Spin-Coupling and Other Explicit Many-Body Effects in Time-Dependent Density-Functional Theory (TDDFT)

Andrei Ipatov, Felipe Cordova, and <u>Mark E. Casida</u>

Institut de Chimie Moléculaire de Grenoble (ICMG)

Laboratoire d'Études Dynamiques et Structurales de la Sélectivité (LÉDSS)

Équipe de Chimie Théorique (LÉDSS-ÉCT)

Université Joseph Fourier (Grenoble I)

F-38041 Grenoble

France

e-mail: Mark.Casida@UJF-Grenoble.FR

Crosstalks in the Physics of Many-Body Systems

Institut Henri Poincaré

Paris, France

Thursday 7 December 2006

45 min

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"I'm on the verge of a major breakthrough, but I'm also at that point where chemistry leaves off and physics begins, so I'll have to drop the whole thing."

Difficultés de Communication (Language Problems)

For the purposes of this talk :

Chemist = chemical physicist/physical chemist

Physicist = solid state (or other) physicist

$$DFT \neq ab\,initio$$

Brief Biased History of Density-Functional Theory (DFT)

Pre 1964 : Thomas-Fermi-Dirac and Slater's Xα methods

1964 : Hohenberg-Kohn theorems provide a formal justification

1965 : Kohn-Sham reformulation of DFT

1970s : Xα tried in Quantum Chemistry and many hands were burned

Dark Period : DFT is an outcast in Quantum Chemistry

1980s : rich period for development of DFT algorithms and functionals

1994 : First version of **Gaussian** with DFT

1998 : Nobel Prize in Chemistry to John Pople and Walter Kohn

Maturity : DFT is an accepted tool in Quantum Chemistry

DFT doesn't always work but it no longer means the method is evil.

# DFT still doesn't always work, but the method is no longer evil!

- *Ab initio* theory seemed to be "running out of steam" (and granting agencies were increasing pressure for technological impact)
- DFT provides a practical method to extrapolate *ab initio* accuracy to molecules of practical interest
- Validation on small systems still necessary for each new property and class of molecules before applying DFT to larger systems
- And DFT is continuing to improve ...

Problem : Conventional DFT is Limited to the Ground Stationary State

Chemistry is also : • Optical materials
• Spectroscopy
• Photochemistry

Chemistry is can involve many surfaces.
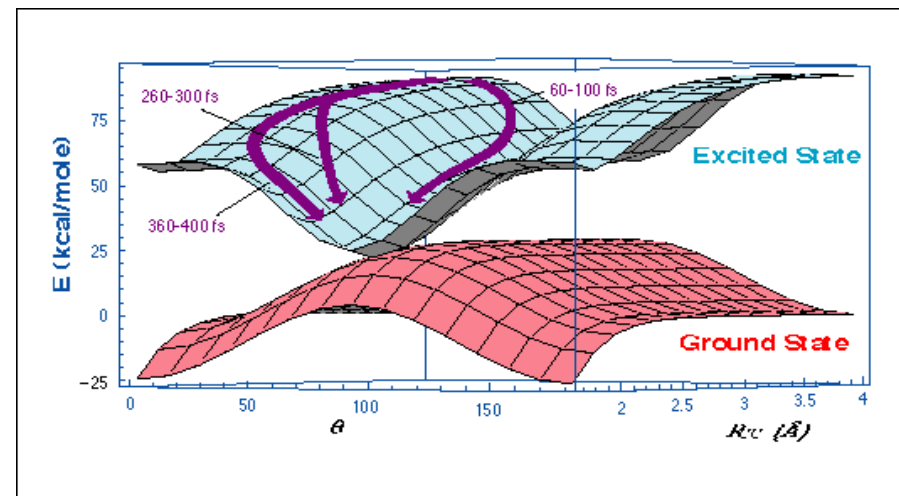
Time-Dependent Density-Functional Theory (TDDFT) aims to overcome this limitation.

THE TWO HOHENBERG-KOHN THEOREMS

[Phys. Rev. 136, B864 (1964)]

1st HK Theorem: The external potential is determined up to an additive constant by the ground state charge density.

Corollary:

$$\rho \rightarrow N,\, v_{ext} + C \rightarrow \hat{H} + C \rightarrow \Psi_I,\, \omega_I = E_I - E_0$$

2nd HK Theorem: The ground state energy and density may be determined by minimizing

$$E = F[\rho] + \int v_{ext}(\vec{r})\,\rho(\vec{r})\,d\vec{r}$$

The functional F[ρ] is "universal" in the sense that it does not depend on v_{ext}.

Introducing N orthonormal Kohn-Sham orbitals allows the most important contributions to the total energy to be written exactly.

$$E=\sum_{i\sigma} n_{i\sigma} <\psi_{i\sigma}|-\frac{1}{2}\nabla^2+v_{ext}|\psi_{i\sigma}> +\frac{1}{2}\int\int\frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{|\vec{r}_1-\vec{r}_2|}d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho]$$

where

$$\rho(\vec{r})=\sum_{i\sigma} n_{i\sigma}|\psi_{i\sigma}(\vec{r})|^2$$

Minimizing subject to the orbital orthnormality constraint gives
the Kohn-Sham equation.

$$[-\frac{1}{2}\nabla^2+v_{ext}(\vec{r})+\int\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}'+v_{xc}(\vec{r})]\psi_{i\sigma}(\vec{r})=\varepsilon_{i\sigma}\psi_{i\sigma}(\vec{r})$$

where the exchange-correlation potential is
$$v_{xc}[\rho](\vec{r})=\frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}$$

DFT

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d\vec{r}\,' + v_{xc}(\vec{r})\right] \psi_{i\sigma}(\vec{r}) = \varepsilon_{i\sigma}\psi_{i\sigma}(\vec{r})$$

where
$$v_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}$$

HF

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d\vec{r}\,' + \hat{\Sigma}_x^\sigma\right] \psi_{i\sigma}(\vec{r}) = \varepsilon_{i\sigma}\psi_{i\sigma}(\vec{r})$$

where
$$\hat{\Sigma}_x^\sigma \psi_{i\sigma} = -\sum_j n_{j\sigma}\psi_{j\sigma} \int \frac{\psi*_{j\sigma}(\vec{r}\,')\psi_{i\sigma}(\vec{r}\,')}{|\vec{r}\,'-\vec{r}|} d\vec{r}\,'$$

- DFT is exact when E_{xc} is exact, but HF is always an approximation.
- v_{xc} is a simple multiplicative operator but the HF exchange operator is an integral operator.

Up to this point everything is formal, hence exact.

We need to approximate E_{xc} in order to have a practical theory.

- No practical exact form is known for E_{xc}.

- E_{xc} must be approximated in practice.

- Is there a systematic hierarchy of appromations?

- Axel Becke talked of 3 generations of functionals

- John Perdew had a vision inspired by the Bible ...

