Time-Dependent Density-Functional Theory (TD-DFT) for Molecules
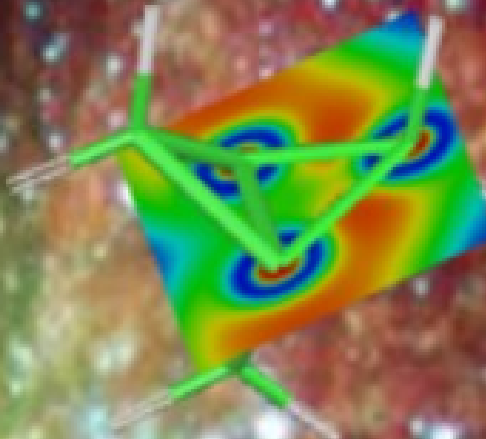
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Département de Chimie Moléculaire (DCM, UMR CNRS/UGA 5250)
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ASESMA
12 June 2025
90 minutes

ASESMA

OUTLINE

I. MOTIVATION

II. GROUND-STATE THEORY

III. QUANTUM CHEMISTRY FOR EXCITED STATES

IV. TD-DFT

V. HOW WELL DOES IT WORK IN PRACTICE?

VI. CONCLUSION

Why not?
New idea for
the synthesis.

**

Try it out.

*

An idea for
a synthesis.

**

"I haven't failed.
I've just found
10,000 ways
that won't work."

Thomas Edison

H_3C, CH_3, CH_3

No

***

*** **Yes**

Characterize
the product.
Did you get the
right molecule?

Publish
(but don't
mention the
10,000 failures)
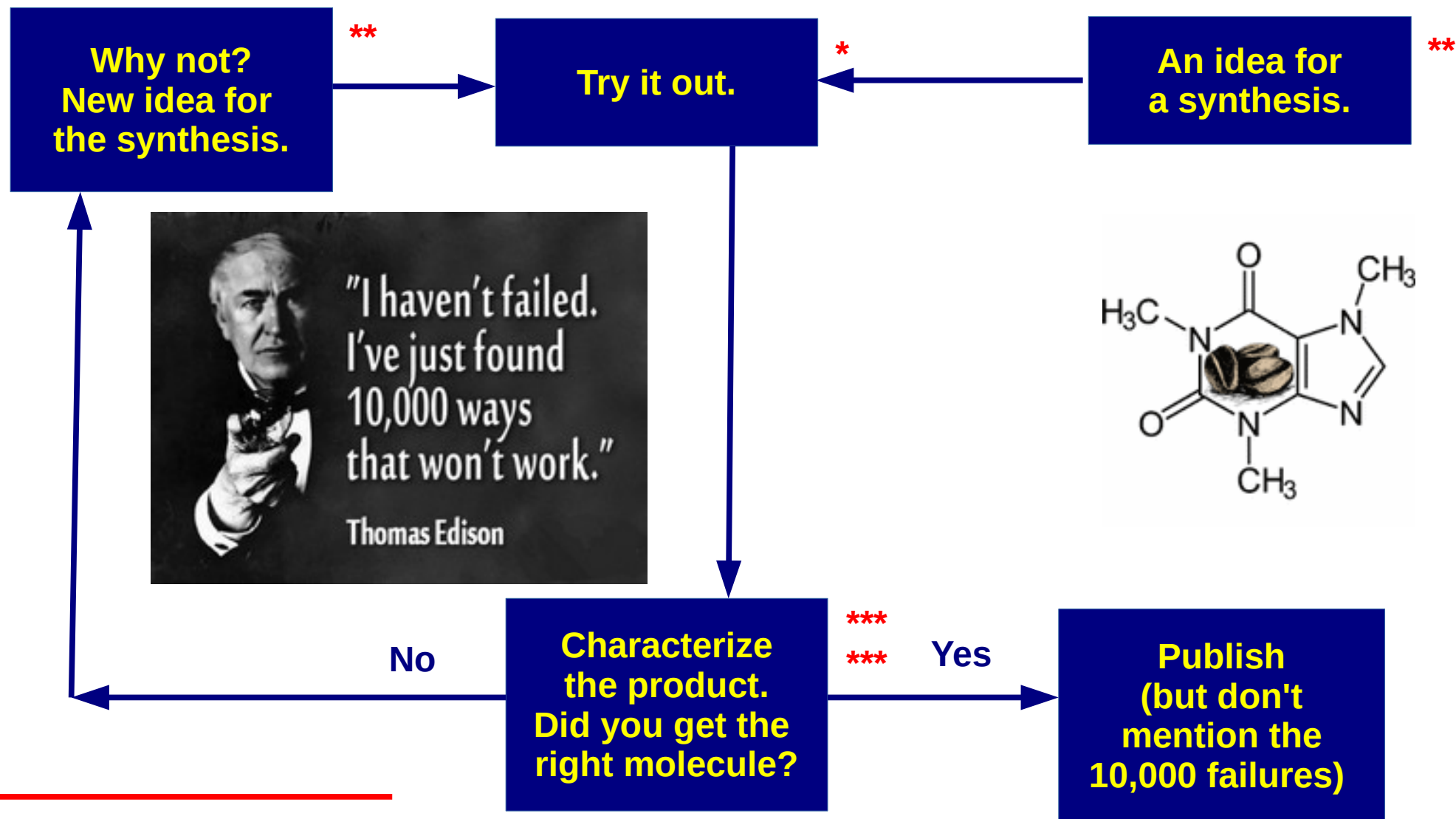
* Physical chemistry and theoretical chemistry are here.

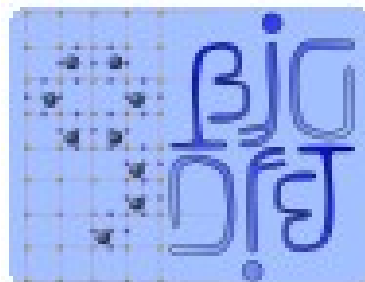**These days *experimentalists* have access to Quantum Chemistry programs and *are expected to be able to use them*.**

Gaussian

Amsterdam density functional

deMon
density of Montréal

GAMESS

NWCHEM
HIGH-PERFORMANCE COMPUTATIONAL CHEMISTRY SOFTWARE

QUANTUMESPRESSO

CP2K

siesta
TM

Abinit

BigDFT

fiesta!

FHI-aims
The ab initio materials simulation package

ASESMA 2025, Accra, Ghana

and many others!

4

These days *experimentalists* have access to Quantum Chemistry programs and *are expected to be able to use them*.

http://www.demon-software.com/public_html/index.html
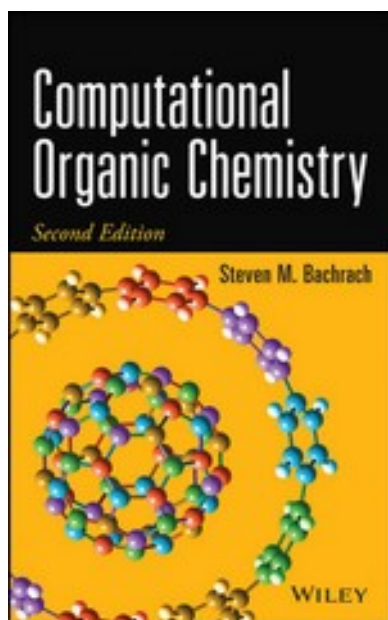
A member of the ETSF software suite:

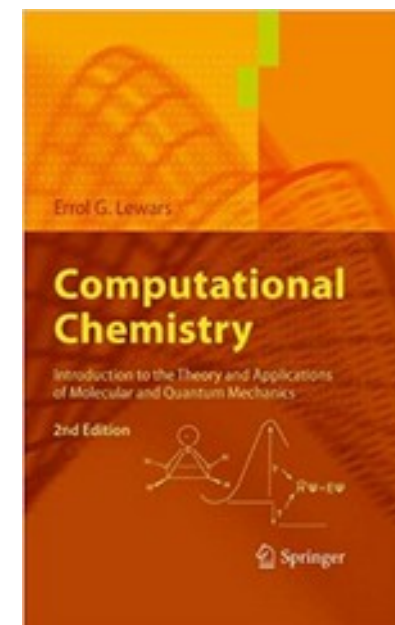https://www.etsf.eu/resources/software/codes
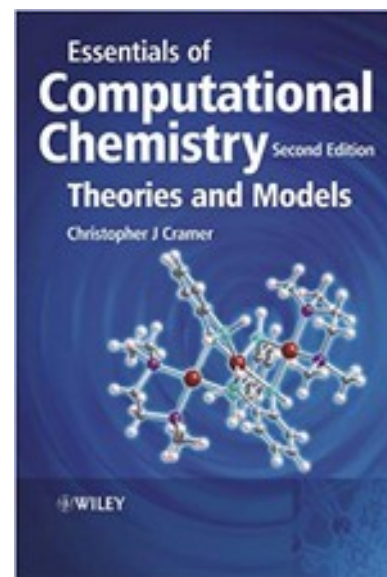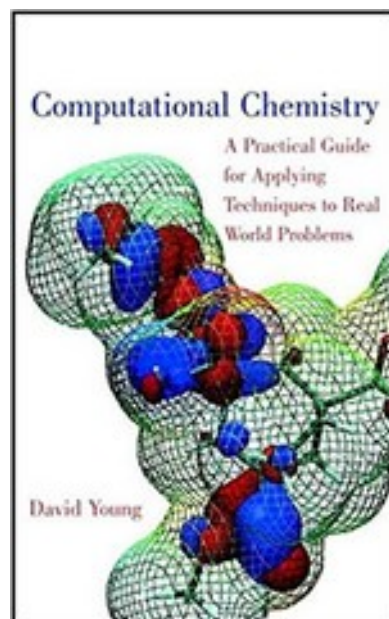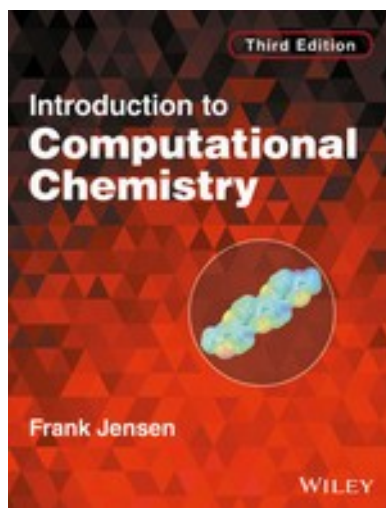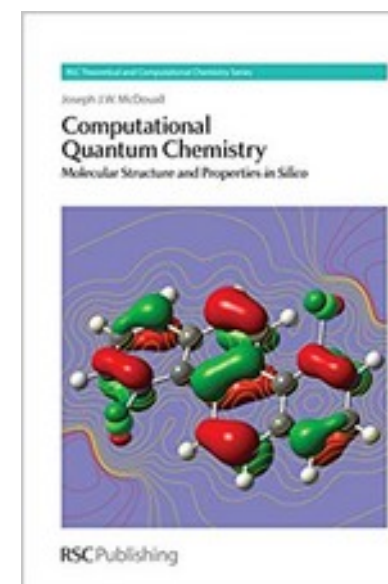https://sites.unimi.it/etsf/software/

(Needs updating!)

COMPUTATIONAL CHEMISTRY: The name of a course where experimentalists learn to use the tools developed and built by theoretical chemists

and probably many more!

Geometric and Electronic Structures of Nickel(II) Complexes of Redox Noninnocent Tetradentate Phenylenediamine Ligands

Jérémie Ciccione,[†] Nicolas Leconte,[*,†] Dominique Luneau,[‡] Christian Philouze,[†] and Fabrice Thomas[*,†]

[†]Chimie Inorganique Redox, Département de Chimie Moléculaire (UMR CNRS 5250), Université Grenoble Alpes, UMR-5250, 38041 Grenoble Cedex 9, France

[‡]Laboratoire des Multimatériaux et Interfaces (UMR CNRS 5615), Université Claude Bernard Lyon 1, 69622 Villeurbanne cedex, France

 Supporting Information

ABSTRACT: Five tetradentate ligands based on the N,N'-bis(2-amino-3,5-di-*tert*-butylphenyl)-*o*-phenylenediamine backbone were prepared, with different substituents at positions 4 and 5 (CH_3 (**3a**), p-CH_3O-C_6H_4 (**3b**), H (**3c**), Cl (**3d**), F (**3e**)). Their [reaction] with a nickel(II) salt in air affords the neutral species **4(a-e)**, which were isolated [as cr]ystals. **4(a-e)** feature two antiferromagnetically exchange-coupled diiminose-[miquinonat]e moieties, both located on peripheral rings, and a diamidobenzene bridging [...] of **4(a-e)** with 1 equiv of $AgSbF_6$ yields the cations **4(a-e)⁺**, which harbor a [diimin]osemiquinonate radical. Significant structural differences were observed within [... **4**]**b⁺** is mononuclear and contains a localized diiminosemiquinonate moiety. In [...]⁺ is a dimer wherein the diiminosemiquinonate radical is rather delocalized over [periph]eral [...]
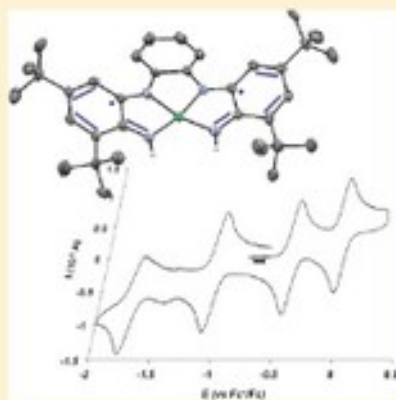
Fabrice THOMAS

Denis MAGERO

OBJECTIVES FOR THIS ULTRA-SHORT COURSE

- Teach some wave function theory because TD-DFT looks very much like wave function theory and one must not put the cart before the horse.
- Give the essentials of TD-DFT.
- Discuss problems of TD-DFT and helpful techniques to surmount them as time allows.
- Try to minimize the math and physics but *never* be afraid to include it when it appears helpful.

WARNING!
I shall probably repeat somethings you already know or from previous lectures. THIS IS INTENTIONAL.

BUT CHEMISTRY IS A PHYSICAL SCIENCE

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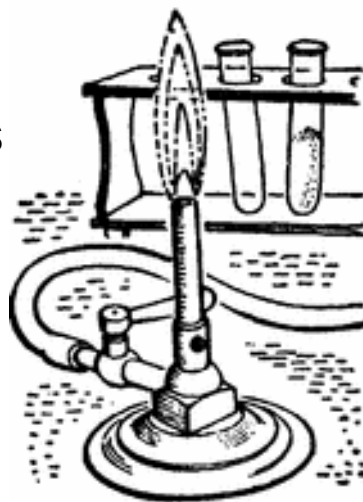
* "A chemist who is not at the same time a physicist is nothing at all."

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Let Us Be Quantum Mechanics and Look Under the Hood
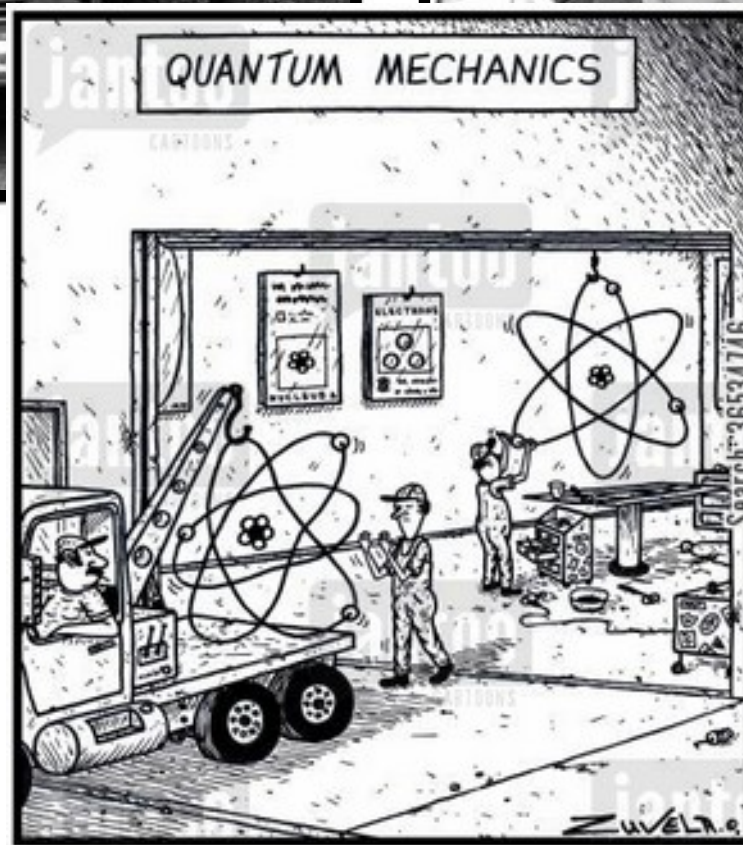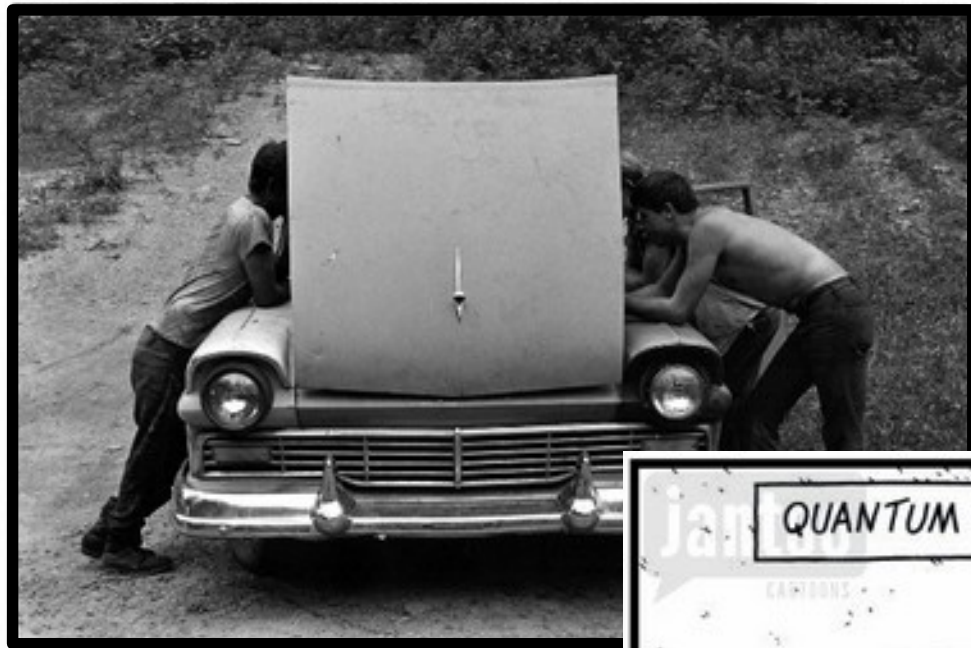
"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble."

Paul Adrien Maurice DIRAC
Proceedings of the Royal Society of London. Series A,
Containing Papers of a Mathematical and Physical Character,
Vol. 123, Page 714 (6 April 1929)

Let us concentrate on the electronic problem!

$$\hat{H}_e(\boldsymbol{r};\boldsymbol{R})\Psi_I^e(\boldsymbol{x};\boldsymbol{R})=E_I^e(\boldsymbol{R})\Psi_I^e(\boldsymbol{x};\boldsymbol{R}) \qquad \textbf{(1)}$$

$$\hat{H}\Psi_I(\boldsymbol{x})=E_I\Psi_I(\boldsymbol{x}) \qquad \textbf{(2)}$$

"The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation."

Paul Adrien Maurice DIRAC
Proceedings of the Royal Society of London. Series A,
Containing Papers of a Mathematical and Physical Character,
Vol. 123, Page 714 (6 April 1929)

714

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

§ 1. Introduction.

The general theory of quantum mechanics is now almost complete, the imperfections that still remain being in connection with the exact fitting in of the theory with relativity ideas. These give rise to difficulties only when high-speed particles are involved, and are therefore of no importance in the consideration of atomic and molecular structure and ordinary chemical reactions, in which it is, indeed, usually sufficiently accurate if one neglects relativity variation of mass with velocity and assumes only Coulomb forces between the various electrons and atomic nuclei. The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.

1926 : Schrödinger equation
1927 : Heitler-London VB theory

Dirac's 1929 paper is actually about the symmetric group applied to justify the Heitler-London VB theory for many-electron systems.

We want to solve

$$\hat{H}\Psi_I = E_I\Psi_I \,;\, E_0 \leq E_1 \leq E_2 \leq \cdots \qquad \textbf{(1)}$$

We will use the variational principle

$$E_0 \leq W[\Psi] = \frac{\langle \Psi_{trial} | \hat{H} | \Psi_{trial} \rangle}{\langle \Psi_{trial} | \Psi_{trial} \rangle} \qquad \textbf{(2)}$$

Valid for every test function Ψ_{test}, satisfying the same boundary conditions as Ψ_I.

* Quantum Chemistry 101 ?

Electrons are fermions:

$$\Psi(1,2,\cdots,j,\cdots,i,\cdots,N)=-\Psi(1,2,\cdots,i,\cdots,j,\cdots,N) \quad \text{(1)}$$

$$\text{where} \quad i=\vec{x}_i \quad \text{(2)}$$

The simplest function satisfying equation (1) is a
Slater determinant:
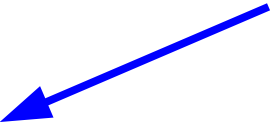
$$\Phi=\left|\psi_1,\psi_2,\cdots,\psi_N\right|=\frac{1}{\sqrt{N!}}\,det\begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix} \quad \text{(3)}$$
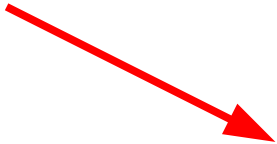
$$\text{where} \quad \langle\psi_i|\psi_j\rangle=\delta_{i,j} \quad \text{(4)}$$

$$E = \sum_i n_i \langle \psi_i | \hat{h} | \psi_i \rangle + E_{SCF} = \sum_i n_i \epsilon_i - E_{SCF} \quad \textbf{(1)}$$

$$E_{SCF} = E_H + E_x \quad \textbf{(2)}$$

$$E_H = \frac{1}{2} \int \int \frac{\rho(1)\rho(2)}{r_{12}} d1 \, d2 \quad \textbf{(3)}$$

$$E_x = -\frac{1}{2} \int \int \frac{|\gamma(1,2)|^2}{r_{12}} d1 \, d2 \quad \textbf{(4)}$$

The test function is a Slater determinant.

