Time-Dependent Density-Functional Theory with Molecules in Mind

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Rhône-Alpes Associated Node

DCEN211
Kyoto, Japan
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60 min.

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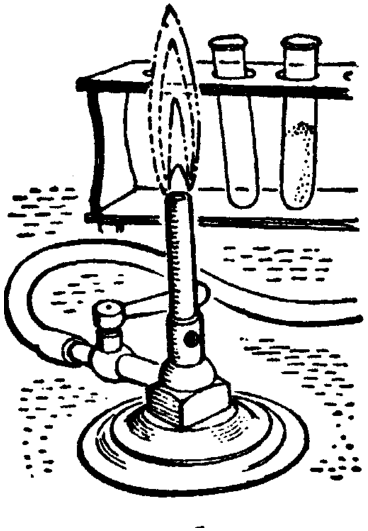
I. Interdisciplinarity
II. Our Interests
III. DFT
IV. TD-DFT
V. Successes/Problems/Solutions
VI. Conclusion

“*Ein Chemiker, der nicht gleichzeitig Physiker ist,
ist gar nichts.*”*
Robert Eberhard Wilhelm Bunsen (1811-1899)

- Spectroscopy for chemical characterization
- Photochemistry
- A nifty little burner -->
- and quite a few other things



*** “A chemist who is not at the same time a physicist is nothing at all.”**

"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."

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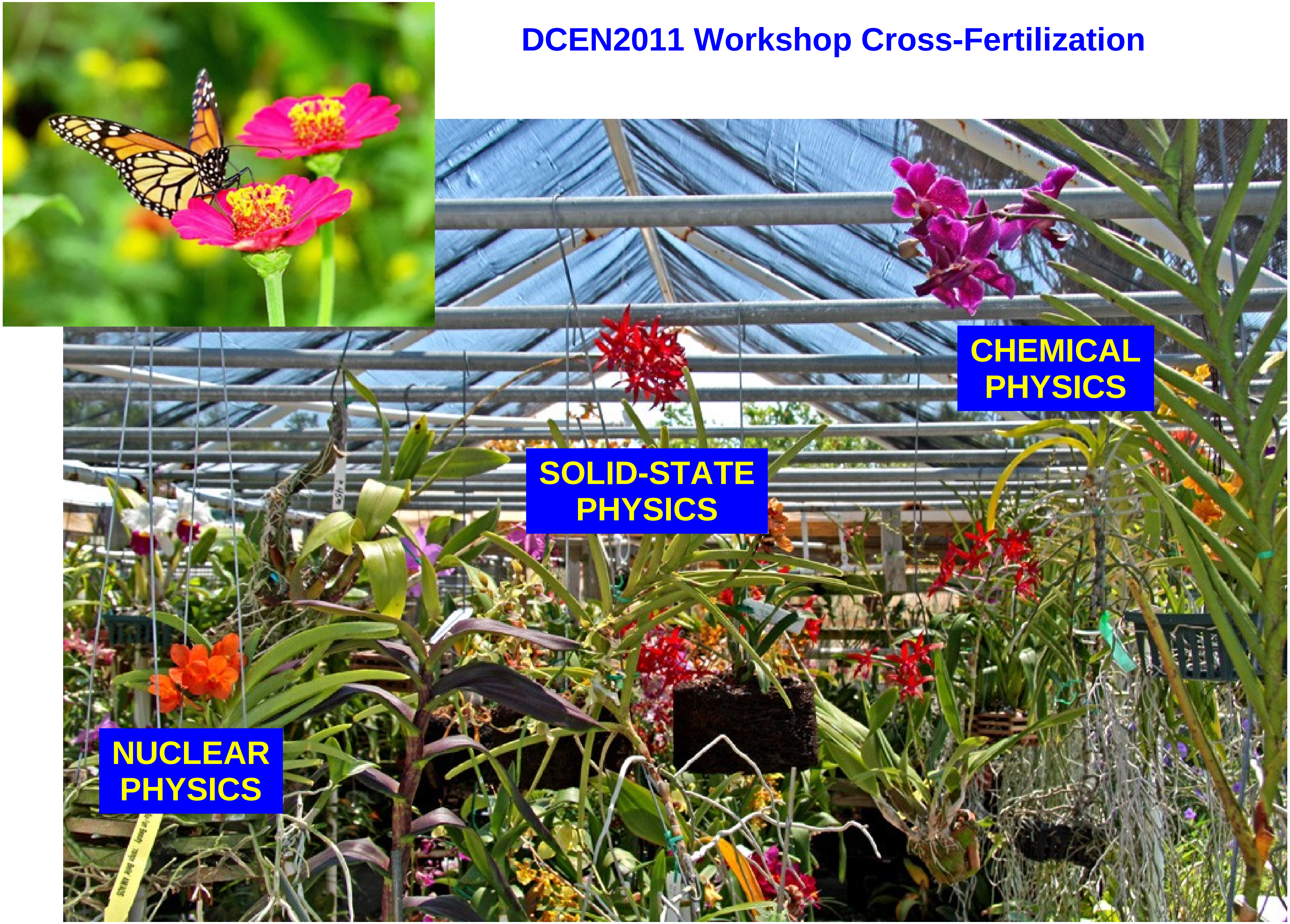
DCEN2011 Workshop Cross-Fertilization



Quick Comparison of Different Fields

Nuclear Physics:
- Finite systems
- *No Born-Oppenheimer separation*
- *Complicated and incompletely-known forces*

Chemical Physics:
- Finite systems
- Born-Oppenheimer separation
- Simple well-characterized forces

Solid-State Physics:
- *Infinite systems*
- Born-Oppenheimer separation
- Simple well-characterized forces

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DuPont Chemical Company Motto

1935
“Better things for better living ... through chemistry.”

1982
“Better things for better living.”

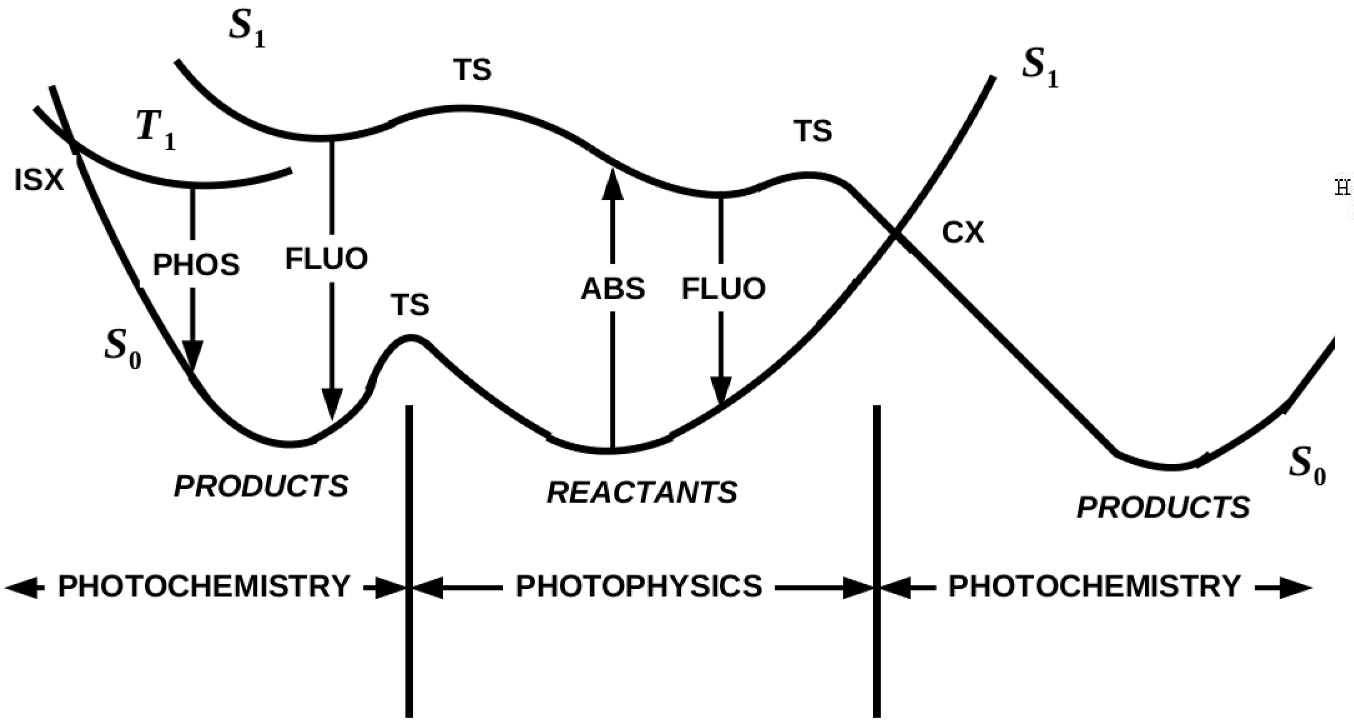
1999
“The miracles of science.”

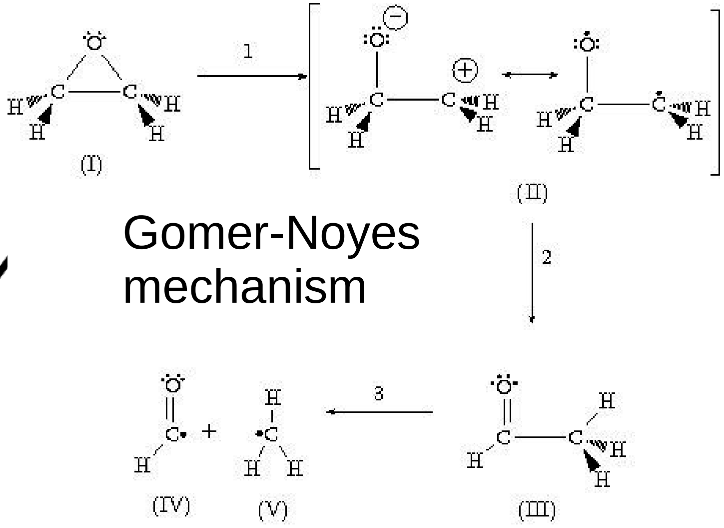
In my e-mail signature:

"Improving theory for better chemistry."

Photoprocesses

Mark E. Casida, Bhaarathi Natarajan, and Thierry Deutsch, **http://arxiv.org/abs/1102.1849** in *Fundamentals of Time-Dependent Density-Functional Theory*, edited by E.K.U. Gross, Miquel Marques, Fernando Noguiera, and Angel Rubio (Springer: *in press*).
"**Non-Born-Oppenheimer dynamics and conical intersections**"





Gomer-Noyes mechanism

Challenge: Photodynamics calculations require fast on-the-fly calculation of forces.

Photochemical Molecuar Devices (PMDs)

Definition:* “structurally organized and functionally integrated systems capable of elaborating the energy and information input of photons to perform *complex functions*”

- Light harvesting
- Conversion of light into chemical or electrical energy
- Collection of information in a molecular shift register
- Etc.

Components of PMDs include switches, spacers, leads, catalytic centers, etc.

The problem is to fabricate and assemble components into working devices.

Challenge: Modeling of complex systems.

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* From J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, and C. Coudret, *Chem. Rev.* **94**, 993 (1994).

Dye-sensitized solar cells (DSSCs)

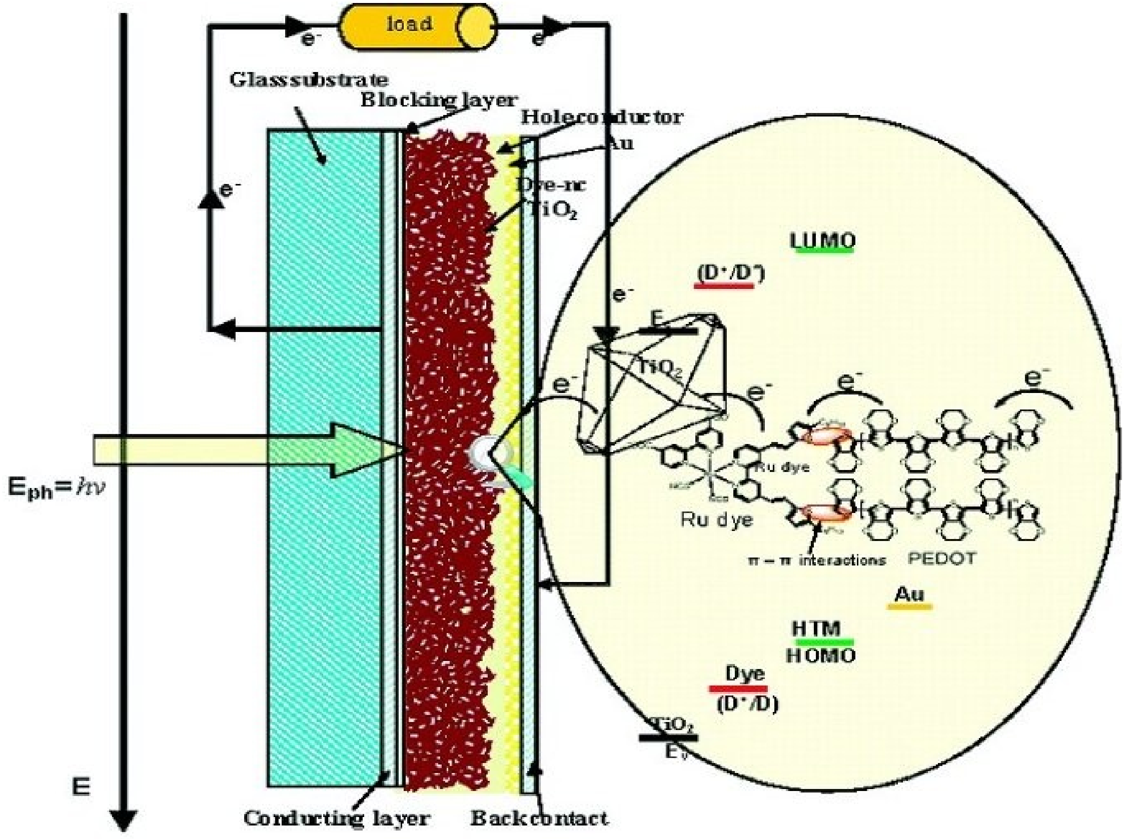

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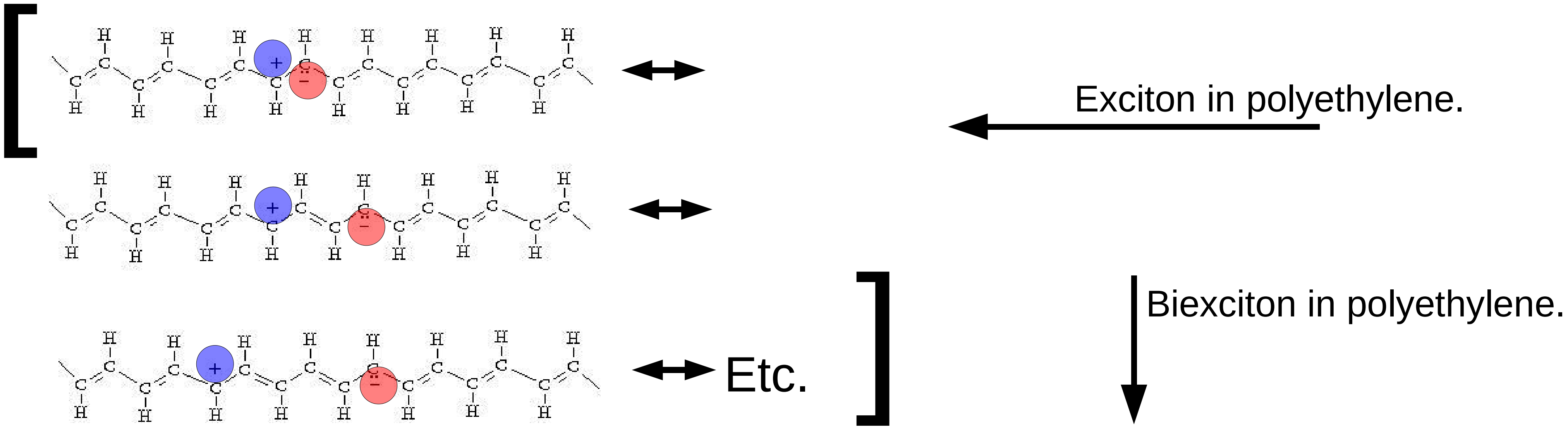
*Image from: *Acc. Chem. Res.* **42**, 1827 (2009)

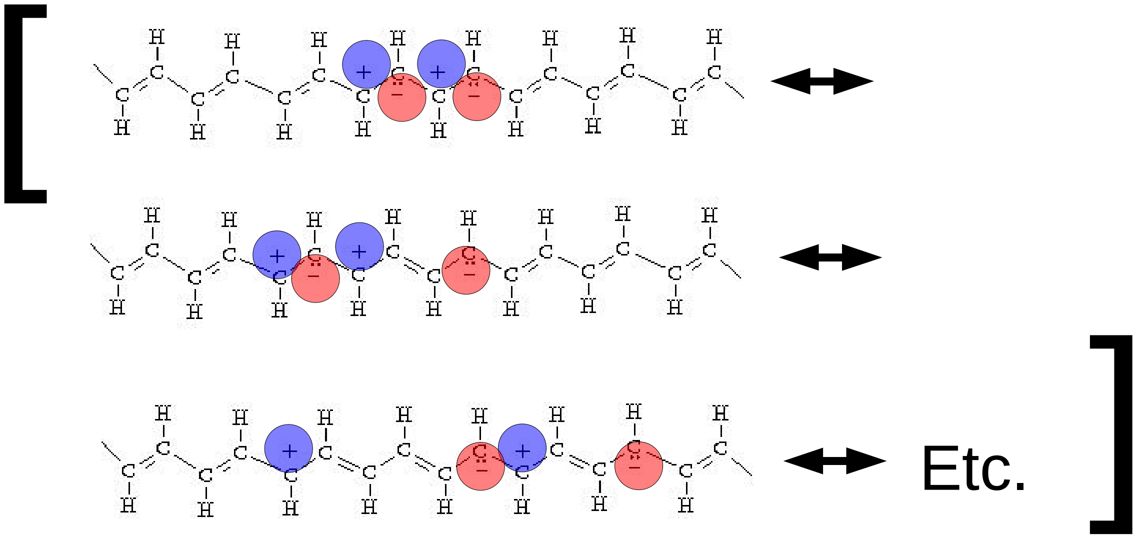
Excitons



Etc.

Exciton in polyethylene.

Biexciton in polyethylene.

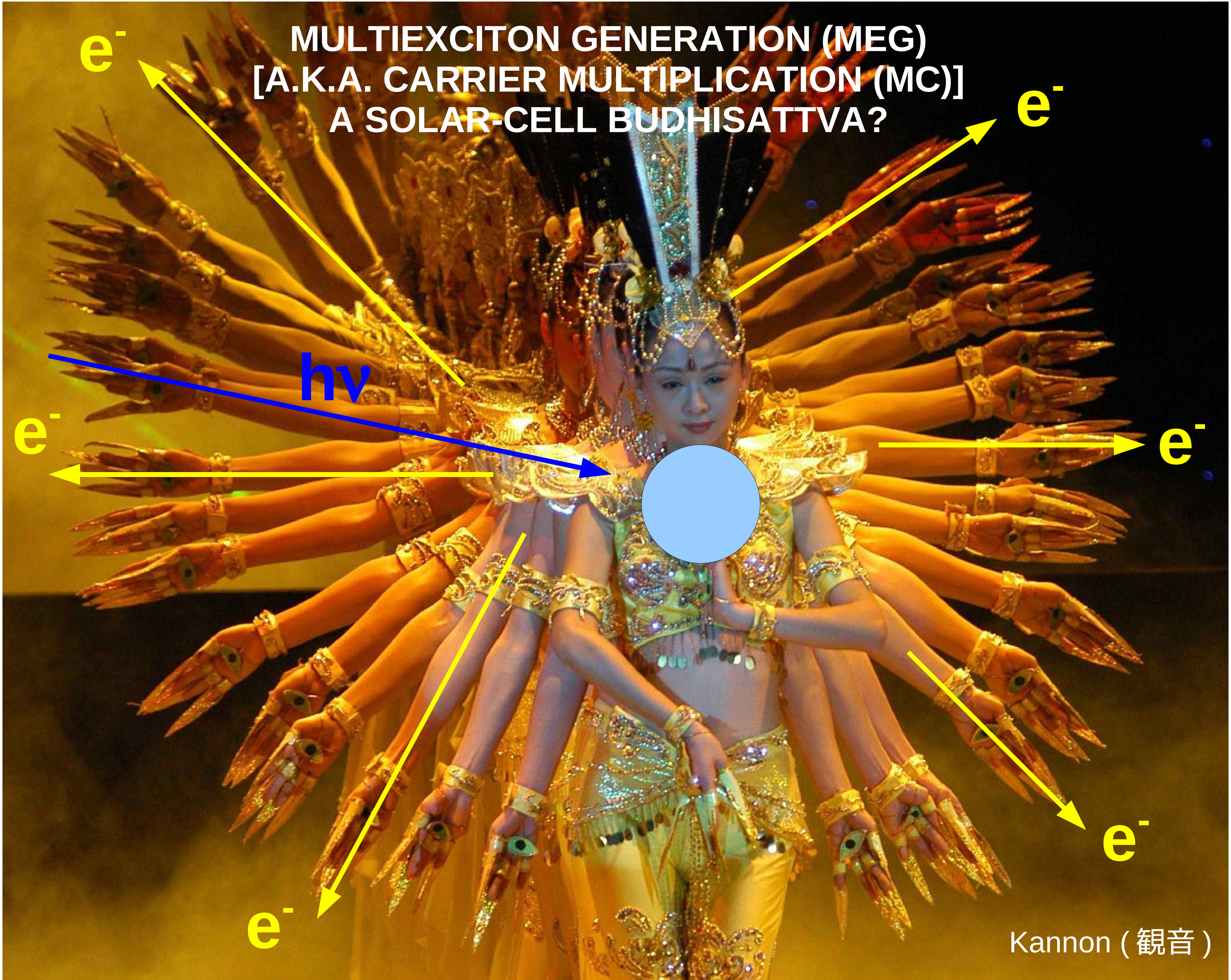


Etc.

Challenges:

- ***System size.***
- ***Charge-transfer excitations.***
- ***Polaron coupling.***
- ***Dynamics.***
- ***“Photochemistry++”***

MULTIEXCITON GENERATION (MEG)
[A.K.A. CARRIER MULTIPLICATION (MC)]
A SOLAR-CELL BUDHISATTVA?



Kannon (観音)

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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:

$$\rho \rightarrow N, v_{ext} + C \rightarrow \hat{H} + C \rightarrow \Psi_I, \omega_I = E_I - E_0 \qquad (1)$$

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

$$E = F[\rho] + \int v_{ext}(\vec{r})\rho(\vec{r})\,d\vec{r} \qquad (2)$$

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

Levy-Lieb Constrained Variational Principle

$$F[\rho]=min_{\Psi\to\rho}\frac{\langle\Psi|\hat{T}+V_{ee}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad (1)$$

- Avoids *v*-representablity
- Assumes the density is *N*-representable (it is!)
- The functional is known! (but not practical)

Extension to Ensemble Theory:

$$F[\rho]=min_{D\to\rho}tr\left[\left(\hat{T}+V_{ee}\right)D\right] \quad (2)$$

$$\hat{D}=\sum_I p_I|\Psi_I><\Psi_I| \quad (3)$$

Probability of observing system *I* with state Ψ_I.

The Kohn-Sham Formulation
[*Phys. Rev.* 140, A1133 (1965)]

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

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

where

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

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

$$[-\frac{1}{2}\nabla^2 + v_{ext}(\vec{r}) + \int \frac{\rho(\vec{r}\,')}{|\vec{r} - \vec{r}\,'|} d\vec{r}\,' + v_{xc}(\vec{r})]\psi_{i\sigma}(\vec{r}) = \varepsilon_{i\sigma}\psi_{i\sigma}(\vec{r}) \quad (3)$$

where the exchange-correlation potential is

$$v_{xc}[\rho](\vec{r}) = \frac{\delta E_{xc}[\rho]}{\delta \rho(\vec{r})} \quad (4)$$

Functional Derivatives

Definition

$$E_{xc}[\rho+\delta\rho]-E_{xc}[\rho]=\int\frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})}\delta\rho(\vec{r})\,d\vec{r} \qquad (1)$$

We will need ...

$$v_{xc}[\rho](\vec{r})=\frac{\delta E_{xc}[\rho]}{\delta\rho(\vec{r})} \qquad (2)$$

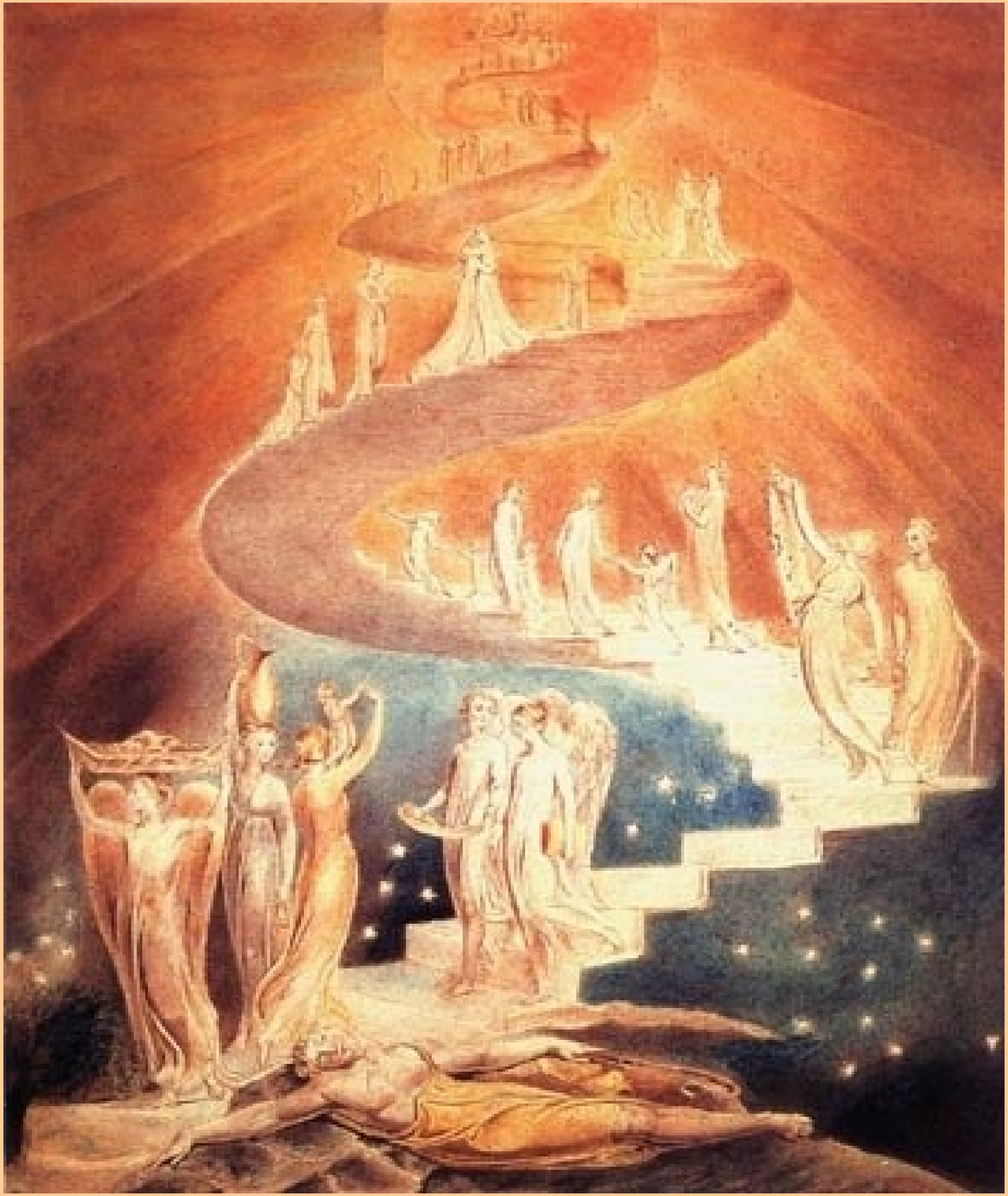
$$f_{xc}[\rho](\vec{r}_1,\vec{r}_2)=\frac{\delta^2 E_{xc}[\rho]}{\delta\rho(\vec{r}_1)\delta\rho(\vec{r}_2)} \qquad (3)$$

even

$$g_{xc}[\rho](\vec{r}_1,\vec{r}_2,\vec{r}_3)=\frac{\delta^3 E_{xc}[\rho]}{\delta\rho(\vec{r}_1)\delta\rho(\vec{r}_2)\delta\rho(\vec{r}_3)} \qquad (4)$$

Taking Stock

- So far everything is *pure* density-functional theory (only depends on ρ .)
- Nowadays pure DFT is *pure* spin-DFT (depends upon ρ_α and ρ_β .)
- Most people no longer do pure DFT (pure Kohn-Sham) but rather do *generalized* Kohn-Sham (GKS) which includes an orbital dependence.