John P. Perdew and Karla Schmidt, in *Density Functional Theory and Its Applications to Materials*, edited by V.E. Van Doren, K. Van Alseoy, and P. Geerlings (American Institute of Physics, 2001).
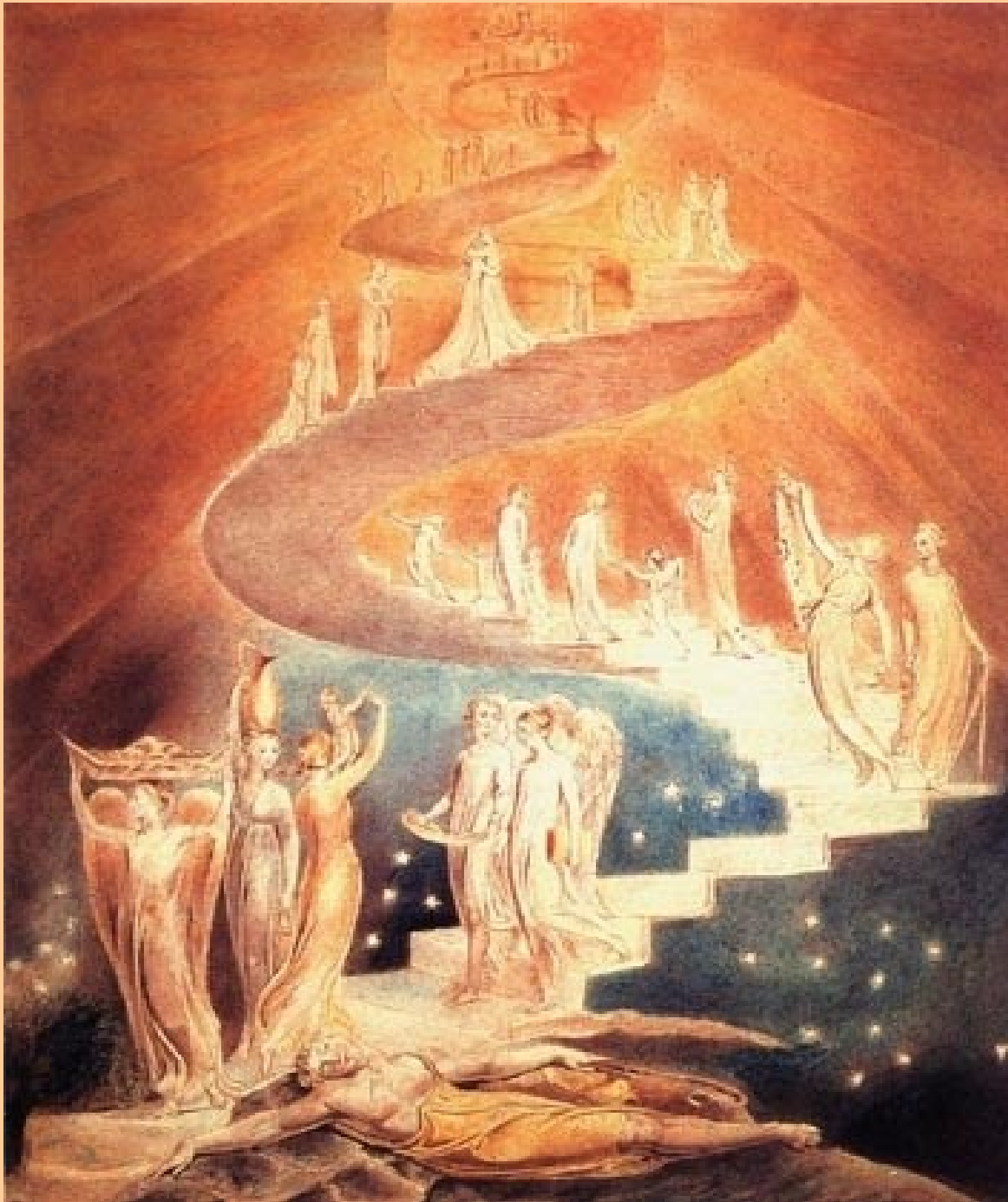
« Jacob's ladder »
William Blake
water color
1799-1800
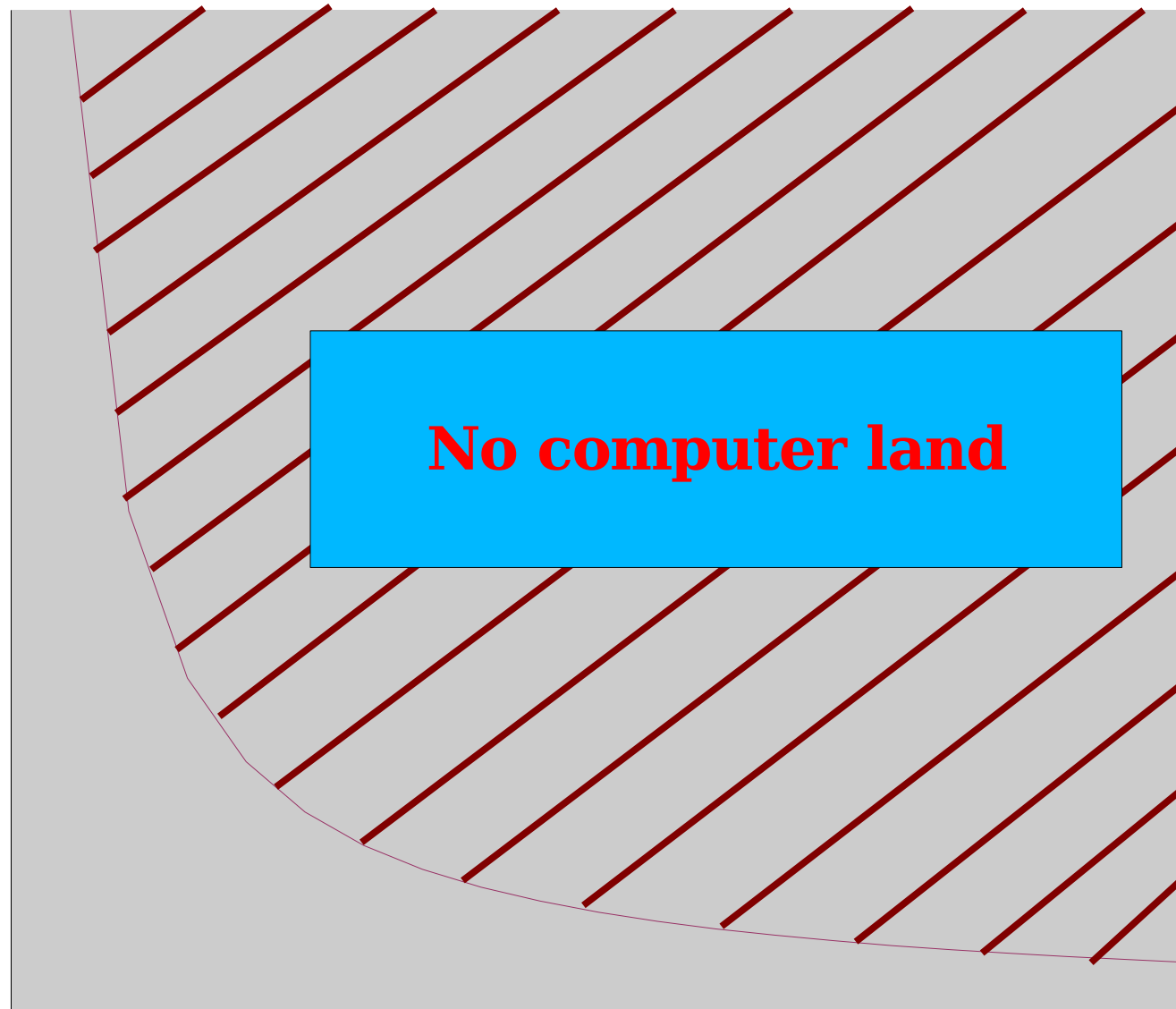
WHERE WE EXPECT CONVENTIONAL DFT TO WORK

- Nondegenerate ground states are best
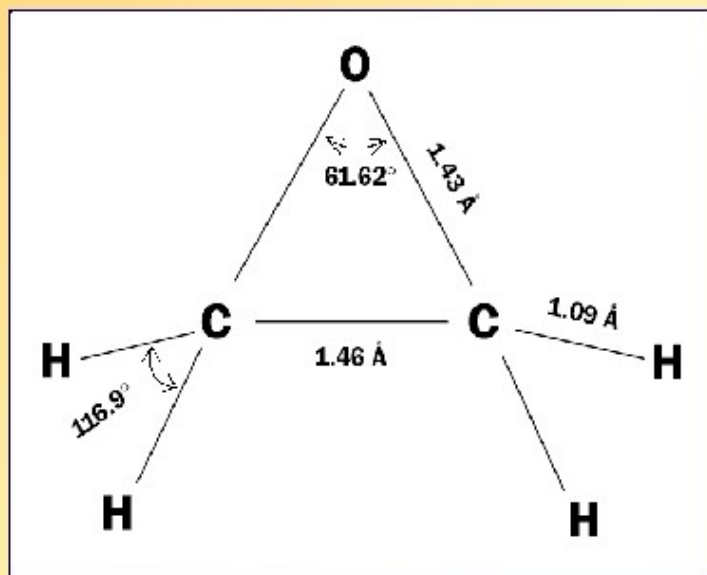- When a single determinant is a reasonable first approximation for the interacting system
- Strong bonding (strong H bonds but not weak H bonds or van der Waals molecules) with bonds involving an integer number of electrons
- Neutrals or cations (not anions)
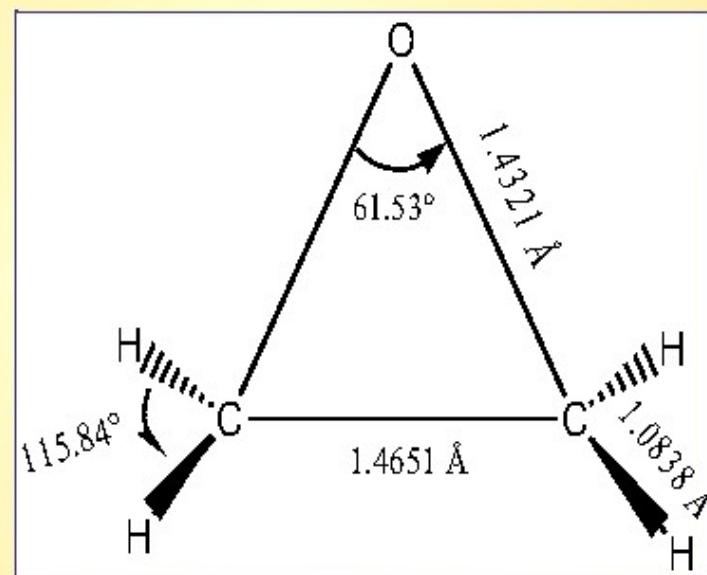- Not too much charge transfer

DFT may also work outside these limits, but testing is required on a case-by-case basis!

Ground State Equilibrium Geometry

Experimental structure of Ethylene Oxide
(From C. Hirose, *Bull. Chem. Soc. Jpn,* **47**, No. 6 (1947), pp. 1311-1318.)