We minimize the variational energy subject to the condition that the orbitals are orthonormal. The result is

$$\hat{f}\,\psi_i = \epsilon_i\,\psi_i \qquad \text{(1)}$$

The Fock operator:

$$\hat{f} = \hat{h} + \hat{v}_{SCF} \qquad \text{(2)}$$

Self-consistent field (SCF) :

$$\hat{v}_{SCF} = v_H + \hat{\Sigma}_x = \hat{J} - \hat{K} \qquad \text{(3)}$$

Physics notation   Chemistry notation

SELF-CONSISTENT FIELD CYCLES

Guess the MOs → These are the "old" MOs

↓

Use the "old" MOs to calculate the "old" total energy.

↓

Use the "old" MOs to construct the "old" MO self-consistent field.

↓

Solve the orbital Schrödinger equation with the "old" self-consistent field to find "new" MOs.

↓

Use the "new" MOs to calculate "new" total energy.

→ Is the "new" total energy close enough to the "old" total energy?

no ↑

SCF iterations

The "new" MOs are now the new "old" Mos and the "new" total energy is now the new "old" total energy.

yes ↓

Converged

Wolfgang PAULI

John C. SLATER

Douglas Rayner HARTREE

Vladimir FOCK

Inga FISCHER-HJALMARS*

C.A. Coulson and Miss I. Fischer, "XXXIV. Notes on the molecular orbital treatment of the hydrogen molecule", *Phil. Mag.* **40**, 386 (1949).

* Lest we forget the heroines among our heroes!

In the HF approximation, in the absence of orbital relaxation:

Ionization potential (IP)

$$M + IP \rightarrow M^+ + e^- (v=0) \qquad \text{(1)}$$

$$-IP_i = E_N - E_{N-1}(i^{-1}) = \epsilon_i \qquad \text{(2)}$$

The occupied orbitals "see" N-1 electrons.

Electron affinity (EA)

$$M + e^- (v=0) \rightarrow M^- + EA \qquad \text{(3)}$$

$$-EA_a = E_{N+1}(a^{+1}) - E_N = \epsilon_a \qquad \text{(4)}$$

The unoccupied orbitals "see" N electrons.

Tjalling Charles
KOOPMANS

Analysis of results

Physical model ✓

Mathematical formalism ✓

DEVELOPMENT CYCLE

Numerical method

Calculations

TEST CYCLE

Computer Program

Applications

Choosing and collecting a set of comparison data

ENGINEERING CYCLE

Performance profiling

Cleaning, documentation, etc.

Optimisation
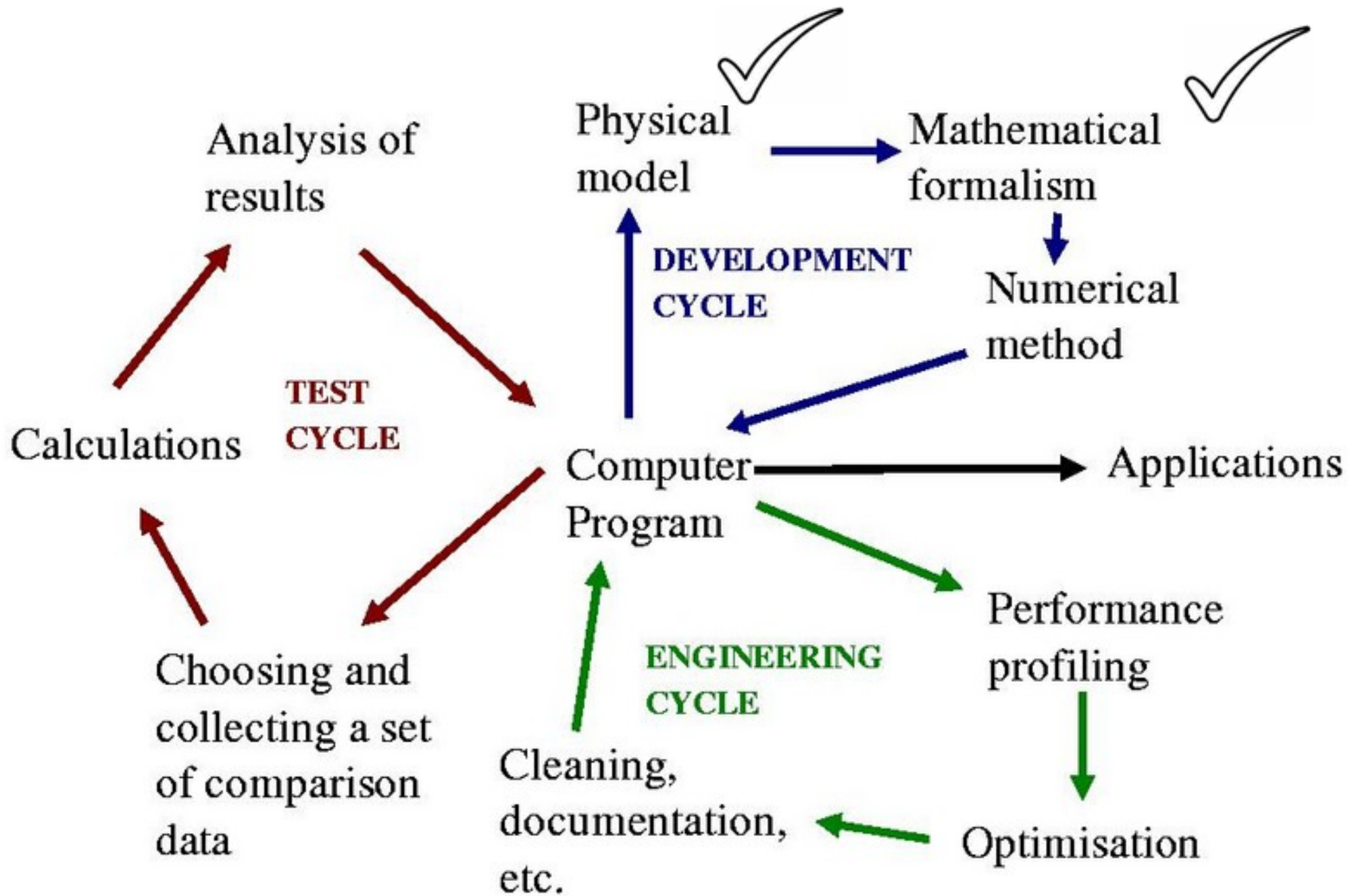
Want to solve the molecular orbital (MO) equation,

$$\hat{f}\,\psi_i = \epsilon_i\,\psi_i \qquad \textbf{(1)}$$

Expand each MO in a basis of atomic orbitals (AOs),

$$\psi_i = \sum_\nu \chi_\nu\, c_{\nu,i} \qquad \textbf{(2)}$$

Either (i) rigorously by finding the MO coefficients $c_{\nu,i}$ by doing a variational minimization of the energy or (ii) heuristically by inserting Eq. (2) in Eq. (1) and projecting:

$$\sum_\nu \hat{f}\,\chi_\nu\, c_{\nu,i} \approx \epsilon_i \sum_\nu \chi_\nu\, c_{\nu,i} \qquad \textbf{(3)}$$

$$\sum_\nu \langle \chi_\mu | \hat{f} | \chi_\nu \rangle\, c_{\nu,i} = \epsilon_i \sum_\nu \langle \chi_\mu | \chi_\nu \rangle\, c_{\nu,i} \qquad \textbf{(4a)} \qquad \text{N equations in N unknowns}$$

$$f\,\vec{c}_i = \epsilon_i\, s\,\vec{c}_i \qquad \textbf{(4b)}$$

Walter KOHN (9 March 1923 - 19 April 2016)

- Father of modern DFT
- Theoretical physicist and a great friend to chemists
- 1998 Nobel prize in Chemistry

Walter KOHN

Pierre C. HOHENBERG

<u>Theorem (HK1)</u>

For a nondegenerate ground state, the external potential is determined by the charge density up to an arbitrary additive constant (i.e., an energy zero.)

$$\rho(\vec{r}) \quad \xrightarrow{\text{1-1}} \quad v_{ext}(\vec{r}) + const. \qquad (1)$$

Fortunately DFT really rests on HK2 which requires only N-representability, not v-representability.

Walter KOHN

Pierre C. HOHENBERG

<u>Theorem (HK2)</u>

The ground state energy and density are determined the variational principle,

$$E = min_\rho \left(F[\rho] + \int v_{ext}(\vec{r}) \rho(\vec{r}) d\vec{r} \right) \qquad (1)$$

The functional F[ρ] is universal in the sense of being independent of v_{ext} .

Theorem (HK2)
The ground state energy and density are determined the variational principle,

$$E = min_\rho \left(F[\rho] + \int v_{ext}(\vec{r}) \rho(\vec{r}) d\vec{r} \right) \qquad (1)$$

The functional F[ρ] is universal in the sense of being independent of v_{ext} .

Proof (Levy-Lieb*)

$$F[\rho] = min_\Psi^{\Psi \to \rho} \langle \Psi | \hat{T} + V_{ee} | \Psi \rangle \qquad (2) \qquad \blacksquare$$

So the exact "unknown" functional is known, but just impossibly difficult to calculate !

* M. Levy, *Proc. Nat. Acad. Sci. USA* **76**, 6062 (1979).
  M. Levy, *Phys. Rev. A* **26**, 1200 (1982).

Mel LEVY

Elliott LIEB

Introducing *N* orthonormal Kohn-Sham orbitals allows us to give an exact description of an important part of the total energy.

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

where

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

Variational minimization subject to the orbital orthonormality contraint gives the Kohn-Sham equation.

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

where the exchange-correlation (xc) potential is

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

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 need ...

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

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

and sometimes also

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

WANTED

COMPUTATIONALLY CONVENIENT EFFECTIVE APPROXIMATIONS, TYPICALLY OF THE FORM

$$F[\rho] = \int f[\rho](\vec{r})\rho(\vec{r})\,d\vec{r}$$
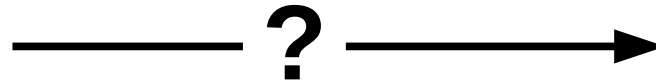
Density-
Functional
Theory

- Formally exact
- Computationally useless
- What DFAs try to approximate

Density-
Functional
Approximations

- Never exact
- But computationally useful
- Try to approximate the behavior of DFT

Red bubble t-shirts http://www.redbubble.com/

?

« *Le but n'est pas toujours placé pour être atteint, mais pour servir de point de mire ou de direction.* »*****
   --- Joseph Joubert (p. 221 of *Receuil des pensées de M. Joubert* by F.-R. De Chateaubriand, 1838)

* The target is not always meant to be hit, but rather to show where we should aim.

Taking Stock

- Up to this point, we have only discussed *pure* DFT (depends only on ρ .)
- Today pure DFT is pure spin-DFT (depends on ρ_α and on ρ_β .)
- Today we really see pure DFT (pure Kohn-Sham). Most people use some type of generalized Kohn-Sham (GKS) that includes an orbital dependence.
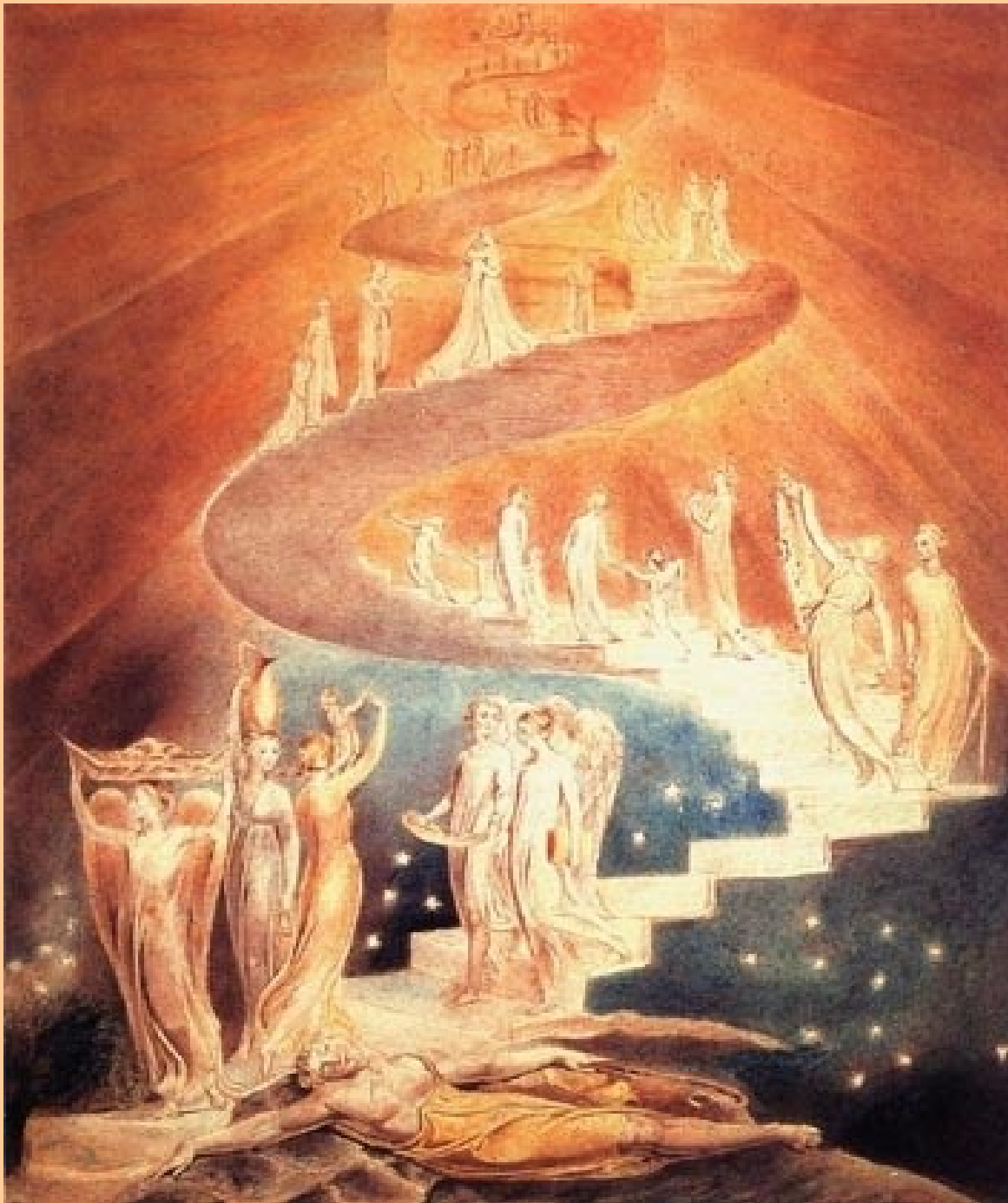
"Jacob's Ladder"
William Blake
watercolor
1799-1800

Jacob's Ladder
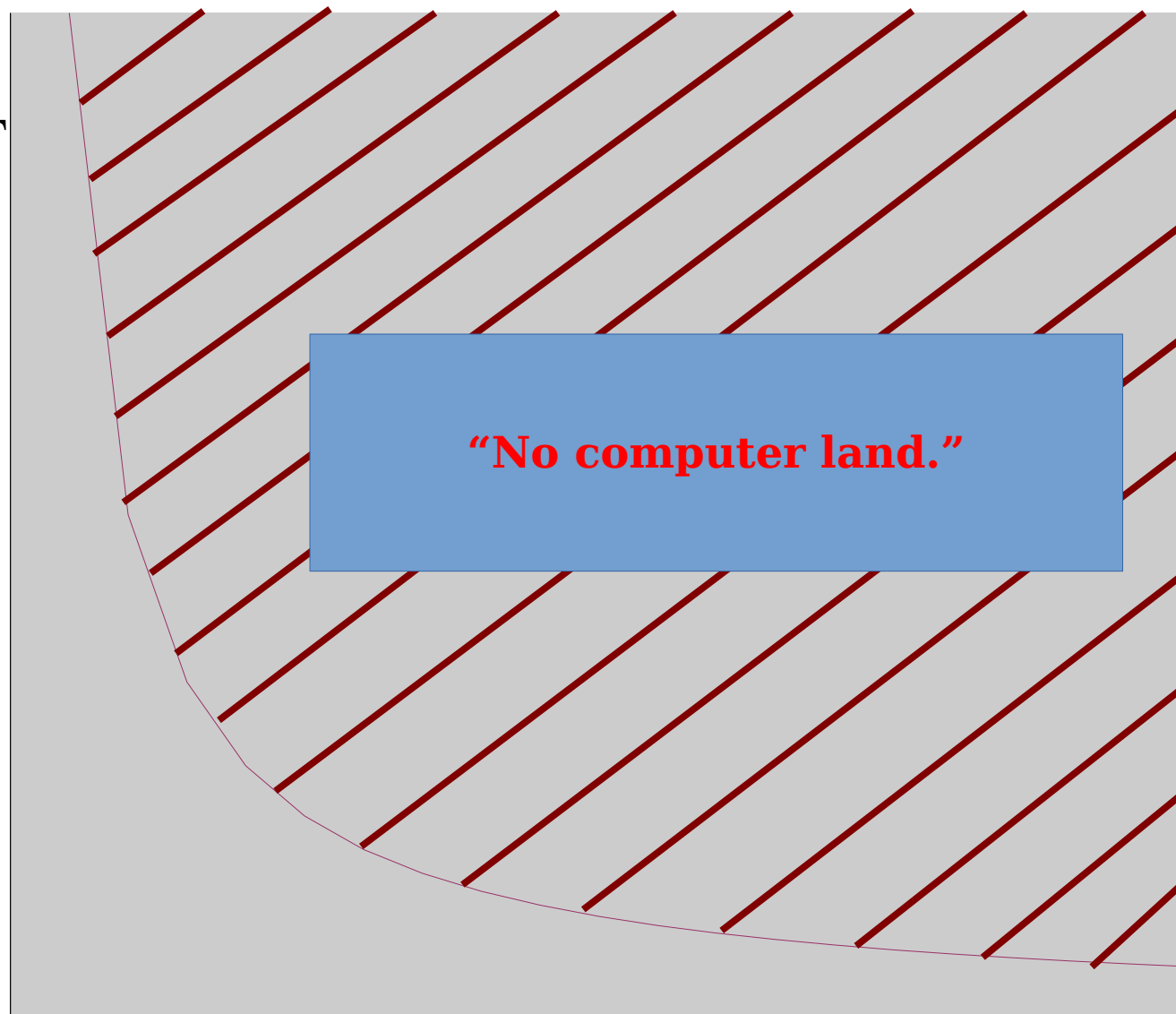
MBPT   *ab initio* DFT

$\hat{K}_x^{HF}$ hybrid/OEP

$\tau(\vec{r}) = \sum_i n_i |\nabla \psi_i|^2$ mGGA*

$$x(\vec{r}) = \frac{|\nabla \rho(\vec{r})|}{\rho(\vec{r})^{4/3}} \quad \text{GGA}$$

pure DFT

$\rho(\vec{r})$ LDA

HARTREE WORLD

* or include $\nabla^2 \rho$

"No computer land."

Size of the molecule →

** 1 kcal/mol or better precision

Range-Separated Hybrids (RSH*)

The favorite type of GKS is less
And less B3LYP and more and
More a RSH.

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

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

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

The RSH idea came originally from Andreas Savin (Université Pierre et Marie Curie, Paris.)

TD-DFT applications:
 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).

* because Nature is not always short-sighted.

Semi-empirical (molecular-modeling-type) formula designed to interpolate between two physical limits: "*the asymptotic part that is described very accurately by [TD-DFT] (for atomic or molecular fragments) and the short-range regime for which standard [DFAs] often yield a rather accurate description of the exchange-correlation problem*".

$$E_{\text{disp}} = \sum_{A,B} \sum_{n=6,8,10,\dots} s_n \frac{C_n^{A,B}}{R_{A,B}^n \left[1 + 6\left(\dfrac{R_{AB}}{s_{r,n} R_0^{A,B}}\right)^{-\alpha_n}\right]}$$

$$- \sum_{A,B,C} \frac{\sqrt{C_6^{AB} C_6^{AC} C_6^{BC}} \left(3\cos\theta_a \cos\theta_b \cos\theta_c + 1\right)}{\left(R_{AB} R_{BC} R_{CA}\right)^3 \left[1 + 6\left(\dfrac{\bar{R}_{ABC}}{s_{r,3} R_0^{A,B}}\right)^{-\alpha_3}\right]}$$

* S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *J. Chem. Phys.* **132**, 154104 (2010). "A consistent and accurate *ab initio* parameterization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu"

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All of the orthonormal orbitals, taken together, form a complete (infinite) basis set that can be used to expand any one-electron wave function.

Similarly, all of the (infinitely many) *N*-electron Slater determinants, taken together, Constitute a complete basis set that may be used to expand any *N*-electron wave function.

This type of N-electron expansion is called "*complete CI*" and it is just a nice dream!

$$\Psi = C_0 \Phi + \sum_{i,a} C_{ai} \Phi_i^a + \sum_{i,j,a,b} C_{abji} \Phi_{ij}^{ab} + \cdots \qquad \textbf{(1)}$$

An expansion in all of possible determinants made from a finite orbital basis is called "*full CI*" and is only possible for small basis sets (and hence for small molecules).

For normal sized orbital basis sets, we can only do *"truncated CI"*.