“Jacob's ladder”
William Blake
water color
1799-1800

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).

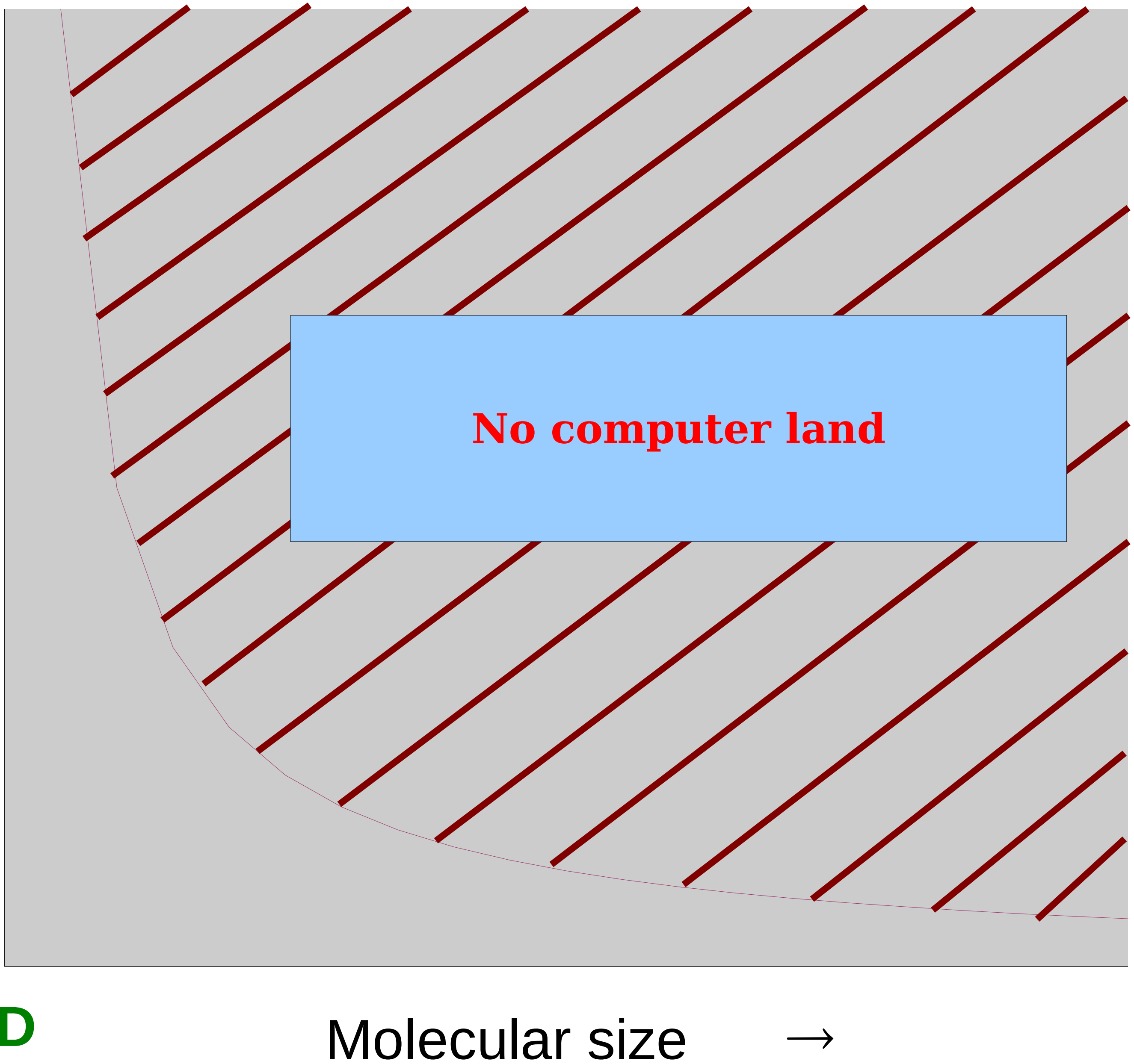
See also J.P. Perdew, A. Ruzsinsky, L.A. Constantin, J. Sun, and G.I. Csonka, *J. Chem. Theory Comput.* **5**, 902 (2009). “Some Fundamental Issues in Ground-State Density-Functional Theory: A Guide for the Perplexed”

Jacob's ladder

THEORETICAL CHEMISTRY HEAVEN

MBPT	*ab initio* DFT
$\hat{K}_x^{HF}$	hybrid/OEP
$\tau(\vec{r}) = \sum_i n_i \lvert\nabla\psi_i\rvert^2$	mGGA*
$x(\vec{r}) = \frac{\lvert\nabla\rho(\vec{r})\rvert}{\rho(\vec{r})^{4/3}}$	GGA
Pure DFT	
$\rho(\vec{r})$	LDA

HARTREE WORLD



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* or include $\nabla^2\rho$

Range-Separated Hybrids (RSH)*

Modern GKS is
- less and less B3LYP
- more and more RSH

$$\frac{1}{r_{12}} = \underbrace{\frac{erfc\left(\gamma r_{12}\right)}{r_{12}}}_{SHORT\ RANGE} + \underbrace{\frac{erf\left(\gamma r_{12}\right)}{r_{12}}}_{LONG\ RANGE}$$

Molecules:
- SR <-> DFT
- LR <-> WF (e.g. HF)

Solids:
- SR <-> WF
- LR <-> DFT

Idea originally due to Andreas Savin (Université Pierre et Marie Curie, Paris, France.)

Applications in TDDFT:
- Y. Tawada, T. Tsuneda, S. Yanagisawa, T. Yanai, and **K. Hirao**, *J. Chem. Phys.* **120**, 8425 (2004).
- S. Tokura, T. Tsuneda, and **K. Hirao**, *J. Theoretical and Computational Chem.* **5**, 925 (2006).
- O.A. Vydrov and G.E. Scuseria, *J. Chem. Phys.* **125**, 234109 (2006).
- M.J.G. Peach, E.I. Tellgrent, P. Salek, T. Helgaker, and D.J. Tozer, *J. Phys. Chem. A* **111**, 11930 (2007).
- E. Livshits and R. Baer, *Phys. Chem. Chem. Phys.* **9**, 2932 (2007).

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* Because Nature is often, *but not always*, nearsighted.

Fluctuation-Dissipation Theorem

Quantity closely related to xc-hole of DFT

$$i\chi(\mathbf{1},\mathbf{2}) = \langle \Psi_0 | [\tilde{\rho}(\mathbf{1}), \tilde{\rho}(\mathbf{2})] | \Psi_0 \rangle = i\Pi(\mathbf{1},\mathbf{1}^+;\mathbf{2},\mathbf{2}^+)$$

$$\tilde{\rho}(\mathbf{1}) = \hat{\rho}(\mathbf{1}) - \langle \Psi_0 | \hat{\rho}(\mathbf{1}) | \Psi_0 \rangle \qquad \boldsymbol{i} = (i, t_i) = (x_i, y_i, z_i, t_i)$$

Electron repulsion energy

$$\langle \Psi_0 | v_{e,e} | \Psi_0 \rangle = \langle \Phi | v_{e,e} | \Phi \rangle + \frac{1}{2} \int \frac{1}{r_{12}} \left(i\chi(\mathbf{1},\mathbf{2},) - i\chi_0(\mathbf{1},\mathbf{2}) \right)$$

Correlation energy

$$\Delta E_{corr} = \frac{1}{2} \int_0^1 d\lambda \int \frac{1}{r_{12}} \left(i\chi_\lambda(\mathbf{1},\mathbf{2}) - i\chi_0(\mathbf{1},\mathbf{2}) \right)$$

5th rung functionals from TDDFT (RPA and beyond)

A.L. Fetter and J.D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill Book Company, New York, 1971), p. 152.

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TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY (TDDFT)
[E. Runge and E.K.U. Gross, *Phys. Rev. Lett.* 52, 997 (1984)]

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

1st Theorem: $v_{ext}(\mathbf{r}t)$ is determined by $\rho(\mathbf{r}t)$ up to an additive function of time

Corollary: $$\rho(\mathbf{r}t) \rightarrow N, v_{ext}(\mathbf{r}t) + C(t) \rightarrow \hat{H}(t) + C(t) \rightarrow \Psi(t) e^{-i\int_{t_0}^{t} C(t')dt'} \qquad (1)$$

(RG1 assumes functions with Taylor series.)

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

$$A[\rho] = \int_{t_0}^{t} < \Psi(t') | i\frac{\partial}{\partial t'} - \hat{H}(t') | \Psi(t') > dt' \qquad (2)$$

(RG2 suffers from a “causality paradox.”)

Ways to Resolve the Causality Paradox

A. K. Rajagopal, *Phys. Rev. A* **54**, 3916 (1996). “Time-dependent variational principle and the effective action in density-functional theory and Berry’s phase”

Keldysh action

R. van Leeuwen, *Phys. Rev. Lett.* **80**, 1280 (1998). “Causality and symmetry in time-dependent density-functional theory”
R. van Leeuwen, *Int. J. Mod. Phys. A* **15**, 1969 (2001). “Key concepts in time-dependent density-functional theory”

Liouville space pathways

S. Mukamel, *Phys. Rev. A* **71**, 024503 (2005). “Generalized time-dependent density-functional-theory response functions for spontaneous density fluctuations and nonlinear response: Resolving the causality paradox”

Most recently
G. Vignale, *Phys. Rev. A* **77**, 062511 (2008). “Real-time solution of the causality paradox of time-dependent density-functional theory”

Continued Healthy (?) Debate

- J. Schirmer and A. Dreuw, *Phys. Rev. A* **75**, 022513 (2007). “Critique of the foundations of time-dependent density-functional theory”
- N.T. Maitra, K. Burke, and R. van Leeuwen, *Phys. Rev. A* **75**, 022513 (2007). “Comment on 'Critique of the foundations of time-dependent density-functional theory'”
- J. Schirmer and A. Dreuw, *Phys. Rev. A* **78**, 056502 (2008). “Reply to 'Comment on “Critique of the foundations of time-dependent density-functional theory”'”
- J. Schirmer, *Phys. Rev. A* **82**, 052510 (2010). “Modifying the variational principle in the action-integral-functional derivation of time-dependent density-functional theory”
- G. Vignale, *Phys. Rev. A* **93**, 046501 (2011). “Comment on 'Modifying the variational principle in the action-integral-functional derivation of time-dependent density-functional theory'”

Comments:

- The issue is not about whether a correct xc-action can be formulated, but whether any of the existent formulations are useful for developing approximate functionals.
- If ever you are given an approximate xc-action functional, you will most likely use the (Vignale-corrected) Frenkel-Dirac action to derive the corresponding time-dependent Kohn-Sham equation.

TIME-DEPENDENT KOHN-SHAM EQUATION

[E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984)]

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

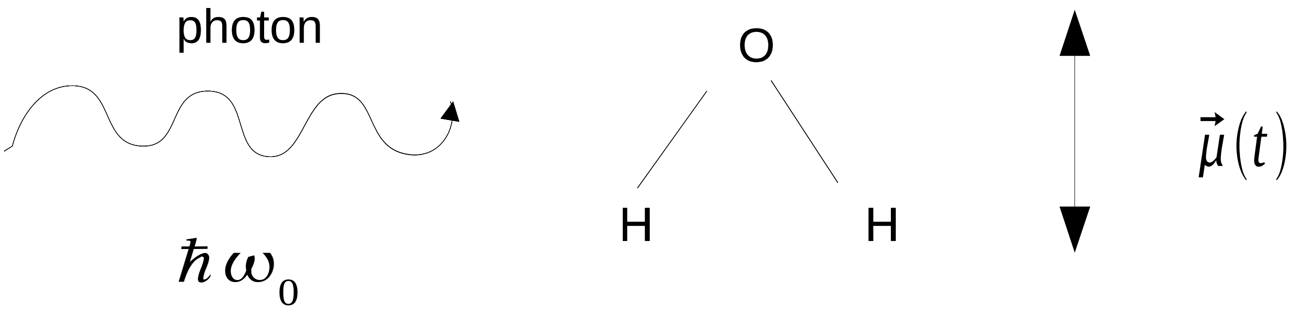
where $\rho(\boldsymbol{r}\,t)=\sum_{i\sigma} n_{i\sigma}|\psi_{i\sigma}(\boldsymbol{r}\,t)|^2$ (2)

and $v_{xc}(\boldsymbol{r}\,t)=\frac{\delta A_{xc}[\rho]}{\delta\rho(\boldsymbol{r}\,t)}$ (3)

Comment: More generally, if you don't start from the ground stationary state,

$$v_{xc}(\boldsymbol{r},t)=v_{xc}[\rho,\Psi_{0,}\Phi_0](\boldsymbol{r},t) \qquad (4)$$

Electric-Field Induced Electronic Polarization



- Classical model of a photon

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

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

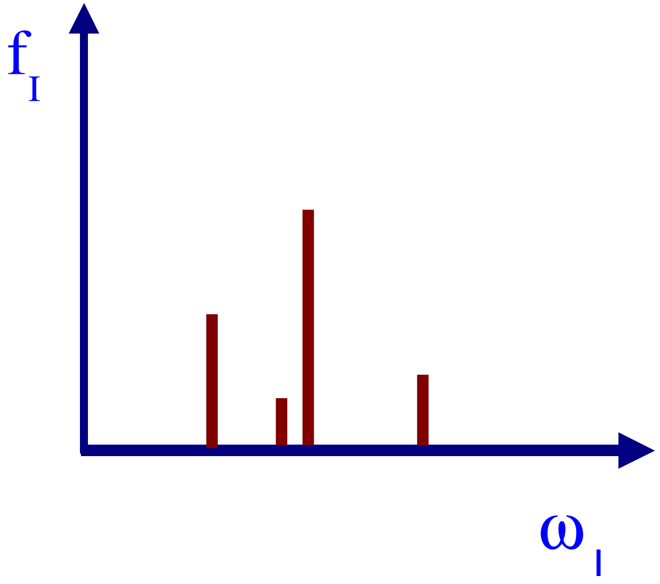
- Induced dipole moment

$$\delta\vec{\mu}(t) = -e\left(<\Psi_0|\vec{r}|\delta\Psi_0(t)> + <\delta\Psi_0(t)|\vec{r}|\Psi_0>\right)$$

THE DYNAMIC POLARIZABILITY

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

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



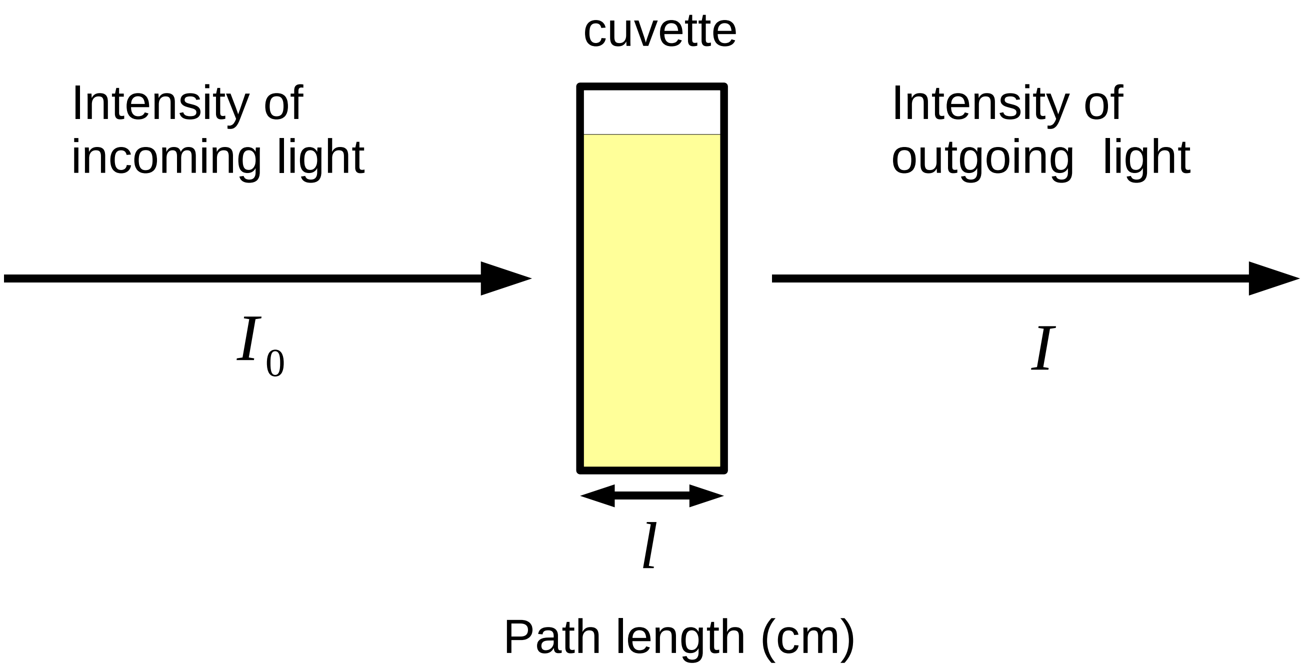
Sum-over-states (SOS) theorem

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

$$f_I=\frac{2}{3}\omega_I(|<\Psi_0|x|\Psi_I>|^2+|<\Psi_0|y|\Psi_I>|^2+|<\Psi_0|z|\Psi_I>|^2)$$

How to make computationally convenient?

Beer's Law*



cuvette

Intensity of
incoming light

I_0

Intensity of
outgoing light

I

l

Path length (cm)

Absorbance (unitless) $A=\log_{10}\frac{I_0}{I}$ (1) Concentration (mol/L) C

Beer's law $A=\epsilon C l$ (2) Molar extinction coefficient (L/mol.cm) ϵ

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* August Beer (1825-1863). The term Beer's law appears to date from 1889.

THEORETICAL MOLAR EXTINCTION COEFFICIENT

For a single transition,

$$f_I = \frac{m_e c \, 4\pi \epsilon_0 \ln(10)}{\pi N_A e^2} \int \epsilon(\nu) \, d\nu \qquad (1)$$

$$\epsilon(\nu) = \frac{\pi N_A e^2}{m_e c \, 4\pi \epsilon_0 \ln(10)} f_I \delta(\nu - \nu_I) \qquad (2)$$

For several transitions,

$$\epsilon(\nu) = \frac{\pi N_A e^2}{m_e c \, 4\pi \epsilon_0 \ln(10)} S(\nu) \qquad (3)$$

$$S(\nu) = \sum_I f_I \delta(\nu - \nu_I) \qquad (4)$$

REAL-TIME CALCULATION OF SPECTRA*

Literally introduce

$$\boldsymbol{\varepsilon}(t) = \boldsymbol{\varepsilon} \cos \omega_0 t \qquad (1)$$

$$v_{appl}(\boldsymbol{r}\,t) = \boldsymbol{\varepsilon}(t) \cdot \boldsymbol{r} \qquad (2)$$

Propogate in time :

$$\left[-\frac{1}{2}\nabla^2 + v_{ext}(\boldsymbol{r}\,t) + \int \frac{\rho(\boldsymbol{r}'\,t)}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' + v_{xc}(\boldsymbol{r}\,t) \right] \psi_i(\boldsymbol{r}\,t) = i\frac{\partial}{\partial t}\psi_i(\boldsymbol{r}\,t) \qquad (3)$$

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* For example, in the **Octopus** code, an open-source code based, in part, upon the original code developed by George Bertsch and **Kazuhiro Yabana** and, in part, on another code by Angel Rubio, Xavier Blase, and Stephen G. Louie, with major rewriting by Alberto Castro and Miquel Marques.

REAL-TIME CALCULATION OF SPECTRA*

Dynamic polarizability

$$\alpha(\omega)=\sum_{I\neq 0}\frac{f_I/2\omega_I}{\omega+\omega_I}-\sum_{I\neq 0}\frac{f_I/2\omega_I}{\omega-\omega_I} \quad (1)$$

Laurentzian function

$$L(\omega)=\frac{1}{\pi}\frac{\eta}{(\omega-\omega_I)^2+\eta^2} \quad (2)$$

Spectral function

$$S(\omega)=\frac{2\omega}{\pi}\Im\alpha(\omega+i\eta) \quad (3)$$

$$S(\omega)=\frac{2\omega}{\pi}\Im\left[\sum_{I\neq 0}\frac{f_I/2\omega_I}{\omega+i\eta+\omega_I}-\sum_{I\neq 0}\frac{f_I/2\omega_I}{\omega+i\eta-\omega_I}\right] \quad (4a)$$

$$=\frac{\omega}{\omega_I}f_I\left[\sum_{I\neq 0}\frac{\eta}{(\omega-\omega_I)^2+\eta^2}-\sum_{I\neq 0}\frac{\eta}{(\omega+\omega_I)^2+\eta^2}\right] \quad (4b)$$

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* For example, in the **Octopus** code.

REAL-TIME CALCULATION OF SPECTRA*

Calculate

$$\Delta\boldsymbol{\mu}(t) = -\sum_i n_i \langle\psi_i(t)|\mathbf{r}|\psi_i(t)\rangle - \boldsymbol{\mu}(t=0) \tag{1}$$

Dynamic polarizability

$$\Delta\boldsymbol{\mu}(t) = \int \boldsymbol{\alpha}(t-t')\boldsymbol{\epsilon}_{appl}(t')\,dt' + HOT \tag{2}$$

Convolution theorem

$$\Delta\boldsymbol{\mu}(\omega) = \boldsymbol{\alpha}(\omega)\boldsymbol{\epsilon}_{appl}(\omega) + HOT \tag{3a}$$

$$\alpha(\omega) = \frac{\Delta\boldsymbol{\mu}(\omega)}{\boldsymbol{\epsilon}_{appl}(\omega)} \tag{3b}$$

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* For example, in the **Octopus** code.

FREQUENCY/ENERGY FORMULATION

Mark E. Casida in *Recent Advances in Density Functional Methods, Part I,*
edited by D.P. Chong (Singapore, World Scientific, 1995), p. 155.
"Time-dependent density-functional response theory for molecules"

"RPA" equation

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

where

$$A_{ij\sigma,kl\tau}(\omega) = \delta_{\sigma,\tau}\delta_{i,k}\delta_{j,l}(\varepsilon_{i\sigma}-\varepsilon_{j\sigma}) + K_{ij\sigma,kl\tau}(\omega) \quad (2)$$

$$B_{ij\sigma,kl\tau}(\omega) = K_{ij\sigma,lk\tau}(\omega) \quad (3)$$

Coupling matrix

$$K_{ij\sigma,kl\tau} = \int\int \psi^*_{i\sigma}(\vec{r})\psi_{j\sigma}(\vec{r}) f^{\sigma,\tau}_{Hxc}(\vec{r},\vec{r}\,';\omega)\psi_{k\tau}(\vec{r}\,')\psi^*_{l\tau}(\vec{r}\,')\,d\vec{r}\,d\vec{r}\,' \quad (4)$$

*Note: Original formulation did **not** assume the adiabatic approximation!*

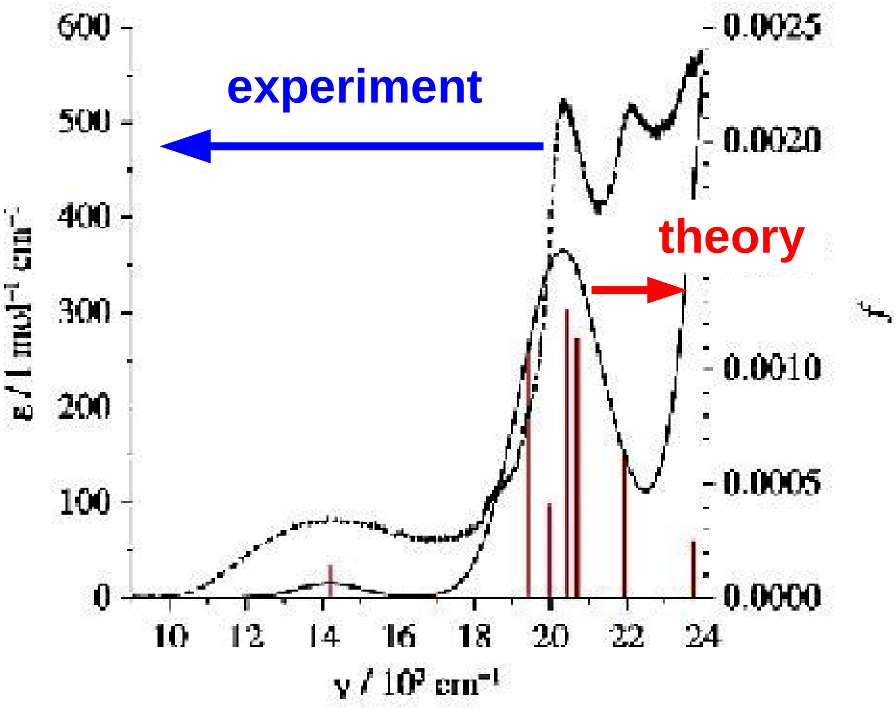
GAUSSIAN BROADENING

Normalized gaussian

$$g(\nu)=\sqrt{\frac{\alpha}{\pi}}e^{-\alpha\nu^2} \qquad (1)$$

Full width at half maximum (FWHM)

$$FWHM=2\sqrt{\frac{\ln 2}{\alpha}} \qquad (2)$$



$$\epsilon(\nu)=\frac{\pi N_A e^2}{m_e c\, 4\pi\epsilon_0 \ln(10)} \times \sum_I f_I\, g(\nu-\nu_I) \qquad (3)$$

One program that does this:
spectrum.py
by Pablo Baudin and M.E.C.