Theoretical structure of Ethylene Oxide
(Determined with B3LYP and 6-311++G**(2d,2p) basis set)

F. Cordova, L. Joubert Doriol, A. Ipatov, M.E. Casida, and A. Vela, *in preparation.*

ΔSCF and MULTIPLET SUM METHOD

ΔSCF

- Formally exact for the first ionization potential (I) and electron affinity (A)
- Reasonable for singlet-triplet excitation energy (ω_T)

- Often used, often successful
- Slater's transition state method sometimes used $\int_0^1 E(n)\,dn \approx \epsilon(n=1/2)$

Multiplet Sum Method (MSM)
- Clearly described in an article by Ziegler, Rauk, and Baerends
- Nicely developed by Daul
- Sometimes the form of a multideterminantal wavefunction may be guessed from symmetry
- The MSM provides a first-order perturbation estimate
- May be used for singlet-singlet excitation energy (ω_S)

T. Ziegler, A. Rauk, and E.J. Baerends, Theor. Chim. Acta **4**, 877 (1977)
C. Daul, Int. J. Quantum Chem. **52**, 867 (1994)

Kernels :
$$f_H(\vec{r}_1, \vec{r}_2) = \frac{1}{r_{12}}$$
$$f_{xc}^{\sigma,\tau}(\vec{r}_1, \vec{r}_2) = \frac{\delta^2 E_{xc}[\rho_\uparrow, \rho_\downarrow]}{\delta \rho_\sigma(\vec{r}_1) \delta \rho_\tau(\vec{r}_2)}$$

"Mullikan (charge cloud) notation" :

$$\left(p\, q \middle| f \middle| p'\, q' \right) = \int \int \psi_p^*(1) \psi_q(1) f(1,2) \psi_{p'}^*(2) \psi_{q'}(2)\, d1\, d2$$

"Fortran" index convention

$$\underbrace{a\, b\, c\, d \ldots g\, h}_{\text{unoccupied}}\, \underbrace{i\, j\, k\, l\, m\, n}_{\text{occupied}}\, \underbrace{o\, p\, q \ldots x\, y\, z}_{\text{free}}$$

IONIZATION POTENTIAL, I_i

ΔSCF : $\qquad -I_i = E\left(\begin{array}{c} \overline{}\ \ a \\ \uparrow\!\downarrow\ \ i \end{array} \right) - E\left(\begin{array}{c} \overline{}\ \ a \\ \downarrow\ \ i \end{array} \right)$

Slater's transition state :

$$-I_i = \epsilon_{i\uparrow}(n_{i\uparrow} = 1/2)$$

In terms of parent N electron qauntities :

$$-I_i = \epsilon_i - \frac{1}{2}\left(ii \left| f_H \right| ii \right) + \left\langle i \left| v_{xc}^{\uparrow}\left[\rho_\uparrow - \frac{1}{2}\rho_i , \rho_\downarrow \right] \right| i \right\rangle$$

After linearization :

$$-I_i = \epsilon_i - \frac{1}{2}\left(ii \left| f_H + f_{xc}^{\uparrow,\uparrow} \right| ii \right)$$

Orbital energy corrected for relaxation

ELECTRON AFFINITY, A_a

ΔSCF :

$$-A_a = E\left(\begin{array}{c}\text{—↑— a}\\ \text{↑↓— i}\end{array}\right) - E\left(\begin{array}{c}\text{—— a}\\ \text{↑↓— i}\end{array}\right)$$

Slater's transition state :

$$-A_a = \epsilon_{a\uparrow}\left(n_{a\uparrow}=1/2\right)$$

In terms of parent N electron quantities :

$$-A_a = \epsilon_a - \frac{1}{2}\left(aa\left|f_H\right|aa\right) + \left\langle a\left|v_{xc}^{\uparrow}\left[\rho_{\uparrow}+\frac{1}{2}\rho_a,\rho_{\downarrow}\right]\right|a\right\rangle$$

After linearization :

$$-A_a = \epsilon_a + \frac{1}{2}\left(aa\left|f_H+f_{xc}^{\uparrow,\uparrow}\right|aa\right)$$

Orbital energy corrected for relaxation

TRIPLET EXCITATION ENERGY

ΔSCF : $\qquad \omega_T = E(\quad\uparrow\ a\ \ \uparrow\ i\ ) - E(\quad\uparrow\ a\ \ \uparrow\downarrow\ i\ )$

Slater's transition state :

$$\omega_T = \epsilon_{a\uparrow}(n_{a\uparrow}=n_{i\downarrow}=1/2) - \epsilon_{i\downarrow}(n_{a\uparrow}=n_{i\downarrow}=1/2)$$

In terms of parent quantities :

$$\omega_T = \epsilon_a - \epsilon_i + \frac{1}{2}\left(aa-ii\middle| f_H + f_{xc}^{\uparrow,\uparrow}\middle| aa-ii\right) + E_{xc}[\rho_\uparrow + \rho_a, \rho_\downarrow - \rho_i] - E_{xc}[\rho_\uparrow, \rho_\downarrow]$$

After linearization :

$$\omega_T = \epsilon_a - \epsilon_i + \underbrace{\frac{1}{2}\left(aa-ii\middle| f_H + f_{xc}^{\uparrow,\uparrow}\middle| aa-ii\right) + \left(aa\middle| f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\uparrow,\downarrow}\middle| ii\right)}_{charge\ transfer\ term}$$

SINGLET EXCITATION ENERGY

Ziegler-Rauk-Baerends (Daul) Multiplet Sum Method :

$$\omega_T = 2\,E\left(\quad \substack{a \\ i} \quad \right) - E\left(\quad \substack{a \\ i} \quad \right)$$

Slater's transition and linearization :

$$\omega_S = \epsilon_a - \epsilon_i + \underbrace{\frac{1}{2}\left(\,aa - ii\,\middle|\,f_H + f_{xc}^{\uparrow,\uparrow}\,\middle|\,aa - ii\,\right)}_{charge\,transfer\,term} - \left(\,aa\,\middle|\,f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\uparrow,\downarrow}\,\middle|\,ii\,\right)$$

COMPARISON WITH HARTREE-FOCK

DFT

$$\omega_T = -\left(A_a - I_i\right) - \left(aa\left|f_H\right|ii\right) - \left(aa\left|f_{xc}^{\uparrow\downarrow}\right|ii\right)$$

$$\omega_S = -\left(A_a - I_i\right) - 2\left(aa\left|f_{xc}^{\uparrow\uparrow}\right|ii\right) - \left(aa\left|f_H\right|ii\right) + \left(aa\left|f_{xc}^{\uparrow\downarrow}\right|ii\right)$$

$$\left(aa\left|f_{xc}^{\uparrow\downarrow}\right|ii\right) \rightarrow 0 \qquad \text{No correlation}$$

$$\left(aa\left|f_{xc}^{\uparrow\uparrow}\right|ii\right) \rightarrow -\left(ai\left|f_H\right|ia\right) \qquad \text{Exchange integral}$$

HF

$$\omega_T = \epsilon_a - \epsilon_i - \left(aa\left|f_H\right|ii\right)$$

$$\omega_S = \epsilon_a - \epsilon_i + 2\left(ai\left|f_H\right|ia\right) - \left(aa\left|f_H\right|ii\right)$$

TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY (TDDFT)
[according to E. Runge and E.K.U. Gross, Phys. Rev. Lett. <u>52</u>, 997 (1984)]

For a system, intially in its ground state, exposed to time-dependent perturbation :

1st Theorem: v_{ext} (rt) is determined by ρ(rt) up to an additive function of time

Corollary: $\quad \rho(\vec{r}t) \rightarrow N, v_{ext}(\vec{r}\,t) + C(t) \rightarrow \hat{H}(t) + C(t) \rightarrow \Psi(t)\, e^{-i\int_{t_0}^{t} C(t')dt'}$

2nd Theorem: The time-dependent density is a stationary point of the action

$$A[\rho] = \int_{t_0}^{t} < \Psi(t')|i\frac{\partial}{\partial t'} - \hat{H}(t')|\Psi(t')> dt'$$

[Actually, the time-dependent density should rather be generated by the Keldysh action. See R. van Leeuwen, Int. J. Mod. Phys. B **15**, 1969 (2001).]

THE TIME-DEPENDENT KOHN-SHAM EQUATION

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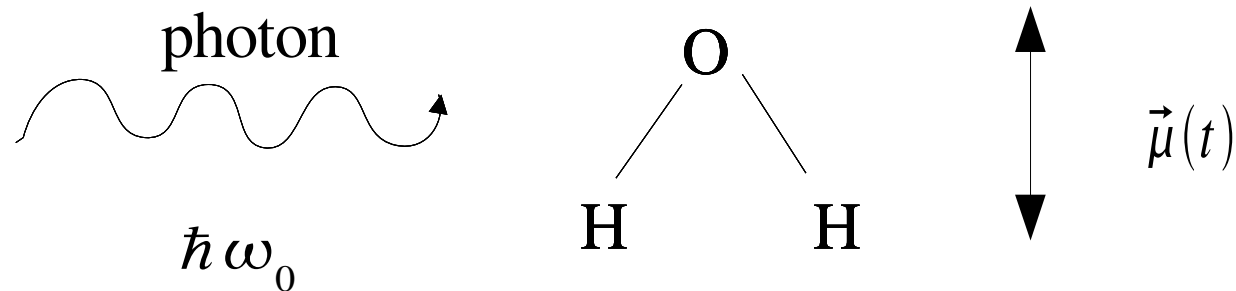
where