Ψ_{test} = truncated CI **(1)**

Using this trial function in a variation calculation is a *linear variation* and special theorems apply.

$$\boldsymbol{H}\, \vec{C}_I = E_I \vec{C}_I \quad \textbf{(2)}$$

$$H = \begin{vmatrix} H_{0,0} & \vec{H}_{0,1}^{+} & \cdots \\ \vec{H}_{0,1} & \boldsymbol{H}_{1,1} & \cdots \\ \vdots & \vdots & \ddots \end{vmatrix} \quad \textbf{(3a)} \qquad\qquad \vec{C}_I = \begin{pmatrix} C_0 \\ \vec{C}_2 \\ \vdots \end{pmatrix} \quad \textbf{(4a)}$$

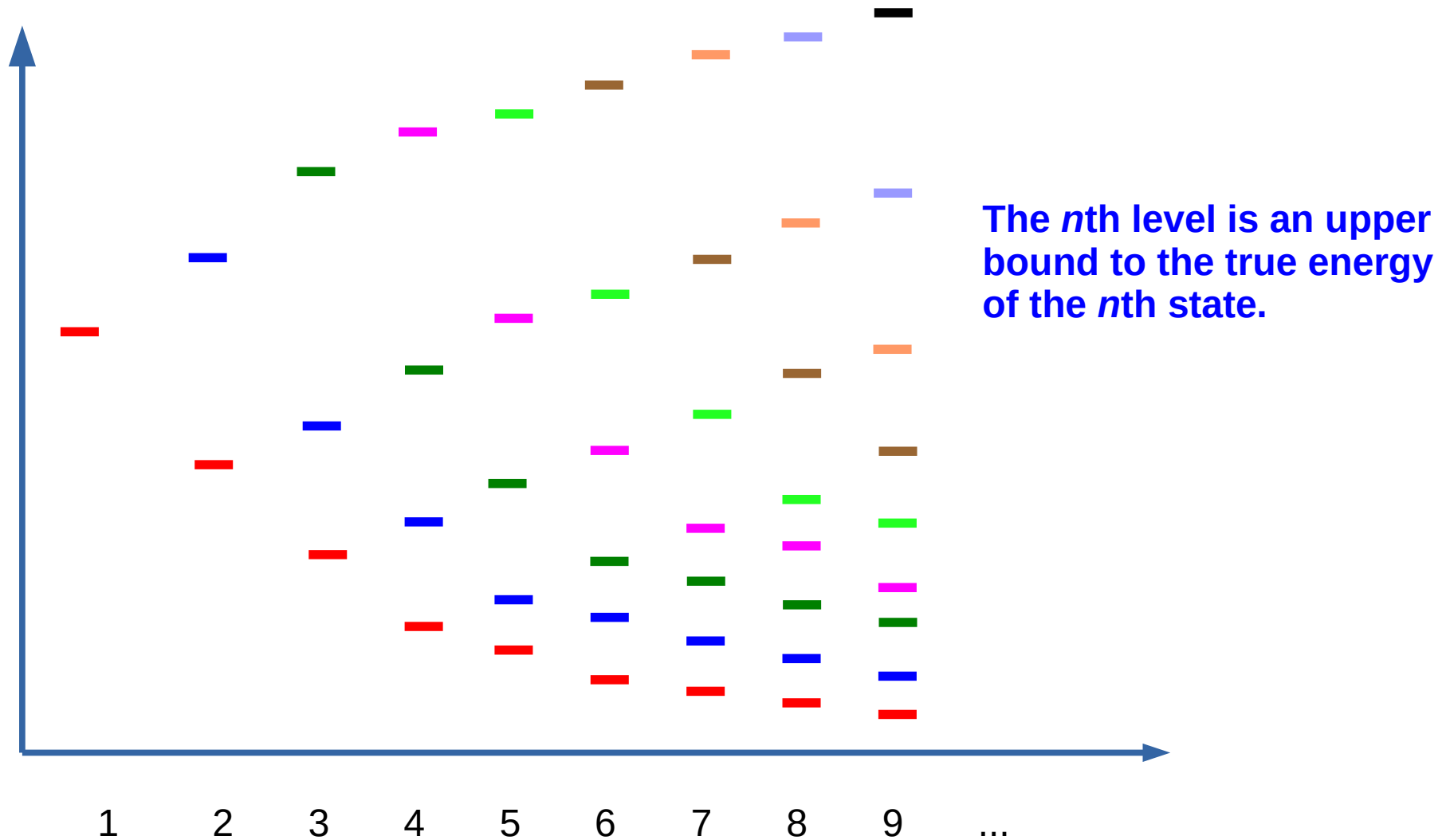$$H_{0,0} = \langle \Phi | \hat{H} | \Phi \rangle = E_{\text{HF}} \quad \textbf{(3b)} \qquad\qquad \left(\vec{C}_1 \right)_{ai} = C_{ai} \quad \textbf{(4b)}$$

$$\left(\vec{H}_{0,1} \right)_{ai} = \langle \Phi_i^a | \hat{H} | \Phi \rangle = f_{a,i} = 0 \quad \textbf{(3c)} \qquad \text{(Brillouin's theorem)}$$

$$\left(\boldsymbol{H}_{1,1} \right)_{ai,bj} = \delta_{i,j}\, \delta_{a,b}\, E_{\text{HF}} + A_{ai,bj} \quad \textbf{(3d)}$$

Only for *linear* variations (such as CI):

The *n*th level is an upper bound to the true energy of the *n*th state.

$$\begin{bmatrix} H_{0,0} & \vec{H}_{0,1}^{+} \\ \vec{H}_{0,1} & \boldsymbol{H}_{1,1} \end{bmatrix} \begin{pmatrix} C_0 \\ \vec{C}_1 \end{pmatrix} = E \begin{pmatrix} C_0 \\ \vec{C}_1 \end{pmatrix} \qquad \text{(1)}$$

$$\begin{bmatrix} E_{\mathrm{HF}} & \vec{0}^{+} \\ \vec{0} & \boldsymbol{A} + E_{\mathrm{HF}} \end{bmatrix} \begin{pmatrix} C_0 \\ \vec{C}_1 \end{pmatrix} = E \begin{pmatrix} C_0 \\ \vec{C}_1 \end{pmatrix} \qquad \text{(2)}$$

$$\boldsymbol{A}\,\vec{C}_1 = \left(E - E_{HF} \right) \vec{C}_1 = \omega\, \vec{C}_1 \qquad \text{(3)}$$

How do we solve such a big eigenvalue equation?

Block Davidson Diagonalisation

Ernest R. Davidson, J. Comp. Phys. **17**, 87 (1975).
"The iterative calculation of a few of the lowest eigenvalues and corresponding eigenvectors of large real-symmetric matrices"

Ernest R. Davidson, Comp. Phys. Comm. **53**, 49 (1989).
"Super-matrix methods"

C.W. Murray, S.C. Racine, and E.R. Davidson,
J. Comp. Phys. **103**, 382 (1992).
"Improved algorithms for the lowest few eigenvalues and associated eigenvectors of large matrices"

Algorithm

Want to solve $\quad A\vec{x}=a\vec{x}$

1) guess $\quad \vec{x}_0$

2) calculate correction $\quad \delta\vec{x}=(a-D)^{-1}(A-a)\vec{x}_0$

3) if $\quad |\delta\vec{x}|<\epsilon$ then we are converged

4) orthonormalize with respect to $\quad \vec{x}_0$ to obtain $\vec{x}_1$

5) set up projected (2 x 2) matrix $\quad \tilde{A}=\begin{bmatrix} \vec{x}_0^+ A\vec{x}_0 & \vec{x}_0^+ A\vec{x}_1 \\ \vec{x}_1^+ A\vec{x}_0 & \vec{x}_1^+ A\vec{x}_1 \end{bmatrix}$

6) solve $\quad \tilde{A}\vec{c}=\tilde{a}\vec{c}$

7) update $\quad \vec{x}_0=c_0\vec{x}_0+c_1\vec{x}_1$

8) repeat until converged
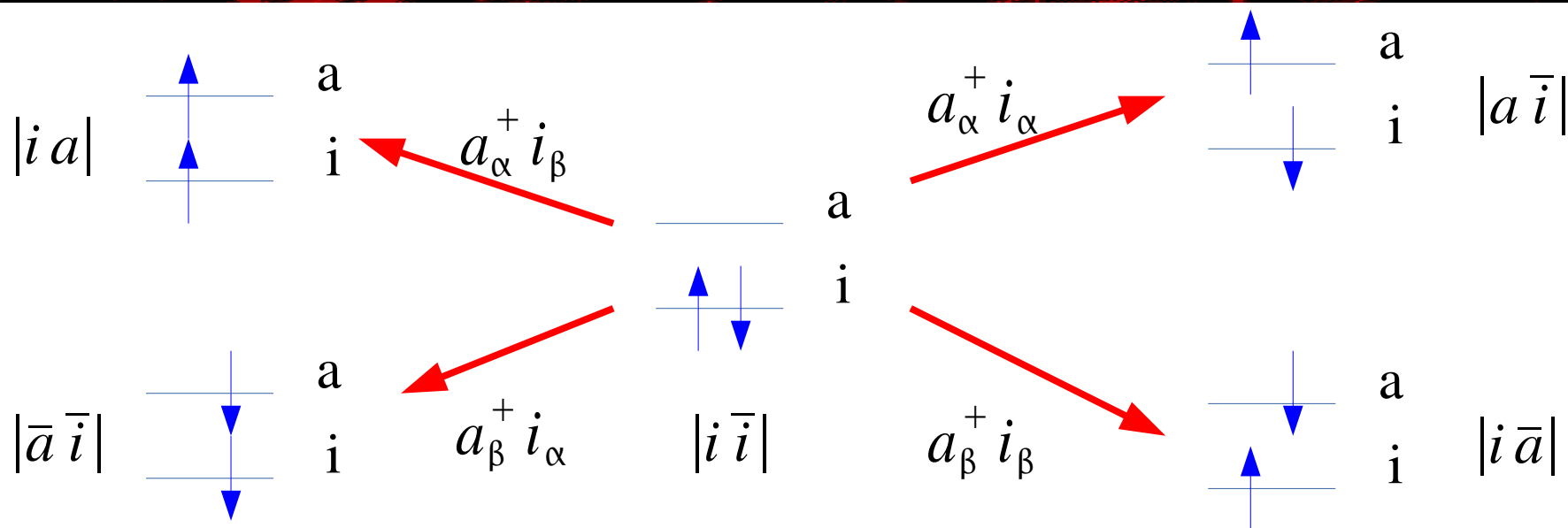
Block Davidson Diagonalisation : Pyridine Results

Vertical Excitation Energies in eV (oscillator strength)

State	Full diagonalization[a]	Davidson (40 states)[b]	Davidson (30 states)[b]	Davidson (20 states)[b,d]	Davidson (10 states)[b]	Davidson (10 states)[c]
45	9.983579					
44	9.982837					
13	8.261103	8.261105	8.261103	8.261104		
12	8.237879	8.237889	8.237879	8.237880		
11	8.101488	8.101494	8.101489	8.101492		
10	7.514902	7.514903	7.514904	7.514908	7.514908	
9	7.336417 (0.300983)	7.336417 (0.300977)	7.336415 (0.300978)	7.336417 (0.300879)	7.336418 (0.300999)	
8	7.317097	7.317098	7.317097	7.317100	7.317099	
7	7.258573	7.258573	7.258573	7.258573	7.258575	
6	7.234619	7.234620	7.234621	7.234619	7.234623	
5	7.221868	7.221869	7.221870	7.221875	7.221871	7.231149
4	7.023707	7.023707	7.023707	7.023707	7.023709	7.044960
3	6.688117 (0.059847)	6.688117 (0.059828)	6.688117 (0.059847)	6.688124 (0.059683)	6.688117 (0.059882)	6.694428 (0.058550)
2	6.596621	6.596621	6.596621	6.596621	6.596626	6.606604
1	4.403893	4.403898	4.403895	4.403895	4.403898	4.574847
No. iterations		20	13	13	11	8
Memory	38MB	43MB	43MB	6MB	43MB	8MB
user time	38.24	14.52	14.49	13.01	7.77	8.15
system time	999.63	196.96	157.07	142.28	129.56	113.39

Exact up to numerical convergence.
***Not* an approximation!**

TWO-ORBITAL TWO-ELECTRON MODEL (TOTEM)*

$|i\,a|$ a, i

$a_\alpha^+ i_\beta$

$a_\alpha^+ i_\alpha$ a, i $|a\,\bar{i}|$

a

i

$|\bar{a}\,\bar{i}|$ a, i

$a_\beta^+ i_\alpha$ $|i\,\bar{i}|$ $a_\beta^+ i_\beta$

a, i $|i\,\bar{a}|$

	Ψ_{S,M_S}
Singlet	$\Psi_{0,0} = \dfrac{1}{\sqrt{2}}\left(|a\,\bar{i}| + |i\,\bar{a}| \right)$
Triplets	$\Psi_{1,0} = |i\,a|$ $\Psi_{1,0} = \dfrac{1}{\sqrt{2}}\left(|a\,\bar{i}| - |i\,\bar{a}| \right)$ $\Psi_{1,-1} = |\bar{a}\,\bar{i}|$

* two-orbital two-electron model.

$$\left[\begin{matrix} \epsilon_a - \epsilon_i + [ai|ia] - [aa|ii] & [ai|ia] \\ [ai|ia] & \epsilon_a - \epsilon_i + [ai|ia] - [aa|ii] \end{matrix}\right]\left(\begin{matrix} X_{ai\alpha} \\ X_{ai\beta} \end{matrix}\right) = \omega \left(\begin{matrix} X_{ai\alpha} \\ X_{ai\beta} \end{matrix}\right)$$

Singlet type excitation

$$\left(\begin{matrix} X_{ai\alpha} \\ X_{ai\beta} \end{matrix}\right) = \left(\begin{matrix} 1 \\ 1 \end{matrix}\right) \quad \Rightarrow \quad \omega = \epsilon_a - \epsilon_i + 2[ai|ia] - [aa|ii]$$

Triplet type excitation

$$\left(\begin{matrix} X_{ai\alpha} \\ X_{ai\beta} \end{matrix}\right) = \left(\begin{matrix} 1 \\ -1 \end{matrix}\right) \quad \Rightarrow \quad \omega = \epsilon_a - \epsilon_i - [aa|ii]$$

THE ZIEGLER-RAUK-BAERENDS (DAUL) MULTIPLET SUM METHOD*

$$E_S = \langle \Psi_{0,0} | \hat{H} | \Psi_{0,0} \rangle = \langle a\,\bar{i} | \hat{H} | a\,\bar{i} \rangle + \langle a\,\bar{i} | \hat{H} | i\,\bar{a} \rangle$$

$$E_T = \langle \Psi_{1,0} | \hat{H} | \Psi_{1,0} \rangle = \langle a\,\bar{i} | \hat{H} | a\,\bar{i} \rangle - \langle a\,\bar{i} | \hat{H} | i\,\bar{a} \rangle$$

	Ψ_{S,M_S}
Singlet	$\Psi_{0,0} = \dfrac{1}{\sqrt{2}}\left(|a\,\bar{i}| + |i\,\bar{a}| \right)$
Triplets	$\Psi_{1,0} = |i\,a|$
	$\Psi_{1,0} = \dfrac{1}{\sqrt{2}}\left(|a\,\bar{i}| - |i\,\bar{a}| \right)$
	$\Psi_{1,-1} = |\bar{a}\,\bar{i}|$

$\Rightarrow$

$$E_S + E_T = 2\langle a\,\bar{i} | \hat{H} | a\,\bar{i} \rangle$$

$\Rightarrow$

$$\boxed{E_S = 2\langle a\,\bar{i} | \hat{H} | a\,\bar{i} \rangle - \langle ia | \hat{H} | ia \rangle}$$

because

$$\boxed{E_T = \langle ia | \hat{H} | ia \rangle}$$

---

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

A consequence of Koopmans' theorem is that the TOTEM formulae are almost never accurate enough to be useful.

HF

DFT

OUTLINE

I. MOTIVATION
II. GROUND-STATE THEORY
III. QUANTUM CHEMISTRY FOR EXCITED STATES
IV. TD-DFT
V. HOW WELL DOES IT WORK IN PRACTICE?
VI. CONCLUSION

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

Given a system, initially in its ground state, exposed to a time-dependent perturbation:

1st Theorem (RG1): $v_{ext}(rt)$ is determined by $\rho(rt)$ up to an arbitrary additive function of time.

Corollary:

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

(RG1 has only been proven for functions whose time dependence can be expanded in a Taylor series.)

2nd Theorem (RG2): The time-dependent charge-density is a stationary point of the Frenkel-Dirac action

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

[RG2 suffers from a "causality paradox". But this difficulty now seems to have been solved by G. Vignale, *Phys. Rev. A* **77**, 062511 (2008). "Real-time solution of the causality paradox of time-dependent density-functional theory"]

TIME-DEPENDENT KOHN-SHAM EQUATION

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

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

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

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

Remark: If the initial state is not the ground state, then

$$v_{xc}(\boldsymbol{r},t)=v_{xc}[\rho,\Psi_0,\Phi_0](\boldsymbol{r},t) \quad \text{(4)}$$

TD-DFT ADIABATIC APPROXIMATION (AA)

Assume that the exchange-correlation (xc) potential responds instantaneously and without memory to any change in the time-dependent density.

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

$$\rho_t(\boldsymbol{r}) = \rho(\boldsymbol{r}\,t)$$

This defines "conventional TD-DFT".

ELECTRONIC POLARIZATION INDUCED BY THE APPLICATION OF A TIME-DEPENDENT ELECTRIC FIELD
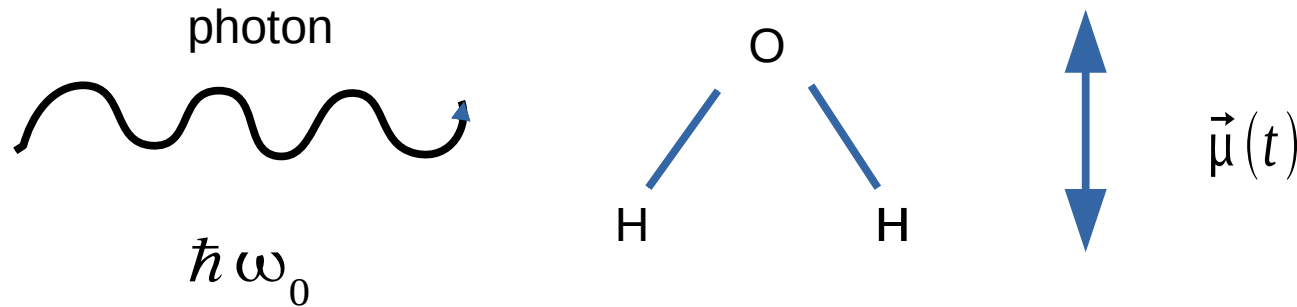
Classical model of a photon

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

$$v(\vec{r}\, t) = e\, \vec{\varepsilon}(t) \cdot \vec{r} \qquad \text{(2)}$$

Induced dipole moment

$$\delta \vec{\mu}(t) = -e \left(<\Psi_0|\vec{r}|\delta\Psi_0(t)> + <\delta\Psi_0(t)|\vec{r}|\Psi_0> \right) \qquad \text{(3)}$$

The linear response for a property a $\qquad \delta <\hat{a}>(t)$

to the perturbation b $\qquad \hat{b}(t)=\hat{b}\cos\omega_0 t$ **(1)**

$$\hat{H}\Psi_I = E_I\Psi_I \qquad \textbf{(2)}$$

$$[\hat{H}+\hat{b}(t)]\Psi_0(t)=i\hbar\frac{\partial}{\partial t}\Psi_0(t) \qquad \textbf{(3)}$$

$$\Psi_0(t)=[\Psi_0+\delta\Psi_0(t)+\ldots]e^{-iE_0 t/\hbar} \qquad \textbf{(4)}$$

which allows us to deduce the 1st order equation

$$\hat{b}(t)\Psi_0=(i\hbar\frac{\partial}{\partial t}-\hat{H}+E_0)\delta\Psi_0(t) \qquad \textbf{(5)}$$

Fourier transforms

$$f(\omega) = \int_{-\infty}^{+\infty} e^{i\omega t} f(t)\, dt \qquad \textbf{(1)}$$

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{-i\omega t} f(\omega)\, d\omega \qquad \textbf{(2)}$$

Joseph Fourier
Prefect of the Isère
(Grenoble)
1802-1815

Transform the 1$^{\text{st}}$ order equation

$$\hat{b}(t)\Psi_0 = \left(i\hbar\frac{\partial}{\partial t} - \hat{H} + E_0\right)\delta\Psi_0(t) \qquad \textbf{(3)}$$

$$\hat{b}(\omega)\Psi_0 = \left(\hbar\omega - \hat{H} + E_0\right)\delta\Psi_0(\omega) \qquad \textbf{(4)}$$

Solve by Rayleigh-Schrödinger perturbation theory!

$$\delta\Psi_0(\omega) = \sum_{I \neq 0} \Psi_I \frac{<\Psi_I|\hat{b}(\omega)|\Psi_0>}{\omega - \omega_I} \qquad \textbf{(5)} \quad \text{where} \quad \hbar\omega_I = E_I - E_0 \;(\hbar = 1) \quad \textbf{(6)}$$

TIME REPRESENTATION

Since

$$\int_{-\infty}^{+\infty} e^{i\omega t} \cos \omega_0 t \, dt = \pi \left[\delta(\omega + \omega_0) + \delta(\omega - \omega_0) \right] \qquad \textbf{(1)}$$

$$\int_{-\infty}^{+\infty} e^{i\omega t} \sin \omega_0 t \, dt = \frac{\pi}{i} \left[\delta(\omega + \omega_0) - \delta(\omega + \omega_0) \right] \qquad \textbf{(2)}$$

we find

$$\delta \Psi_0(t) = \left(\sum_{I \neq 0} \Psi_I \frac{\omega_I < \Psi_I | \hat{b} | \Psi_0 >}{\omega_0^2 - \omega_I^2} \right) \cos \omega_0 t$$

$$\qquad \qquad \qquad \qquad \qquad \qquad \textbf{(3)}$$

$$- i \left(\sum_{I \neq 0} \Psi_I \frac{\omega_0 < \Psi_I | \hat{b} | \Psi_0 >}{\omega_0^2 - \omega_I^2} \right) \sin \omega_0 t$$

RESPONSE OF AN ARBITRARY PROPERTY

$$\delta <\hat{a}>(t) = <\Psi_0|\hat{a}|\delta\Psi_0(t)> + <\delta\Psi_0(t)|\hat{a}|\Psi_0>$$

(1)

Electronic polarizabilities, NMR chemical shifts

$$\delta <\hat{a}>(t) = \left(\sum_{I\neq 0}\frac{2\omega_I \Re e <\Psi_0|\hat{a}|\Psi_I><\Psi_I|\hat{b}|\Psi_0>}{\omega_0^2 - \omega_I^2}\right)\cos\omega_0 t$$

$$+\sum_{I\neq 0}\left(\frac{2\omega_0 \Im m <\Psi_0|\hat{a}|\Psi_I><\Psi_I|\hat{b}|\Psi_0>}{\omega_I^2 - \omega_0^2}\right)\sin\omega_0 t$$

(2)

Circular dichroïsme

$$\mu_i(t) = \mu_i + \sum_j \alpha_{i,j}(\omega)\, \varepsilon_j \cos \omega t + \cdots \qquad \text{(1)}$$

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

Sum-over-states (SOS*)

$$\alpha(\omega) = \sum_{I \neq 0} \frac{f_I}{\omega_I^2 - \omega^2} \qquad \text{(3)}$$

f_I

ω_I
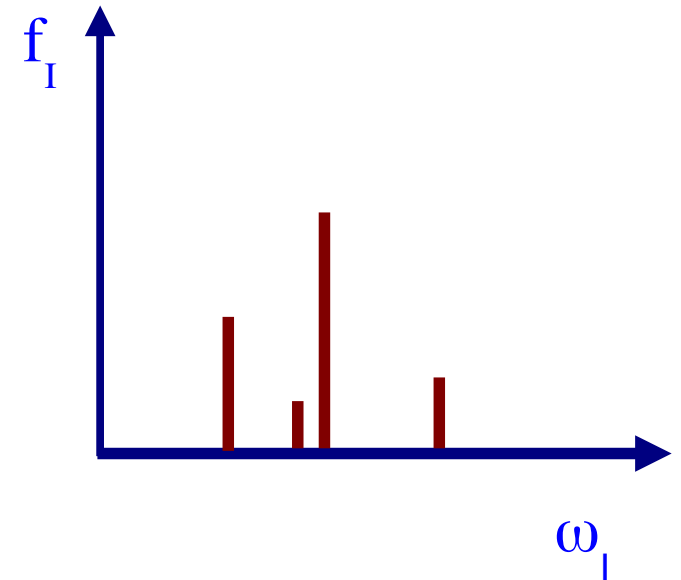
$$f_I = \frac{2}{3}\omega_I \left(|<\Psi_0|x|\Psi_I>|^2 + |<\Psi_0|y|\Psi_I>|^2 + |<\Psi_0|z|\Psi_I>|^2 \right) \qquad \text{(4)}$$

The idea here is to present a method which is relatively "easy" and "elegant" to understand but which gives us the same equations as response theory.