For various reasons, only an order of magnitude agreement with experiment is expected.

All is exact up to this point!

(Even fractional occupation numbers have been included
in my original formulation of LR-TDDFT.)

TDDFT ADIABATIC APPROXIMATION (AA)

Assume xc-potential responds instantaneously and without memory to any temporal change of the charge density.

$$v_{xc}(\mathbf{r}t) = \frac{\delta A_{xc}[\rho]}{\delta \rho(\mathbf{r}t)} \longrightarrow v_{xc}(\mathbf{r}t) = \frac{\delta E_{xc}[\rho_t]}{\delta \rho_t(\mathbf{r})}$$

$$\rho_t(\mathbf{r}) = \rho(\mathbf{r}t)$$

This defines "conventional TDDFT."

TAMM-DANCOFF APPROXIMATION (TDA)

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

B=**0** defines the Tamm-Dancoff approximation

$$\boldsymbol{A}\vec{X}_I=\omega_I\vec{X}_I \qquad (1)$$

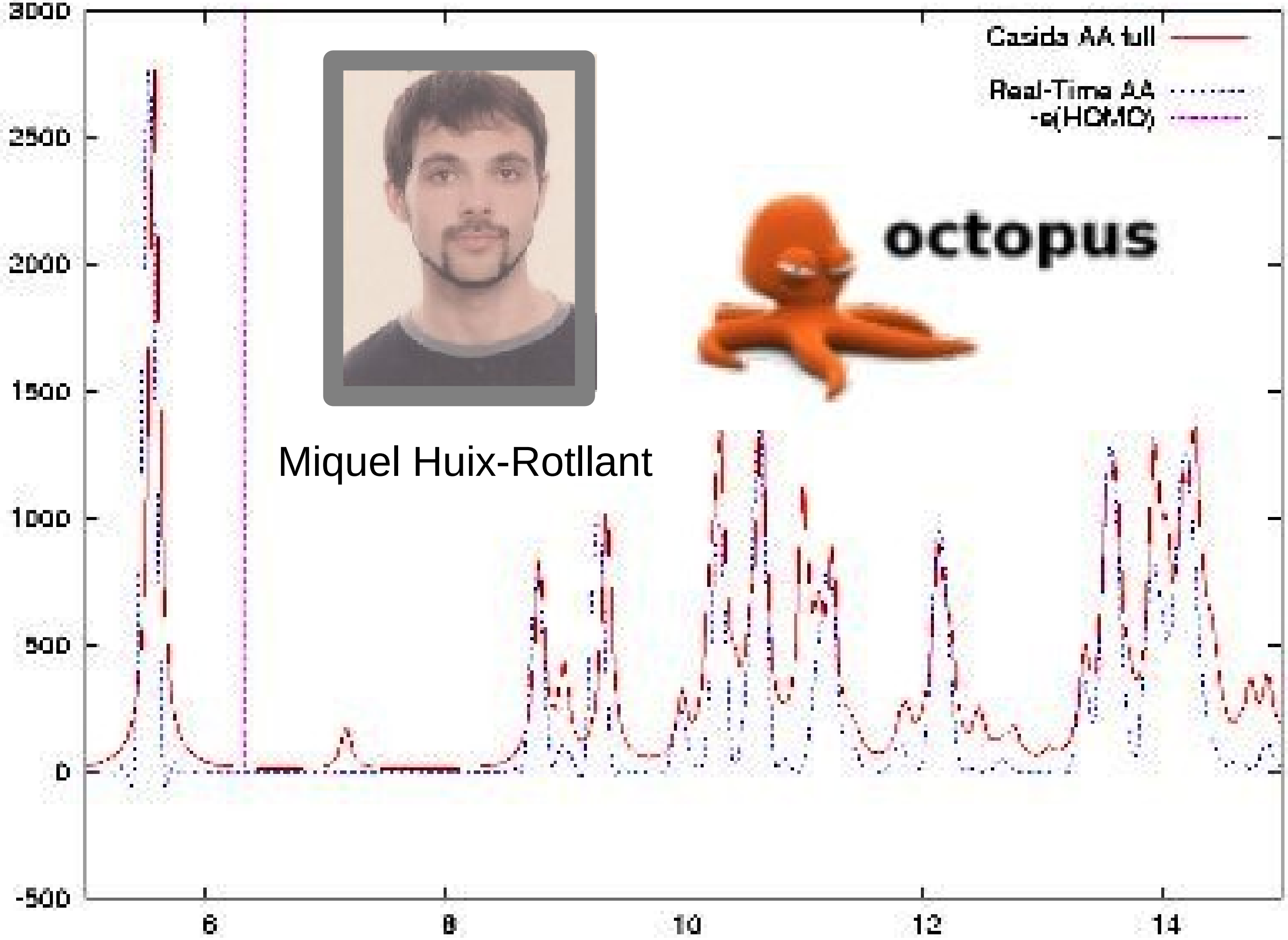
Loose Thomas-Reiche-Kuhn (TRK) sum rule,

$$\sum_I f_I=N \quad , \qquad (2)$$

but gain elsewhere.

Spectrum of Butadiene (CH_2=CH-CH=CH_2)

Finite Difference Method



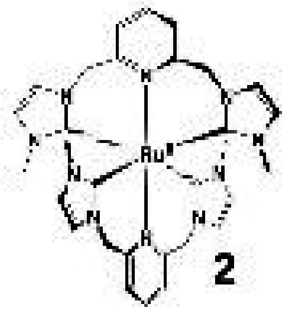
Miquel Huix-Rotllant

Note: Only x and y components drawn in the real-time propagation

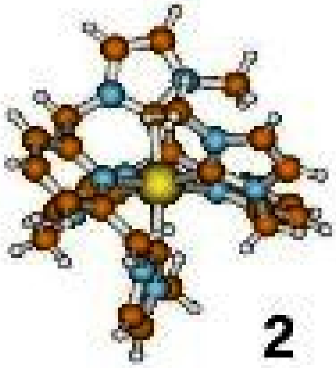
Casida's Equation (GAUSSIAN)

C. Muhavini Wawire

TD-B3LYP/LANL2DZ+ECP



2



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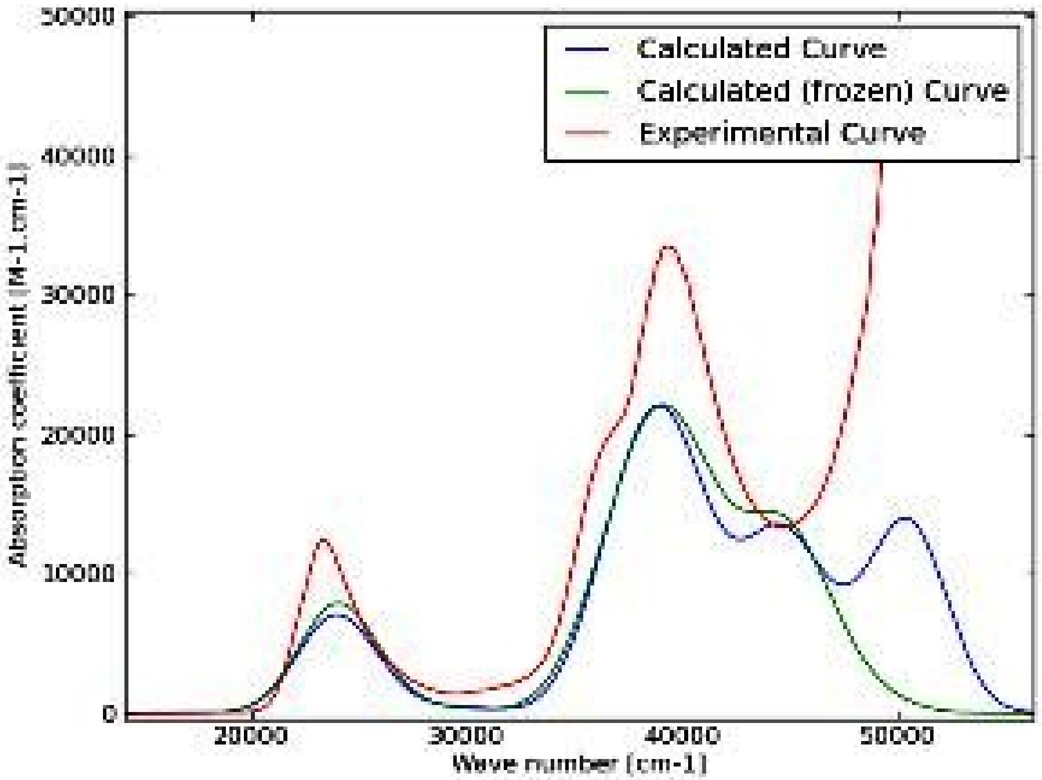
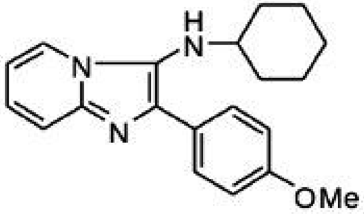
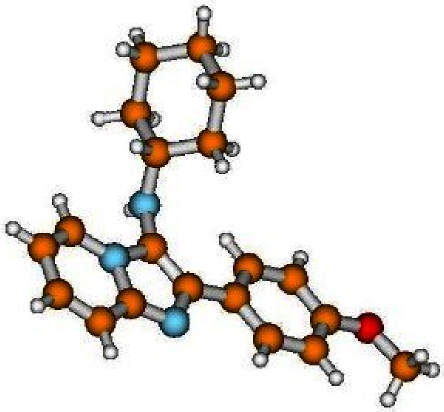


C.M. Wawire, D. Jouvenot, F. Loiseau, P. Baudin, S. Liatard, L. Njenga, G.N. Kamau, and M.E. Casida, "Density-Functional Study of Lumininescent Ruthenium Complexes: $[Ru(bpy)_3]^{2+}$, $[Ru(tpy)_2]^{2+}$, $[Ru(CNC)_2]^{2+}$, $[Ru(CNC)(tpy)]^{2+}$, and $[Ru(benzi)_2]^{2+}$ (bpy=2,2'-bipyridine; tpy=2,2':6',2"-terpyridine; CNC=2,6-bis-N-(N-methylimidazolidene)methylpyridine; benzi=2,6-bis-N-(N-methylbenzimidazolylidene)methylpyridine)", *in preparation*.

Casida's Equation (BIGDFT)

Bhaarathi Natarajan





TD-LDA-TDA/wavelets

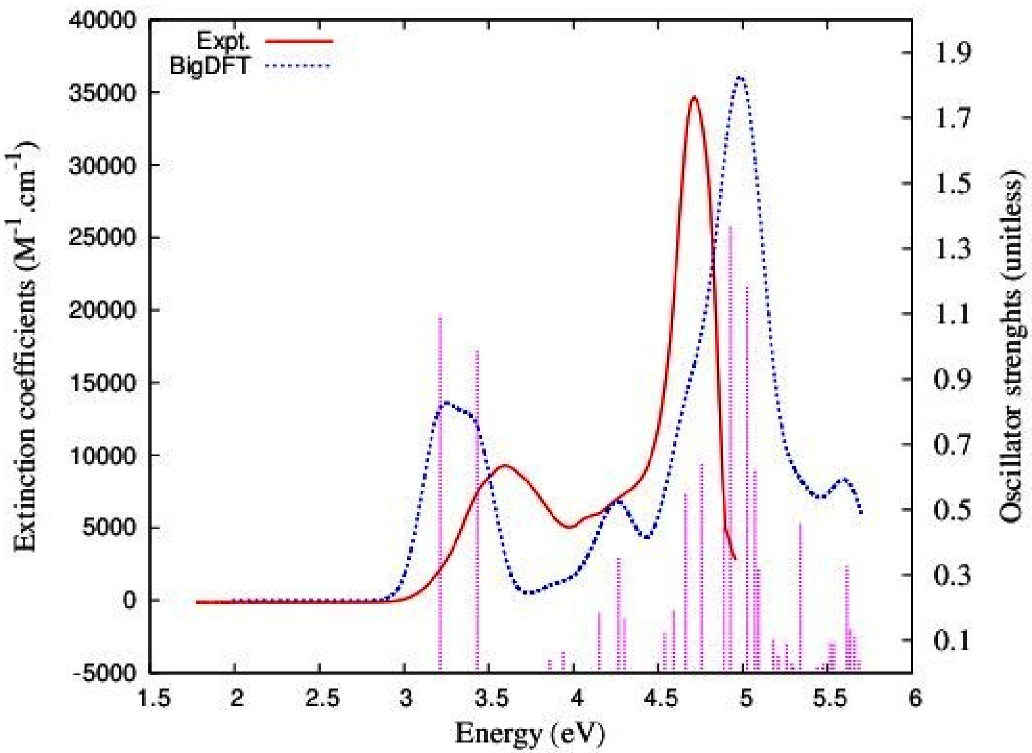
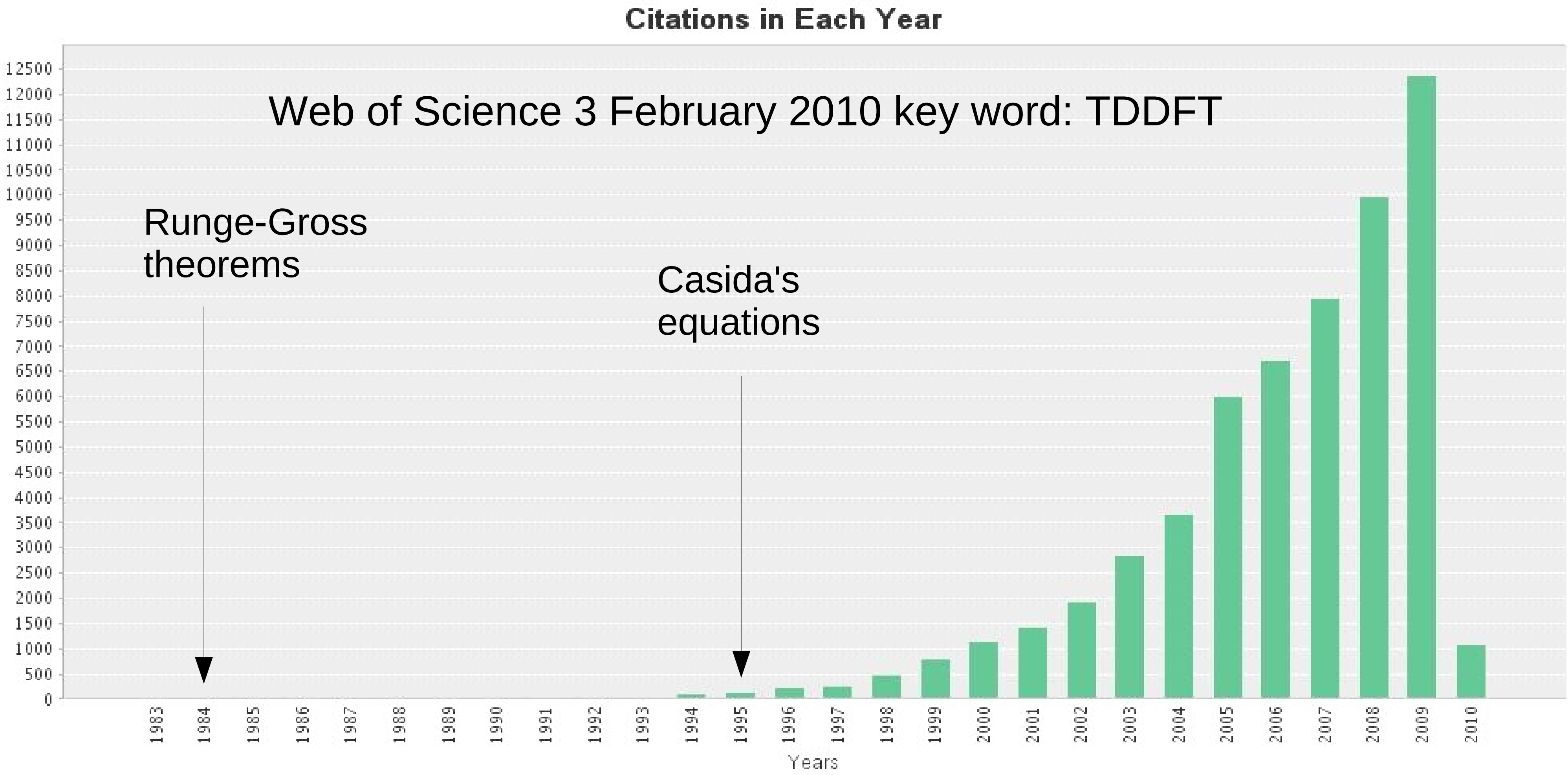


FIG. 6: Comparison of theoretical and measured absorption spectra for Flugi **6** (left y-axis). The magnitude of the BIGDFT curve has been divided by a factor of ten (see text). Both theoretical and experimental curves show qualitative agreement with the oscillator strength stick-spectra which however is in different units (right y-axis).

B. Natarajan, L. Genovese, M.E. Casida, T. Deutsch, O.N. Burchak, C. Philouze, and M.Y. Balakirev, **arXiv:1108.3475v1**, *Chem. Phys.* , *submitted.*
"Wavelet-Based Linear-Response Time-Dependent Density-Functional Theory"

I. Interdisciplinarity
II. Our Interests
III. DFT
IV. TD-DFT
V. Successes/Problems/Solutions
VI. Conclusion

TDDFT is the Main Single-Determinantal Theory for Excited States


Citations in Each Year

Web of Science 3 February 2010 key word: TDDFT

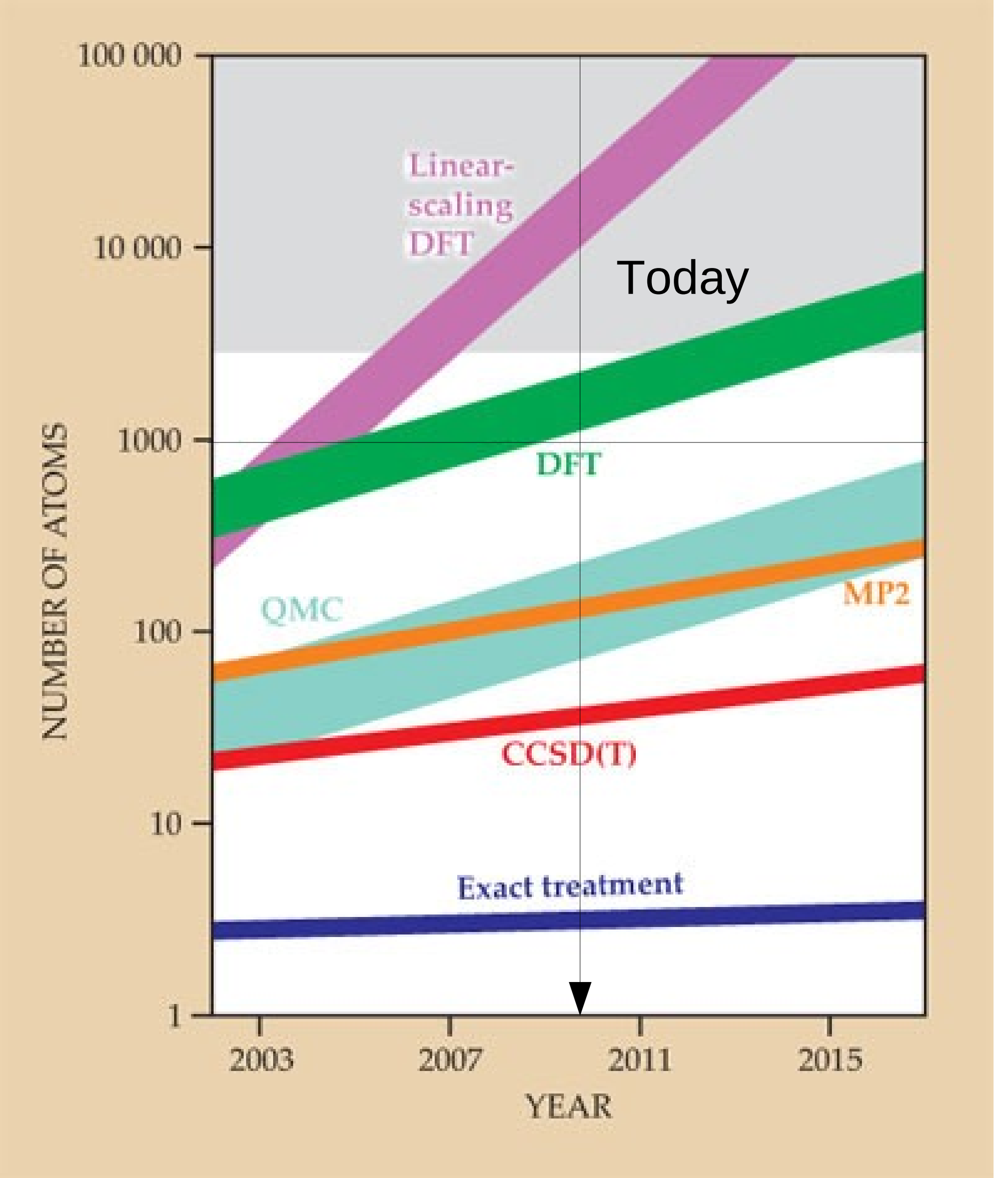
Runge-Gross theorems

Casida's equations

Present-day conventional TDDFT is not ultra-sophisticated, but often gives acceptably good results.

... applications in nanotechnology?

M. Head-Gordon and E. Artacho,
“Chemistry on the computer”,
***Physics Today* 61(4), 58 (2008).**

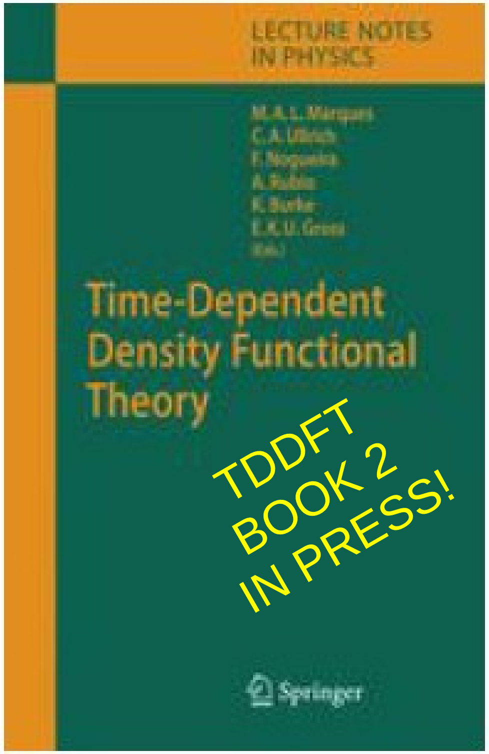


Computational chemistry/physics oriented towards nanotechnology is now typically done with DFT and will most likely be done with linear-scaling DFT in the future.

TDDFT will follow the same trends as DFT.

Problem with linear-scaling:
Scaling and accuracy varies with method and type of system (energy gap).

RECENT WORKS ON TDDFT



LECTURE NOTES IN PHYSICS

M.A.L. Marques
C.A. Ullrich
F. Nogueira
A. Rubio
K. Burke
E.K.U. Gross
(Eds.)

Time-Dependent Density Functional Theory

Springer

TDDFT BOOK 2 IN PRESS!

Special Issue:
"Time-Dependent Density-Functional Theory", Guest edited by M.A.L. Marques and A. Rubio, *Phys. Chem. Chem. Phys.* vol. **11**, issue 22, pp. 4421-4688 (2009).

Special Issue:
"Time-Dependent Density-Functional Theory for Molecules and Solids", Guest edited by M.E. Casida, H. Chermette, and D. Jacquemin, *J. Mol. Struct. (Theochem)*, vol. **914** (2009).

Book:
Time-Dependent Density Functional Theory, Edited by M.A.L. Marques, C.A. Ullrich, F. Nogueira, A. Rubio, K. Burke, and E.K.U. Gross, *Lecture Notes in Physics vol. 706* (Springer: Berlin, 2006).

Special Issue:
"Open Problems and New Solutions in Time-Dependent Density-Functional Theory", Guest edited by R. Baer, L. Kronik, and S. Kümmel, *Chem. Phys.* (2011).

☺

We began with successes ...

☹

... Let us continue with a few failures and how they might be corrected.

☺

(But this is not the place for a complete review ...) ☹

Also not a complete review:

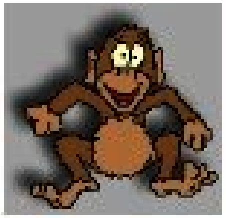
Mark E. Casida and Miquel Huix-Rotllant, **arXiv:1108.0611v1**,
Annu. Rev. Phys. Chem. **63**, xxxx (2012). (in press)
"Progress in Time-Dependent Density-Functional Theory"

Where Conventional TDDFT Works Best

- When the ground-state DFT answer is good
- Low energy excitations of dominant single excitation character
- Not too much “charge-transfer” (really density relaxation) character
- Reasonably localized excitations

(“TDDFT has a way of bringing out the worst behavior in functionals.”)