$$\rho(\vec{r}\,t)=\sum_{i\sigma}n_{i\sigma}|\psi_{i\sigma}(\vec{r}\,t)|^2$$

and

$$v_{xc}(\vec{r}\,t)=\frac{\delta A_{xc}[\rho]}{\delta\rho(\vec{r}\,t)}$$

EXCITED-STATES ARE OBTAINED FROM LINEAR RESPONSE THEORY

photon

O

H   H

$\vec{\mu}(t)$

$\hbar\omega_0$

- Classical model of a photon

$$\vec{\varepsilon}(t) = \vec{\varepsilon}\cos\omega_0 t$$

$$v(\vec{r}\,t) = e\,\vec{\varepsilon}(t)\cdot\vec{r}$$

- Induced dipole moment

$$\delta\vec{\mu}(t) = -e\,(<\Psi_0|\vec{r}|\delta\Psi_0(t)> + <\delta\Psi_0(t)|\vec{r}|\Psi_0>)$$
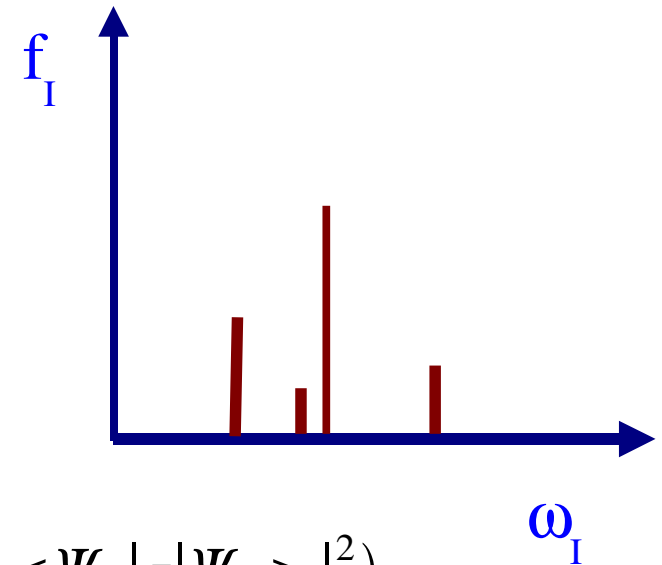
DYNAMIC POLARIZABILITY

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

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

Sum-over-states theorem (SOS)

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

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

MATRIX EQUATIONS

[Mark E. Casida in Recent Advances in Density Functional Methods, Part I, edited by D.P. Chong (Singapore, World Scientific, 1995), p. 155]

$$\alpha_{xz}(\omega) = -2\,\vec{x}^{+}(A-B)^{1/2}\left[\omega^2\mathbf{1} - (A-B)^{1/2}(A+B)(A-B)^{1/2}\right](A-B)^{1/2}\,\vec{z}$$

where

$$A_{ij\sigma kl\tau}(\omega) = \delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}(\varepsilon_{j\sigma} - \varepsilon_{j\sigma}) + K_{ij\sigma,kl\tau}(\omega)$$

$$B_{ij\sigma,kl\tau}(\omega) = K_{ij\sigma,lk\tau}(\omega)$$

PSEUDO-EIGENVALUE PROBLEM

The poles of the dynamic polarizability are the solutions of the pseudo-eigenvalue problem,

$$\boldsymbol{\Omega}(\omega_I)\vec{F}_I = \omega_I^2 \vec{F}_I$$

where

$$\boldsymbol{\Omega} = (\boldsymbol{A} - \boldsymbol{B})^{1/2}(\boldsymbol{A} + \boldsymbol{B})(\boldsymbol{A} - \boldsymbol{B})^{1/2}$$

These equations are variously known as
- the RPA equations (which is really confusing)
- the "Casida equations"
- or LR-TDDFT

In principle these equations take all spectroscopically allowed transitions into account when the functional is exact. This is not a problem because it is well-established that the number of solutions of such an equation can exceed the dimension of the matrix Ω.

Up to this point everything is formal, hence exact.

We need to approximate A_{xc} in order to have a practical theory.

In general

$$v_{xc}(\vec{r}\,t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(\vec{r}\,t)}$$

Supposing that the reaction of the self-consistant field to variations in the charge density is instantaneous and without memory gives the adiabatic approximation,

$$v_{xc}(\vec{r}\,t) = \frac{\delta E_{xc}[\rho_t]}{\delta \rho_t} \qquad \text{where} \qquad \rho_t(\vec{r}) = \rho(\vec{r}\,t)$$

E_{xc} functionals are inherited from conventional DFT

<u>Theorem</u>: The adiabatic approximation limits TDDFRT to 1e excitations.

<u>Reasoning</u>: 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.

<u>Alternatively</u>: 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").

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<u>Theorem</u>: The adiabatic approximation limits the poles of the nonlinear response to 1e excitations.

<u>Proof</u>: 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,

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

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

* S. Tretiak and V. Chernyak, J. Chem. Phys. **119**, 8809 (2003).

WHERE WE EXPECT CONVENTIONAL TDDFT TO WORK

- DFT should already be working for the ground state
- Excitations below the TDDFT ionization threshold ($-\varepsilon_{HOMO}$) which is too low
- Excitations with little or no charge density relaxation (charge transfer excitations are underestimated by 1 or 2 eV)
- Single electron excitations (avoid polyenes and free radicals)

TDDFT may also work outside these limits, but testing is required on a case-by-case basis!

Principle Singlet Excitation Energies (eV) and Oscillator Strengths

TDHF	TDLDA	TDB3LYP	Expt.
9.14 (0.0007)	6.01 (0.0309)	6.69 (0.0266)	7.24(s) [a] [b] [c]
9.26 (0.0050)	6.73 (0.0048)	7.14 (0.0060)	7.45(w) [b]
9.36 (0.0635)	6.78 (0.0252)	7.36 (0.0218)	7.88(s) [a], 7.89(s) [b]
9.56 (0.0635)	7.61 (0.0035)	7.85 (0.0052)	
9.90 (0.0478)	7.78 (0.0304)	8.37 (0.0505)	
9.93 (0.0935)	8.13 (0.0014)	8.39 (0.0168)	
8.15 (0.0405)	8.40 (0.0419)		

[a] Gas phase UV absorption spectrum [LD49].
[b] Obtained by a photoelectic technique [LW58].
[b] Gas phase UV absorption spectrum [FAHP59].
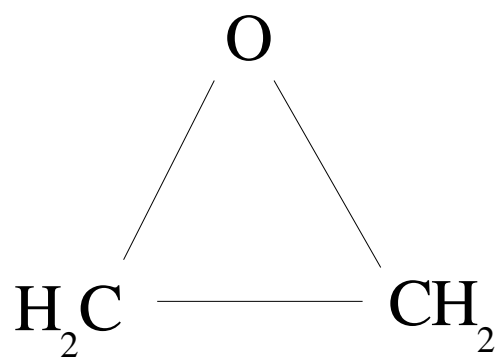
Excitation energy (eV)	Transition electronic
6.69	$1^1B_1[2b_1(n) \rightarrow 7a_1(3s)]$
7.14	$2^1B_1[2b_1(n) \rightarrow 8a_1(3pz)]$
7.36	$2^1A_1[2b_1(n) \rightarrow 3b_1(3px)]$

Additional Approximations

TAMM-DANCOFF APPROXIMATION (TDA)

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

$$\begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{vmatrix} \vec{X}_I \\ \vec{Y}_I \end{vmatrix} = \omega_I \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{vmatrix} \vec{X}_I \\ \vec{Y}_I \end{vmatrix}$$

B=0 defines the Tamm-Dancoff approximation

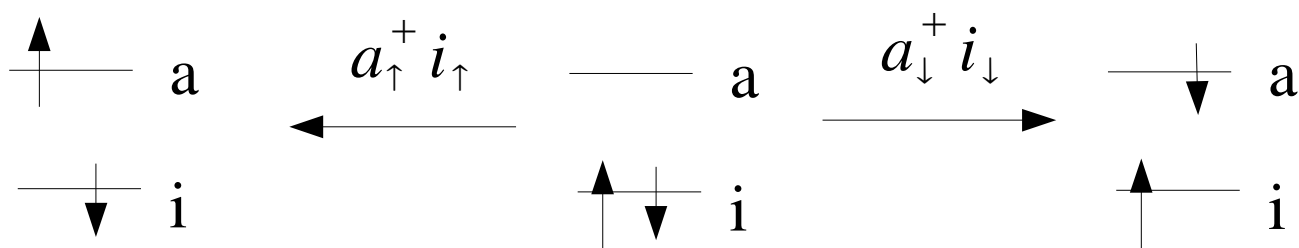$$A \vec{X}_I = \omega_I \vec{X}_I$$

$$\boxed{CIS = TDHF + TDA}$$

TDDFT reference : S. Hirato and M. Head-Gordon, Chem. Phys. Lett. **314**, 291 (1999)

TWO ORBITAL APPROXIMATION (2OA)

Because DFT orbitals are "preprepared" for describing excitation energies :
They see the same number of electrons and hence relaxation is minimal.

$$\omega_T = \epsilon_a - \epsilon_i + \left(ia \left| f_{xc}^{\uparrow\uparrow} - f_{xc}^{\uparrow\downarrow} \right| ia \right)$$

$$\omega_S = \epsilon_a - \epsilon_i + \left(ia \left| 2 f_H + f_{xc}^{\uparrow\uparrow} + f_{xc}^{\uparrow\downarrow} \right| ia \right)$$

Comparison with ΔSCF is not obvious (though results are often similar)