The EOM

$$\breve{H}\,\hat{O}^+ = \left[\hat{H},\hat{O}^+\right] = \omega\,\hat{O}^+ \qquad \text{(1)}$$

has excitation-type solutions

$$\left[\hat{H},|I><0|\right] = (E_I - E_0)\,|I><0| \qquad \text{(2)}$$

and de-excitation-type solutions

$$\left[\hat{H},|0><I|\right] = (E_0 - E_I)\,|0><I| \qquad \text{(3)}$$

(it also has other solutions, but these are all we care about here!)

Let us seek a solution of the form

$$\hat{O}^+ = \sum_{ai} a^+ i\, X_{ai} + \sum_{ai} i^+ a\, Y_{ai} \qquad \text{(4)}$$

$$\breve{H}\hat{O}^+ = [\hat{H}, \hat{O}^+] = \omega\hat{O}^+ \qquad \text{(1)}$$

$$\hat{O}^+ = \sum_{ai} a^+ i \, X_{ai} + \sum_{ai} i^+ a \, Y_{ai} \qquad \text{(2)}$$

Inserting (2) into (1) and using the "metric"

$$(\hat{A}|\hat{B}) = \langle \Phi | [\hat{A}^+, \hat{B}] | \Phi \rangle \qquad \text{(3)}$$

gives us

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} \qquad \text{(4)}$$

with

$$A_{ai,bj} = \delta_{i,j}\delta_{a,b}(\epsilon_a - \epsilon_i) + (ai|f_H|jb) - (ab|f_H|ji) \qquad \text{(5)}$$

$$B_{ai,bj} = (ib|f_H|ja) - (jb|f_H|ia) \qquad \text{(6)}$$

https://arxiv.org/pdf/1008.1478

22   Mark E. Casida and Miquel Huix-Rotllant

(a)

(b)

(c)
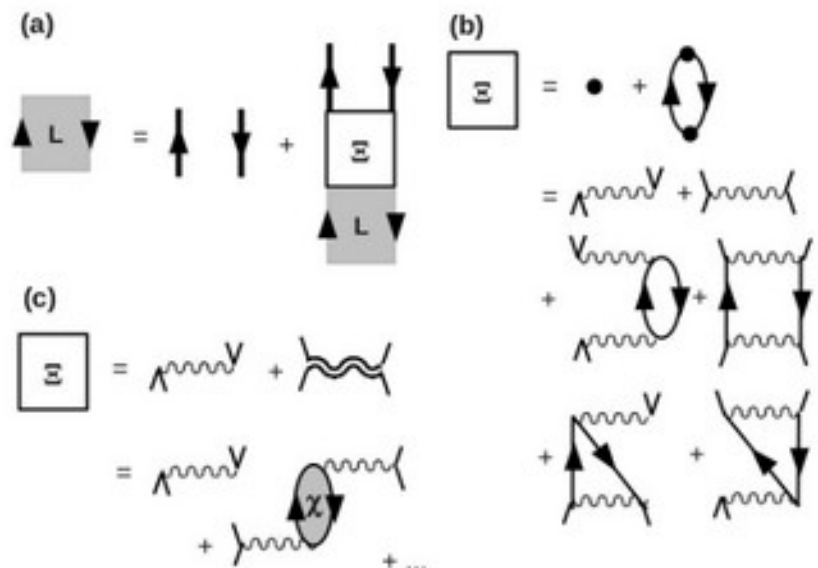
Fig. 10 Time-unordered (Feynman and Abrikosov) ph-propagator diagrams: (a) BSE, (b) second-order self-energy quantum chemistry approximation, (c) *GW* self-energy solid-state physics approximation. Note in part (c) that the solid-state physics literature will often turn the v and w wiggly lines at right angles to each other to indicate the same thing that we have indicated here by adding tab lines.

$$A_{ia,jb} = i \quad \square \quad a$$

$$+ \quad j \;\; b \quad i \;\; a$$

$$+ \quad j \;\; b \quad i \;\; a$$

$$A_{ai,bj} = \delta_{i,j}\,\delta_{a,b}\left(\epsilon_a - \epsilon_i\right) + \left(ai|f_H|jb\right) - \left(ab|f_H|ji\right)$$
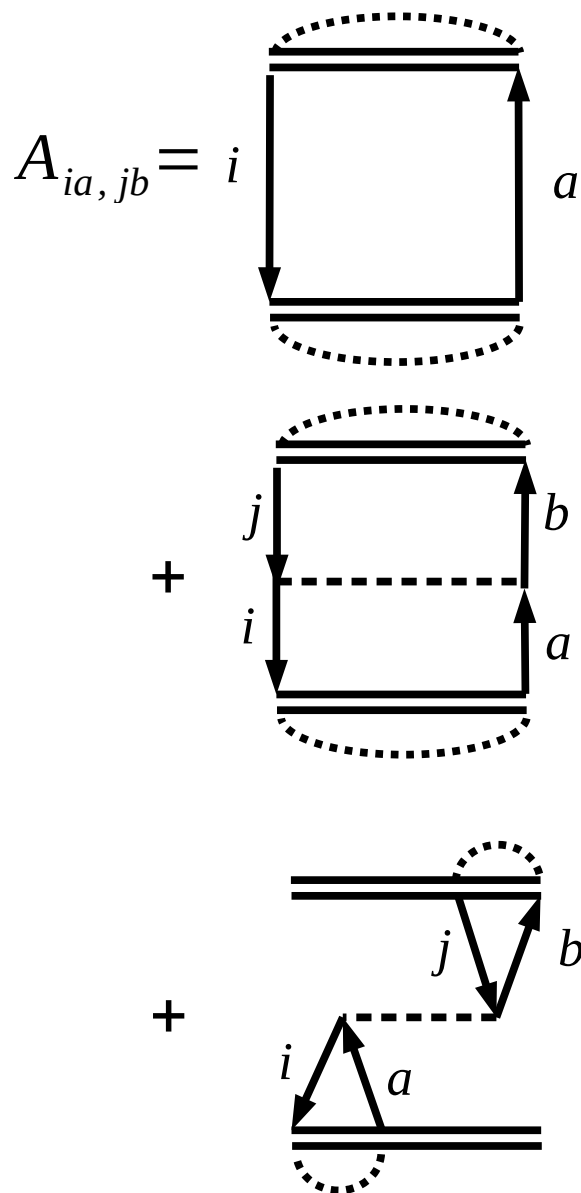
Mark E. Casida in *Recent Advances in Density Functional Methods, Part I,*
edited by D.P. Chong (Singapore, World Scientific, 1995), p. 155.
"Time-dependent density-functional response theory for molecules"

"RPA" equation

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

or

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

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

Coupling matrix

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

Remark: The general formulation does not make the adiabatic approximation.

excitation

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} \qquad \textbf{(1)}$$

corresponding de-excitation

$$\begin{bmatrix} A & B \\ B^* & A^* \end{bmatrix} \begin{pmatrix} \vec{Y}^* \\ \vec{X}^* \end{pmatrix} = -\omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{pmatrix} \vec{Y}^* \\ \vec{X}^* \end{pmatrix} \qquad \textbf{(2)}$$

$$\begin{bmatrix} A & B=0 \\ B^*=0 & A^* \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} \qquad (1)$$

$$A\,\vec{X} = \omega\,\vec{X} \qquad (2)$$

This looks like CIS !!
(and is actually the
same as CIS if we
start from TD-HF)

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The Dynamic Polarizability of the Nitrogen Molecule

C. Jamorski, M.E. Casida, and D.R. Salahub, J. Chem. Phys. **104**, 5134 (1996).

DYNAMIC MEAN POLARIZABILITY
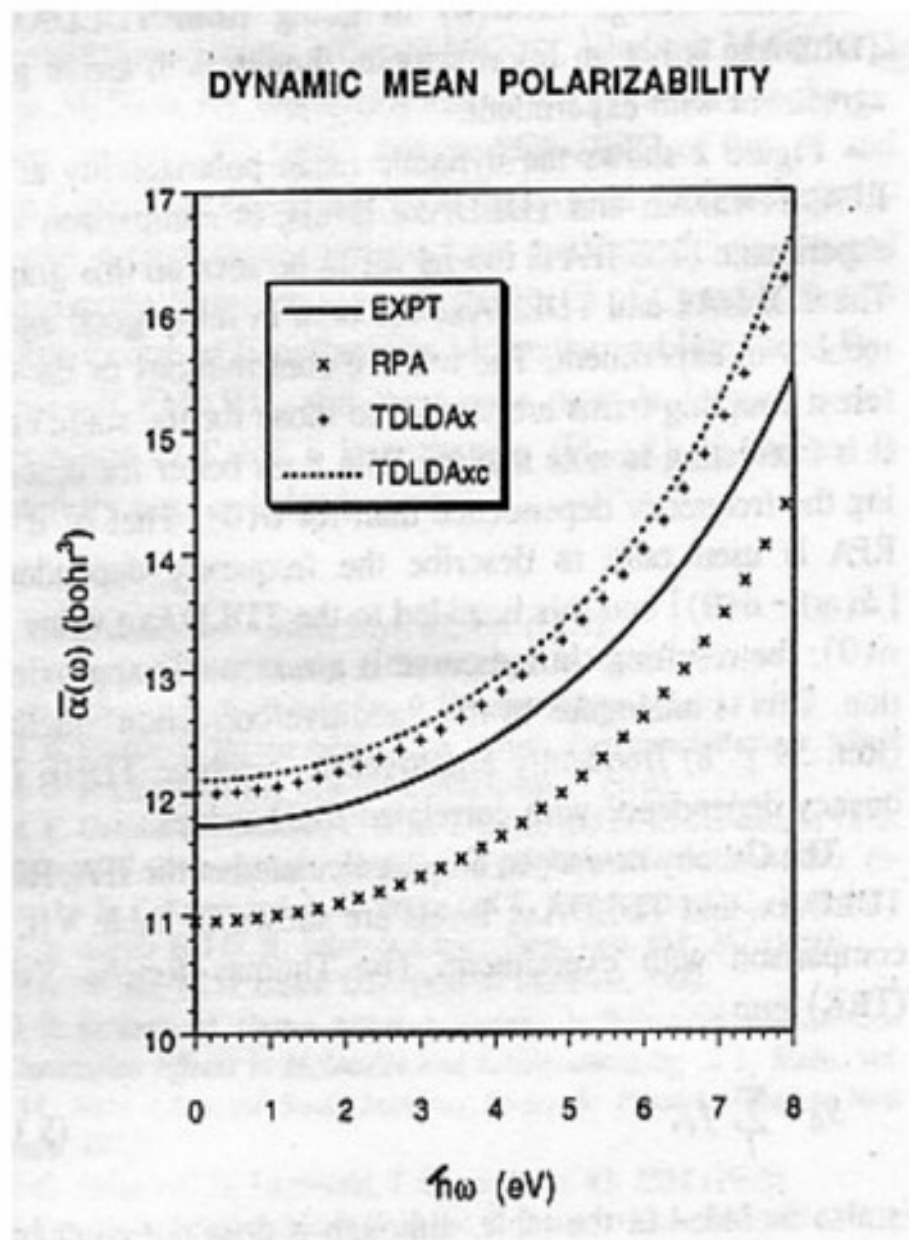
N₂ π -> π * Excitations

C. Jamorski, M.E. Casida, and
D.R. Salahub, J. Chem. Phys.
104, 5134 (1996).

CORRELATION BETWEEN COUPLED AND UNCOUPLED
STATES FOR THE π → π* TRANSITIONS IN NITROGEN
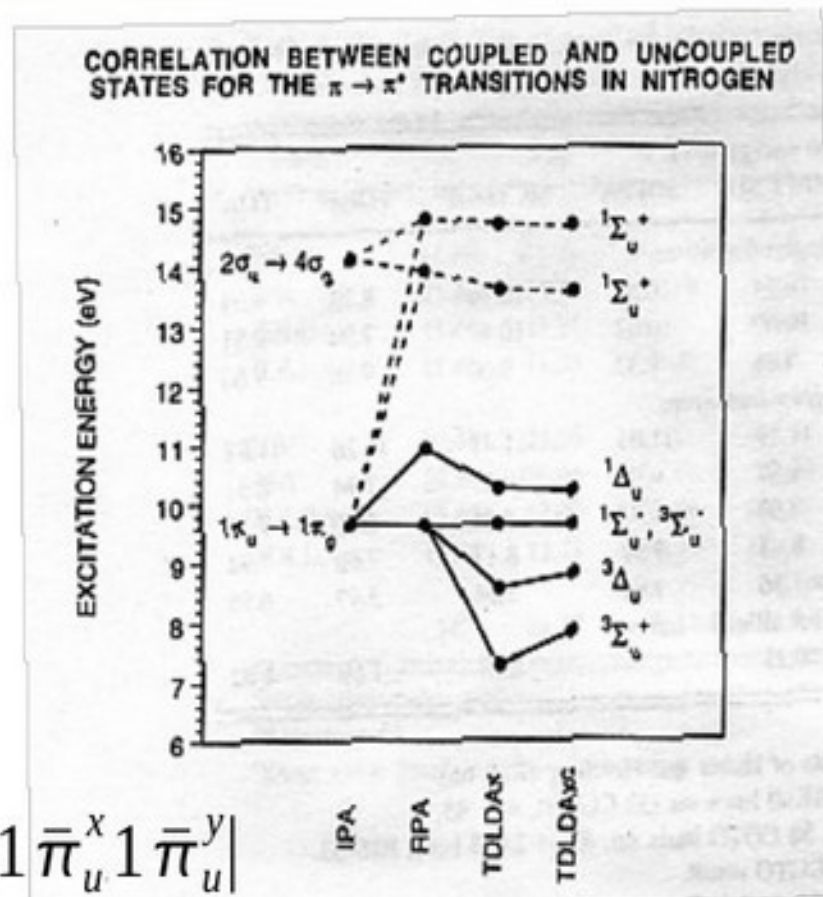
$$\Sigma_u^+ \Rightarrow \left|1\pi_g^x 1\pi_u^y 1\bar{\pi}_u^x 1\bar{\pi}_u^y\right| + \left|1\pi_u^x 1\pi_g^y 1\bar{\pi}_u^x 1\bar{\pi}_u^y\right|$$

$$\Sigma_u^- \Rightarrow \left|1\pi_g^y 1\pi_u^y 1\bar{\pi}_u^x 1\bar{\pi}_u^y\right| - \left|1\pi_u^x 1\pi_g^x 1\bar{\pi}_u^x 1\bar{\pi}_u^y\right|$$

$$\Delta_u \Rightarrow \left|1\pi_g^x 1\pi_u^y 1\bar{\pi}_u^x 1\bar{\pi}_u^y\right| - \left|1\pi_u^x 1\pi_g^y 1\bar{\pi}_u^x 1\bar{\pi}_u^y\right|,$$

$$\left|1\pi_u^x 1\pi_g^x 1\bar{\pi}_u^x 1\bar{\pi}_u^y\right| + \left|1\pi_u^x 1\pi_g^x 1\bar{\pi}_u^x 1\bar{\pi}_u^y\right|$$

72

BEER'S LAW*

cuvette

incident intensity

transmitted intensity

I_0

I

l

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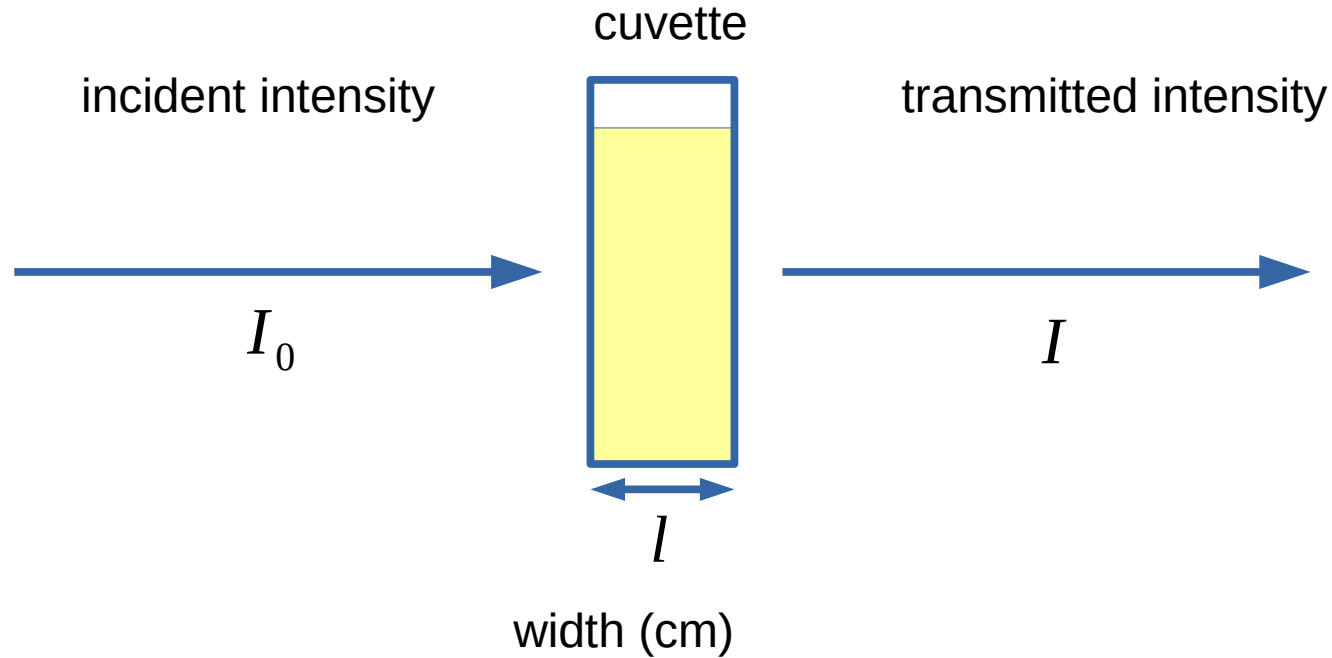
Absorbance (unitless)
$$A = \log_{10} \frac{I_0}{I}$$
(1)   Concentration (mol/L) C

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

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

$$\epsilon = \frac{A}{cl}$$

λ (nm)
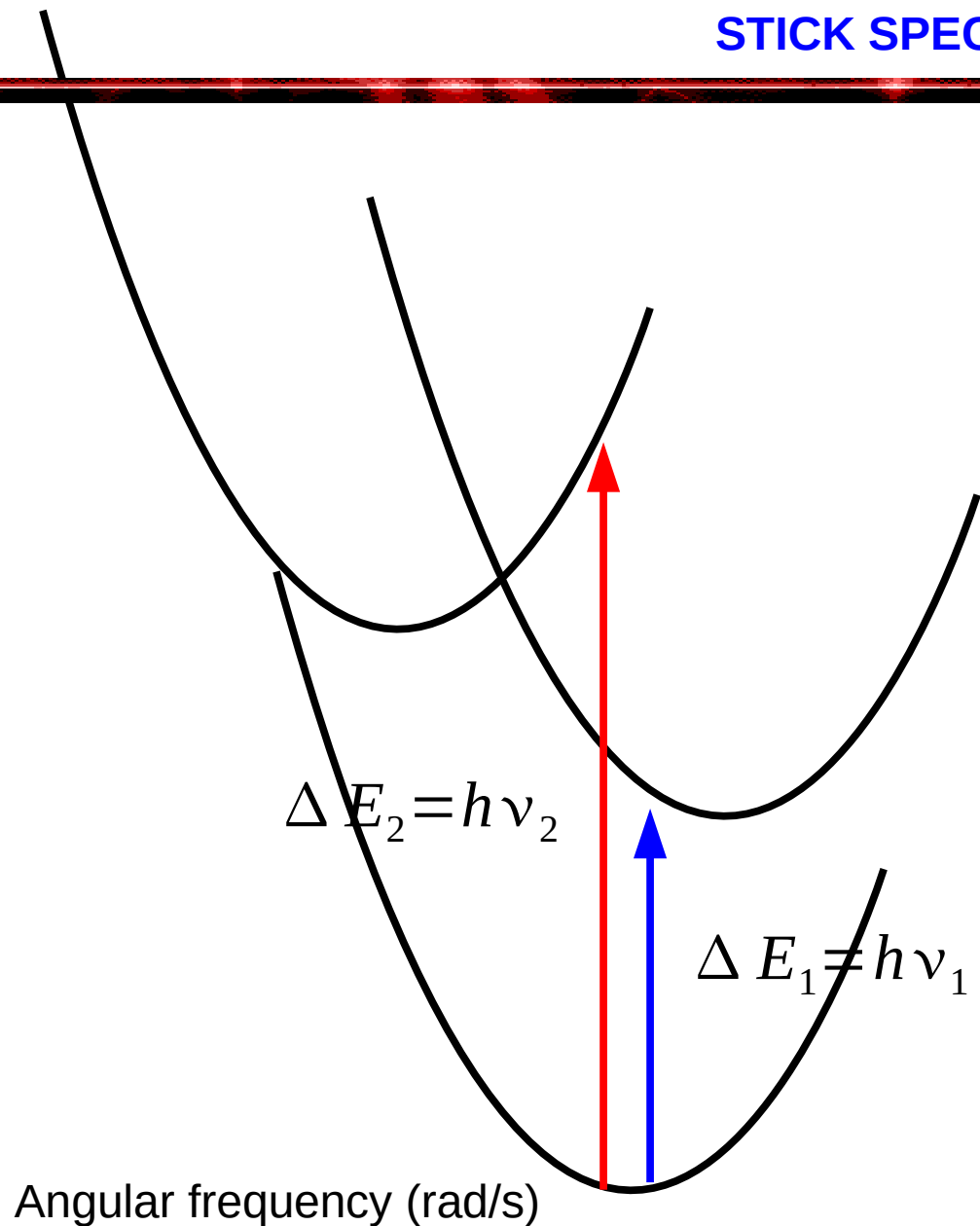
- Vertical transition (ground-state equilibrium geometry)
- Neglect vibrations (and rotations)
- Neglect other contributions to the width of the peaks (e.g., solvent, spectrometer artifacts)
- Average over rotations
- Dipole-dipole approximation

$\Delta E_2 = h\nu_2$

$\Delta E_1 = h\nu_1$

Spectral function (units: cm)

$$S(\nu) = \sum_I f_I \delta(\nu - \nu_I) \qquad (1)$$

Oscillator strength (unitless)

$$f_I = \frac{2\omega_I m_e}{3\hbar} |\langle \Psi_0 | r | \Psi_I \rangle|^2 \qquad (2)$$

Angular frequency (rad/s)

$$\omega = 2\pi\nu \quad (3) \qquad h\nu = \hbar\omega \quad (4)$$

More about oscillator strengths ...