M.E. Casida, "Jacob's ladder for time-dependent density-functional theory: Some rungs on the way to photochemical heaven" in *Accurate Description of Low-Lying Molecular States and Potential Energy Surfaces*, ACS Symposium Series 828, edited by Mark R. Hoffmann and Kenneth G. Dyall (ACS Press: Washington, D.C., 2002).



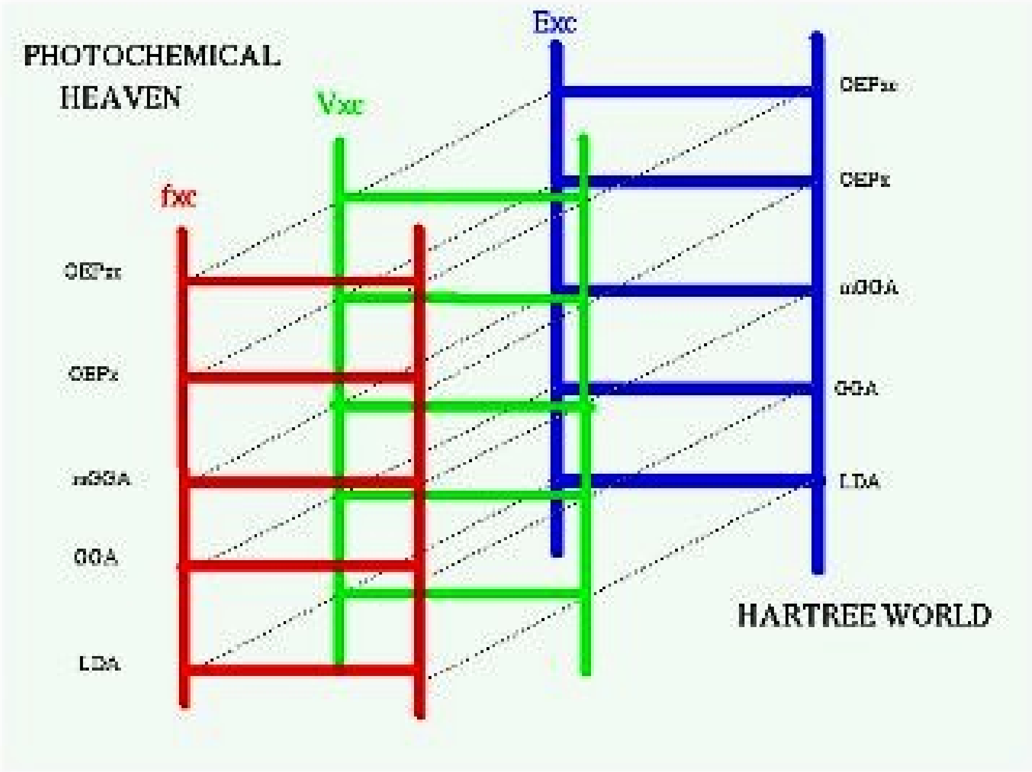


FIG. 1: Jacob's jungle gym for TDDFT.

$$v_{xc} = \frac{\delta E_{xc}}{\delta \rho} \quad (1)$$

$$f_{xc} = \frac{\delta^2 E_{xc}}{\delta \rho \, \delta \rho} \quad (2)$$

$$g_{xc} = \frac{\delta^2 E_{xc}}{\delta \rho \, \delta \rho \, \delta \rho} \quad (3)$$

Failures and Corrections

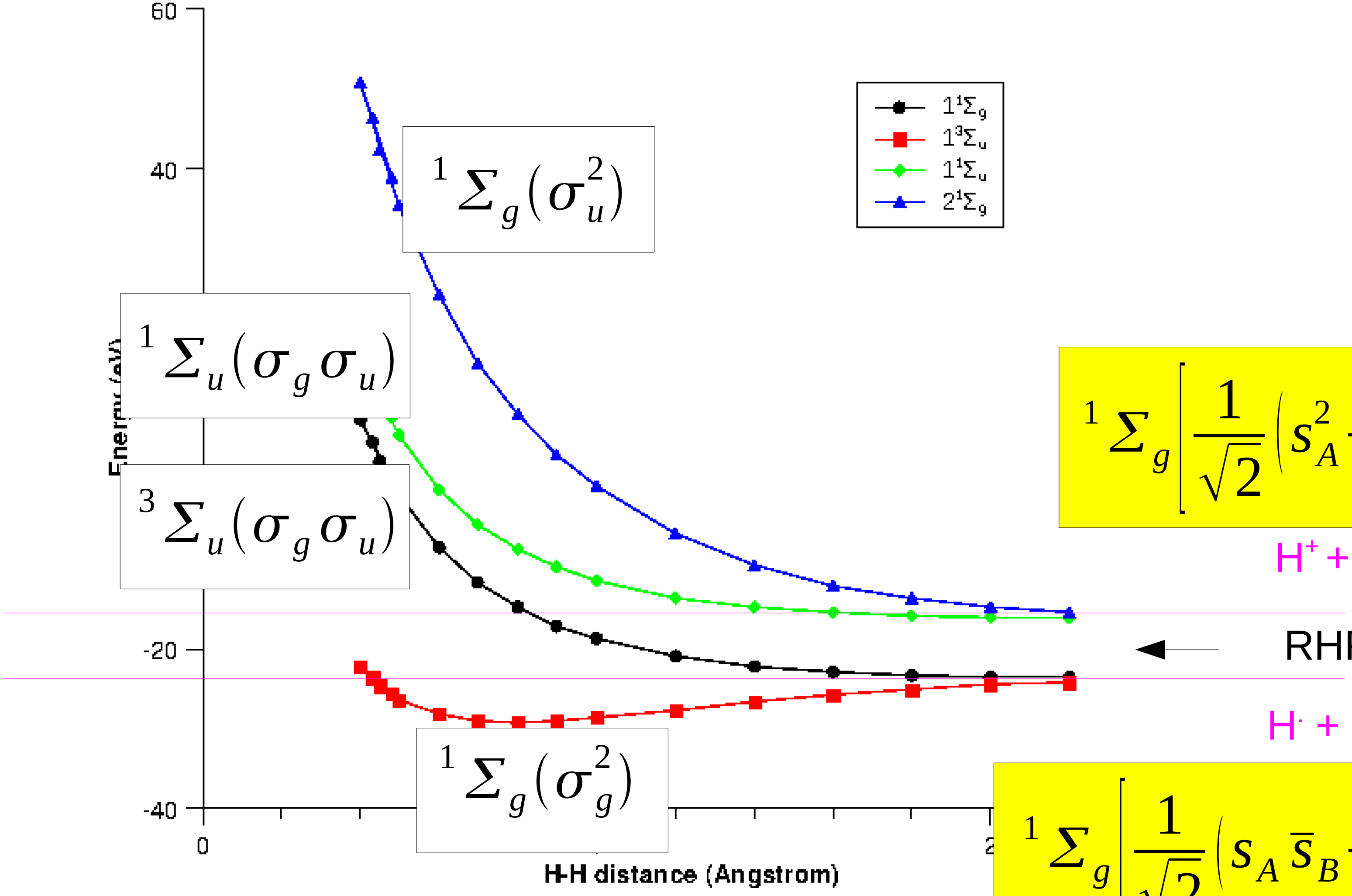
(i) Failure originating in E_{xc}

(ii) Failures originating in v_{xc}

(iii) Failures orignating in f_{xc}

WAVE FUNCTION THEORY

H_2



$^1\Sigma_g(\sigma_u^2)$

$^1\Sigma_u(\sigma_g\sigma_u)$

$^3\Sigma_u(\sigma_g\sigma_u)$

$^1\Sigma_g(\sigma_g^2)$

$$^1\Sigma_g\left[\frac{1}{\sqrt{2}}\left(s_A^2 - s_B^2\right)\right]$$

$H^+ + H:^-$

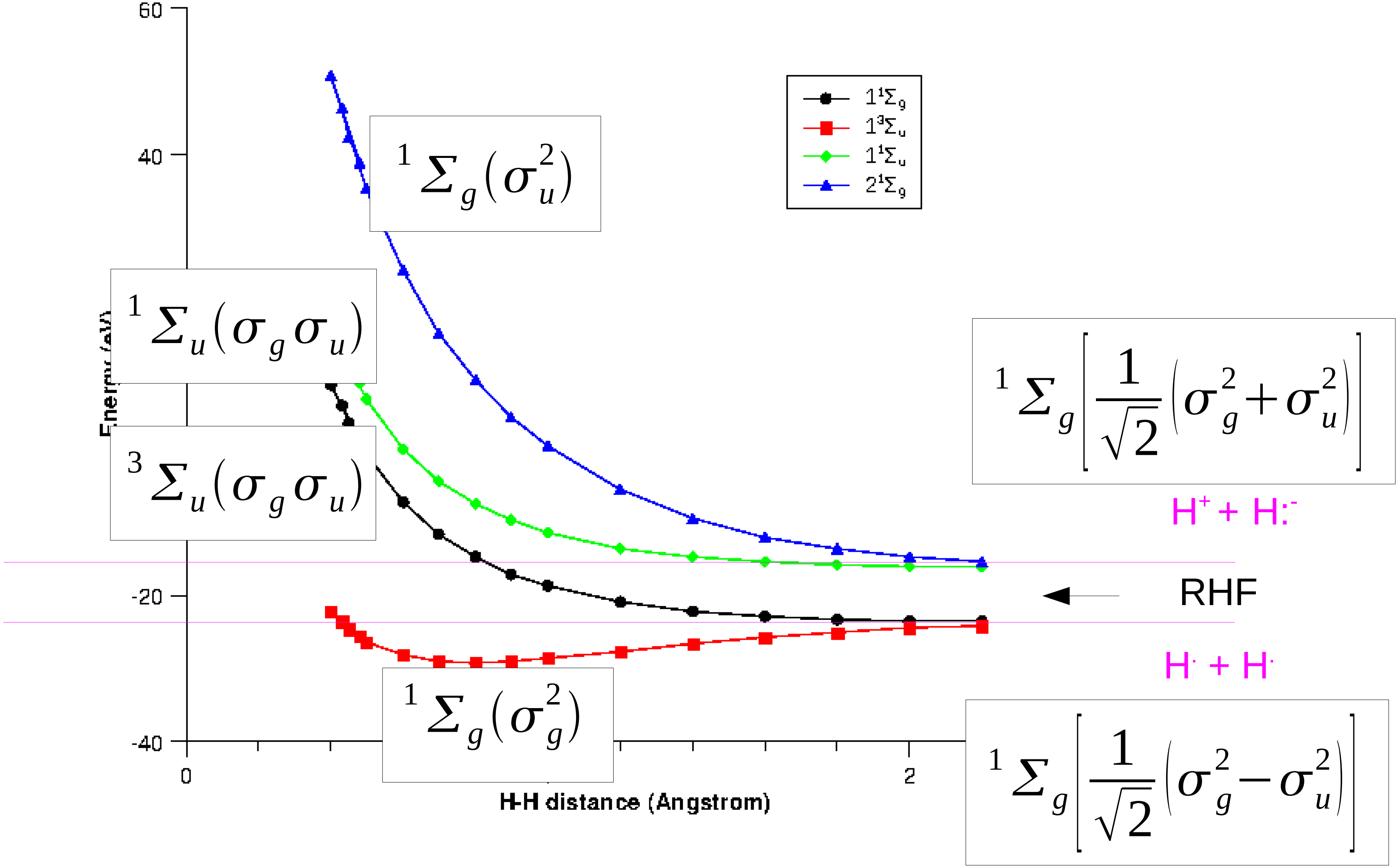
RHF

$H^\cdot + H^\cdot$

$$^1\Sigma_g\left[\frac{1}{\sqrt{2}}\left(s_A\bar{s}_B + s_B\bar{s}_A\right)\right]$$

WAVE FUNCTION THEORY

H_2



$^1\Sigma_g(\sigma_u^2)$

$^1\Sigma_u(\sigma_g\sigma_u)$

$^3\Sigma_u(\sigma_g\sigma_u)$

$^1\Sigma_g(\sigma_g^2)$

$^1\Sigma_g\left[\frac{1}{\sqrt{2}}\left(\sigma_g^2+\sigma_u^2\right)\right]$

$H^+ + H:^-$

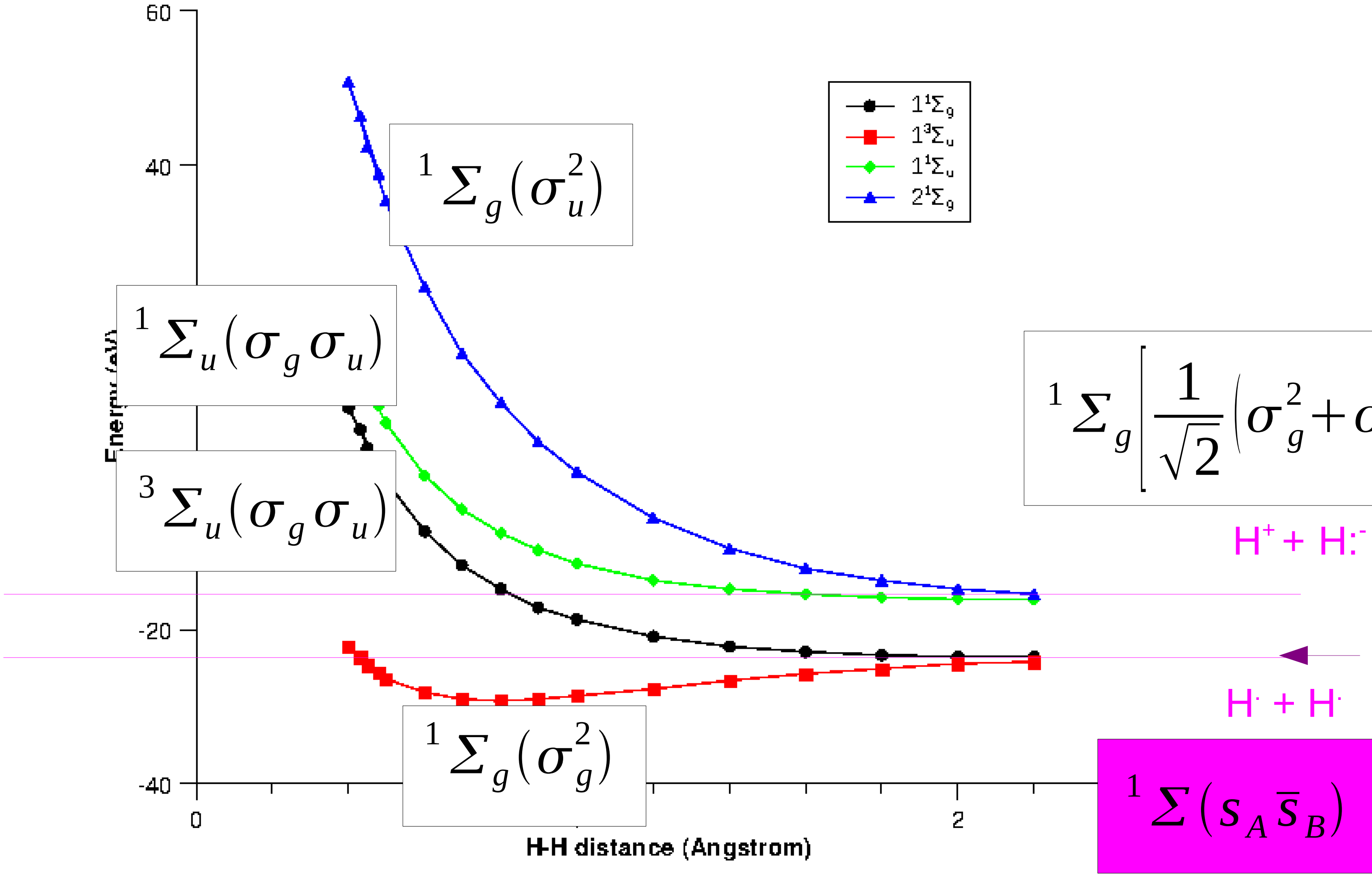
RHF

$H^\cdot + H^\cdot$

$^1\Sigma_g\left[\frac{1}{\sqrt{2}}\left(\sigma_g^2-\sigma_u^2\right)\right]$

WAVE FUNCTION THEORY

H_2



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

$${}^1\Sigma_u(\sigma_g\sigma_u)$$

$${}^3\Sigma_u(\sigma_g\sigma_u)$$

$${}^1\Sigma_g\left[\frac{1}{\sqrt{2}}\left(\sigma_g^2+\sigma_u^2\right)\right]$$

$H^+ + H:^-$

UHF

$H^\cdot + H^\cdot$

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

$${}^1\Sigma(s_A\bar{s}_B)$$

Can “cheat” for ground state by breaking symmetry but not for excited states!

DENSITY-FUNCTIONAL THEORY

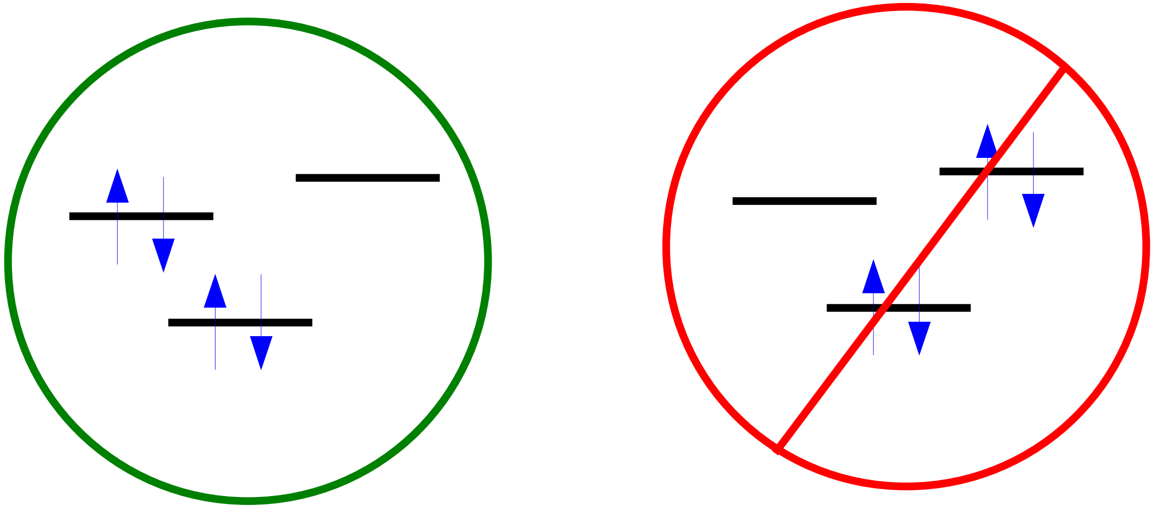
Exact theory

Ground state singlet belonging to the totally symmetric irrep

⇒ $\rho_\alpha = \rho_\beta$ ⇒ $v_{xc}^{\alpha} = v_{xc}^{\beta}$ ⇒ No symmetry breaking expected!

Assumes noninteracting v-representability (NVR)

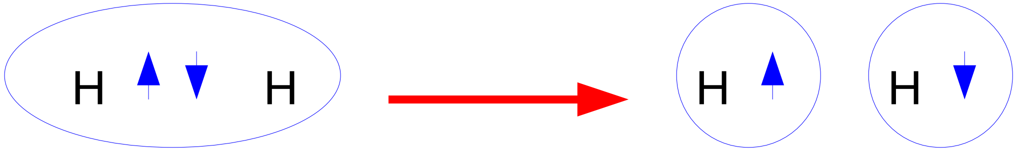
NVR: There is a fictitious Kohn-Sham system of noninteracting electrons *with integer occupation number* whose ground state gives the density of the interacting system.



Traditional workaround is the ensemble formulation with fractional occupation numbers.

STABILITY ANALYSIS*

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



(1)

Try arbitrary unitary transformations of spin orbitals

$$\psi_r^{\lambda}(\vec{r}) = e^{i\lambda(\hat{R}+i\hat{I})}\psi_r(\vec{r}) \qquad (2)$$

Find

$$E_\lambda = E_0 + \lambda^2 \left[\vec{R}^+ (A-B)\vec{R} + \vec{I}^+ (A+B)\vec{I}\right] + O(\lambda^3) \qquad (3)$$

But another form of the LR-TDHF equation is

$$(A+B)(A-B)\vec{Z}_I = \omega_I^2 \vec{Z}_I \qquad (4)$$

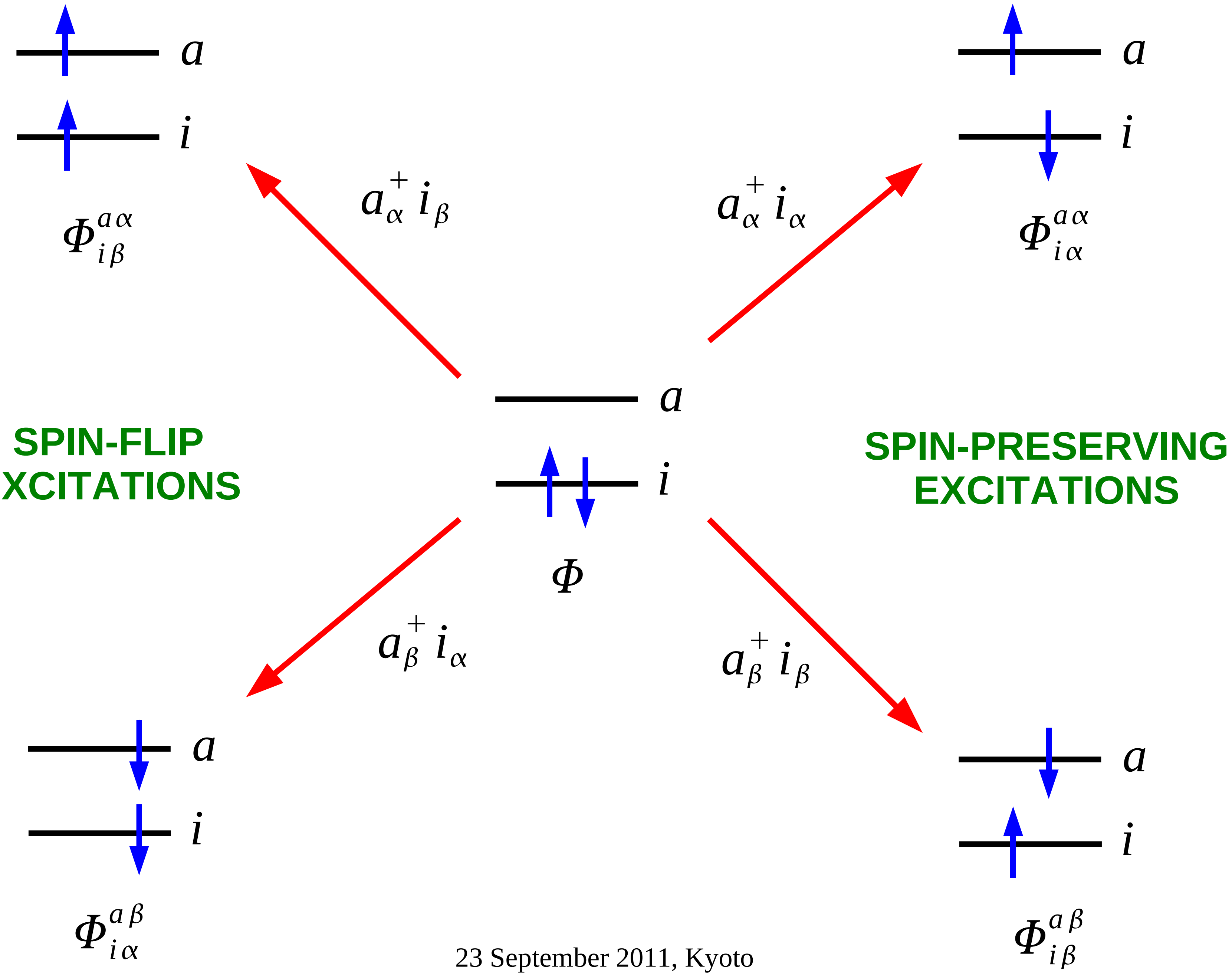
Conclude :

Symmetry breaking if imaginary excitation energies (triplet and singlet instabilities)

---

* J. Cizek and J. Paldus, *J. Chem. Phys.* **47**, 3976 (1967).

Two-Orbital Two-Electron Model (TOTEM)



SPIN-FLIP EXCITATIONS

SPIN-PRESERVING EXCITATIONS

Two-Orbital Two-Electron Model (TOTEM)

$$\begin{bmatrix} (\Delta\epsilon)(\Delta\epsilon + K_{\alpha,\alpha}) & (\Delta\epsilon) K_{\alpha,\beta} \\ (\Delta\epsilon) K_{\beta,\alpha} & (\Delta\epsilon)(\Delta\epsilon + K_{\beta,\beta}) \end{bmatrix} \begin{pmatrix} F_\alpha \\ F_\beta \end{pmatrix} = \omega^2 \begin{pmatrix} F_\alpha \\ F_\beta \end{pmatrix} \tag{1}$$

Triplet energy

$$\omega_T = \sqrt{(\Delta\epsilon)\left[\Delta\epsilon + 2\left(K_{\alpha,\alpha} - K_{\alpha,\beta}\right)\right]} \tag{2}$$

Singlet energy

$$\omega_S = \sqrt{(\Delta\epsilon)\left[\Delta\epsilon + 2\left(K_{\alpha,\alpha} + K_{\alpha,\beta}\right)\right]} \tag{3}$$

Suggests 3 types of instabilities => Actually there are 8 types!*

---

* H. Fukutome, "Unrestricted Hartree-Fock theory and its applications to molecules and chemical reactions", *Int. J. Quant. Chem.* **20**, 955-1065 (1981).