HARTREE-FOCK (HF) STATIC EXCHANGE (SX)

$$\omega_T = \epsilon_a(i^{-1}) - \epsilon_i - \left(ia\middle|f_H\middle|ai\right)$$

$$\omega_S = \epsilon_a(i^{-1}) - \epsilon_i + \left(ia\middle|f_H\middle|ai\right)$$

where

$$\epsilon_a(i^{-1}) = \epsilon_{a\uparrow}\left(\begin{array}{c}\overline{\qquad}\ a \\ \underline{\quad}\ i \\ \downarrow\end{array}\right) = \epsilon_a - \left(aa\middle|f_H\middle|ii\right) + \left(ia\middle|f_H\middle|ai\right)$$

$$\epsilon_i = \epsilon_i\left(\begin{array}{c}\overline{\qquad}\ a \\ \uparrow\underline{\quad}\ i \\ \downarrow\end{array}\right)$$

(See **deMon-StoBe** for a ΔSCF-based version of SX)

COMPARISON OF HF SX AND TDDFT

TDDFT

$$\omega_T = \epsilon_a - \epsilon_i + \left(ia \left| f_{xc}^{\uparrow\uparrow} \right| ia \right) - \left(ia \left| f_{xc}^{\uparrow\downarrow} \right| ia \right)$$

$$\omega_S = \epsilon_a - \epsilon_i + 2\left(ia \left| f_H \right| ia \right) + \left(ia \left| f_{xc}^{\uparrow\uparrow} \right| ia \right) + \left(ia \left| f_{xc}^{\uparrow\downarrow} \right| ia \right)$$

$$\left(ia \left| f_{xc}^{\uparrow\downarrow} \right| ia \right) \rightarrow 0 \qquad \text{No correlation}$$

$$\left(ia \left| f_{xc}^{\uparrow\uparrow} \right| ia \right) \rightarrow - \left(ai \left| f_H \right| ia \right) \qquad \text{Exchange integral}$$

HF SX

$$\omega_T = \epsilon_a(i^{-1}) - \epsilon_i - \left(ia \left| f_H \right| ai \right)$$

$$\omega_S = \epsilon_a(i^{-1}) - \epsilon_i + \left(ia \left| f_H \right| ai \right)$$
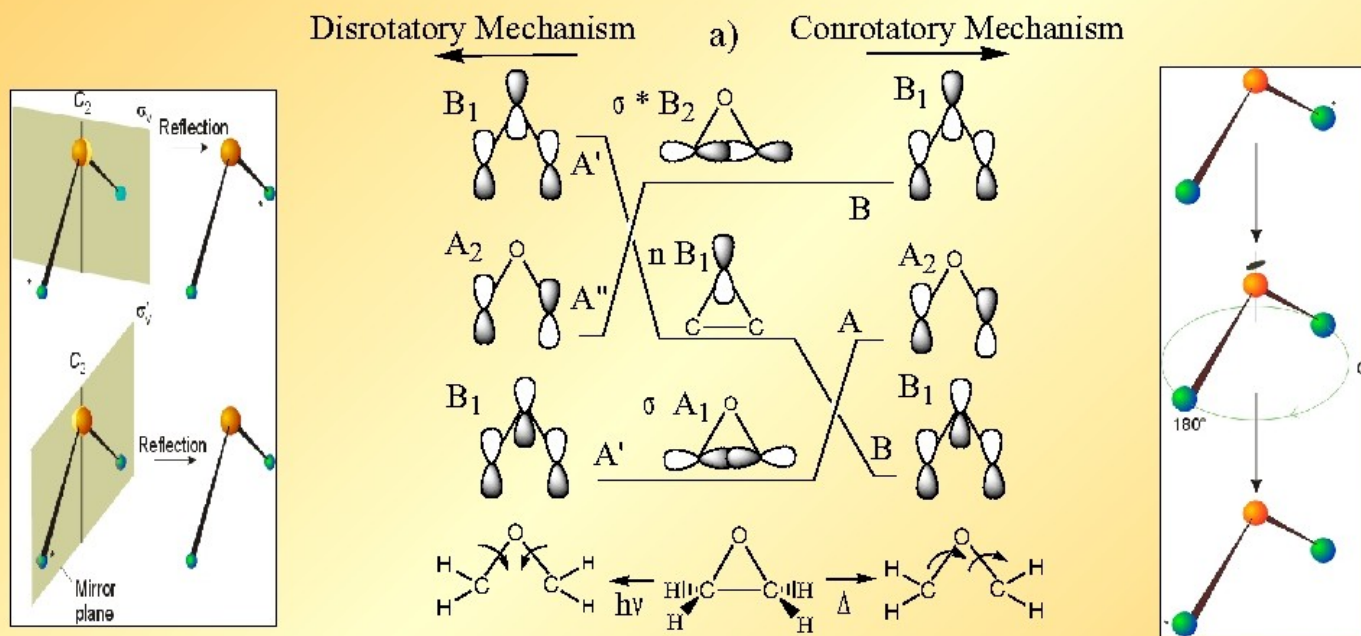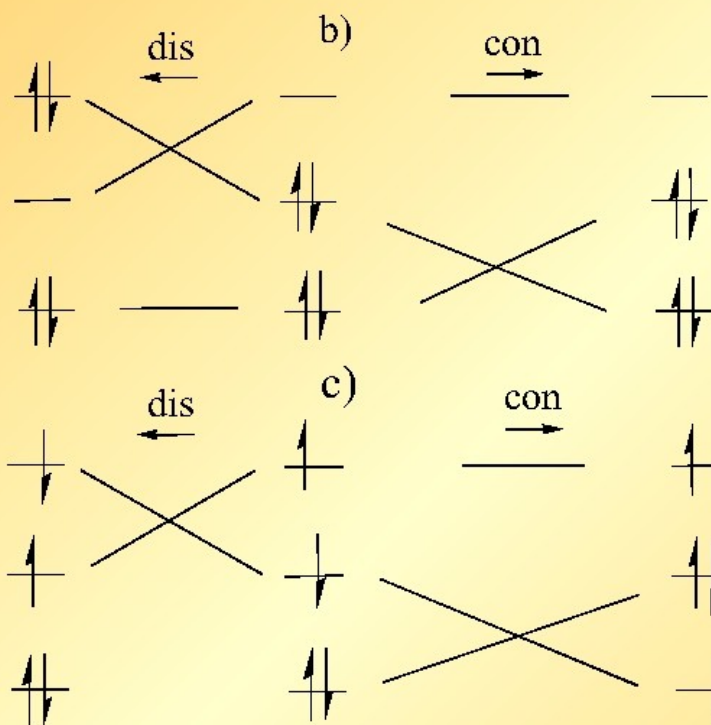
C-C RING OPENING IN OXIRANE

WOODWARD-HOFFMANN THEORY

Oxirane : a good molecule for computational test

F. Cordova, L. Joubert Doriol, A. Ipatov, M.E. Casida, and A. Vela, *in preparation*.

SYMMETRY BREAKING

Given a same orbitals for different spin (SODS) solution, is there a lower energy (symmetry broken) different orbitals for different spin (DODS) solution?

Try arbitrary unitary transformations of spin orbitals

$$\psi_r^\lambda(\vec{r}) = e^{i\lambda(\hat{R}+i\hat{I})}\psi_r(\vec{r})$$

Find

$$E_\lambda = E_0 + \lambda^2\left[\vec{R}^+\left(A-B\right)\vec{R} + \vec{I}^+\left(A+B\right)\vec{I}\right] + O(\lambda^3)$$
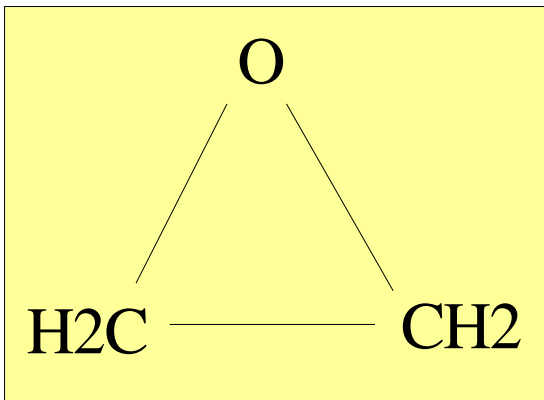
But another form of Casida's equation is

$$\left(A+B\right)\left(A-B\right)\vec{Z}_I = \omega_I^2\vec{Z}_I$$

Conclude :

Symmetry breaking if and only if imaginary triplet excitation energies
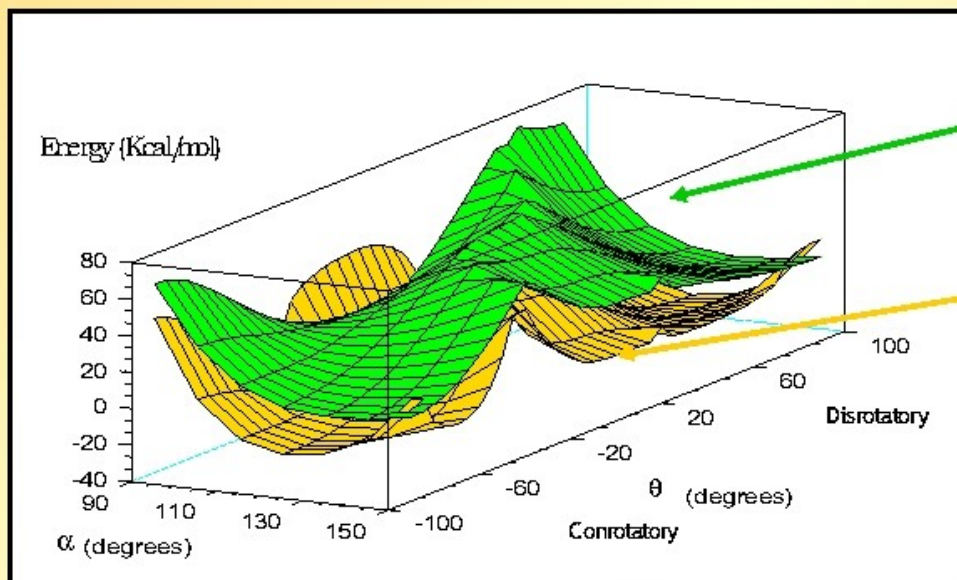
WHAT ABOUT OXIRANE?