If $\quad \left[\hat{x}, \hat{p}_x\right] = +i\hbar \quad$ **(1)** $\qquad$ Plane-wave basis or any sufficiently complete basis set …

Then the following are equivalent:

$$f_I = \frac{2\omega_I m_e}{3\hbar}\left|\langle\Psi_0|\boldsymbol{r}|\Psi_I\rangle\right|^2 \qquad \textbf{(2)} \qquad \text{Length form}$$

$$f_I = \frac{2}{3\hbar\omega_I m_e}\left|\langle\Psi_0|\hat{\boldsymbol{p}}|\Psi_I\rangle\right|^2 \qquad \textbf{(3)} \qquad \text{Momentum form}$$

$$f_I = -\frac{2i}{3\hbar}\langle\Psi_0|\boldsymbol{r}|\Psi_I\rangle\cdot\langle\Psi_I|\hat{\boldsymbol{p}}|\Psi_0\rangle \qquad \textbf{(4)} \qquad \text{Mixed form}$$

The Thomas-Reiche-Kuhn (TRK) or "*f*-Sum" Rule

The sum of the oscillator strengths gives the total number of electrons:

$$\sum_I f_I = N$$

Used
- By experimentalists to normalize their spectra.
- By theoreticians to test their programs (careful: basis-set-dependent answer)

N$_2$

TRK f-sum

TABLE VIII. Comparison of TDLDAxc Cauchy coefficients (in a.u.) with those from other *ab initio* methods and with experiment. $R_{NN}=2.074$ bohr.

Method	Basis set	S_0	S_{-2}[a]	S_{-4}	S_{-6}
		TD-DFRT Calculations			
TDLDAxc	TZVP+	11.48	11.92	32.71	114.5
	BK90	12.96	10.56	31.93	127.98
	Sadlej	10.44	12.11	34.83	131.3
	DSadlej	13.99	12.19	34.00	128.2
	88CGTO	14.04	11.55	29.32	99.12
	106CGTO	14.03	11.73	31.70	121.1
		Experiment[b]			
		14[c]	11.74	30.11	101.8
		Other theory			
TDHF[d]	[11s8p4d1f]	13.96	11.56	27.60	100.51
TDHF[e]	[7s5p3d]		11.44	27.53	83.56
TDHF[f]	DSadlej	14.01	11.54	27.39	83.84
MCTDHF[g]	[11s8p4d1f]		11.06	25.61	68.53
MCTDHF[h]	[8s6p4d1f]			28.92	94.51
SOPPA[i]	DSadlej		11.42	29.24	98.6

[a]Mean static polarizability.
[b]Reference 66.
[c]Exact value equals number of electrons.
[d]Time-dependent Hartree–Fock calculation of Ref. 46.
[e]Time-dependent Hartree–Fock calculation of Ref. 67.
[f]Time-dependent Hartree–Fock calculation of Ref. 44
[g]Multiconfigurational time-dependent Hartree–Fock calculation of Ref. 46. Six orbital active space.
[h]Multiconfigurational time-dependent Hartree–Fock calculation of Ref. 60. Twelve orbital active space.
[i]Second-order polarization propagator approximation calculation of Ref. 44.

$$S_n = \sum_I f_I \omega^n$$

78

C. Jamorski, MEC, and D. R. Salahub, *J. Chem. Phys.* **104**, 5134 (1996).

We assume that the photon absorption process is sudden and use Fermi's (2nd) Golden Rule to obtain (in Gaussian units):

ICBST*

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

You must integrate over all of the spectra coming from the electronic transition!

In SI units, this becomes

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

which makes

$$f_I = (1.44\text{e-}19 \text{ mol.cm.s/L}) \int \epsilon(\nu) \, d\nu \qquad \textbf{(3)}$$

* *It Can Be Shown That*

For a single transition,

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

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

For several transitions,

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

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

GAUSSIAN CONVOLUTION

Normalized gaussian function

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

Full width at half maximum (FWHM)

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

$$\epsilon(\nu) = \frac{\pi N_A e^2}{m_e c \, 4\pi \epsilon_0 \ln(10)} \qquad (3)$$
$$\times \sum_I f_I \, g(\nu - \nu_I)$$
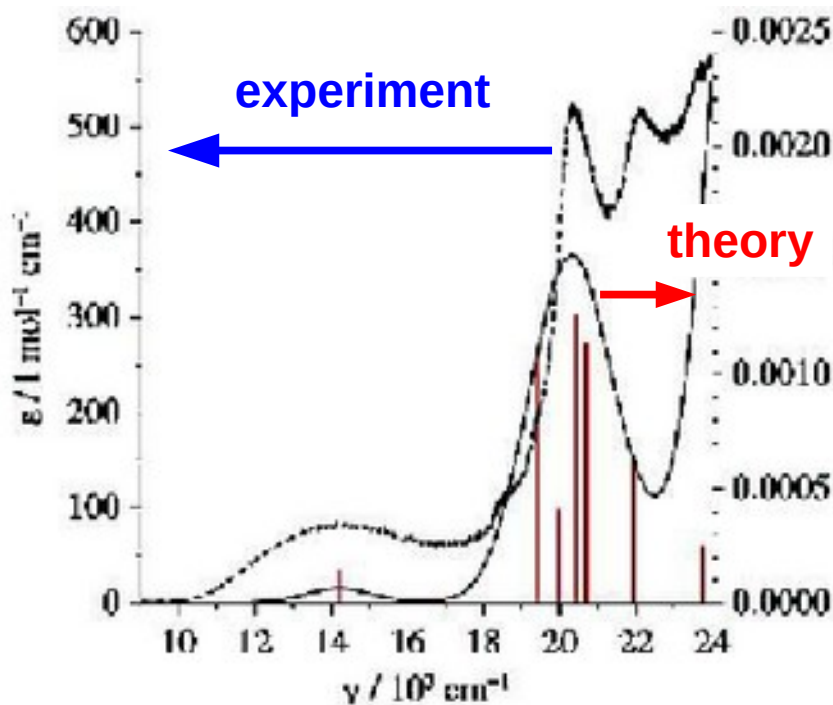
One program:
spectrum.py
By Pablo Baudin and M.E.C.

Normally experiment and properly normalized theoretical spectra have intensities which agree to within an order of magnitude:
- Imperfect spectrometers
- Neglect of vibtational coupling
- Neglect of solvent
- ???

TD-DFT is the Main Single-Determinantal Theory for Excited States

Web of Science 1 May 2025 key word: TDDFT

1984 ← Runge-Gross theorems

Casida equations
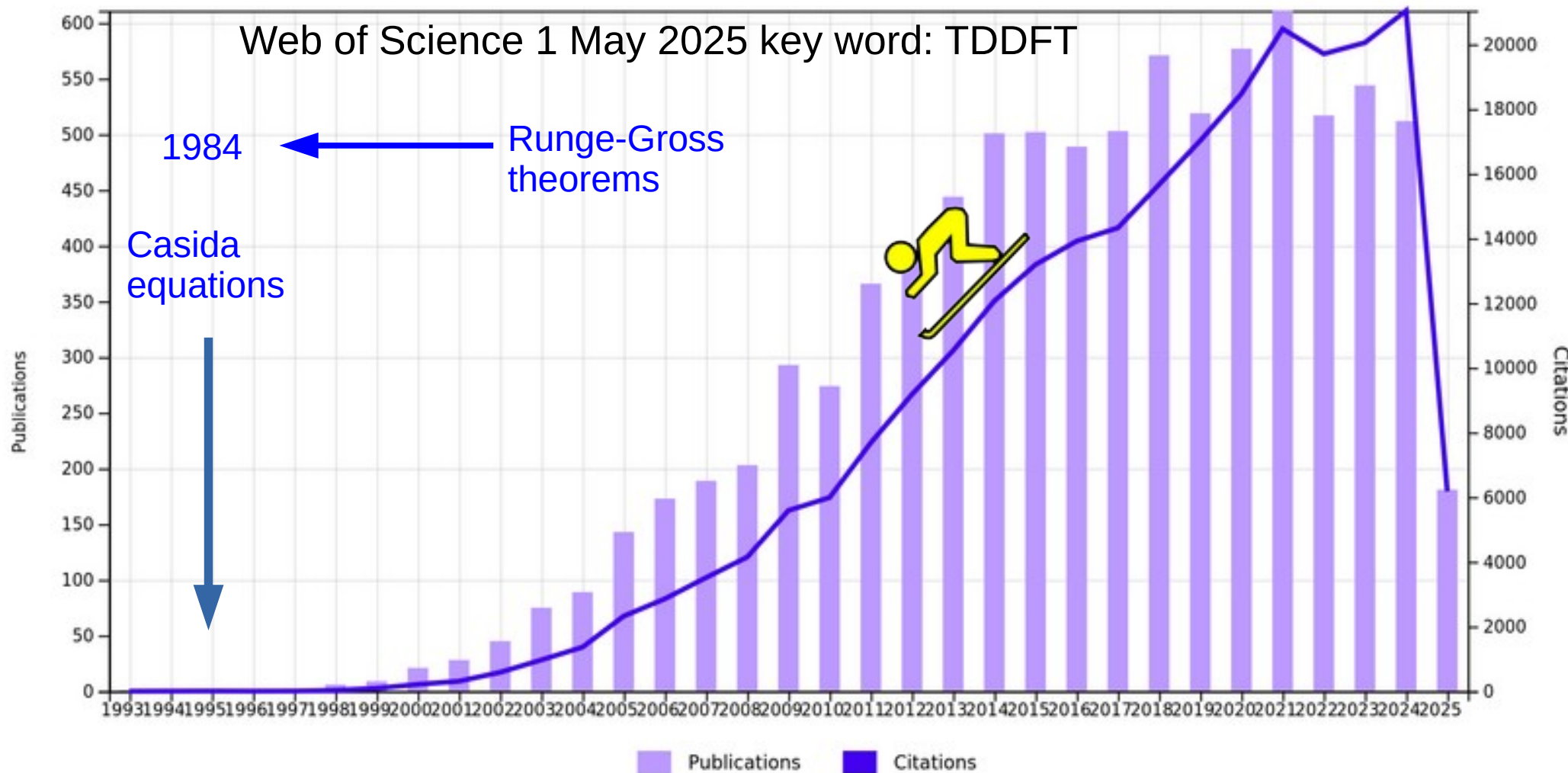
Present-day conventional TDDFT is relatively "simple", but often gives acceptably good results.

Literally introduce

$$\varepsilon(t) = \varepsilon \cos \omega_0 t \qquad (1)$$

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

Propogate in time :

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

Katherine Johnson in *Hidden Figures* turns to Euler's method to solve a critical problem

Basic Time-Dependent (TD) Theory

May solve the time-dependent Schrödinger equation (TDSE), $\hat{H}(t)\Psi(t)=i\dfrac{\partial}{\partial t}\Psi(t)$ (1) , by numerical integration :

Euler's method

$$t_i = i\,\Delta t \quad (2)$$

$$\hat{H}(t_i)\,\Psi(t_i)=i\frac{\Psi(t_{i+1})-\Psi(t_i)}{\Delta t} \quad (3)$$

Solve by "Shooting"

Euler's method
$$\Psi(t_{i+1}) = \Psi(t_i) - i(\Delta t)\hat{H}(t_i)\Psi(t_i) \qquad (1)$$

The solution of a first-order differential equation requires knowing: $\Psi(t_0)$ (2)

(initial value problem)

Calculate

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

Dynamic polarizability

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

Convolution theorem

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

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

Spectral function

$$S(\omega) = \frac{2\omega}{\pi} \Im \alpha(\omega + i\eta) \quad \text{(1)}$$

Dynamic polarizability

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

$$S(\omega) = \frac{2\omega}{\pi} \Im \left[\sum_{I \neq 0} \frac{f_I/2\omega_I}{\omega + i\eta + \omega_I} - \sum_{I \neq 0} \frac{f_I/2\omega_I}{\omega + i\eta - \omega_I} \right] \quad \text{(3a)}$$

$$= \frac{\omega}{\omega_I} f_I \left[\sum_{I \neq 0} \frac{\eta}{(\omega - \omega_I)^2 + \eta^2} - \sum_{I \neq 0} \frac{\eta}{(\omega + \omega_I)^2 + \eta^2} \right] \quad \text{(3b)}$$

Laurentzian function

$$L(\omega) = \frac{1}{\pi} \frac{\eta}{(\omega - \omega_I)^2 + \eta^2} \quad \text{(4)}$$

Finite Difference Method

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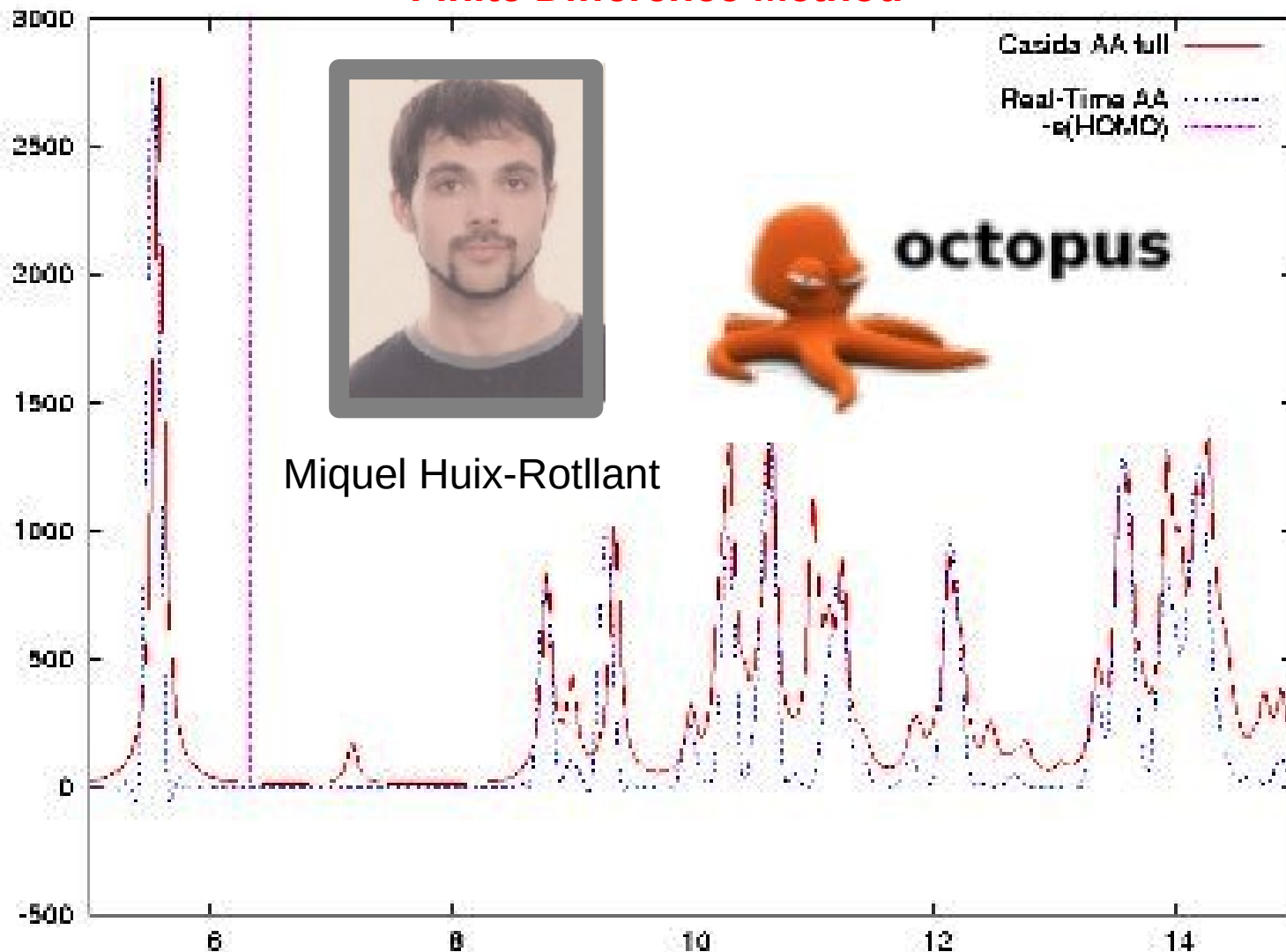
Note: Only x and y components drawn in the real-time propagation

- Allows you to go to high energies in calculated spectra.
- Energy resolution is limited by time of dynamics run.
- Assignment is nontrivial (especially for dark states).

WELL

HOW DOES IT WORK?

- Single electron (particle-hole) excitations
- Calculations without symmetry breaking
- Low-energy excitations
- Localized excitations
- Excitations without too much charge transfer
- Away from conical intersections

Much progress has been made on overcoming these limitations. Only a little can presented here about these problems and their solutions.
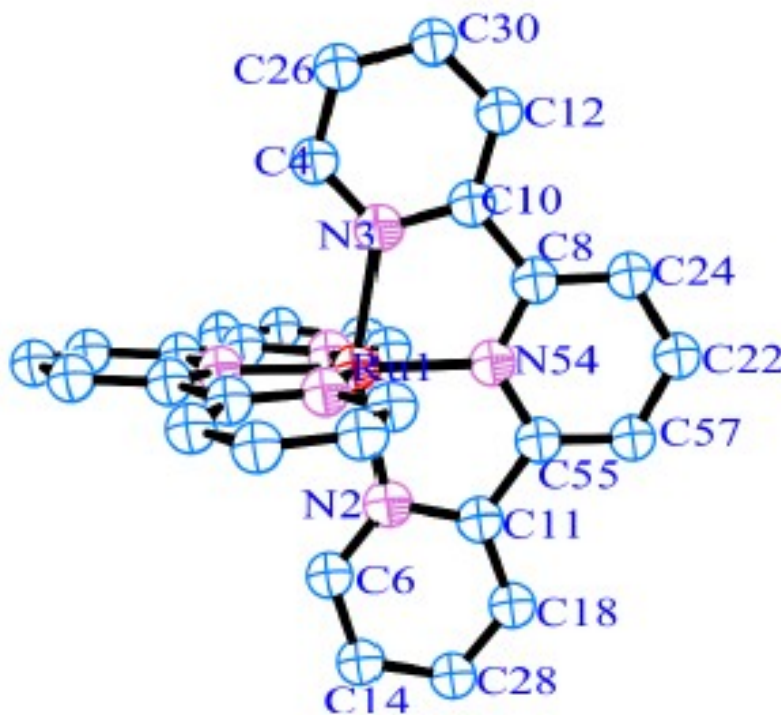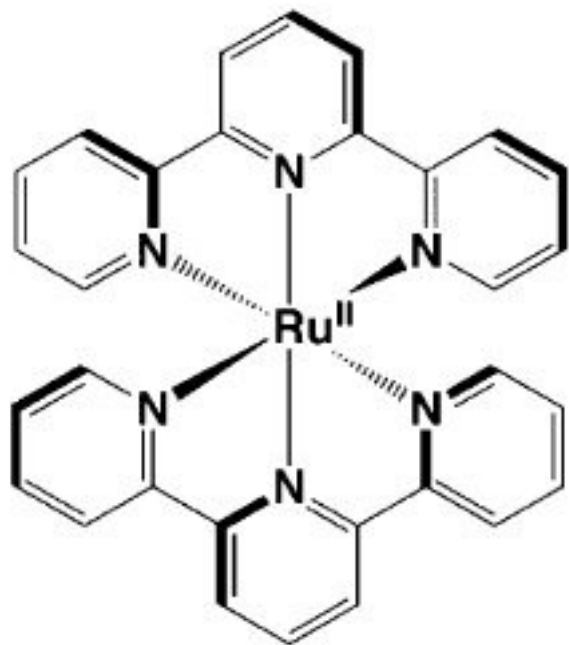
Optimisation beginning with the X-ray structure.