TRIPLET INSTABILITY

$$\Psi_{\lambda}=\left|\sqrt{1-\lambda^{2}}\psi_{i}+\lambda\psi_{a},\sqrt{1-\lambda^{2}}\bar{\psi}_{i}-\lambda\bar{\psi}_{a}\right| \tag{1}$$

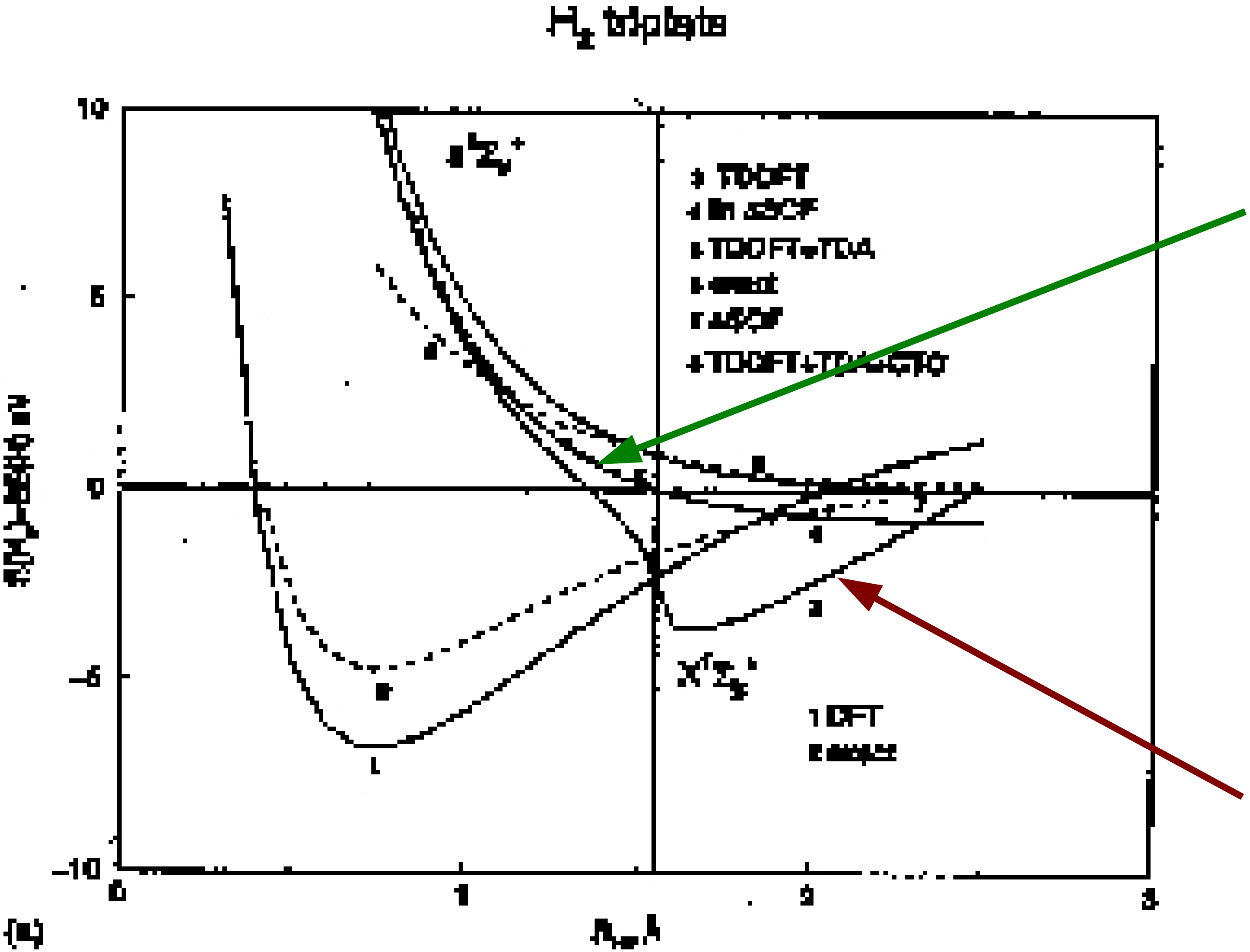
$$E_{\lambda}=E_{0}+2\lambda^{2}\left[\Delta\epsilon+2\left(K_{\alpha,\alpha}-K_{\alpha,\beta}\right)\right]+O\left(\lambda^{3}\right) \tag{2}$$

$$\omega_{T}=\sqrt{\left(\Delta\epsilon\right)\left[\Delta\epsilon+2\left(K_{\alpha,\alpha}-K_{\alpha,\beta}\right)\right]} \tag{3}$$

---

* M.E. Casida, F. Gutierrez, J. Guan, F.-X. Gadea, D.R. Salahub, and J.-P. Daudey, "Charge-transfer correction for improved time-dependent local density approximation excited-state potential energy curves: Analysis within the two-level model with illustration for H_2 and LiH", *J. Chem. Phys.* **113**, 7062 (2000).

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

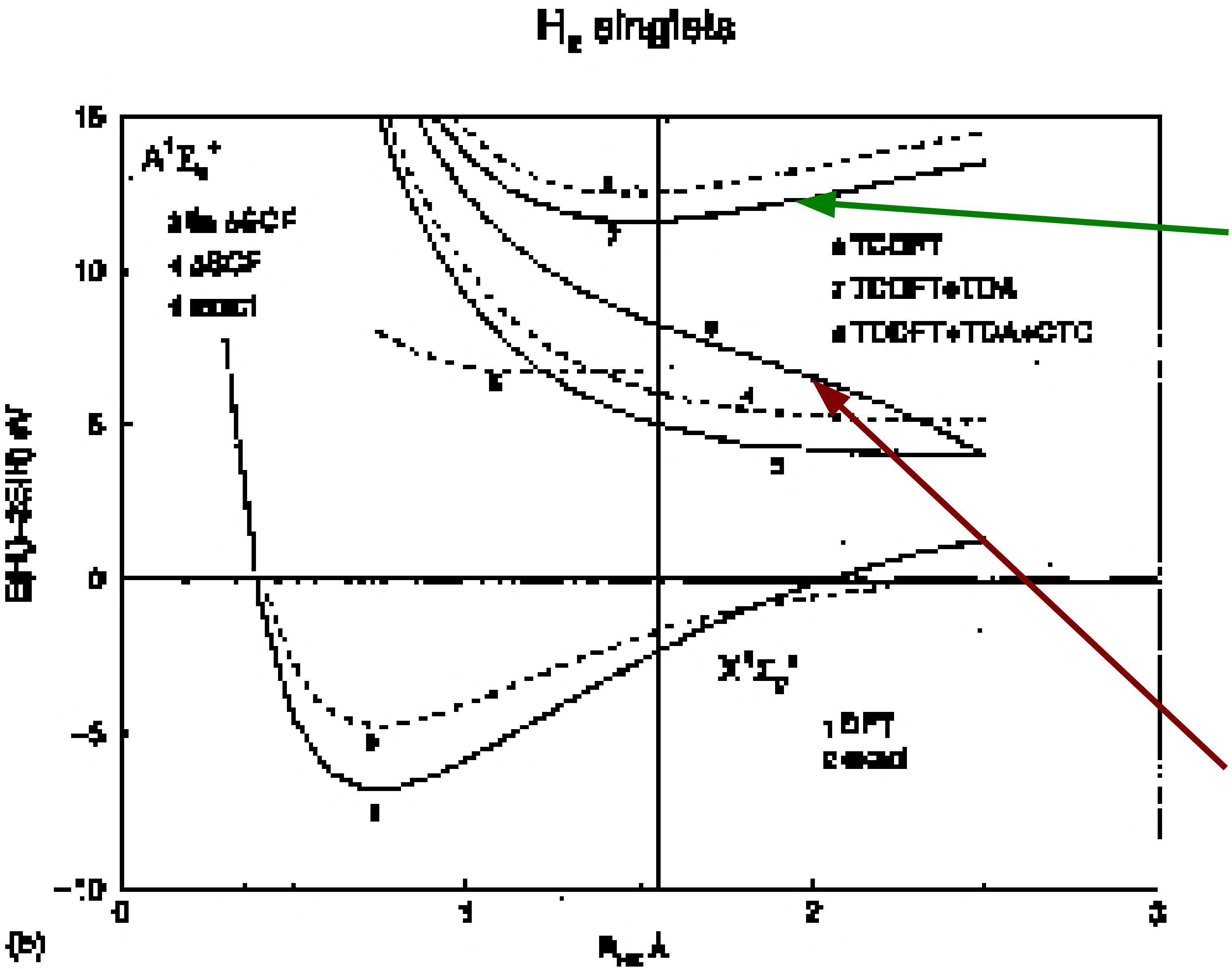


TDA
TDLDA

TDLDA

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

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

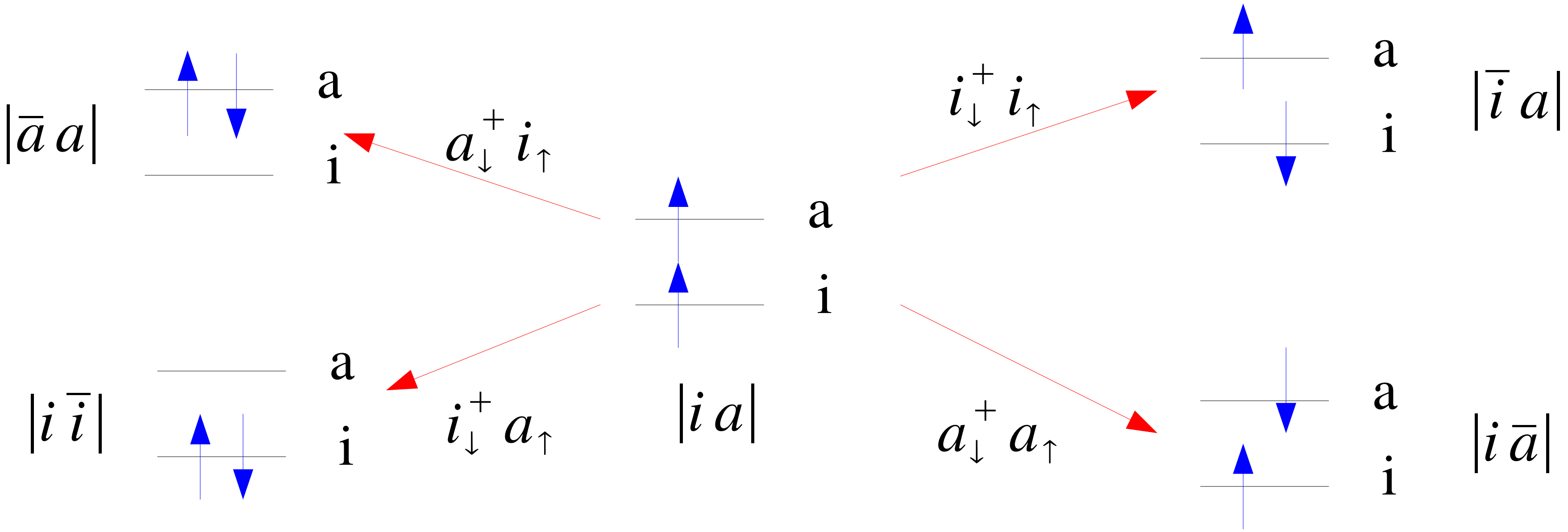


TDA
TDLDA

TDLDA

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

SPIN-FLIP THEORY



ΔM_s=-1 excitations from the lowest triplet allow a simple description where ground, 1-electron singlet, and 2-electron singlet excited states can mix.

Ana Krylov's group has applied this concept at many levels of electronic structure theory.

SF-TDDFT: L.V. Slipchenko and A.I. Krylov, *J. Chem. Phys.* **118**, 6874 (2003).
Y. Shao, M. Head-Gordon, and A.I. Krylov, *J. Chem. Phys.* **118**, 4807 (2003).

NONCOLLINEAR SPIN-FLIP TD-DFT

[F. Wang and T. Ziegler, J. Chem. Phys. **121**, 12191 (2004).]

$$E_{xc}[\rho_\alpha, \rho_\beta] \rightarrow E_{xc}[\rho_+, \rho_-] \tag{1}$$

where

$$\rho_\pm(\vec{r}) = \frac{1}{2}\left(\rho(\vec{r}) \pm s(\vec{r})\right) \tag{2}$$

and the density and spin density are defined in a rotationally invariant way

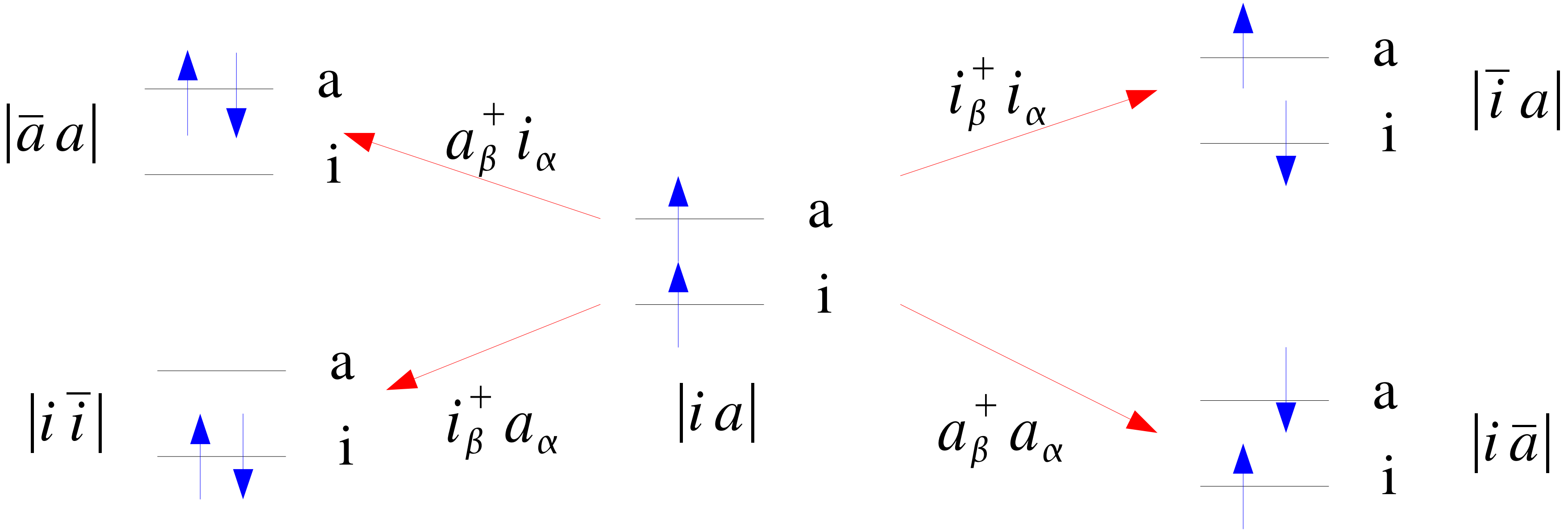
$$\rho(\vec{r}) = \rho_{\alpha,\alpha}(\vec{r}) + \rho_{\beta,\beta}(r) \tag{3}$$

$$s^2(\vec{r}) = \left(\rho_{\alpha,\alpha}(\vec{r}) - \rho_{\beta,\beta}(\vec{r})\right)^2 + 2\left(\rho^2_{\alpha,\beta}(\vec{r}) + \rho^2_{\beta,\alpha}(\vec{r})\right) \tag{4}$$

All the usual definitions are recovered in the collinear limit!

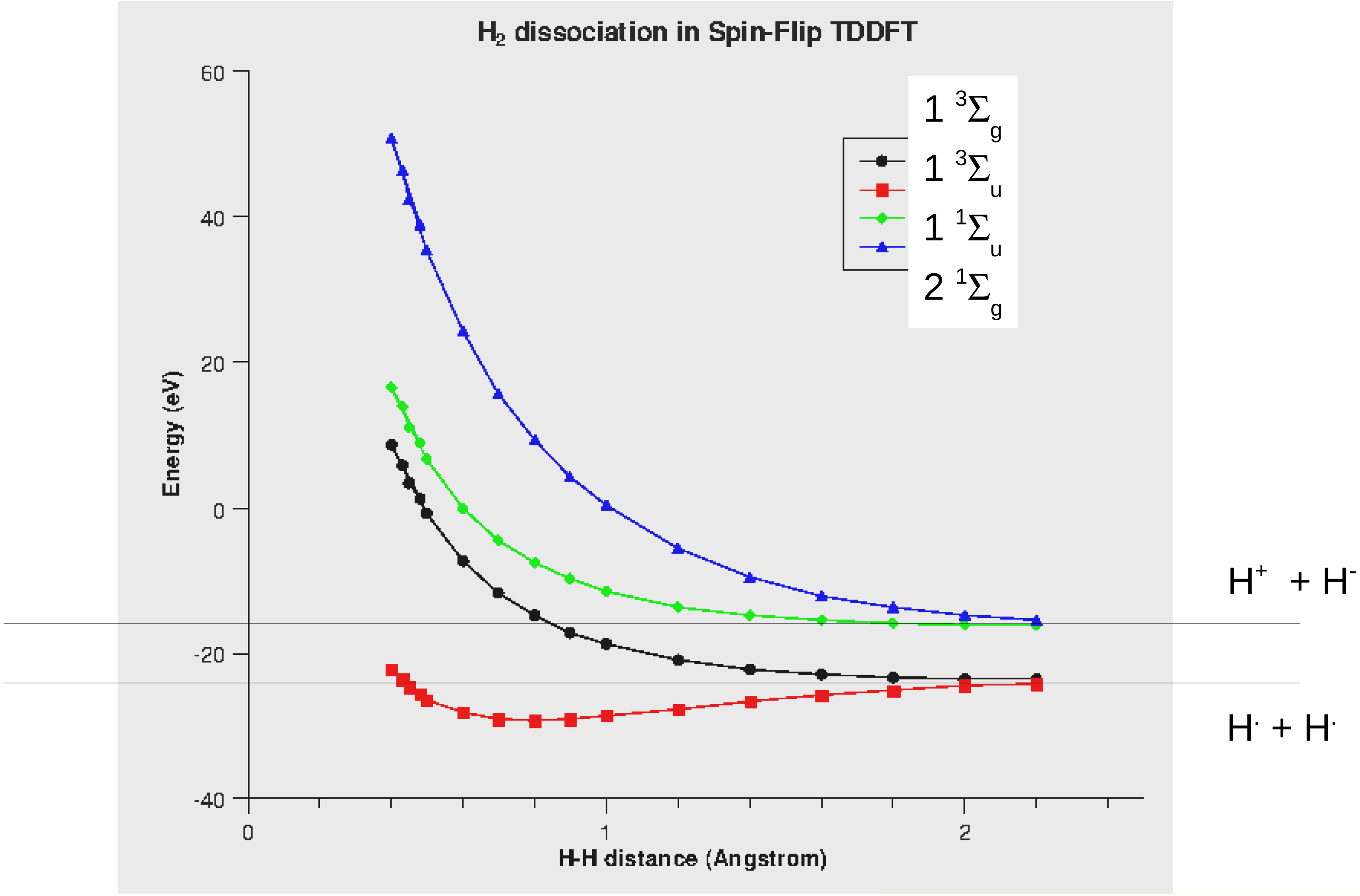
NONCOLLINEAR SPIN-FLIP TD-DFT

[F. Wang and T. Ziegler, J. Chem. Phys. **121**, 12191 (2004).]



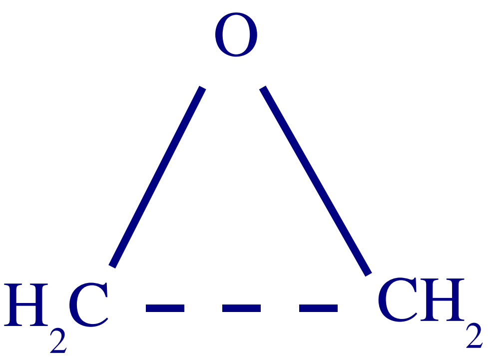
$$\begin{bmatrix} f_{xc}^{\alpha\alpha,\alpha\alpha} & f_{xc}^{\alpha\alpha,\beta\beta} & f_{xc}^{\alpha\alpha,\alpha\beta} & f_{xc}^{\alpha\alpha,\beta\alpha} \\ f_{xc}^{\beta\beta,\alpha\alpha} & f_{xc}^{\beta\beta,\beta\beta} & f_{xc}^{\beta\beta,\alpha\beta} & f_{xc}^{\beta\beta,\beta\alpha} \\ f_{xc}^{\alpha\beta,\alpha\alpha} & f_{xc}^{\alpha\beta,\beta\beta} & f_{xc}^{\alpha\beta,\alpha\beta} & f_{xc}^{\alpha\beta,\beta\alpha} \\ f_{xc}^{\beta\alpha,\alpha\alpha} & f_{xc}^{\beta\alpha,\beta\beta} & f_{xc}^{\beta\alpha,\alpha\beta} & f_{xc}^{\beta\alpha,\beta\alpha} \end{bmatrix} = \begin{bmatrix} f_{xc}^{\alpha,\alpha} & f_{xc}^{\alpha,\beta} & 0 & 0 \\ f_{xc}^{\beta,\alpha} & f_{xc}^{\beta,\beta} & 0 & 0 \\ 0 & 0 & \dfrac{v_{xc}^{\alpha}-v_{xc}^{\beta}}{\rho_\alpha-\rho_\beta} & 0 \\ 0 & 0 & 0 & \dfrac{v_{xc}^{\alpha}-v_{xc}^{\beta}}{\rho_\alpha-\rho_\beta} \end{bmatrix}$$

DISSOCIATION OF H_2



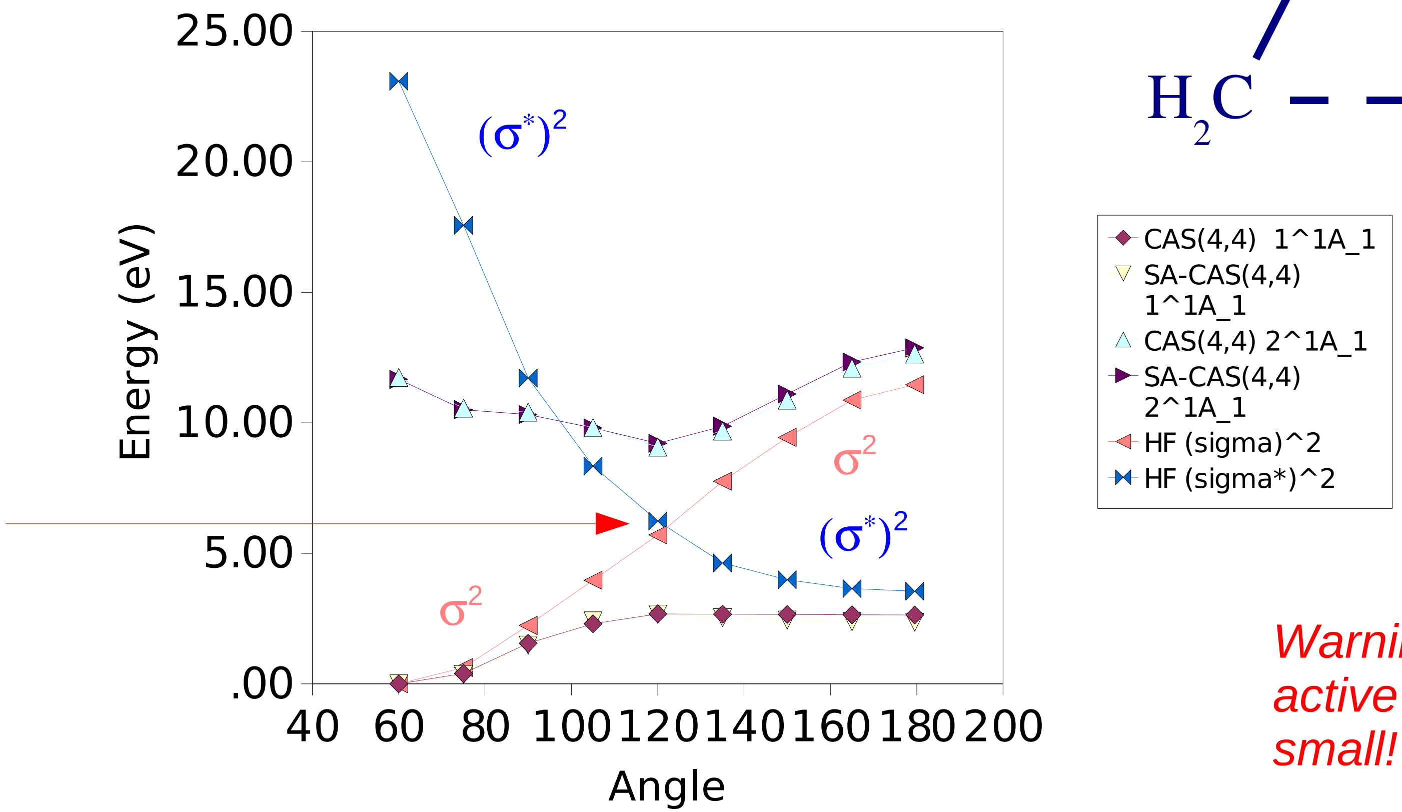
WAVE FUNCTION THEORY

Oxirane CC ring opening



1 & 2 ^1A_1

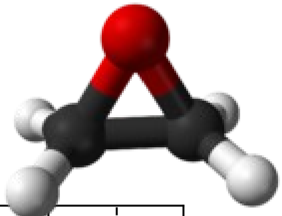
Cusp!