O

H2C —— CH2

Exact DFT
- Singlet ground state
- Same spin up and spin down densities
- Same spin up and spin down exchange-correlation potential
- Same orbitals for different spin (SODS)
- No symmetry breaking

Applied DFT
- Symmetry breaking may occur
- Symmetry breaking may help to describe an otherwise muticonfigurational situation
- But symmetry breaking is an unwanted extra complication when carrying out large numbers of TDDFT calculations (e.g. on-the-fly photochemical dynamics simulations)

93% of the surface shows symmetry breaking
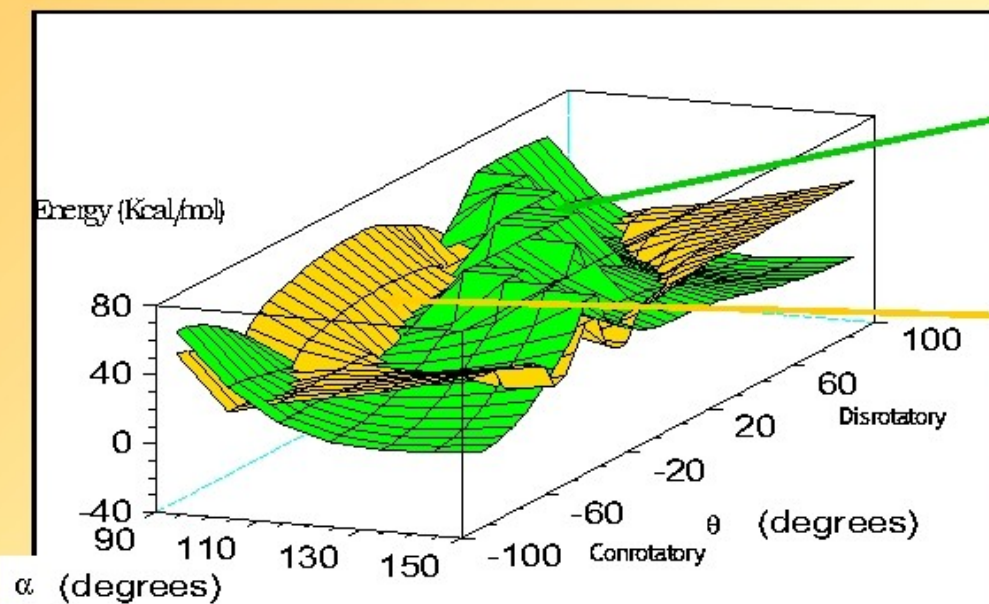
TDB3LYP

Which would you use?

50% of the surface shows symmetry breaking

TDLDA

USE TDA TO DECOUPLE QUALITY OF EXCITED STATE FROM GROUND STATE STABILITY CONDITION

M.E. Casida et al., J. Chem. Phys. **113**, 7062 (2000)

USE TDA TO DECOUPLE QUALITY OF EXCITED STATE FROM GROUND STATE STABILITY CONDITION

M.E. Casida et al., J. Chem. Phys. **113**, 7062 (2000)

Why Are Spectra of Open-Shell Molecules Interesting?

Ionization Spectra

$(2\sigma_g)^{-1}$

$(2\sigma_g)^{-1}$

$(2\sigma_u)^{-1}$

$(3\sigma_g)^{-1}$

$(1\pi_u)^{-1}$

$C_2H_2^+$

C_2H_2

P. Duffy, S.A.C. Clark, C.E. Brion, *et al*. Chem. Phys. **165**, 183 (1992)

DODS FOR EXCITATIONS IN RADICALS

CN radical

S. Hirata and M. Head-Gordon, Chem. Phys. Lett. **302**, 375 (1999).

SODS ANALYSIS OF EXCITATIONS IN RADICALS

SPIN OPERATORS

$$\hat{S}^2 = \sum \hat{P}_{\uparrow\downarrow} + \hat{n}_{\uparrow} + \hat{S}_z\left(\hat{S}_z - \hat{1}\right)$$

$$\hat{S}_z = \frac{1}{2}\left(\hat{n}_{\uparrow} - \hat{n}_{\downarrow}\right)$$

where

$$\hat{n}_{\sigma} = \sum \hat{r}_{\sigma}^{+} \hat{r}_{\sigma}$$

$$\hat{P}_{\uparrow\downarrow} = \sum \hat{r}_{\uparrow}^{+} \hat{s}_{\downarrow}^{+} \hat{s}_{\uparrow} \hat{r}_{\downarrow}$$

- Single determinants are eigenfunctions of S_z but not necessarily of S^2

- Eigenfunctions of S^2 are linear combinations of determinants with different distributions of the same number of up and down spins.

Doublets

$$\left| i\,\bar{i}\,a \right\rangle \qquad \left| i\,\bar{v}\,v \right\rangle$$

$$\left| D_1 \right\rangle = \frac{1}{\sqrt{2}} \left(\left| \bar{i}\,v\,a \right\rangle - \left| i\,v\,\bar{a} \right\rangle \right)$$

$$\left| D_2 \right\rangle = \frac{1}{\sqrt{6}} \left(\left| \bar{i}\,v\,a \right\rangle + \left| i\,v\,\bar{a} \right\rangle - 2 \left| i\,\bar{v}\,a \right\rangle \right)$$

Quadruplet

$$\left| Q \right\rangle = \frac{1}{\sqrt{3}} \left(\left| \bar{i}\,v\,a \right\rangle + \left| i\,v\,\bar{a} \right\rangle + \left| i\,\bar{v}\,a \right\rangle \right)$$

"Extended Singles"
(a type of doubles)

Singlet Coupling   **Doublets**

$$\left| i\, \bar{i}\, a \right\rangle$$

$$\left| i\, \bar{v}\, v \right\rangle$$

$$\left| D_1 \right\rangle = \frac{1}{\sqrt{2}} \left(\left| \bar{i}\, v\, a \right\rangle - \left| i\, v\, \bar{a} \right\rangle \right)$$

Triplet Coupling   **Neither a doublet nor a quadruplet!**

$$\left| TC \right\rangle = \frac{1}{\sqrt{2}} \left(\left| \bar{i}\, v\, a \right\rangle + \left| i\, v\, \bar{a} \right\rangle \right)$$

MISSING: The quadruplet and one of the doublets!

CONSEQUENCES FOR OPEN-SHELL MOLECULES

In the adiabatic approximation,
- Only transitions which conserve S^2 have correct symmetry
- There are too few transitions conserving S^2

!