B3LYP/6-31G(d)+LANL2DZ ECP on Ru

Example prepared by Denis MAGERO with **Gaussian09**.

Table 5. Comparison of parameters for geometries optimized at HF and DFT. Bond lengths are in (Å) and bond angles are in degrees.

	HF	DFT	Exp.[109]	Other Works‡
RuN_2	2.21	2.122	2.074	2.11
RuN_{54}	2.086	2.018	1.984	2.011
RuN_3	2.21	2.122		
$N_{54}C_{55}$	1.336	1.365	1.345	1.36
N_2C_{11}	1.353	1.382	1.374	1.38
$C_{11}C_{55}$	1.489	1.474	1.466	1.47
N_2C_6	1.33	1.354	1.35	1.36
$RuN_{54}C_{55}$	118.132	118.784	119.4	118.8
RuN_2C_{11}	112.473	113.477	113.4	113.8
RuN_2C_6	127.502	127.336	127.5	126.6
$N_{54}RuN_2$	77.002	78.456	78.6	78.9

D. Magero

Gas phase B3LYP calculations give a geometry close to the one measured in the crystal.
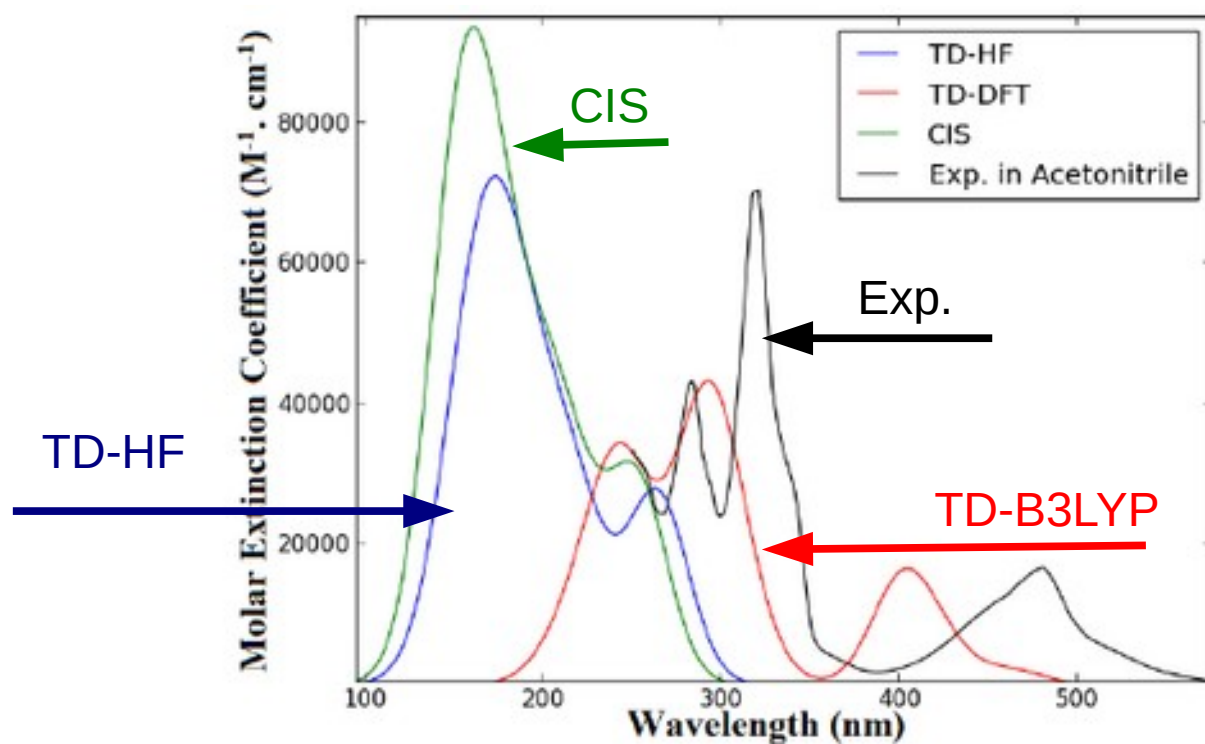
Only the TD-DFT spectrum is close enough to the experiment to allow an assignment.

D. Magero

Figure 7. Comparison of experimental with calculated absorption spectra at different levels of theory; CIS, TD-HF and TD-DFT for [Ru(trpy)$_2$]$^{2+}$. Calculated spectra has been done with 100 singlet states and 6-31G(d) basis set. Experimental spectra; measured at room temperature in acetonitrile [99].

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

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

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!

Energies d'Excitation de CH$_2$O (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!
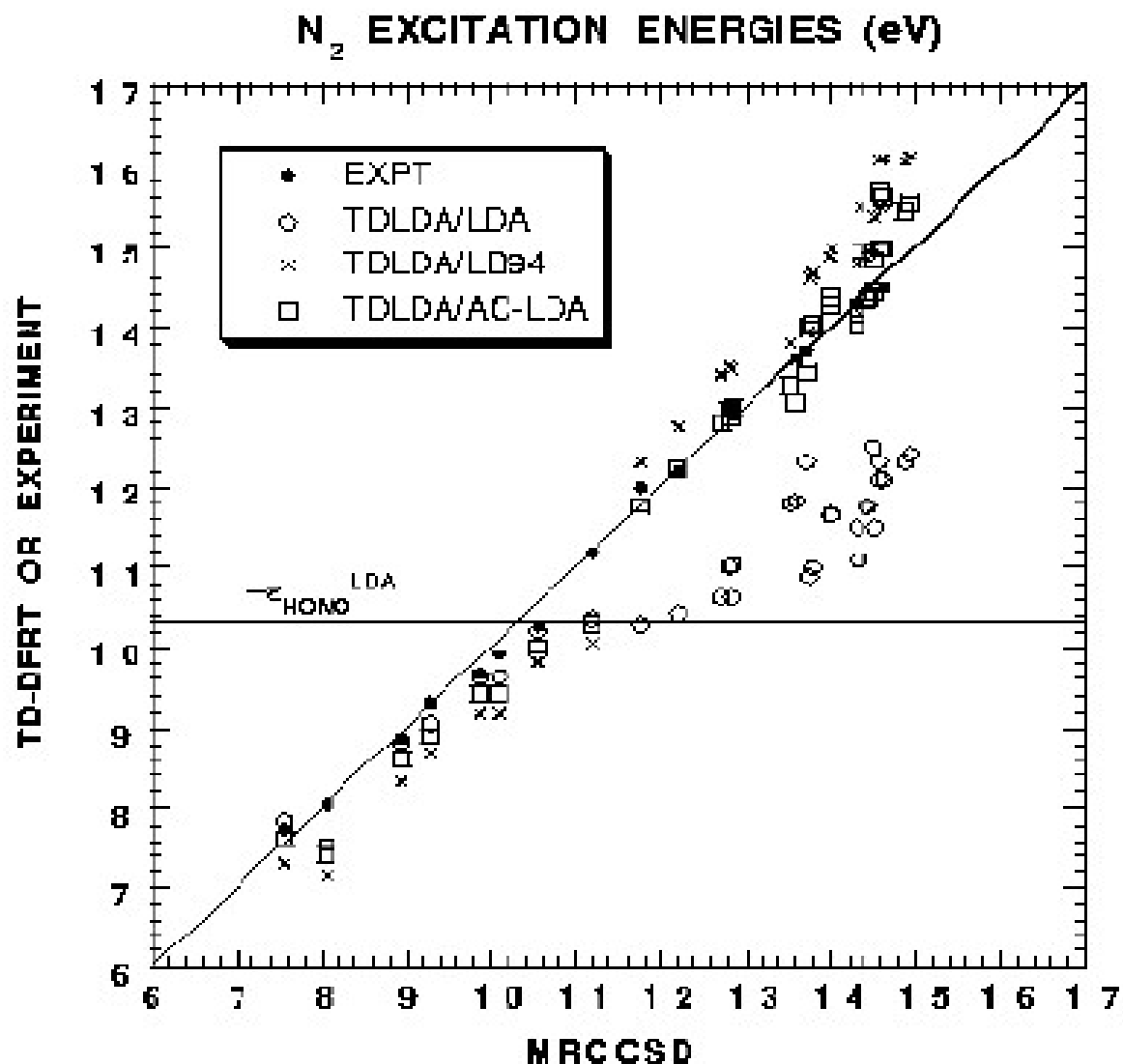
The collapse of high excitation energies is avoided by using exchange-correlation potentials with an improved long range behavior.

OXIRANE C-C RING OPENING
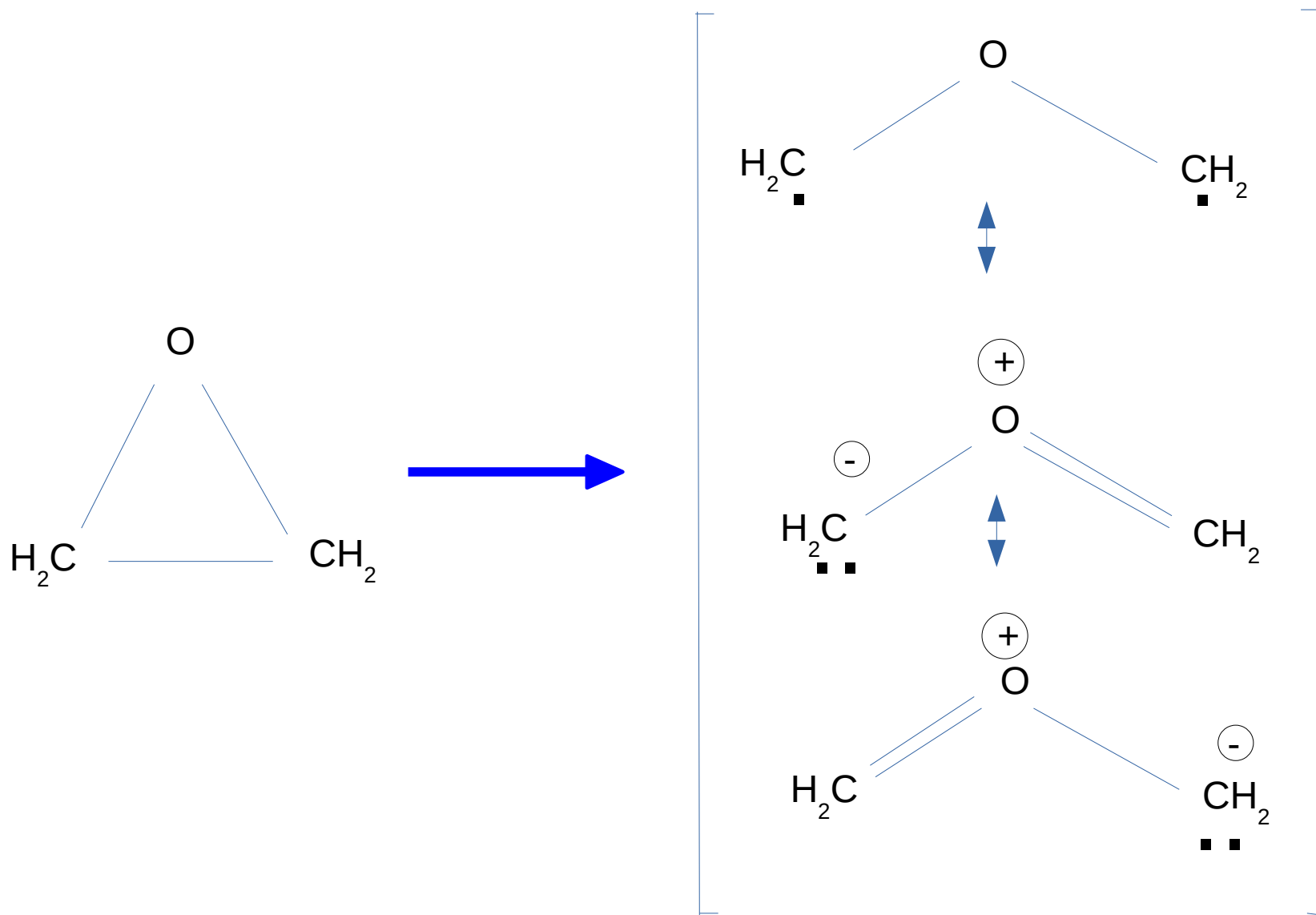
Robert Burns WOODWARD
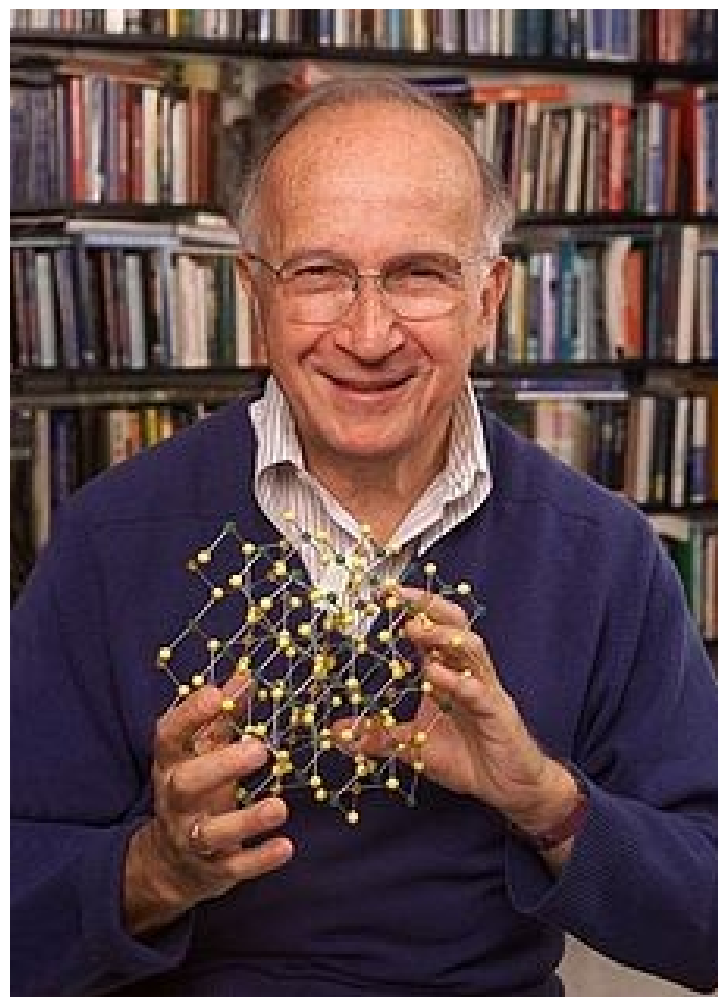
Roald HOFFMANN
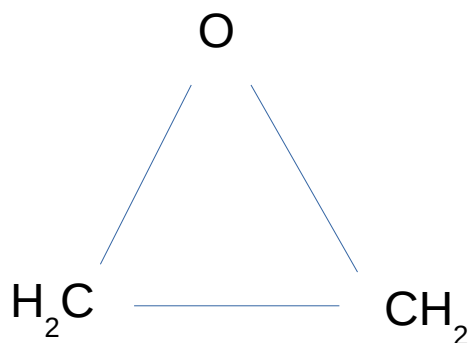
O

H₂C ———— CH₂
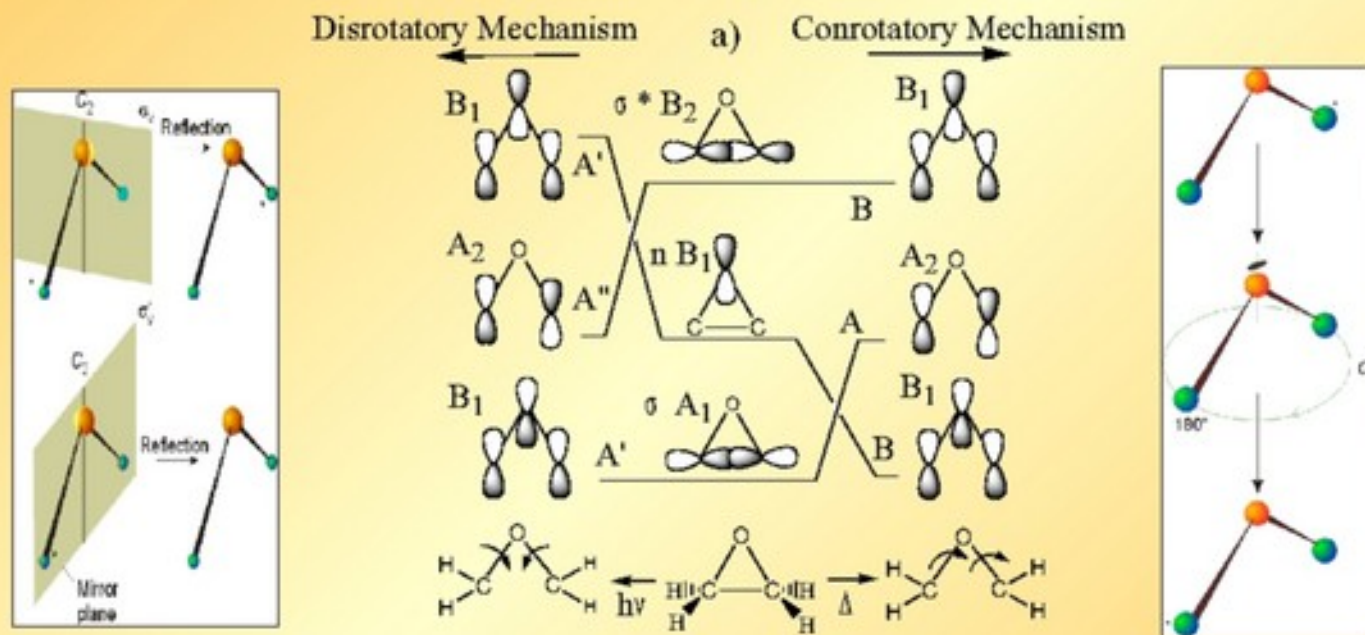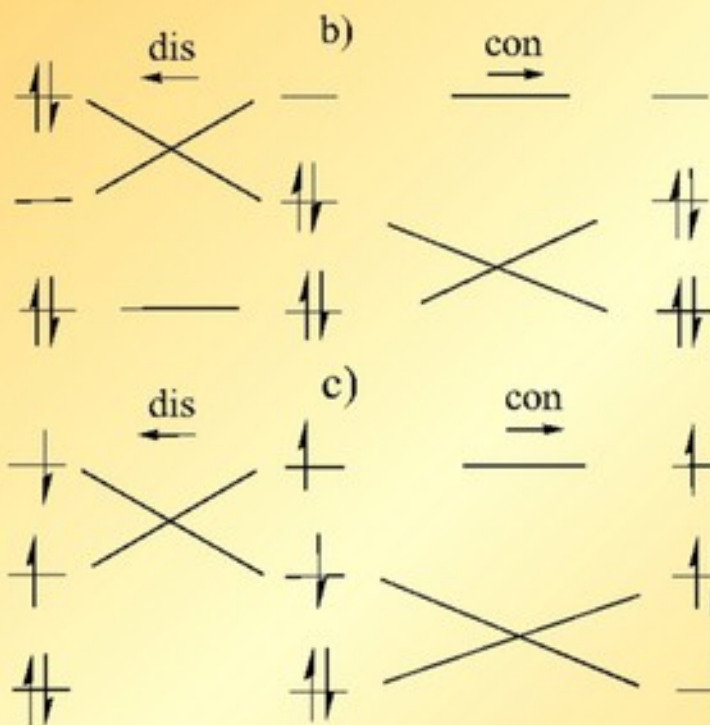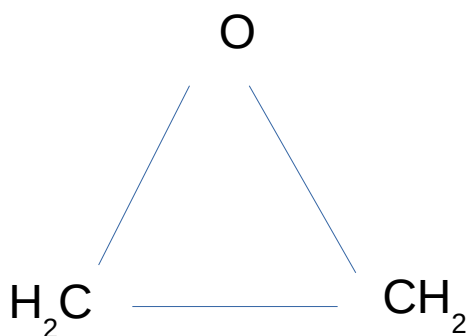
GROUND STATE POTENTIAL ENERGY SURFACE
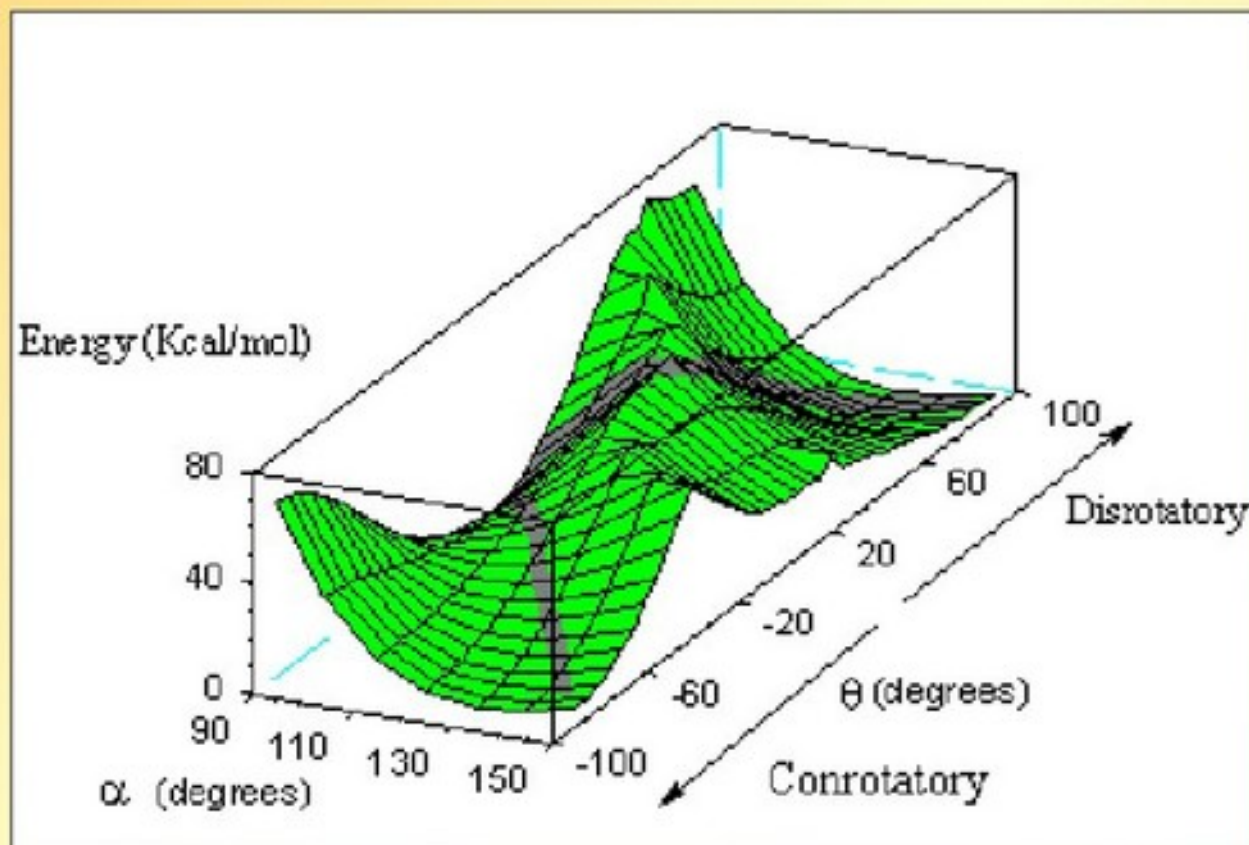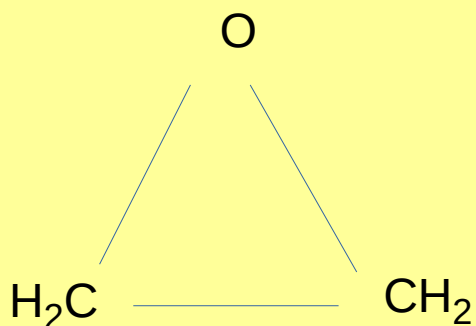
B3LYP

M.E. Casida, A. Ipatov, and F. Cordova, in Time-Dependent Density-Functional Theory, edited by
M.A.L. Marques, C. Ullrich, F. Nogueira, A. Rubio, and E.K.U. Gross, Lecture Notes in Physics
(Springer: Berlin, 2006), pp. 243-257; F. Cordova, L. Joubert Doriol, A. Ipatov, M.E. Casida, and A. Vela, *J. Chem. Phys.*
127, 1764111 (2007).