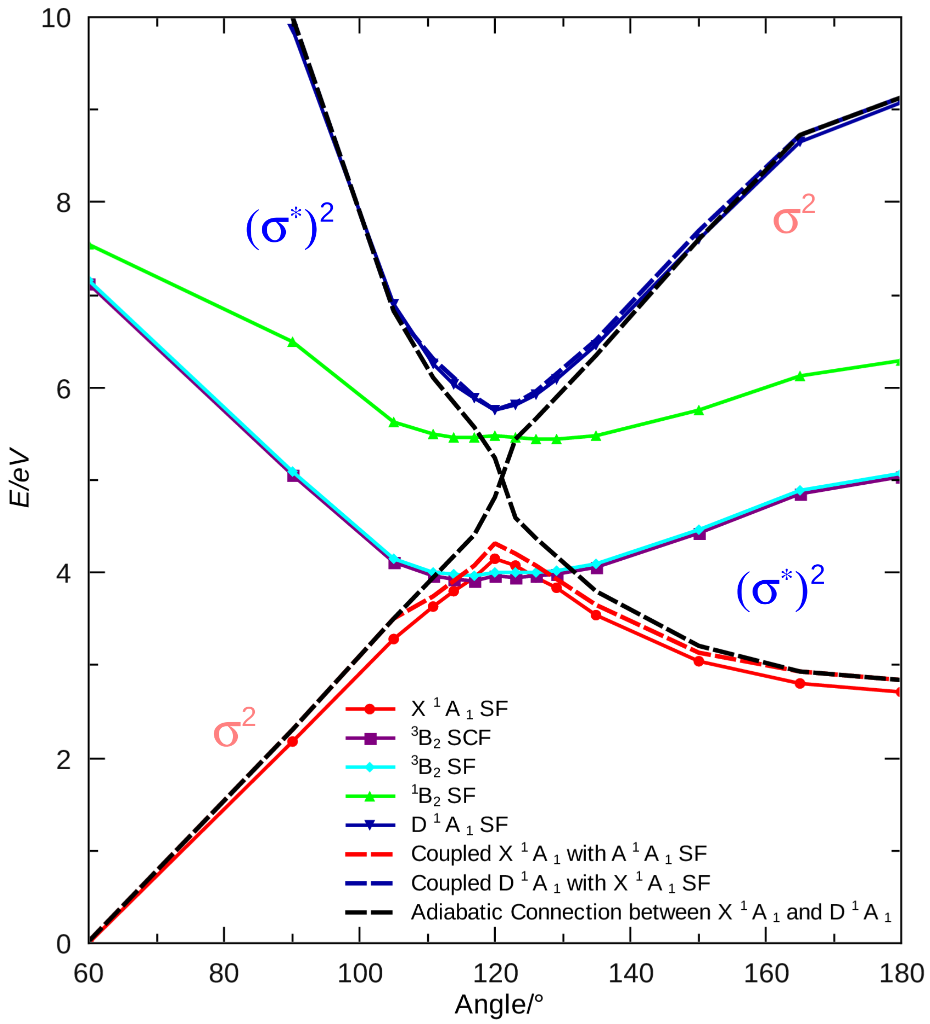


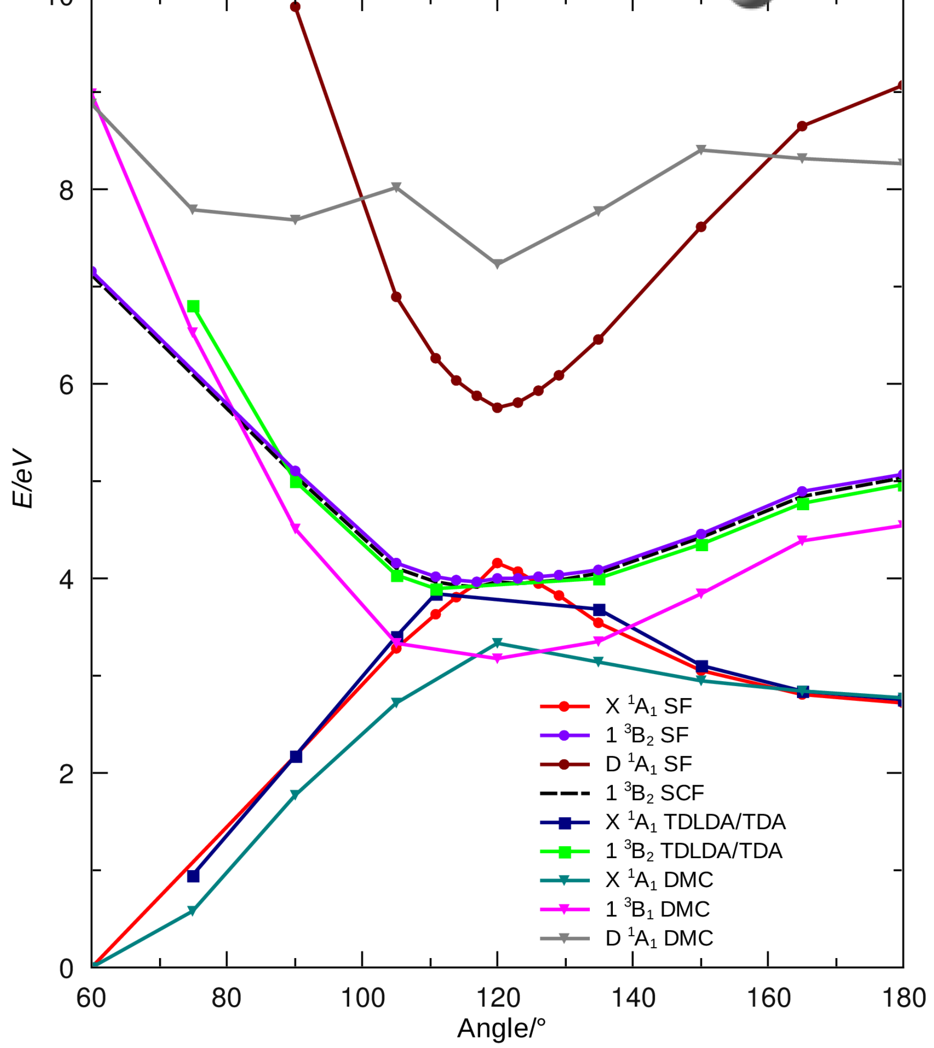
Warning: CAS active space is too small!

Similar situation for rotation around double bond in CH_2=CH_2 .

OXIRANE C_{2v} RING OPENING AVOIDED CROSSING



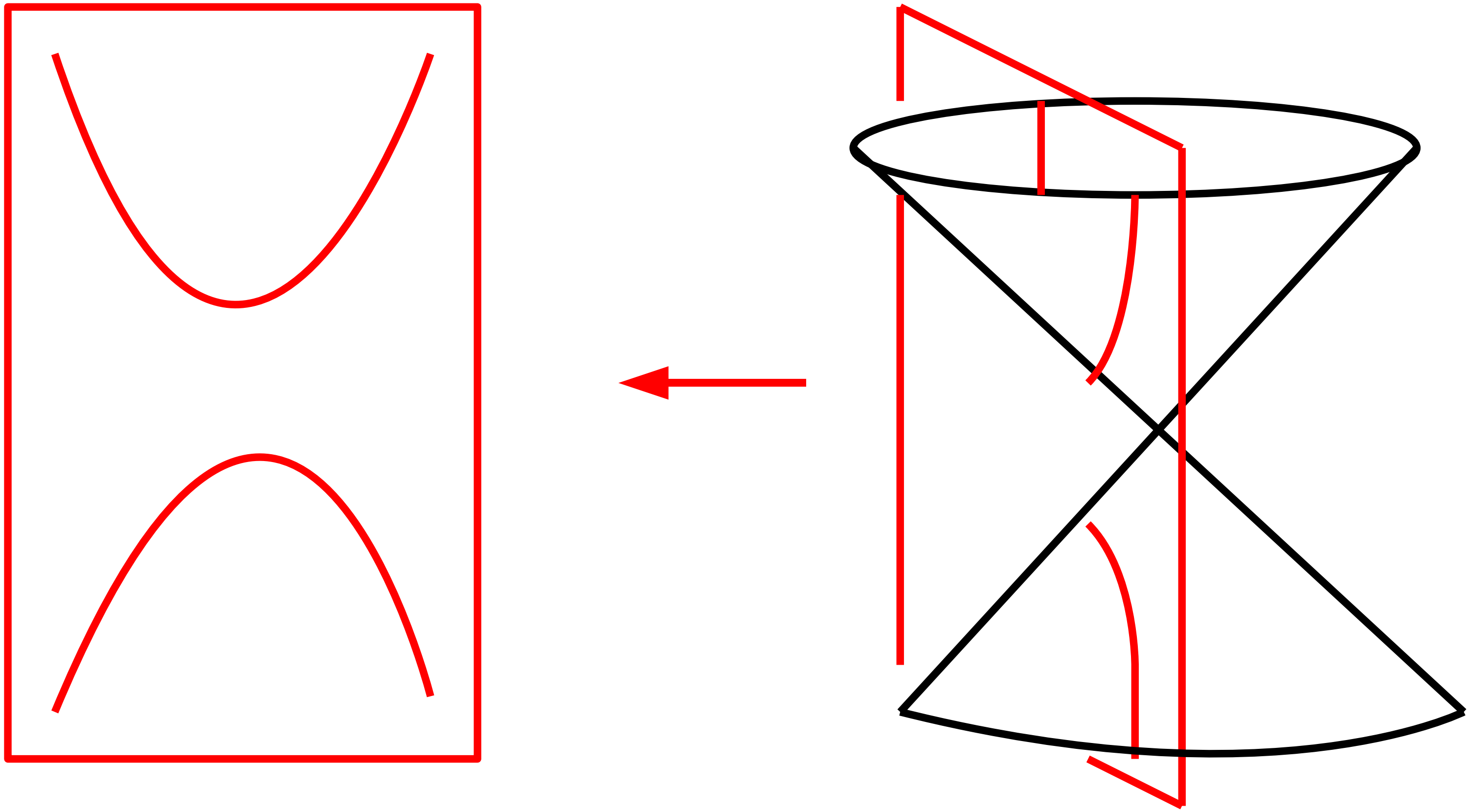




M. Huix-Rotllant, B. Natarajan, A. Ipatov, C. M. Wawire, T. Deutsch, and M. E. Casida, "*Behaviour of Conical Intersections within Noncollinear Spin-Flip Time-Dependent Density-Functional Theory: Oxirane as Test Case*", Phys. Chem. Chem. Phys. **12**, 12811-12825 (2010).

CONICAL INTERSECTIONS AS A DIMENSIONALITY PROBLEM

A conical intersection (CX) is the analogue in N dimensions of avoided crossings in diatomics.



DIMENSIONALITY OF CONICAL INTERSECTIONS

A molecule with **N internal degrees of freedom** has an **N-dimensional potential energy (hyper)surface (PES)** in an **(N+1)-dimensional space**.

$$E_I = E_I(Q_1, Q_2, \ldots, Q_N) \qquad (1)$$

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

$$E_I(Q_{1,} Q_{2,.} \ldots, Q_N) = E_J(Q_{1,} Q_{2,.} \ldots, Q_N) \qquad (2)$$

A conical intersection is **(N-2)-dimensional hyperpoint**.

$$0 = H_{I,J}(Q_{1,} Q_{2,.} \ldots, Q_N) \qquad (3)$$

DIMENSIONALITY OF CONICAL INTERSECTIONS

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$$E_I = E_I(Q_1, Q_2, \ldots, Q_N) \qquad (1)$$

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

$$E_I(Q_{1,} Q_{2,.} .., Q_N) = E_J(Q_{1,} Q_{2,.} .., Q_N) \qquad (2)$$

~~A conical intersection is **(N-2)-dimensional hyperpoint**.~~

$$\xcancel{0 = H_{I,J}(Q_{1,} Q_{2,.} .., Q_N)} \qquad (3)$$

Fails for interaction with the ground state for TDHF TDA (aka CIS) because of Brillouin's theorem.

Also fails for conventional TDDFT.

H_2O
Conical
Intersection

CASSCF

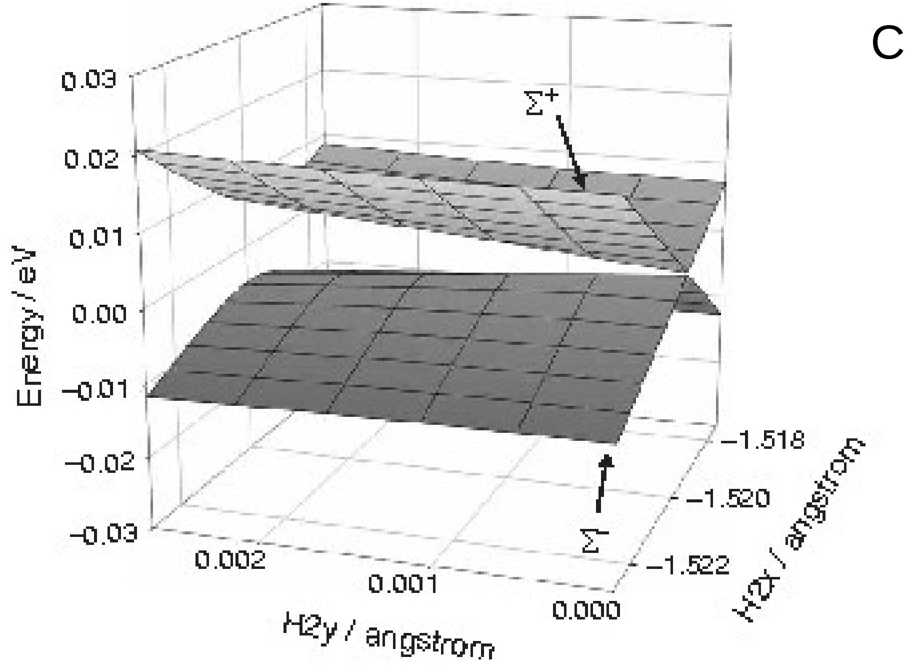


Figure 8. As in figure 7, but using SA3-CAS(6/4)/6-31G. The pronounced conical nature of the intersection is clear, in contrast to figure 7.

CIS

TDB3LYP

Conical intersections and double excitations in time-dependent density functional theory 1047

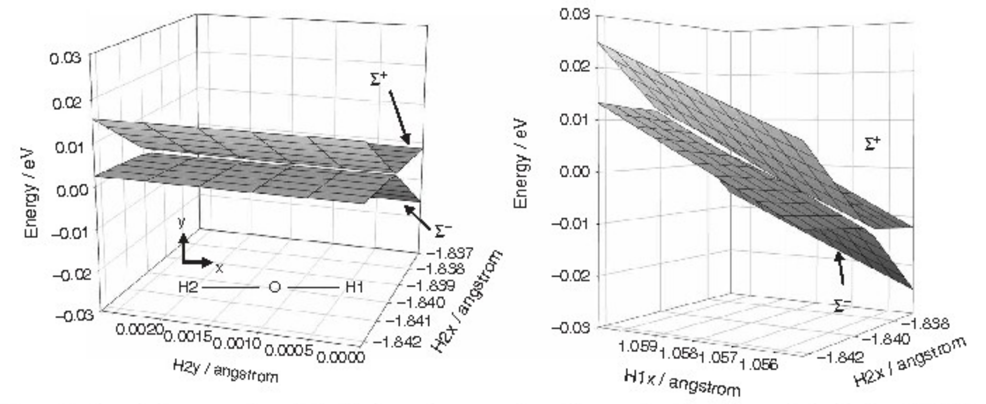


Figure 7. Potential energy surfaces of H_2O in the region surrounding a linear surface intersection calculated using CIS/6-31G. Only one of the three independent displacement coordinates splits the degeneracy. More accurate electronic structure treatments (see figure 8) predict that this intersection is conical and therefore has two branching directions.

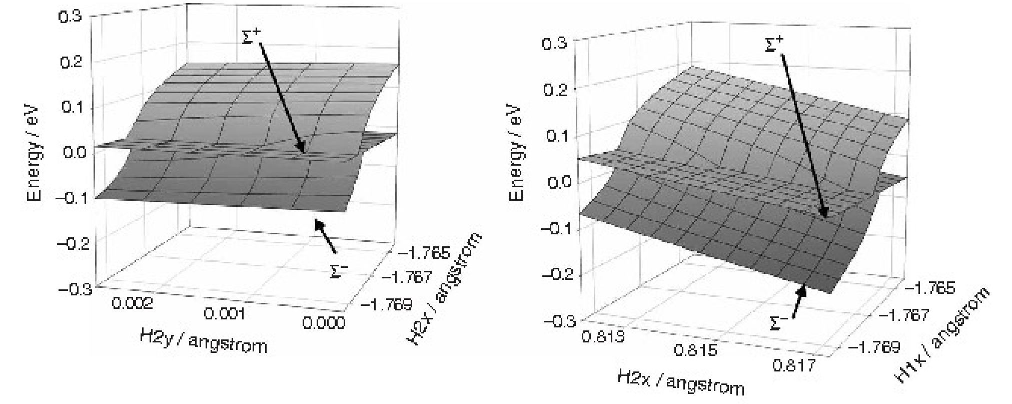
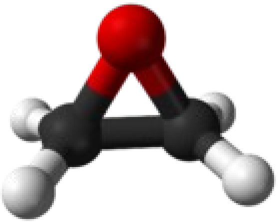
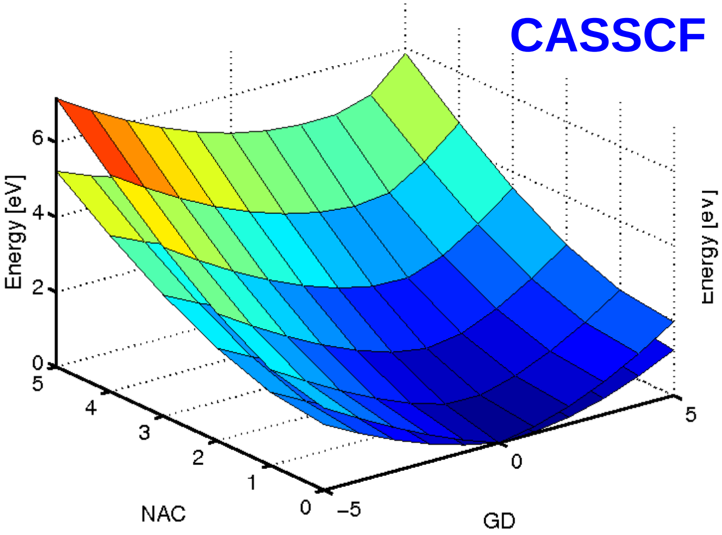


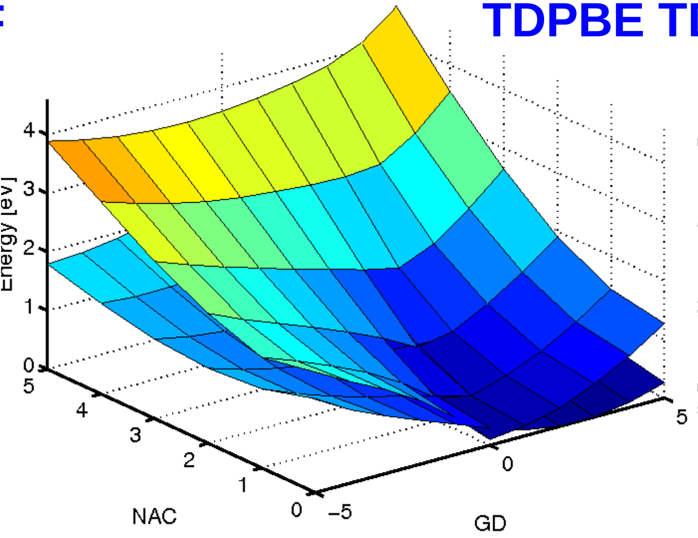
Figure 9. As in figure 7, but using TD-B3LYP/6-31G. As in CIS, only one branching direction is observed instead of the two which should be present. Furthermore, note the change in scale of the energy axis compared to figures 7 and 8.

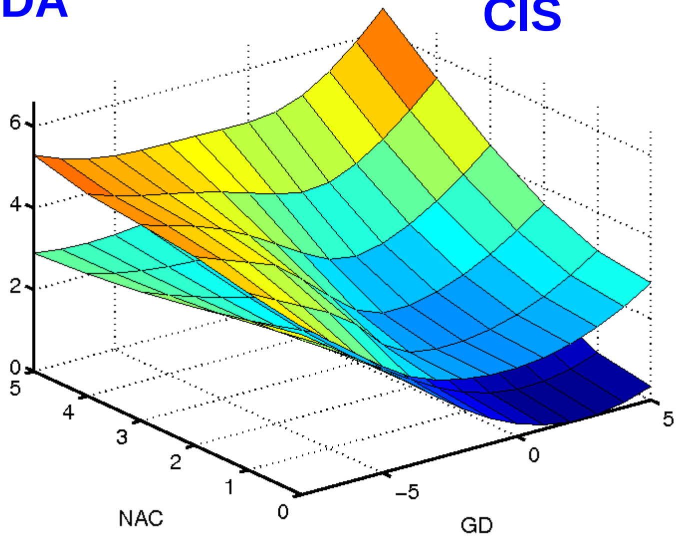
B.G. Levine, C. Ko, J. Quenneville, and T.J. Martinez, *Mol. Phys.* **104**, 1039 (2006).

SF-TDDFT




CASSCF


TDPBE TDA


CIS

SPIN-WAVE INSTABILITY*

Complex orbitals

$$\Psi_\lambda = \left|\sqrt{1-\lambda^2}\psi_i + i\lambda\psi_a, \sqrt{1-\lambda^2}\bar{\psi}_i - i\lambda\bar{\psi}_a\right| \tag{1}$$

$$E_\lambda = E_0 + 2\lambda^2(\Delta\epsilon) + O(\lambda^3) \tag{2}$$

$$\omega_T = \sqrt{(\Delta\epsilon)\left[\Delta\epsilon + 2(K_{\alpha,\alpha} - K_{\alpha,\beta})\right]} \tag{3}$$

$$\omega_S = \sqrt{(\Delta\epsilon)\left[\Delta\epsilon + 2(K_{\alpha,\alpha} + K_{\alpha,\beta})\right]} \tag{4}$$

---

* Axial Spin Current Wave/Paired UHF. See also, N.S. Ostland, “Complex and Unrestricted Hartree-Fock Wavefunctions,” *J. Chem. Phys.* **57**, 2994 (1972).

SPIN-WAVE INSTABILITY

$$\Psi_{\lambda}=\left|\sqrt{1-\lambda^2}\psi_i+i\lambda\psi_a,\sqrt{1-\lambda^2}\bar{\psi}_i-i\lambda\bar{\psi}_a\right| \quad (1)$$

density matrix

$$\hat{\gamma}_{\alpha}=\left(1-\lambda^2\right)|i><i|+i\lambda\sqrt{1-\lambda^2}\left(|a><i|-|i><a|\right)+\lambda^2|a><a| \quad (2)$$

$$\hat{\gamma}_{\beta}=\left(1-\lambda^2\right)|i><i|-i\lambda\sqrt{1-\lambda^2}\left(|a><i|-|i><a|\right)+\lambda^2|a><a| \quad (3)$$

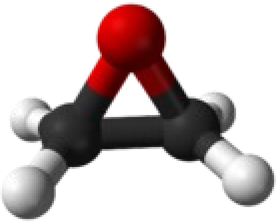
$$\hat{\gamma}=\hat{\gamma}_{\alpha}+\hat{\gamma}_{\beta}=2\left(1-\lambda^2\right)|i><i|+2\lambda^2|a><a| \quad (4)$$

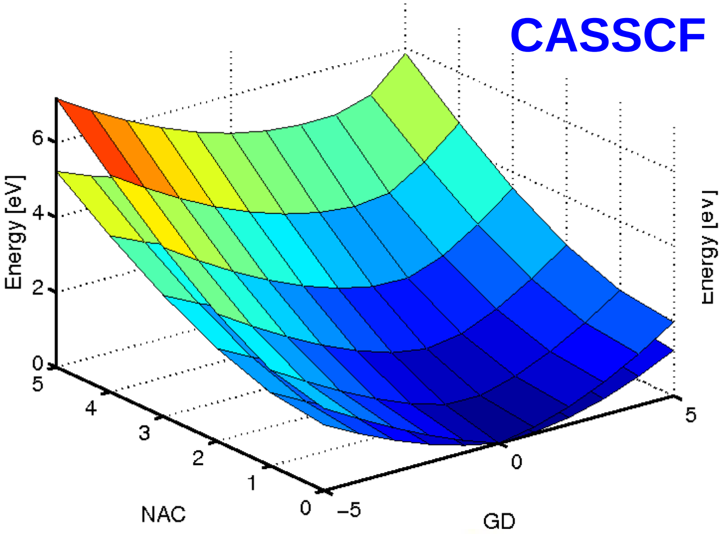
Complex orbitals with integer occupation number
= real orbitals with fractional occupation number (sometimes)

---

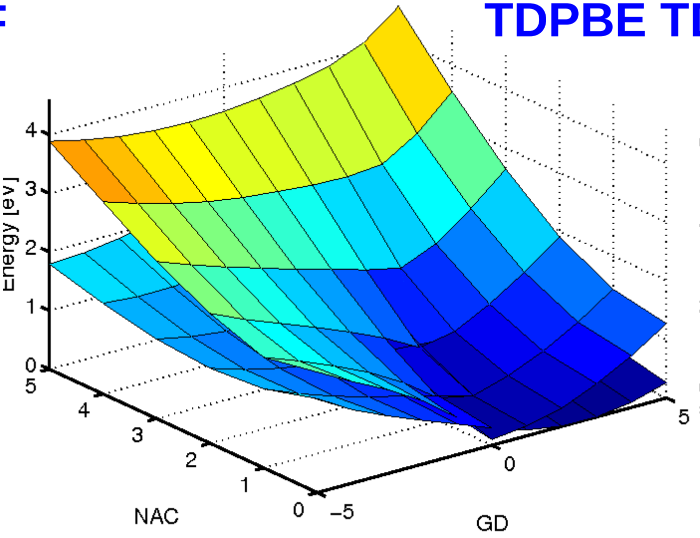
* See also M. Levy, “Electron densities in search of Hamiltonians,” *Phys. Rev. A* **26**, 1200 (1982).