intensity=1

$\omega(S)$

intensity = $\sin^2\theta$

intensity = $\cos^2\theta$

$\omega(\Psi)$ $\omega(\Psi')$
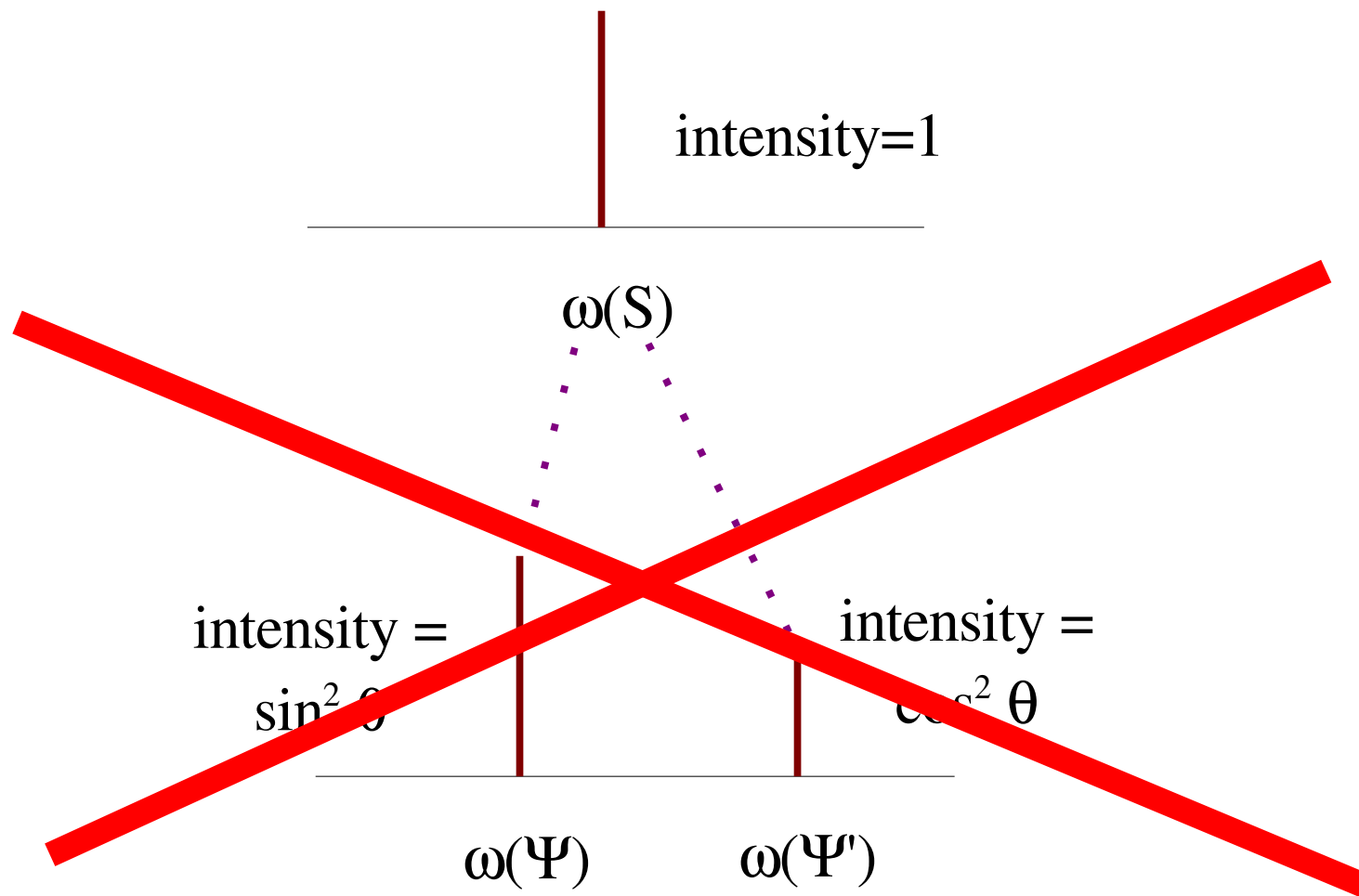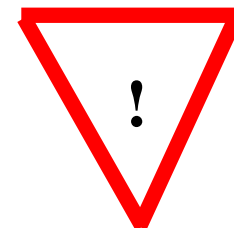
Need a way to calculate spin contamination for TDDFT excited states

BASIC IDEA

Evaluate

$$\langle \Psi | \hat{S}^2 | \Psi \rangle$$

This is a necessary but not a sufficient condition that

$$\hat{S}^2 \Psi = S(S+1)\Psi$$

"Fortran" index convention

$$\underbrace{a\,b\,c\,d\,...\,g\,h}_{unoccupied}\,\underbrace{i\,j\,k\,l\,m\,n}_{occupied}\,\underbrace{o\,p\,q\,...\,x\,y\,z}_{free}$$

Second quantization poor man's notation

$$r_\alpha = \hat{a}_{r\alpha} \qquad r_\alpha^+ = \hat{a}_{r\alpha}^+$$

Number operators

$$\hat{n}_\alpha = \sum r_\alpha^+ r_\alpha \qquad \hat{n}_\beta = \sum r_\beta^+ r_\beta$$

$$\hat{S}_+ = \sum r_\alpha^+ r_\beta \qquad \hat{S}_- = \sum r_\beta^+ r_\alpha \qquad \hat{S}_z = \frac{1}{2}(\hat{n}_\alpha - \hat{n}_\beta)$$

$$\hat{S}^2 = \hat{S}_+ \hat{S}_- + \hat{S}_z(\hat{S}_z - \hat{1}) \quad \Rightarrow \quad \hat{S}^2 = \sum \hat{P}_{\alpha\beta} + \hat{n}_\alpha + \hat{S}_z(\hat{S}_z - \hat{1})$$

Spin transposition operator

$$\hat{P}_{\alpha\beta} = r_\beta^+ s_\alpha^+ s_\beta r_\alpha$$
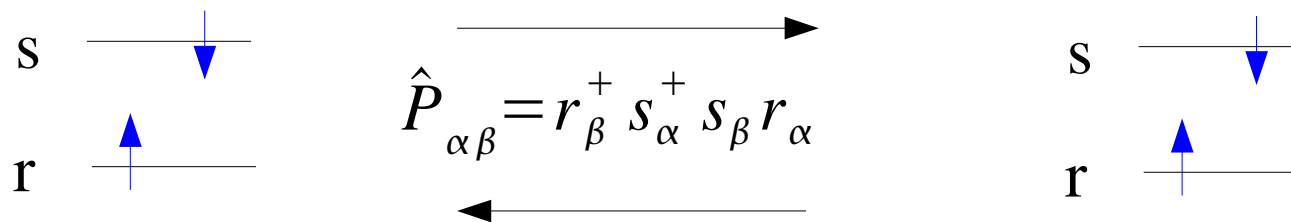
"DODS overlap matrix"

$$\Delta_{r,\bar{s}} = \langle \phi_r | \bar{\phi}_s \rangle \qquad \Delta^+_{\bar{r},s} = \langle \bar{\phi}_r | \phi_s \rangle$$

So

$$\psi^\alpha_r = \phi_r \alpha = \sum \phi_{\bar{s}\alpha} \Delta^+_{\bar{s},r} \qquad\qquad r^+_\alpha = \sum \bar{s}^+ \Delta^+_{\bar{s},r}$$

$$\psi^\beta_r = \bar{\phi}_r \beta = \sum \phi_{s\beta} \Delta_{s,\bar{r}} \qquad\qquad \bar{r}^+_\beta = \sum s^+_\beta \Delta_{s,\bar{r}}$$

And

$$\sum \hat{P}_{\alpha\beta} = \sum \bar{p}^+_\beta s^+_\alpha \bar{q}_\beta r_\alpha \Delta^+_{\bar{p},r} \Delta^+_{\bar{q},s}$$

$$\Phi = \left| \psi_1^\alpha \psi_2^\alpha \ldots \psi_1^\beta \psi_2^\beta \ldots \right|$$

$$\langle \Phi | \hat{S}^2 | \Phi \rangle = \langle \Phi | \sum \hat{P}_{\alpha\beta} | \Phi \rangle + n_\alpha + S_z (S_z - 1)$$

$$\langle \Phi | \sum \hat{P}_{\alpha\beta} | \Phi \rangle = \sum \langle \Phi | \bar{p}_\beta^+ s_\alpha^+ \bar{q}_\beta r_\alpha | \Phi \rangle \Delta_{\bar{p},r}^+ \Delta_{s,\bar{q}}$$

Application of Wick's theorem gives

$$\langle \Phi | \sum \hat{P}_{\alpha\beta} | \Phi \rangle = -\sum^{\text{occ}} |\Delta_{j,\bar{i}}|^2$$

EXCITED-STATE SPIN-CONTAMINATION

• Even in TDHF there is no wave function: obtain 2-electron reduced difference density matrix (2RDDM) from differentiation of excitation energy with respect to electron repulsion integrals (ERI)

• Don't know how to take the derivative of the xc terms with respect to ERIs: just use the TDHF expression.

Are we the first to derive the TDHF spin-contamination expression?

• We use the *un*relaxed density matrix (approximation!)

• Our expression reduces to a previous result in the CIS limit: D. Maurice and M. Head-Gordon, Int. J. Quant. Chem. Symp **29**, 361 (1995).

Result :

$$\Delta \langle \hat{S}^2 \rangle_I = \sum X_{j\bar{a}\downarrow}^{I*} X_{k\bar{a}\downarrow}^{I} \langle \bar{k}|i\rangle \langle i|\bar{j}\rangle$$

$$+ \sum X_{i\bar{a}\uparrow}^{I*} X_{l\bar{a}\uparrow}^{I} \langle l|\bar{j}\rangle \langle \bar{j}|i\rangle$$

$$+ \sum Y_{k\bar{a}\downarrow}^{I*} Y_{j\bar{a}\downarrow}^{I} \langle \bar{k}|i\rangle \langle i|\bar{j}\rangle$$

$$+ \sum Y_{l\bar{a}\uparrow}^{I*} Y_{i\bar{a}\uparrow}^{I} \langle l|\bar{j}\rangle \langle \bar{j}|i\rangle \,,$$

$$- 2\Re \sum X_{ib\uparrow}^{I*} X_{j\bar{a}\downarrow}^{I} \langle b|\bar{a}\rangle \langle \bar{j}|i\rangle$$

$$- 2\Re \sum Y_{j\bar{a}\downarrow}^{I*} Y_{ib\downarrow}^{I} \langle b|\bar{a}\rangle \langle \bar{j}|i\rangle$$

$$- \sum X_{k\bar{b}\downarrow}^{I*} X_{k\bar{a}\downarrow}^{I} \langle \bar{b}|i\rangle \langle i|\bar{a}\rangle$$

$$- \sum Y_{k\bar{a}\downarrow}^{I*} Y_{k\bar{b}\downarrow}^{I} \langle \bar{b}|i\rangle \langle i|\bar{a}\rangle \,,$$

$$- \sum X_{k\bar{b}\uparrow}^{I*} X_{k a\uparrow}^{I} \langle b|\bar{i}\rangle \langle \bar{i}|a\rangle$$

$$- \sum Y_{k a\uparrow}^{I*} Y_{k\bar{b}\uparrow}^{I} \langle b|\bar{i}\rangle \langle \bar{i}|a\rangle \,,$$

$$+ 2\Re \sum X_{ib\uparrow}^{I*} Y_{j\bar{a}\downarrow}^{I} \langle b|\bar{j}\rangle \langle \bar{a}|i\rangle$$

$$+ 2\Re \sum X_{j\bar{a}\downarrow}^{I*} Y_{ib\uparrow}^{I} \langle b|\bar{j}\rangle \langle \bar{a}|i\rangle \,,$$