HF STABILITY ANALYSIS*

Given a spin-restricted solution (same orbitals for different spin), is it possible that there is a lower energy solution with different orbitals for different spin?

(1)
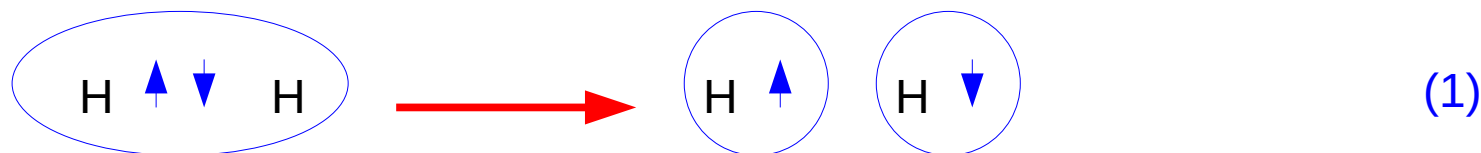
Look at an arbitrary unitary transformation of the orbitals:

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

(2)

We find

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

(3)

But another way to write the EOM matrix equation is

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

(4)

Conclusion :
Symmetry breaking will occur if there are <u>imaginary</u> excitation energies.

* J. Cizek and J. Paldus, *J. Chem. Phys.* **47**, 3976 (1967).
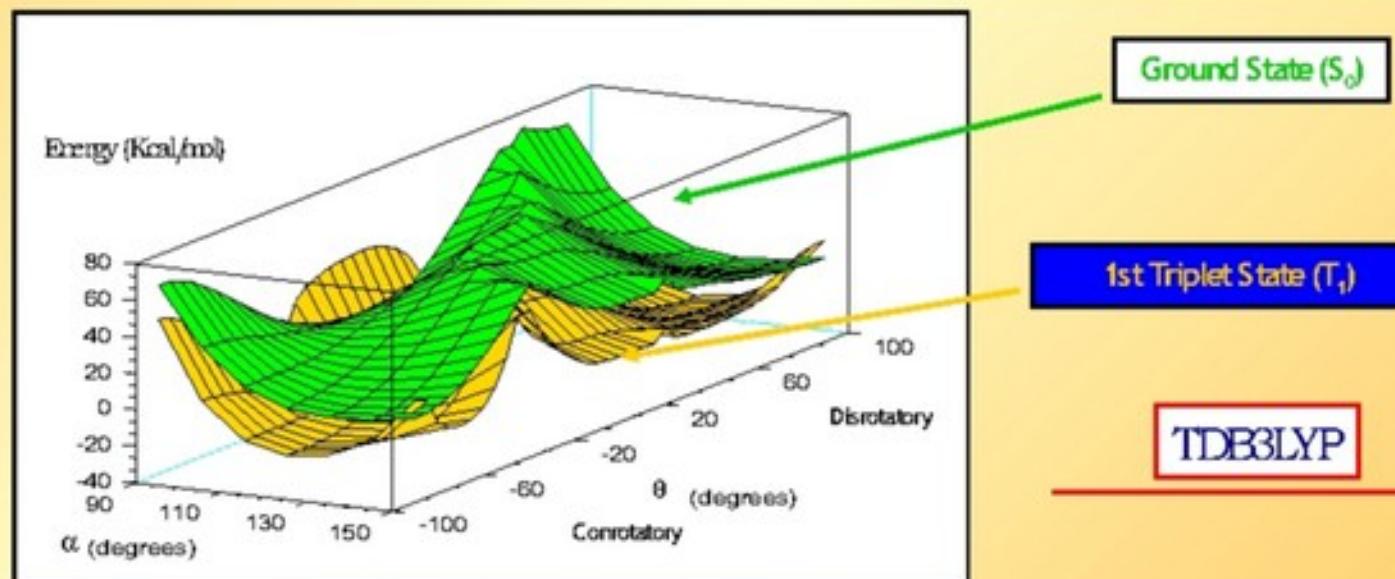
93% of the surface shows symmetry breaking

TDB3LYP

M.E. Casida, A. Ipatov, and F. Cordova, in Time-Dependent Density-Functional Theory, edited by
M.A.L. Marques, C. Ullrich, F. Nogueira, A. Rubio, and E.K.U. Gross, Lecture Notes in Physics
(Springer: Berlin, 2006), pp. 243-257; F. Cordova, L. Joubert Doriol, A. Ipatov, M.E. Casida, and A. Vela,
in Time-Dependent Density-Functional Theory, edited by M.A.L. Marques, C. Ullrich, F. Nogueira, A. Rubio,
and E.K.U. Gross, Lecture Notes in Physics (Springer: Berlin, 2006), pp. 243-257.

Which would you use?
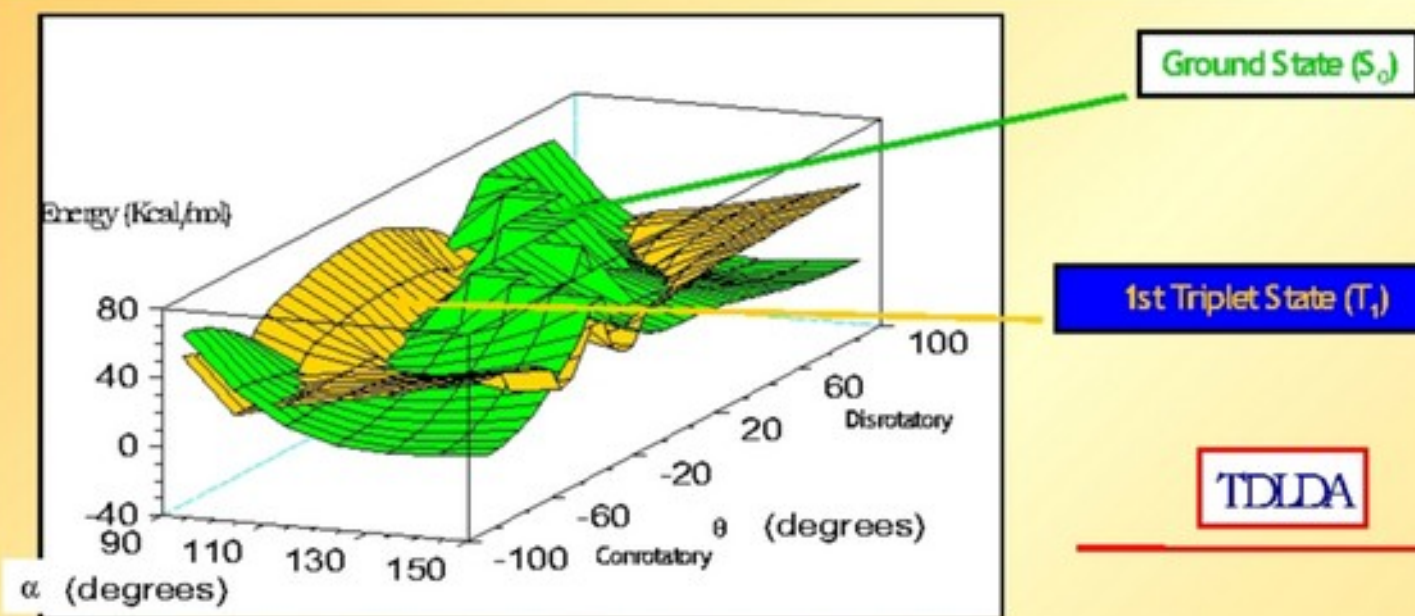
50% of the surface shows symmetry breaking

TDLDA

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A.A.M.H.M. Darghouth, G.C. Correa, S. Juillard, M.E. Casida, A. Humeniuk, and R. Mitrić, "Davydov-Type Excitonic Effects on the Absorption Spectra of Parallel-Stacked and Herringbone Aggregates of Pentacene: Time-Dependent Density-Functional Theory and Time-Dependent Density-Functional Tight Binding", *J. Chem. Phys.* **149**, 134111 (2018).

Spectral effects seen in dye aggregates:

J-aggregates (Jelly/Scheibe) spectrum shifts to lower energies and new narrow peaks appear.

H-aggregates (hypsochromic) spectrum shifts to higher energies.
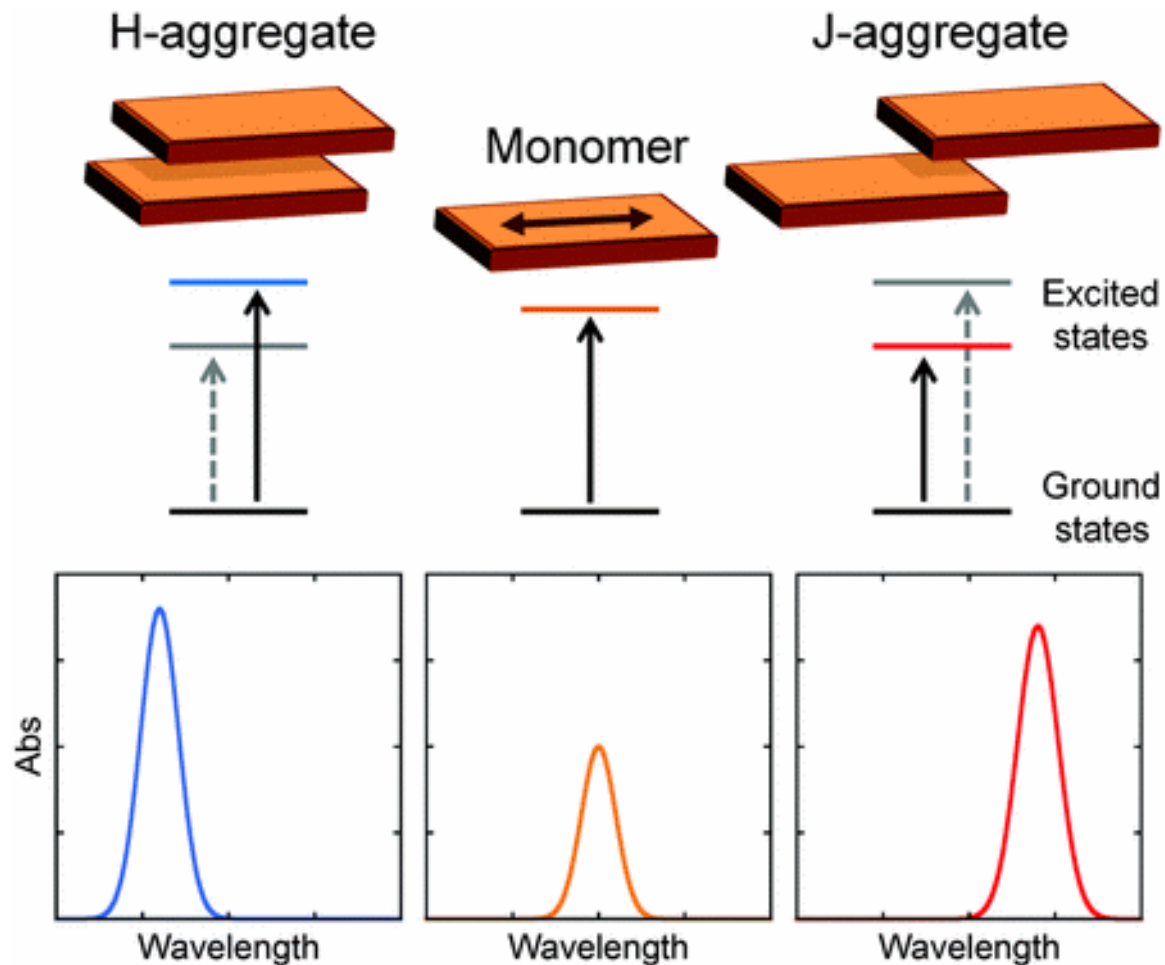
Davydov Splitting in Pentacene
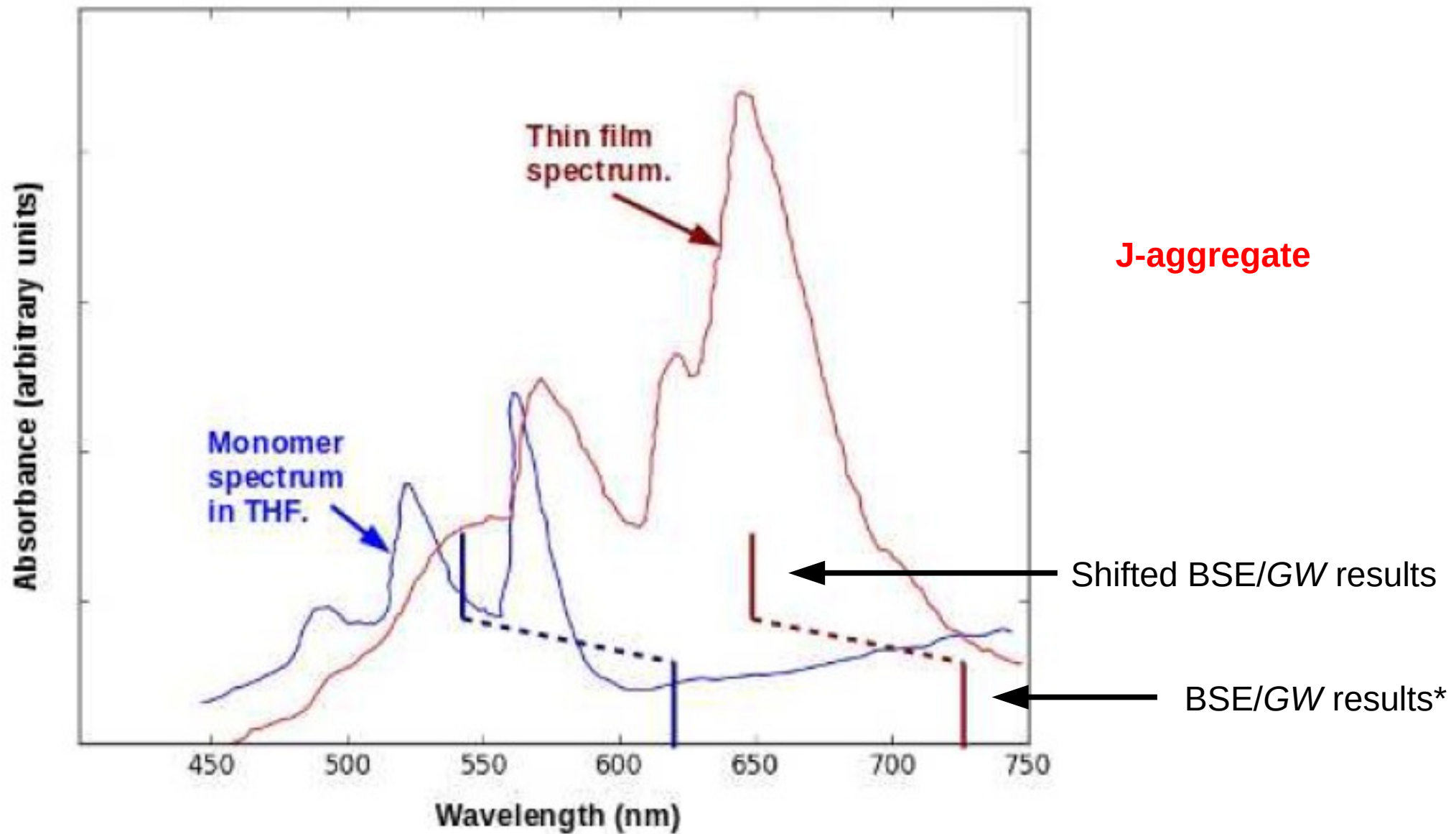
J-aggregate

Shifted BSE/*GW* results

BSE/*GW* results*

* P. Cudazzo, F. Sottile, A. Rubio, and M. Gatti, "Topical Review: Exciton dispersion in molecular Solids," *J. Phys. Condens. Matter* **27**, 113204 (2015).

1. Historical theory (1960s). Necessarily very approximate!
2. Assumes a van der Waals (vdW) dimer.
3. Perturbative. Only zero and first order.
4. Point-dipole point-dipole approximation.

Michael Kasha
(1920-2013)

$$\Psi_1^0 \to \Psi_1^I \quad \text{(1)}$$
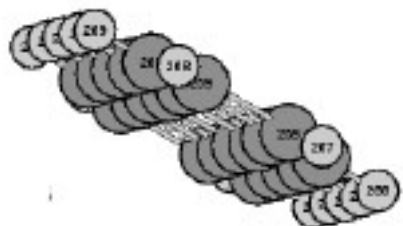
$$\omega = E_1^I - E_1^0 \quad \text{(2)}$$

$$\Psi_2^0 \to \Psi_2^I \quad \text{(3)}$$

$$\omega = E_1^I - E_1^0 \quad \text{(4)}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12} \quad \text{(5)}$$

$$\Psi_0 = \Psi_1^0 \Psi_2^0 \quad \text{(6)}$$

$$\Psi_I = C_1 \Psi_1^I \Psi_2^0 + C_2 \Psi_1^0 \Psi_2^I \quad \text{(7)}$$

* **[KRE65]** M. Kasha, H.R. Rawls, and A. El Bayoumi, "The exciton model in molecular Spectroscopy", *Pure Appl. Chem.* **11**, 371 (1965).