SF-TDDFT

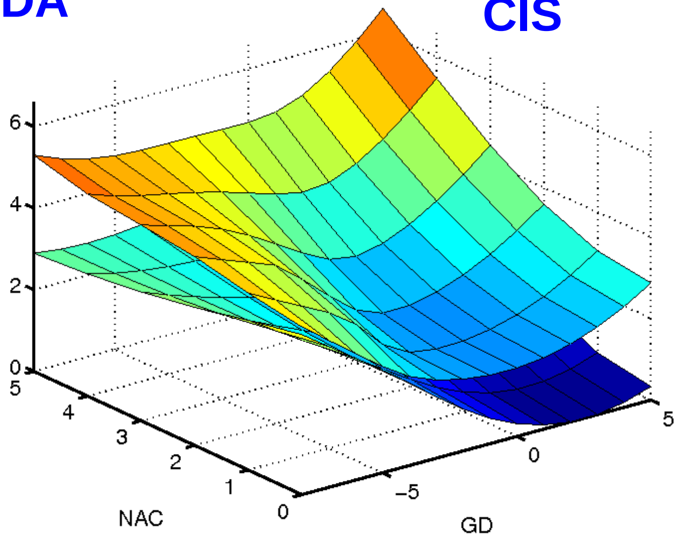




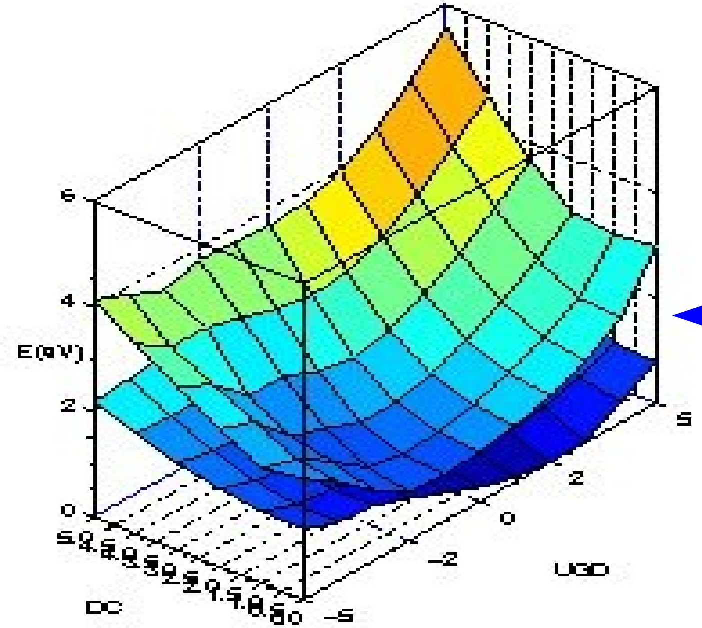
CASSCF



TDPBE TDA



CIS



SF-TDLDA TDA

reference is
lowest triplet

- Easier convergence
- Coupling => true CX
- But the CX is rather approximate

Failures and Corrections

(i) Failure originating in E_{xc}

(ii) Failures originating in v_{xc}

(iii) Failures orignating in f_{xc}

Two-Orbital Two-Electron Model (TOTEM) + TDA

$$\omega_T = \epsilon_a - \epsilon_i + \left(ia \middle| f_{xc}^{\alpha,\alpha} - f_{xc}^{\alpha,\beta} \middle| ai \right) \quad (1)$$

$$\omega_S = \epsilon_a - \epsilon_i + \left(ai \middle| 2 f_H + f_{xc}^{\alpha,\alpha} + f_{xc}^{\alpha,\beta} \middle| ia \right) \quad (2)$$

Interpretation of Kohn-Sham Orbital Energies

When a good quality v_{xc} is used, excitation energies can often be interpreted simply in terms of orbital energy differences,

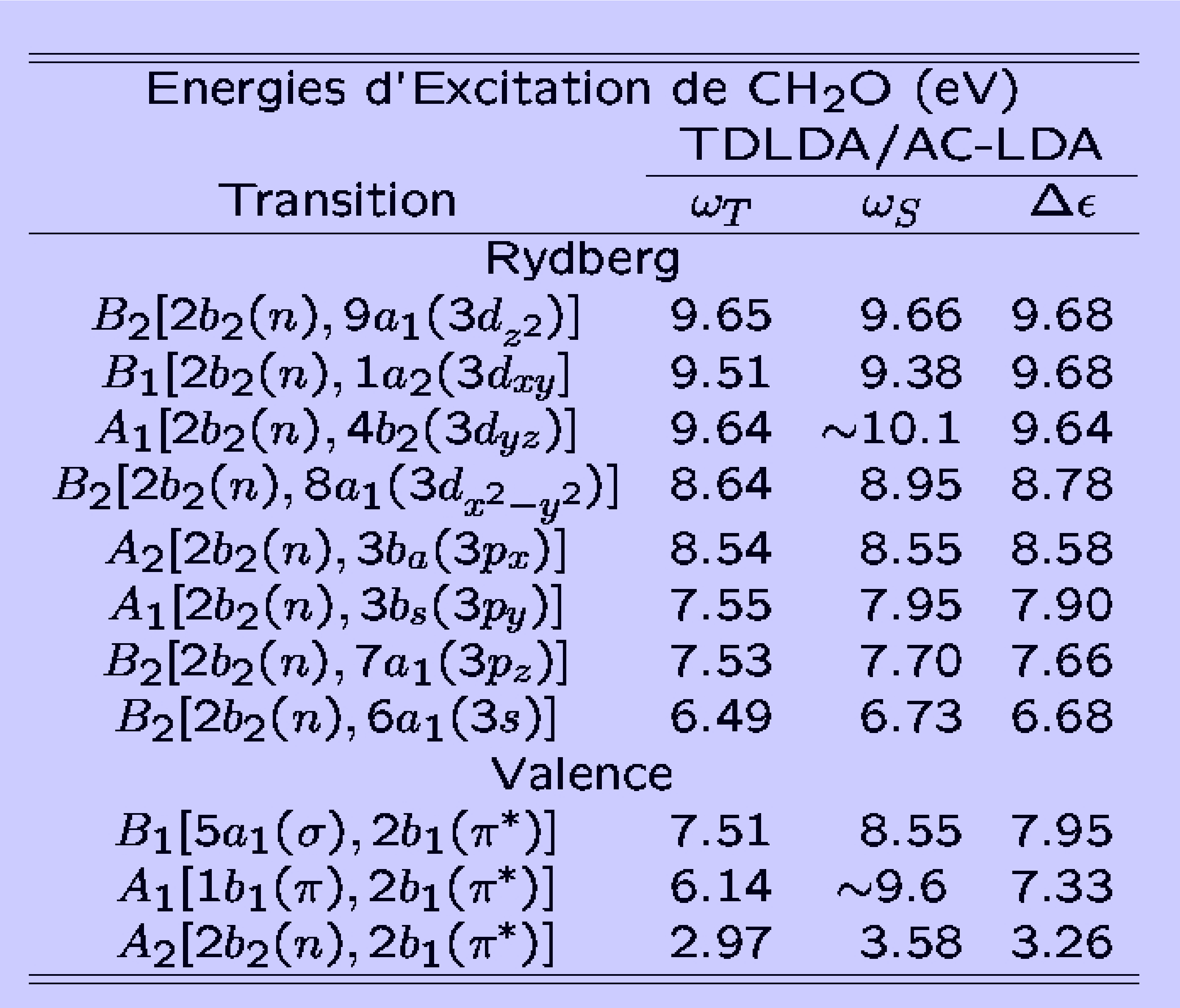
$$\omega_T < \Delta\varepsilon < \omega_S$$

In the case of Rydberg excitations, the energy separation between singlet-triplet pairs becomes very small,

$$\omega_T \approx \Delta\varepsilon \approx \omega_S$$

One consequence is that many unoccupied Kohn-Sham orbitals are bound!

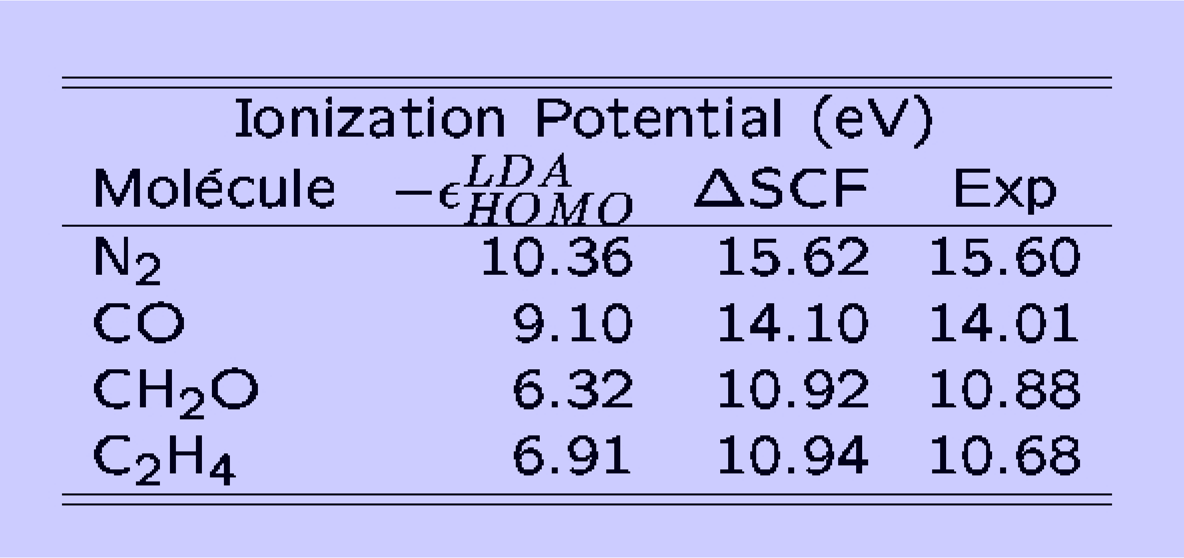
CH_2O Excitation Energies



Energies d'Excitation de CH_2O (eV)

Transition	TDLDA/AC-LDA		
	ω_T	ω_S	$\Delta\epsilon$
Rydberg			
$B_2[2b_2(n), 9a_1(3d_{z^2})]$	9.65	9.66	9.68
$B_1[2b_2(n), 1a_2(3d_{xy}]$	9.51	9.38	9.68
$A_1[2b_2(n), 4b_2(3d_{yz})]$	9.64	~10.1	9.64
$B_2[2b_2(n), 8a_1(3d_{x^2-y^2})]$	8.64	8.95	8.78
$A_2[2b_2(n), 3b_a(3p_x)]$	8.54	8.55	8.58
$A_1[2b_2(n), 3b_s(3p_y)]$	7.55	7.95	7.90
$B_2[2b_2(n), 7a_1(3p_z)]$	7.53	7.70	7.66
$B_2[2b_2(n), 6a_1(3s)]$	6.49	6.73	6.68
Valence			
$B_1[5a_1(\sigma), 2b_1(\pi^*)]$	7.51	8.55	7.95
$A_1[1b_1(\pi), 2b_1(\pi^*)]$	6.14	~9.6	7.33
$A_2[2b_2(n), 2b_1(\pi^*)]$	2.97	3.58	3.26

The Ionization Potential is Minus the HOMO Energy for the Exact Exchange-Correlation Functional

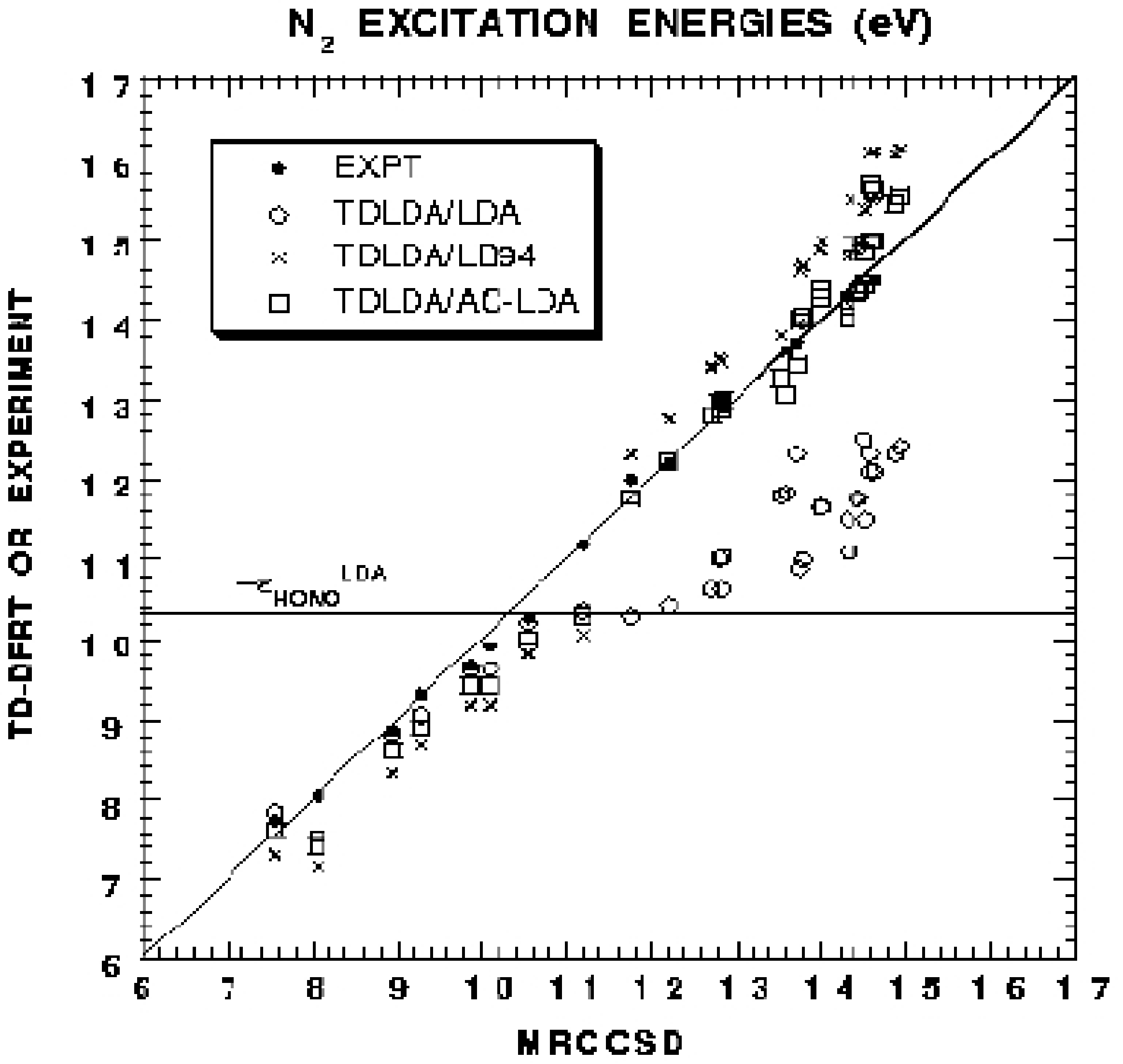


Ionization Potential (eV)

Molécule	$-\epsilon_{HOMO}^{LDA}$	ΔSCF	Exp
N_2	10.36	15.62	15.60
CO	9.10	14.10	14.01
CH_2O	6.32	10.92	10.88
C_2H_4	6.91	10.94	10.68

The vast majority of approximate exchange-correlation potentials v_{xc} underbind the electrons because the potentials go too rapidly to zero at large distance!

The Ionization Threshold is at $-E_{HOMO}$, which is Too Low!



The collapse of high excitation energies is avoided by using exchange-correlation potentials with an improved long range behavior.

Nowadays use RSH.

Failures and Corrections

(i) Failure originating in E_{xc}

(ii) Failures originating in v_{xc}

(iii) Failures orignating in f_{xc}

CONSEQUENCE OF ADIABATIC APPROXIMATION

LR-TDDFT matrix is now independent of frequency.

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

N_{occ} N_{virt} excitation solutions and N_{occ} N_{virt} de-excitation solutions.

Conclude: AA-TDDFT only gives single-electron excitations
(albeit dressed to include some correlation)

Need frequency dependence to include double excitations!

RELATED PROBLEM: UNDERESTIMATED CHARGE TRANSFER EXCITATIONS

$$\omega_T = \epsilon_a - \epsilon_i + \left(ia \middle| f_{xc}^{\alpha,\alpha} - f_{xc}^{\alpha,\beta} \middle| ai \right) \tag{1}$$

$$\omega_S = \epsilon_a - \epsilon_i + \left(ai \middle| 2 f_H + f_{xc}^{\alpha,\alpha} + f_{xc}^{\alpha,\beta} \middle| ia \right) \tag{2}$$

Long-range charge transfer =>

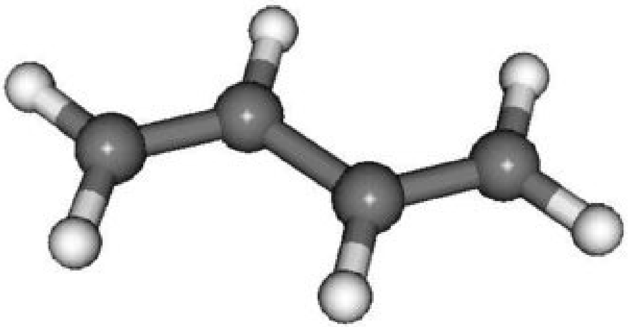
$$\omega_{CT} = \epsilon_a - \epsilon_i < EA - IP \tag{3}$$

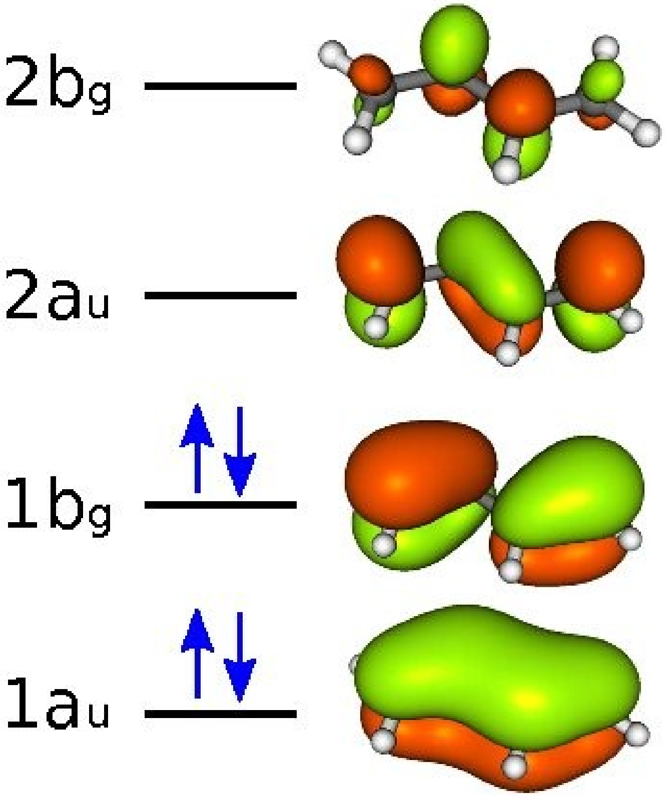
Should have

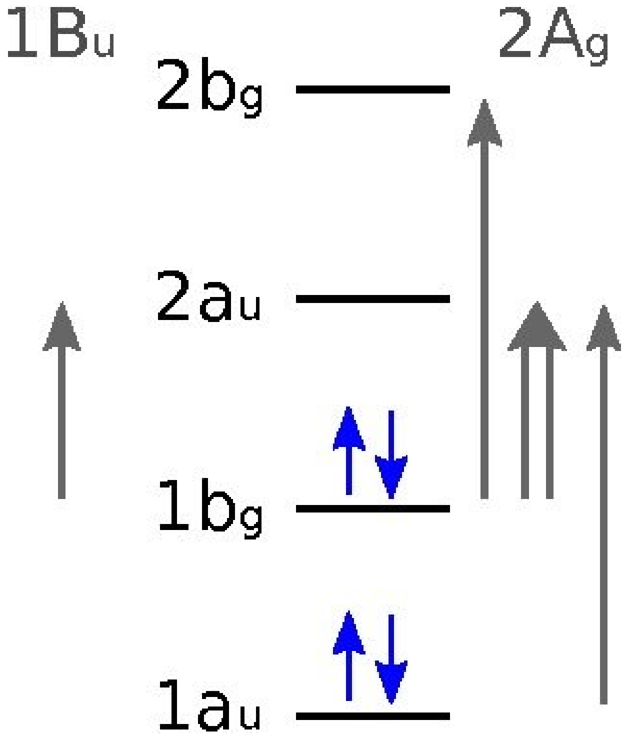
$$\omega_{CT} = EA - IP - \frac{1}{R} \tag{4}$$

A. Dreuw, J.L. Weisman, and M. Head-Gordon, "Long-range charge-transfer excited-states in time-dependent density-functional theory require non-local exchange", *J. Chem. Phys.* **119**, 2943 (2003).

BUTADIENE $CH_2=CH-CH=CH_2$

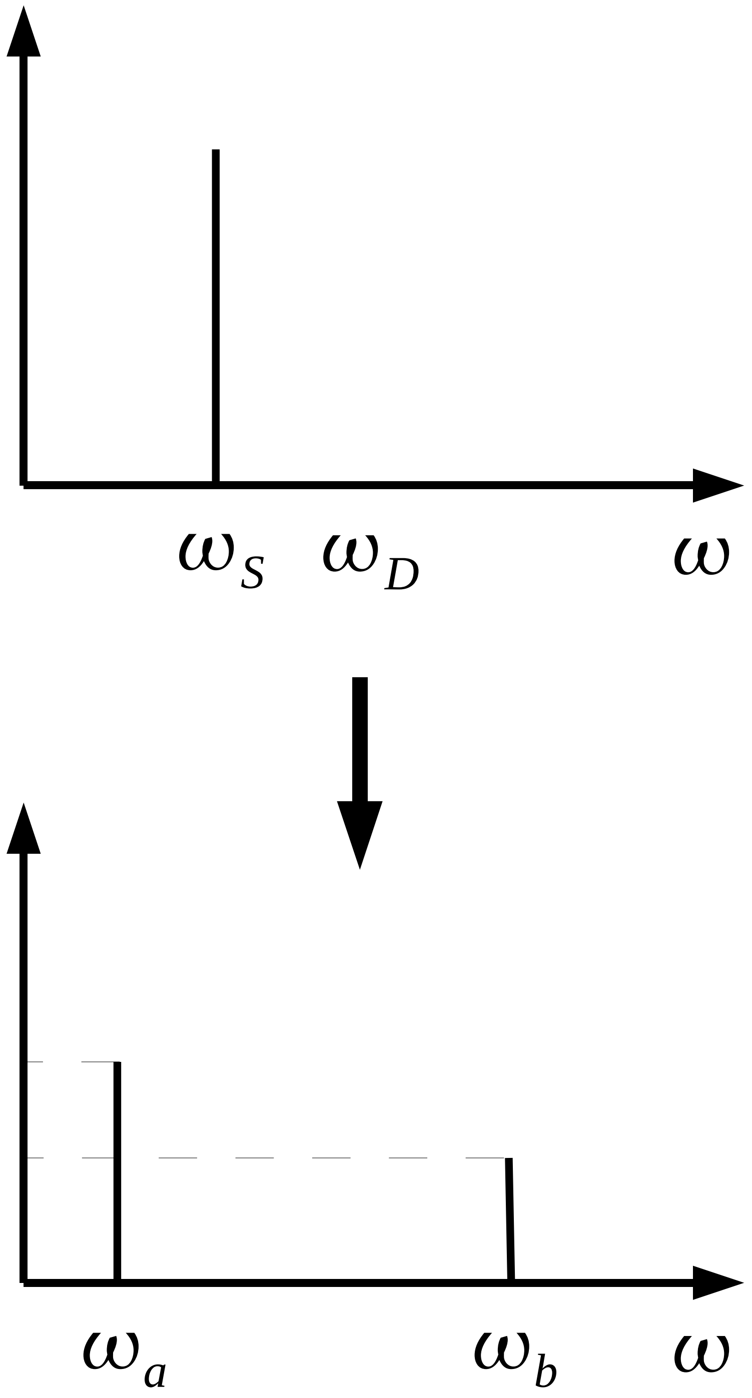






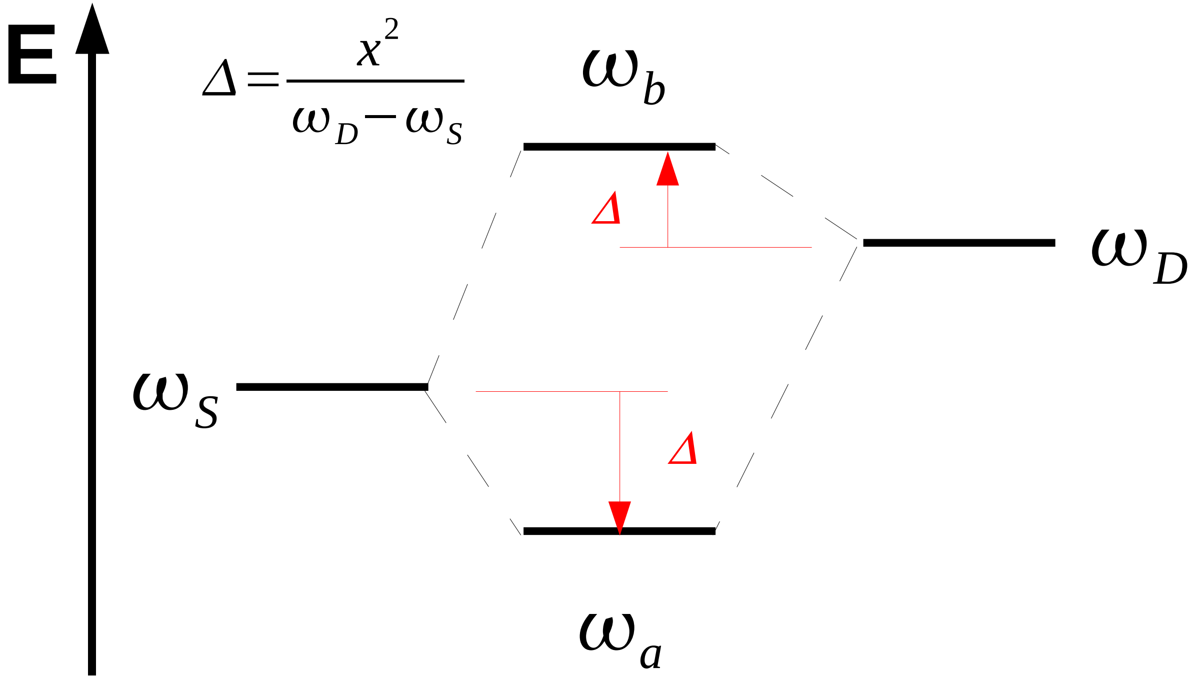
$$\begin{bmatrix} \omega_S & x \\ x & \omega_D \end{bmatrix} \begin{pmatrix} C_S \\ C_D \end{pmatrix} = \omega \begin{pmatrix} C_S \\ C_D \end{pmatrix} \qquad (1)$$

$$\omega = \omega_S + \frac{x^2}{\omega - \omega_D} \qquad (2)$$



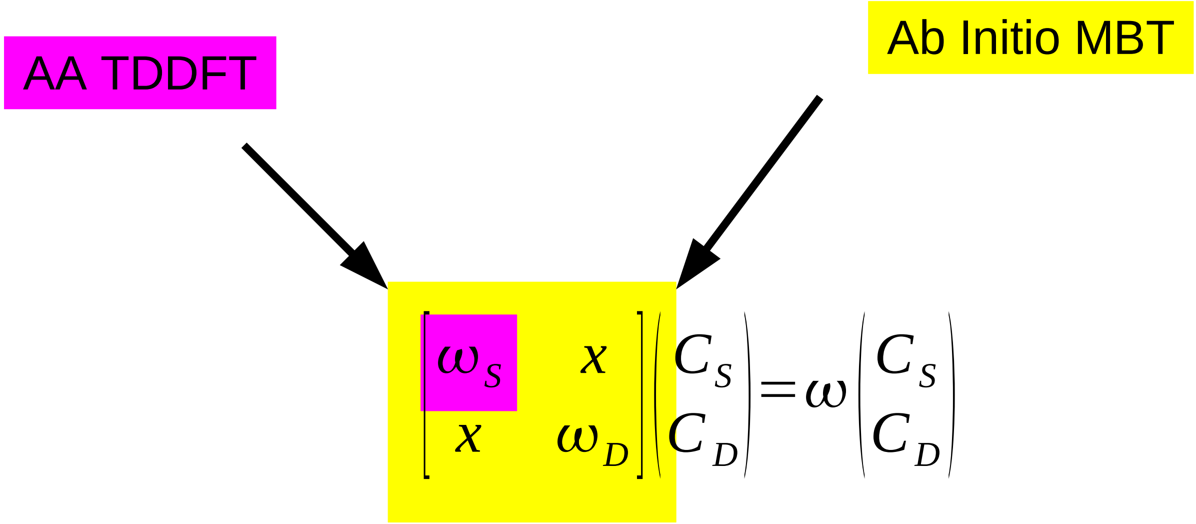
Static correlation

$$\Delta = \frac{x^2}{\omega_D - \omega_S}$$



THE ORIGINAL IDEA

N.T. Maitra, F. Zhang, R.J. Cave, and K. Burke, “Double excitations within time-dependent density-functional theory linear reponse theory”, *J. Chem. Phys.* **120**, 5932 (2004).

