper should be corrected to read
  \[ f_{Hxc}(\omega) = \Lambda_s(\omega) K_{Hxc}(\omega) \Lambda_s(\omega) \]
  where
  \[ K_{Hxc}(\omega) = \left[ \langle \tilde{T}^+_1 | \hat{H} - \hat{h}_s | \tilde{T}^+_1 \rangle_s + K(\omega) \right]_{\text{adiabatic TDDFTx}} + K(\omega) \]
  \[ K(\omega) = \langle \tilde{T}^+_1 | \hat{H} | \tilde{T}^+_2 \rangle_s \left[ \omega \langle \tilde{T}^+_2 | \tilde{T}^+_2 \rangle_s - \langle \tilde{T}^+_2 | \hat{H} | \tilde{T}^+_2 \rangle_s \right]^{-1} \langle \tilde{T}^+_2 | \hat{H} | \tilde{T}^+_1 \rangle_s \]
- Even a static localizer still includes ultranonlocality because it includes derivative discontinuities. (large contribution to charge density transfer corrections in EXX?)
AM OPTIMISTIC THAT WE CAN GET SOME OF THIS IMPLEMENTED AND TESTED

Bhaarathi NATARAJAN, arrives 11 Sept. 2008, codirected by Thierry DEUTSCH and myself. Project name: Development of New Functionals and Algorithms for Time-Dependent Density-Functional Theory (TDDFT) and Implementation in Gaussian- and Wavelet-based Programs

Miquel HUIX I ROTLLANT, arrives end October 2008. Project name: Improvement of TDDFT modeling of the spectroscopy of nanosystems through better understanding of the space-time trade-off in the exchange-correlation functional

Muhavini WAWIRE, arrives ~20 Sept. 2008, codirected by Lydia NJENGA, Geoffrey KAMAU, and myself. Project name: Theoretical Modeling of Molecular Optical Switches
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**SOME CONCLUSIONS AND PERSPECTIVES**

**(TD)DFT** is already useful and used for photochemistry.

TDDFT-TDA gives approximate conical intersections.

We want to understand how 2e excitations arise from the poles of $f_{xc}$.

DFT fails here: but must retest with fractional occupation numbers.

What physics is/is not in the localizer?

Are density-transfer operators responsible for mixing of ground and excited states?
ACKNOWLEDGMENTS AND THANKYOU

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- Claudia Filippi and Ivano Tavernelli, Felipe Cordova and Enrico Tapavicza, Andrei Ipatov
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