A. Ipatov, F. Cordova, and M.E. Casida, *in preparation*.

TABLE VI: Spin contamination in CN excited states.

| State | Excitation Energy (eV) [f] ($\Delta\langle\hat{S}^2\rangle$) | | | | |
	TDLDA[a]	TDLDA[b]	TDLDA TDA[b]	Assign.[c]	Ref. Values[d]
	TDLDA spin up ionization threshold = 9.7 eV				
	TDLDA spin down ionization threshold = 9.5 eV				
7	8.3190	8.3210	8.3210		
	[0.0000]	(0.9967)	(0.9967)		
6	8.0324	8.0334	8.0334		
	[0.0000]	(0.9967)	(0.9967)		
5	8.0518	7.9829	8.0236	$^2\Pi$	8.619
	[0.0027]	(0.0948)	(0.0964)	($5\sigma^{SOMO} \to 2\pi$)	
4	7.4325	7.1807	7.2699	$^{TC}\Delta$	
	[0.0000]	(2.0050)	(1.9838)	($1\pi \to 2\pi$, $1\bar{\pi} \to 2\bar{\pi}$)	
3	6.6347	6.0967	6.4792	$^{TC}\Sigma+$	
	[0.0008]	(1.9928)	(1.9152)	($1\pi \to 2\pi$)	
2	3.2333	2.8364	3.1908	$^2\Sigma+$	3.661
	[0.0366]	(0.1566)	(0.0786)	($4\bar{\sigma} \to 5\bar{\sigma}^{SOMO}$)	
1	1.3576	1.2131	1.3017	$^2\Pi$	1.235
	[0.0029]	(0.0160)	(0.0084)	($1\bar{\pi} \to 5\bar{\sigma}^{SOMO}$)	

[a]GAUSSIAN03.

[b]DEMON2K.

[c]TDLDA TDA.

[d]Multireference configuration interaction vertical excitation energies calculated from the data in Table III of Ref. [47] at $R_e = 2.211$ bohr.

TDDFT $\qquad \chi = \chi_0 + \chi_0 \left[v + f_{xc} \right] \chi_0$

BSE $\qquad {}^4\chi = {}^4\chi_0 + {}^4\chi_0 \left[v + \dfrac{\delta \Sigma_{xc}}{\delta G} \right] {}^4\chi_0$

$$\chi(1,3) = {}^4\chi(1,1;3,3) \qquad \Rightarrow \qquad \chi = \chi_0 + {}^3\chi_0 \left[v + \dfrac{\delta \Sigma_{xc}}{\delta G} \right] {}^3\chi_0$$

Leads to "THE" approximation

$$\chi_0 f_{xc} \chi_0 = {}^3\chi_0 \dfrac{\delta \Sigma_{xc}}{\delta G} {}^3\chi_0$$

Similar on this level:

Reining et al, PRL 88, 066404 (2002);
Sottile PhD thesis and Sottile et al, PRL 91, 056402 (2003)

Bruneval PhD thesis and
Bruneval, Sottile, Olevano, Del Sole, Reining, PRL (2005)

Adragna PhD thesis and Adragna et al, PRB 68, 165108 (2003),
Marini et al PRL 91, 256402 (2003)

Stubner, Tokatly, Pankratov, PRB 70, 245119 (2004)
and Ref. therein

von Barth, Dahlen, van Leeuwen, Stefanucci,
PRB 72, 235109 (2005)

From Lucia Reining's Nanoquanta presentation, September 2006

"THE" approximation is still an approximation

$$f_{xc} = f_{xc}^{quasiparticle} + f_{xc}^{excitonic}$$

$f_{xc}^{excitonic}$ approximated by "THE" approximation

$f_{xc}^{quasiparticle}$ not included in "THE" approximaiton (takes into account
self-energy corrections to KS orbital energies)

<u>Diagrammatic representation of f_{xc}</u>

I.V. Tokatly and O. Pankratov, PRL 86, 2078 (2001)

I.V. Tokatly, R. Stubner, and O. Pankratov, PRB 65, 1131 (2002)

R. Stubner, I.V. Tokatly, and O. Pankratov, PRB 70, 245129 (2004)

PROPAGATOR CORRECTIONS TO TDDFT

M.E. Casida, J. Chem. Phys. **122**, 044110 (2005).

$$\left[\left(\vec{T}_1^+\middle|\hat{h}_s\middle|\vec{T}_1^+\right)_s + K_{Hxc}(\omega_I)\right]\vec{U}_I^{(1)} = \omega_I\left(\vec{T}_1^+\middle|\vec{T}_1^+\right)_s\vec{U}_I^{(1)}$$

$$K_{Hxc}(\omega) = \underbrace{\left(\vec{T}_1^+\middle|\hat{H}-\hat{h}_s\middle|\vec{T}_1^+\right)_s}_{adiabatic\,TDDFTx} + \underbrace{K(\omega)}_{propagator\,correction}$$

$$K(\omega) = \left(\vec{T}_1^+\middle|\hat{H}\middle|\vec{T}_{2+}^+\right)_s\left[\omega\left(\vec{T}_{2+}^+\middle|\vec{T}_{2+}^+\right)_s - \left(\vec{T}_{2+}^+\middle|\hat{H}\middle|\vec{T}_{2+}^+\right)_s\right]^{-1}\left(\vec{T}_{2+}^+\middle|\hat{H}\middle|\vec{T}_1^+\right)_s$$

Note that the propagator correction contains the correlation part of the adiabatic coupling matrix, K(0).

51

PROPAGATOR CORRECTIONS TO TDDFT : DRESSED TDDFT

The present treatment is essentially equivalent to "dressed TDDFT" for the closed-shell case :

$$2\left[q\left|f_{xc}(\omega)\right|q\right]=2\left[q\left|f_{xc}^{A}(\omega_{q})\right|q\right]+\frac{\left|H_{qD}\right|^{2}}{\omega-(H_{DD}-H_{00})}$$

- [MZCB04] N.T. Maitra, F. Zhang, F.J. Cave, and K. Burke, J. Chem. Phys. **120**, 5932 (2004). "Double excitations within time-dependent density functional theory linear response"
- [CZMB04] R.J. Cave, F. Zhang, N.T. Maitra, and K. Burke, Chem. Phys. Lett. **389**, 39 (2004). "A dressed TDDFT treatment of the 21Ag states of butadiene and hexatriene"

2 1Ag VERTICAL EXCITATION ENERGY (eV)
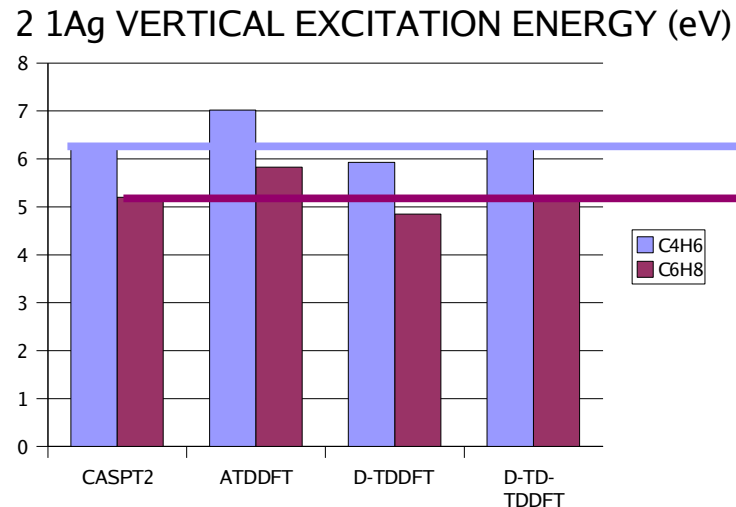
Modifications are needed for the open-shell case.

I. Introduction

II. Review of Conventional DFT

III. ΔSCF and the Multiplet Sum Method

IV. Review of Conventional TDDFT

V. Stability Analysis

VI. Spin-Contamination

VII. Explicit Incorporation of Higher Excitations

VIII. Conclusion

SUMMARY

It has been said that DFT stands for "Darned Fine Theory"
DFT has reached a sort of happy maturity.

It has also been said that TDDFT stands for
"Terribly Difficult Darned Fine Theory" (André Bandrock)
TDDFT is perhaps best described as being an awkward teenager.

- TDDFT has proven its worth as a valuable complement to ab initio excited state methods (especially CASPT2)
- I have tried to emphasize how TDDFT works at a simple level and to contrast it with the ΔSCF method (which gives similar results when both apply)
- I talked about several problems often associated with the breakdown of the single determinantal approximation : symmetry breaking, spin-contamination, explicit higher-order excitations