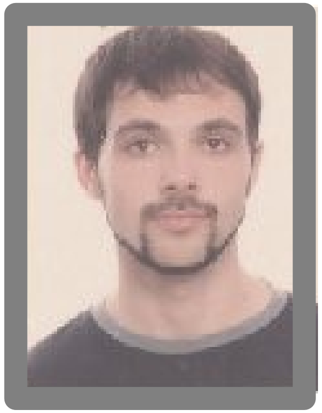


AA TDDFT

Ab Initio MBT

$$\begin{bmatrix}\omega_S & x\\ x & \omega_D\end{bmatrix}\begin{pmatrix}C_S\\ C_D\end{pmatrix}=\omega\begin{pmatrix}C_S\\ C_D\end{pmatrix}$$

- What functional for AA TDDFT?
- What level of MBT?
- How to implement?
- Extensive testing?

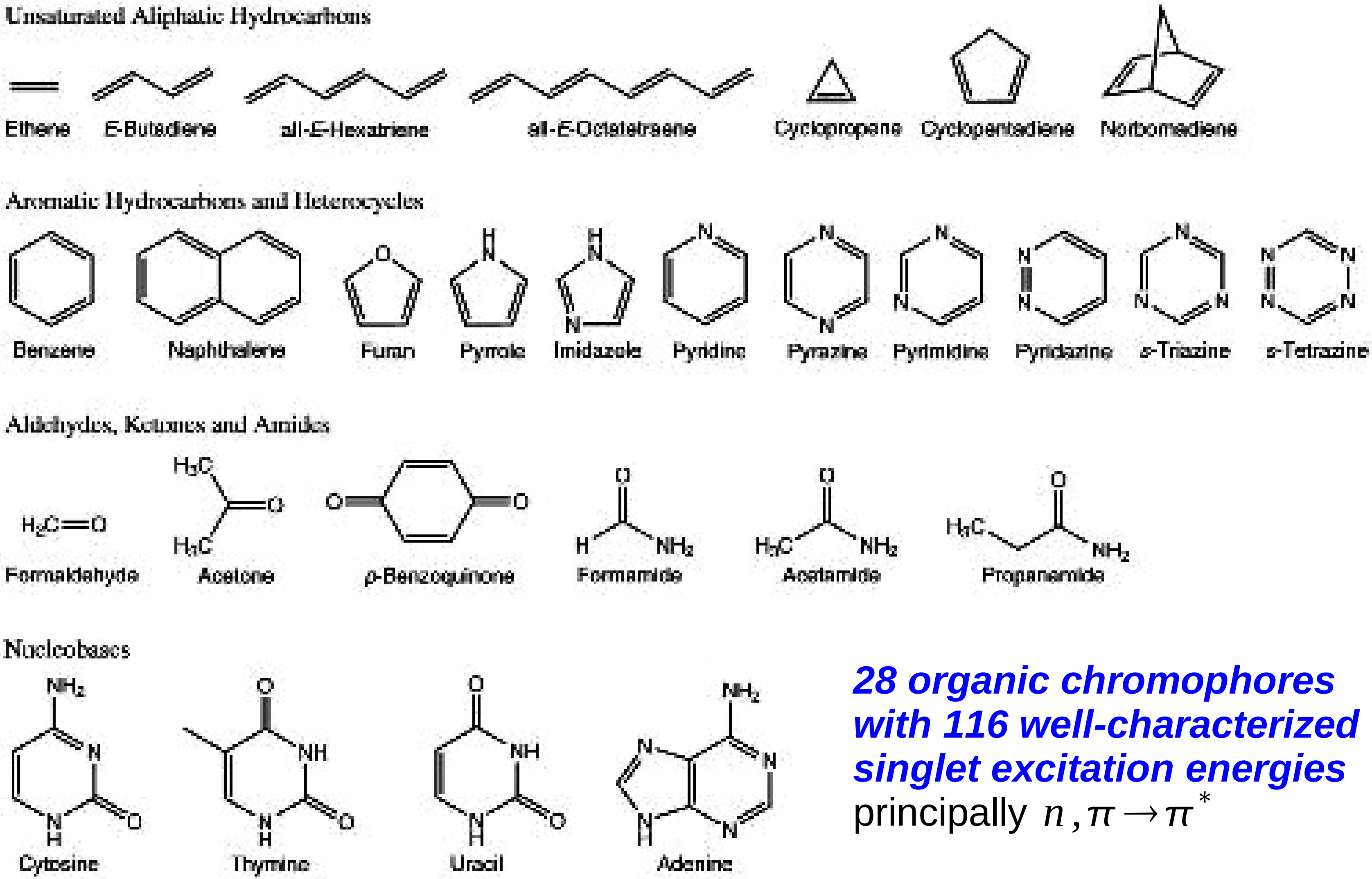


Miquel Huix-Rotllant: Improvement of TDDFT Modeling of the Spectroscopy of Nanosystems Through Better Understanding of the Space-Time Trade-Off in the Exchange-Correlation Functional

M. Huix-Rotllant and M.E. Casida, "Formal Foundations of Dressed Time-Dependent Density-Functional Theory for Many-Electron Excitations", arXiv:1008.1478v1 [cond-mat.mes-hall] 9 Aug 2010.

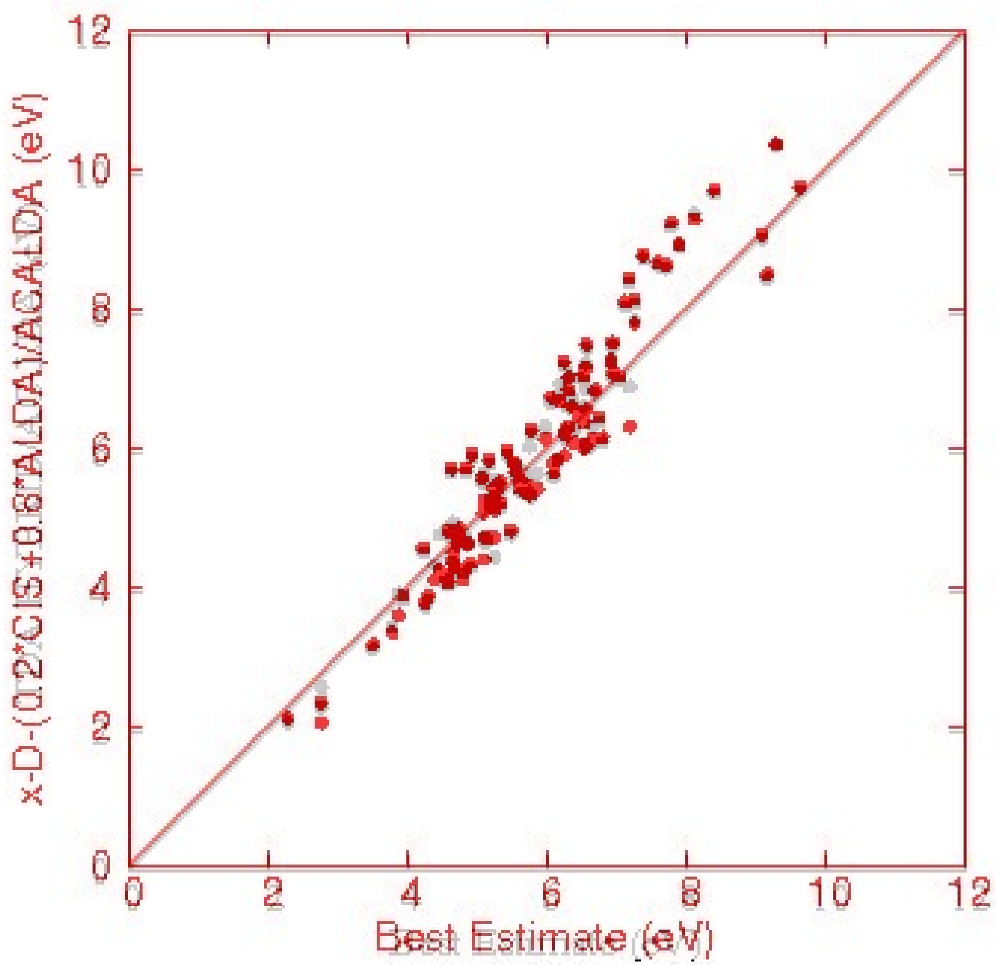
Miquel Huix-Rotllant, A. Ipatov, A. Rubio, and M.E. Casida, "Assessment of Dressed Time-Dependent Density-Functional Theory for the Low-Lying Valence States of 28 Organic Chromophores", *Chem. Phys.,* in press (preprint on-line at Chem Phys and at arXiv).

M. Schreiber, M.R. Silva-Junior, S.P.A. Sauer, and W. Thiel, *J. Chem. Phys.* 128, 134110 (2008).
“Benchmarks for electronically excited states: CASPT2, CC2, CCSD, and CC3”



28 organic chromophores with 116 well-characterized singlet excitation energies
principally $n,\pi \to \pi^*$

EFFECT OF ADDING 10 DOUBLES

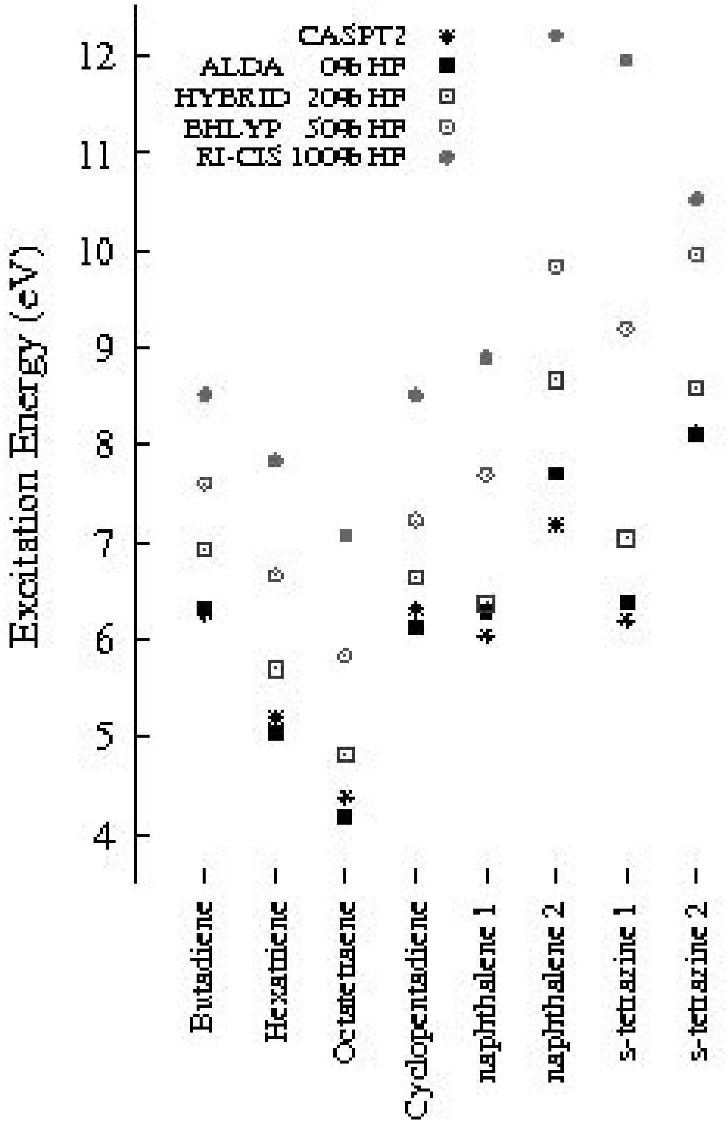


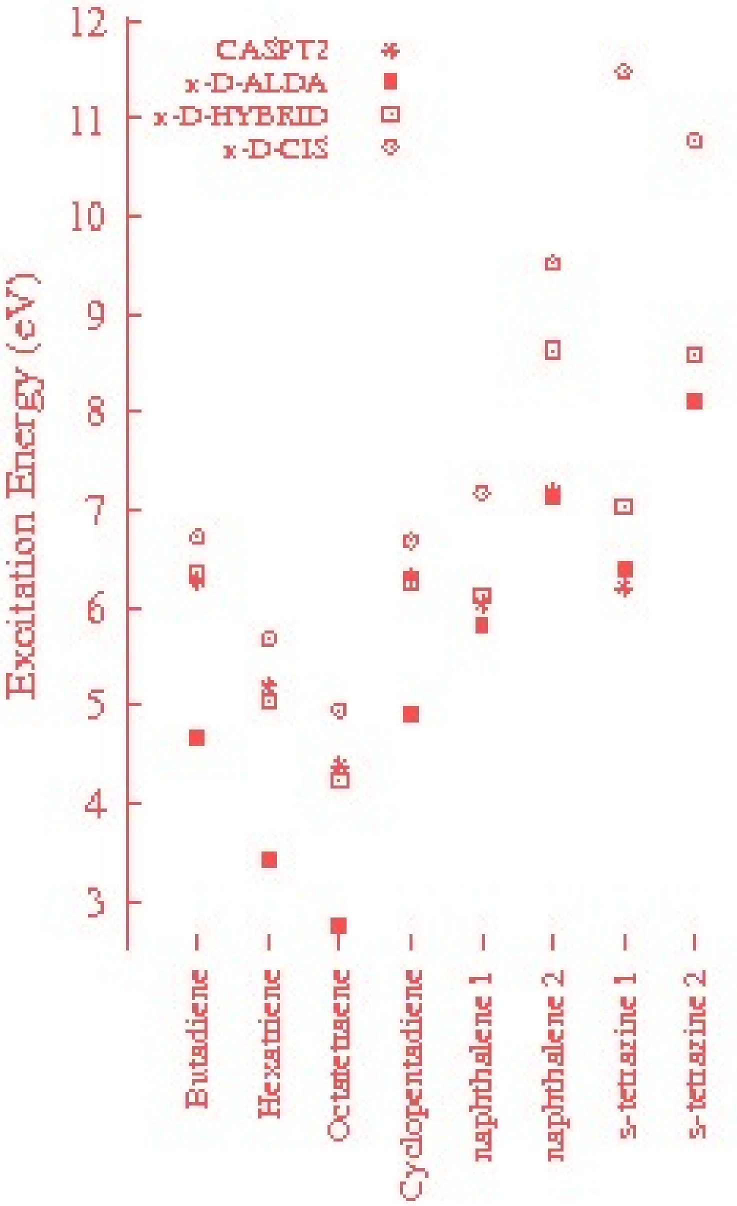
TDhybrid ≈ x-D-TDhybrid

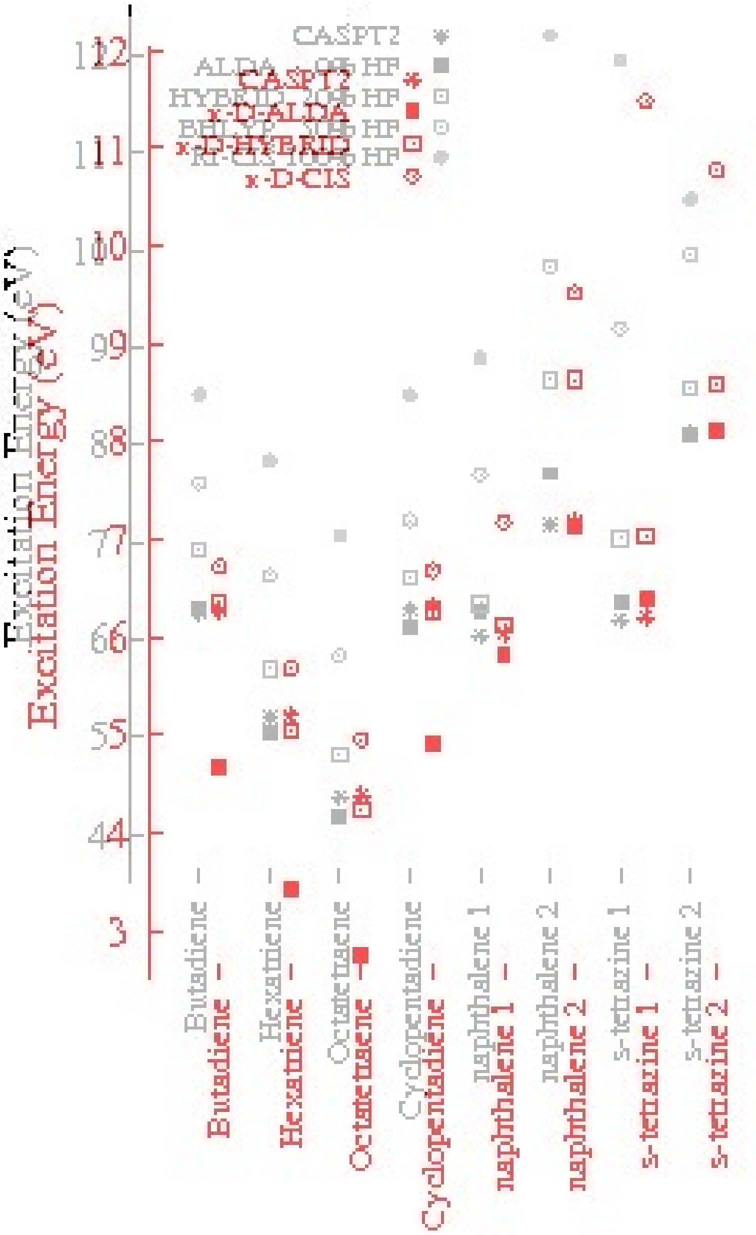
TDhybrid ≈ x-D-TDhybrid

There is almost no difference! (This is a good thing.)

States having more than 10% doubles character according to CCSD calculations.

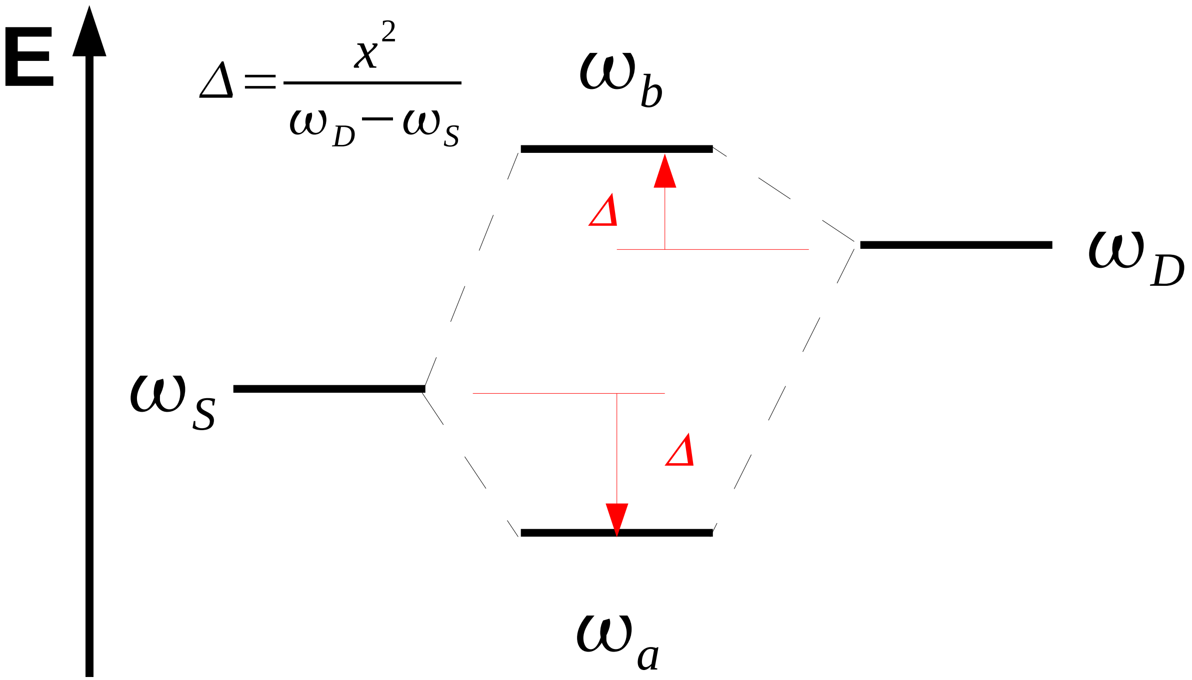






The x-D shifts downwards by an amount which is very dependent on the method to which it is applied.

Static correlation



$$\Delta = \frac{x^2}{\omega_D - \omega_S}$$

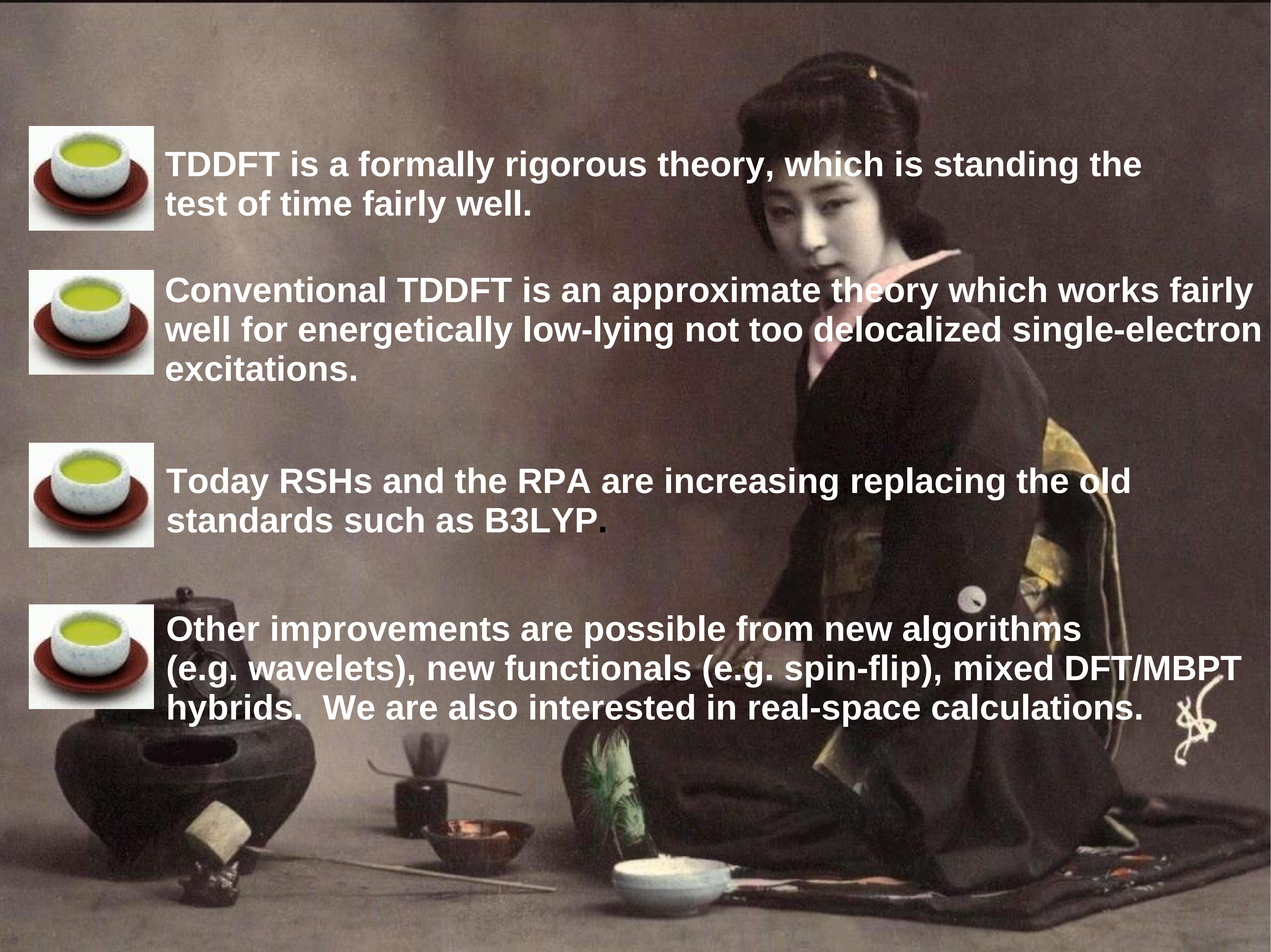
Shift depends upon

- x (basically same for all methods)
- $\omega_D - \omega_S$ (differs from method to method)

OTHER INTERESTING GENERALIZATIONS OF TDDFT

- **Time-Dependent Current-Density Functional Theory**: The Vignale-Kohn current density functional is helpful incorporating ultra long range effects into TDDFT.
- **Time-Dependent Density-Matrix Functional Theory**: Allows the inclusion of fractional occupation numbers (and phases!) in regions of effective noninteracting *v*-representability.

I. Interdisciplinarity
II. Our Interests
III. DFT
IV. TD-DFT
V. Successes/Problems/Solutions
VI. Conclusion



- TDDFT is a formally rigorous theory, which is standing the test of time fairly well.
- Conventional TDDFT is an approximate theory which works fairly well for energetically low-lying not too delocalized single-electron excitations.
- Today RSHs and the RPA are increasing replacing the old standards such as B3LYP.
- Other improvements are possible from new algorithms (e.g. wavelets), new functionals (e.g. spin-flip), mixed DFT/MBPT hybrids. We are also interested in real-space calculations.

Thanks to the organizers of YKIS2011 and DCEN2011:
particularly to Naoyuki Itagaki andd Takashi Nakatsukasa for many messages.
Special thanks also to my dear colleague Kazuhiro Yabana
and to YITP secretary Asako Ando.

Many thanks to you for your attention!
Domo arigato gozaimasu!

Organizations with which I am affiliated and which support our work:

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dépasser les frontières

Chimie Théorique

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Rhône-Alpes Associated Node

nano SCIENCES
FONDATION

deMon
density of Montréal

Mark E. Casida (KASHIDA Maruku), 13 years old
Kyoto, Japan, 1971

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マーク

ma-ru-ku