Ground-State Energy

$$E_0 = \langle \Psi_1^0 \Psi_2^0 | \hat{H} | \Psi_1^0 \Psi_2^0 \rangle \qquad \text{(1)}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12} \qquad \text{(2)}$$

$$E_0 = \langle \Psi_1^0 \Psi_2^0 | \hat{H}_1 | \Psi_1^0 \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{H}_2 | \Psi_1^0 \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \qquad \text{(3)}$$

$$E_0 = \langle \Psi_1^0 | \hat{H}_1 | \Psi_1^0 \rangle \langle \Psi_2^0 | \Psi_2^0 \rangle + \langle \Psi_1^0 | \Psi_1^0 \rangle \langle \Psi_2^0 | \hat{H}_2 | \Psi_2^0 \rangle + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \quad \text{(4)}$$

$$E_0 = E_1^0 + E_2^0 + \langle \Psi_1^0 \Psi_2^0 | \hat{V}_{12} | \Psi_1^0 \Psi_2^0 \rangle \quad \text{(5)}$$

$$E_0 = E_1^0 + E_2^0 + E_{vdW}^0 \qquad \text{(6)}$$

Excited-State Energy

$$\Psi_I = C_1 \Psi_1^I \Psi_2^0 + C_2 \Psi_1^0 \Psi_2^I \qquad \textbf{(1)}$$

$$\begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = E^I \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} \qquad \textbf{(2)}$$

$$A = \langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^I \Psi_2^0 \rangle = \langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^0 \Psi_2^I \rangle \qquad \textbf{(3)}$$

$$B = \langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^I \Psi_2^0 \rangle = \langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^0 \Psi_2^I \rangle \qquad \textbf{(4)}$$

$$\Psi_{\pm}^I = \frac{1}{\sqrt{2}} \left(\Psi_1^I \Psi_2^0 \pm \Psi_1^0 \Psi_2^I \right) \qquad \textbf{(5)}$$

$$E_{\pm}^I = A \pm B \qquad \textbf{(6)}$$

$$A = \langle \Psi_1^I \Psi_2^0 | \hat{H} | \Psi_1^I \Psi_2^0 \rangle \qquad (1)$$

$$B = \langle \Psi_1^0 \Psi_2^I | \hat{H} | \Psi_1^I \Psi_2^0 \rangle \qquad (2)$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{V}_{12} \qquad (3)$$

$$A = E_1^I + E_2^0 + \langle \Psi_1^I \Psi_2^0 | \hat{V}_{12} | \Psi_1^I \Psi_2^0 \rangle = E_1^I + E_2^0 + E_{vdW}^I \qquad (4)$$

$$B = \langle \Psi_1^0 \Psi_2^I | \hat{V}_{12} | \Psi_1^I \Psi_2^0 \rangle = E_{\text{exciton splitting}} \qquad (5)$$

$$E_{\pm}^I = E_1^I + E_2^0 + E_{vdW}^I \pm E_{\text{exciton splitting}} \qquad (6)$$

$$\omega_{\pm}^I = E_{\pm}^I - E^0 = \omega_1^0 + \left(E_{vdW}^I - E_{vdW}^0 \right) \pm E_{\text{exciton splitting}} \qquad (7)$$

$$\vec{\mu}^{I0} = \langle \Psi^I | \vec{r} | \Psi^0 \rangle \quad \text{(1)}$$

$$\vec{\mu}_{\pm}^{I0} = \frac{1}{\sqrt{2}} \langle \Psi_1^I \Psi_2^0 \pm \Psi_1^0 \Psi_2^I | \vec{r} | \Psi_1^0 \Psi_2^0 \rangle \quad \text{(2)}$$

$$\vec{\mu}_{\pm}^{I0} = \frac{1}{\sqrt{2}} \left(\vec{\mu}_1^{I0} \pm \vec{\mu}_2^{I0} \right) \quad \text{(3)}$$

$$f_{\pm}^I = \frac{\omega_{\pm}^I}{3} |\vec{\mu}_1^{I0} \pm \vec{\mu}_2^{I0}|^2 \quad \text{(4)}$$

Example: Parallel stacking $\quad \vec{\mu}_{1/2} \perp \vec{r} \quad$ (5)

$$f_+^I = \frac{4}{3} \omega_1^I |\vec{\mu}_1^{I0}|^2 \quad \text{(6)}$$

$$f_-^I = 0 \quad \text{(7)}$$

Parallel transition dipoles

bright

dark

Monomer levels   Dimer levels   Dipole phase relation

Blue – shift case
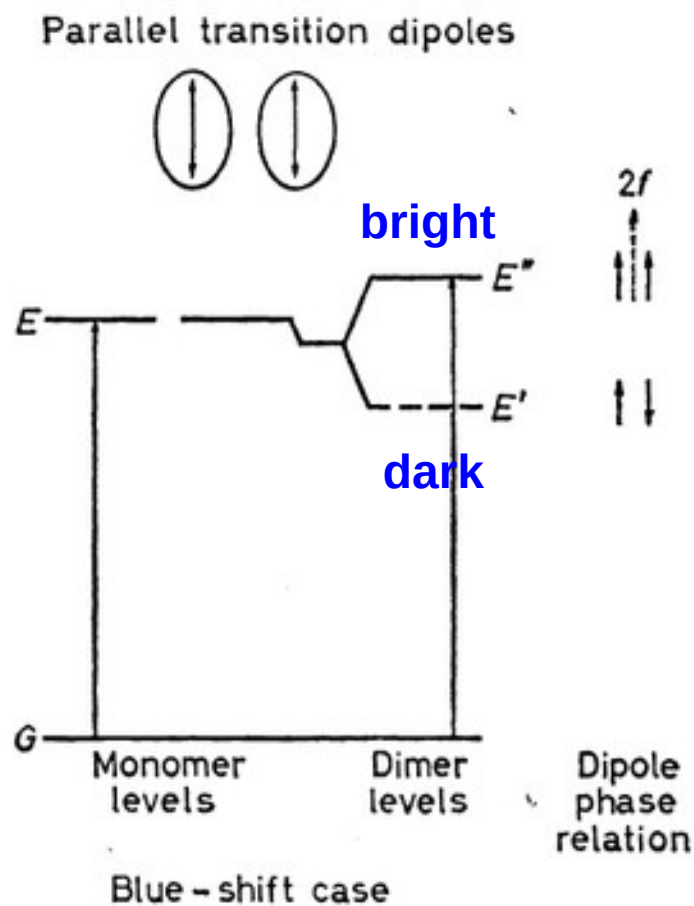
Fig. 1. Ref. **[KRE65]**
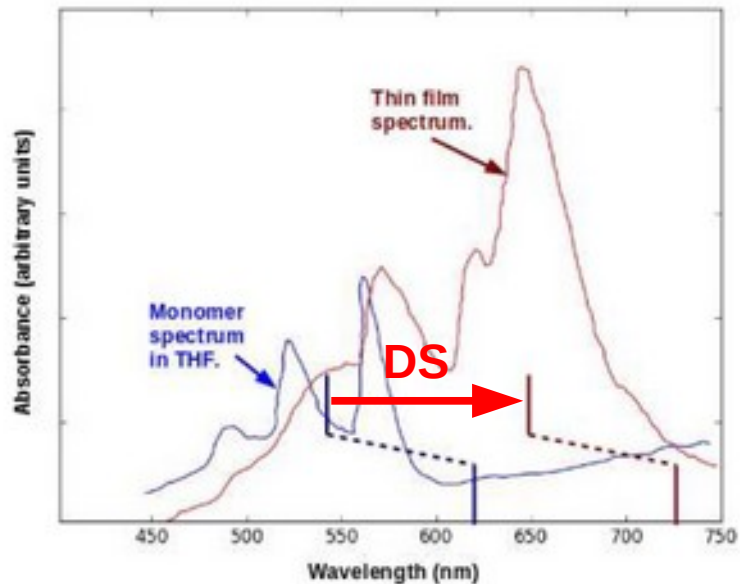
Shift upon aggregation.

$$\omega^I_\pm - \omega^0_1 = \left(E^I_{vdW} - E^0_{vdW} \right) \pm E_{\text{exciton splitting}} \approx \pm DS$$

(1)
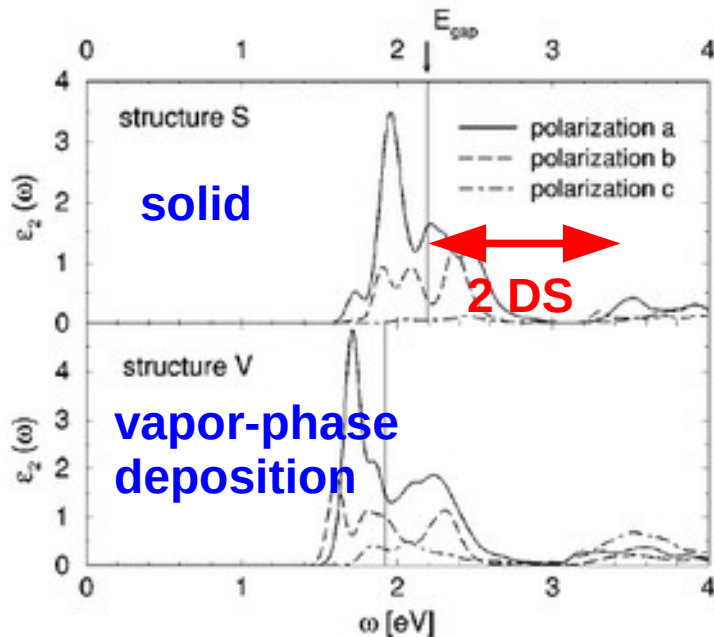
Intensities as a function of light polarization direction.

$$^q f^I_\pm = \frac{\omega^I_\pm}{3} \left| {}^q\mu^{I0}_1 \pm {}^q\mu^{I0}_2 \right|^2$$

(2)

M.L. Tiago, J.E. Northrup, and S.G. Louie, "*Ab initio* Calculation of the electronic and optical properties of Solid pentacene", *Phys. Rev. B* **67**, 115212 (2003).

But Kasha's Model Neglects Charge Transfer!

(d) solid pentacene BSE/*GW*
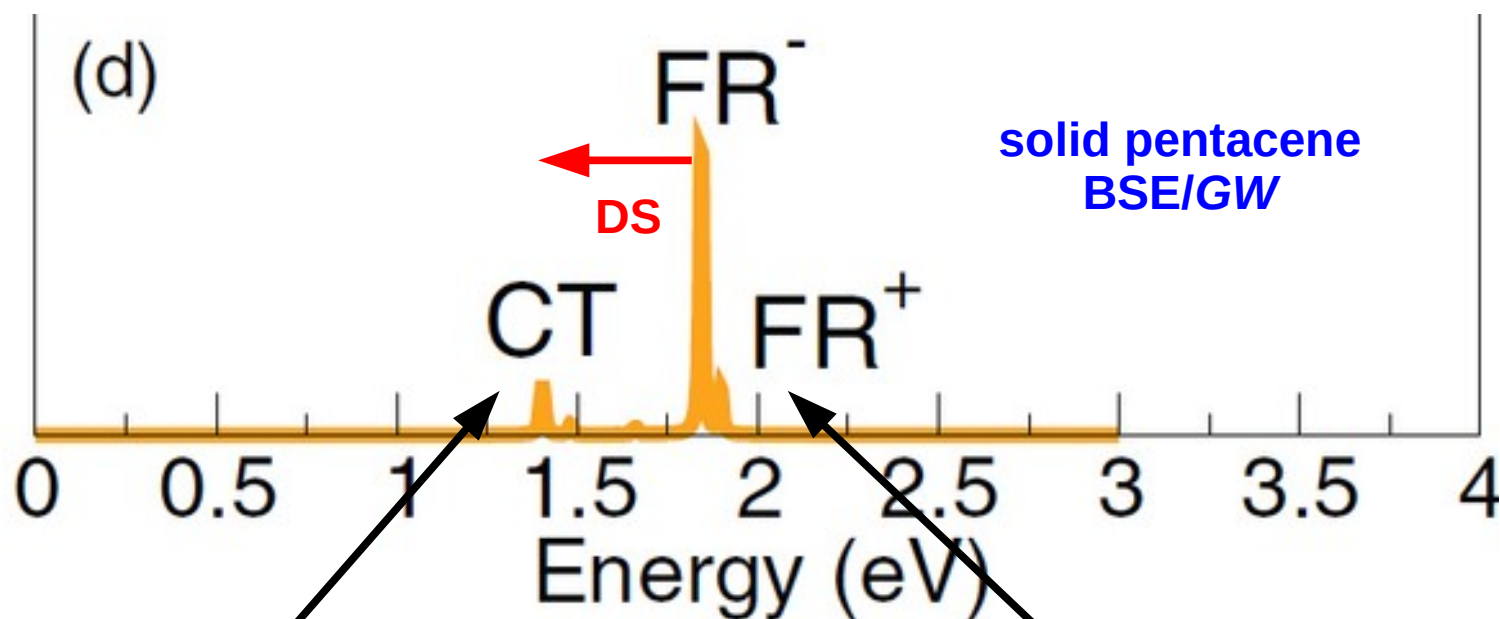
Charge transfer (CT)
(should be sensitive
to choice of functional)

Energy transfer (ET)
(should be insensitive to
choice of functional)

* P. Cudazzo, F. Sottile, A. Rubio, and M. Gatti, "Topical Review: Exciton dispersion in molecular Solids," *J. Phys. Condens. Matter* **27**, 113204 (2015); P. Cudazzo, M. Gatti, A. Rubio, and M. Gatti, "Frenkel versus charge-transfer exciton dispersion in molecular crystals", *Phys Rev. B* **88**, 195152 (2013).

UPPER (1)

LOWER (2)

$\vec{\mu}_{HL} = \langle H|z|L \rangle$

$L = b_{3g}(\pi^*)$

B_{1u}

$H = b_{2u}(\pi)$

$\psi_H(r)\psi_L(r)$

ORBITAL ENERGY

$$\Psi_{B_{1u}} = c_1 \, {}^1(H, L+1) + c_2 \, {}^1(H-1, L) \qquad \text{(1)}$$

$$\Psi_{B_{1u}} = \frac{c_1 + c_2}{\sqrt{2}} \mathrm{ET}_{12} + \frac{c_1 - c_2}{\sqrt{2}} \mathrm{CT}_{12} \qquad \text{(2)}$$

$$\mathrm{ET}_{12}^{+} = \frac{1}{\sqrt{2}} \left[{}^1(H_1, L_1) + {}^1(H_2, L_2) \right] \text{ (3)} \qquad \mathrm{CT}_{12} = \frac{1}{\sqrt{2}} \left[{}^1(H_1, L_2) + {}^1(H_2, L_1) \right] \text{(4)}$$

Let's try to understand how this works ... "simply"!
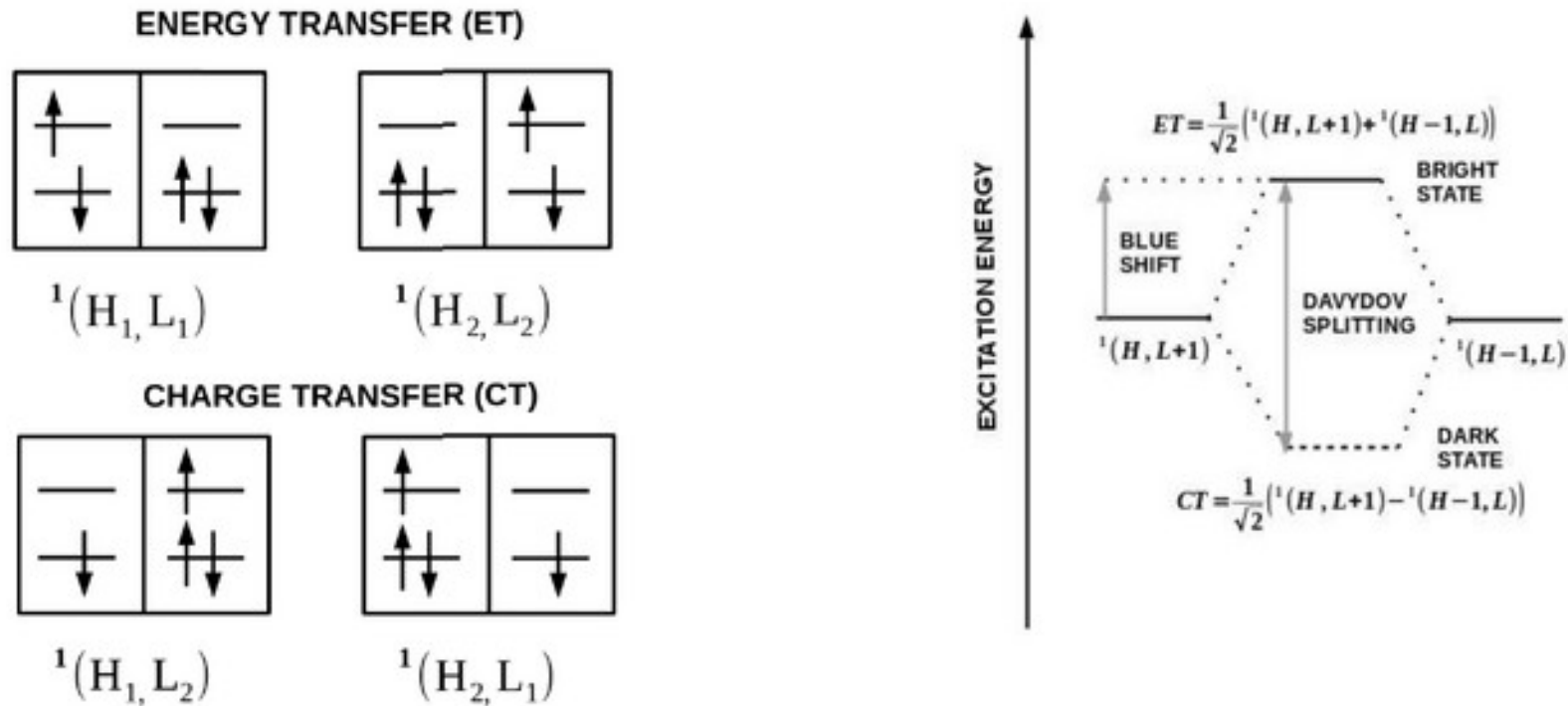
$$\Psi = c_1{}^1(H, L+1) + c_2{}^1(H-1, L) \quad \text{(1)}$$

$$\Psi = \frac{c_1 + c_2}{\sqrt{2}} \text{ET}_{12} + \frac{c_1 - c_2}{\sqrt{2}} \text{CT}_{12} \quad \text{(2)}$$

$$\text{ET}_{12} = \frac{1}{\sqrt{2}}\left[{}^1(H_1, L_1) + {}^1(H_2, L_2)\right] \text{(3)} \qquad \text{CT}_{12} = \frac{1}{\sqrt{2}}\left[{}^1(H_1, L_2) + {}^1(H_2, L_1)\right] \text{(4)}$$

Three Stacked Ethylene Molecules!

$$L+2=\frac{1}{2}\left(L_1+\sqrt{2}L_2+L_3\right)=b_{3g}$$

$$L+1=\frac{1}{\sqrt{2}}\left(L_1-L_3\right)=b_{1u}$$

$$L=\frac{1}{2}\left(L_1-\sqrt{2}L_2+L_3\right)=b_{3g}$$

$$H=\frac{1}{2}\left(H_1+\sqrt{2}H_2+H_3\right)=b_{2u}$$

$$H-1=\frac{1}{\sqrt{2}}\left(H_1-H_3\right)=a_g$$

$$H-2=\frac{1}{2}\left(H_1-\sqrt{2}H_2+H_3\right)=b_{2u}$$
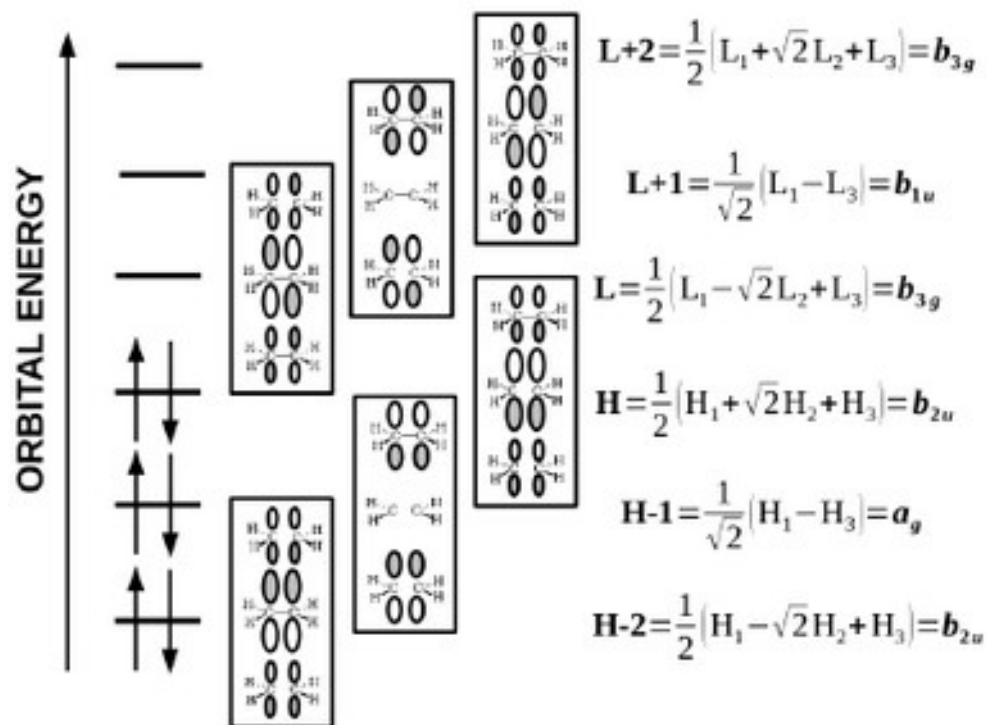
$$
\begin{aligned}
\Psi = &\; c_1 \,^1(H,L) \\
&+ \frac{3c_2 + 2c_3 + 3c_4}{2\sqrt{6}}\left(\frac{\mathrm{ET}_{12} + \mathrm{ET}_{23}}{\sqrt{3}}\right) \\
&+ \sqrt{\frac{2}{3}}c_3 \left\{ \frac{\sqrt{3}}{2}\left[\mathrm{ET}_{13} - \frac{1}{3}\left(\mathrm{ET}_{12} + \mathrm{ET}_{23}\right)\right]\right\} \\
&+ \frac{c_2 - c_4}{\sqrt{2}}\left(\frac{\mathrm{CT}_{12} + \mathrm{CT}_{23}}{\sqrt{2}}\right) \\
&+ \frac{c_2 - 2c_3 + c_4}{2\sqrt{2}}\mathrm{CT}_{13} \\
&+ c_5 \,^1(H-2, L+2),
\end{aligned}
$$

We can apply this to stacked pentacene!!

DS

DS

Model P5   Model P4

Model P3   Model P2

Model P1

$$ET = \frac{1}{\sqrt{2}}\left(^1(H,L+1)+^1(H-1,L)\right)$$

$$CT = \frac{1}{\sqrt{2}}\left(^1(H,L+1)-^1(H-1,L)\right)$$

BRIGHT STATE

BLUE SHIFT

DAVYDOV SPLITTING

$^1(H,L+1)$ $^1(H-1,L)$

DARK STATE

EXCITATION ENERGY

TD-LDA/6-31G(d,p)   TD-B3LYP/6-31G(d,p)

1.67 1.69 1.67   1.96 2.00 1.96

1.20   1.69

TD-CAM-B3LYP/6-31G(d,p)   TD-HF/6-31G(d,p)

2.32 2.54 2.32   2.53 3.73 2.53

2.37   2.62
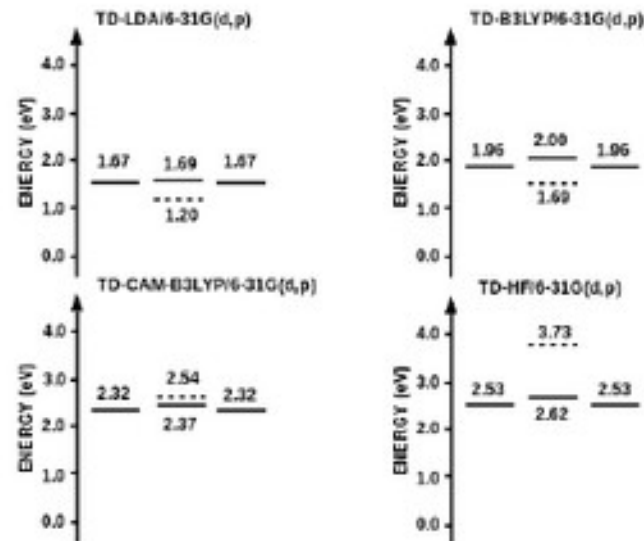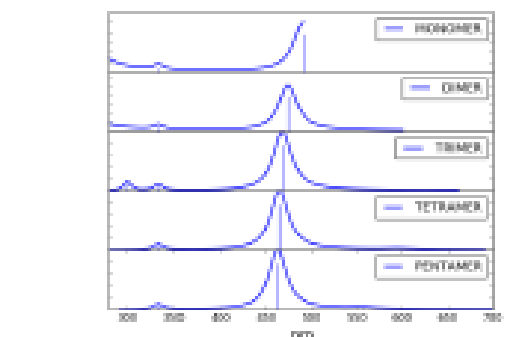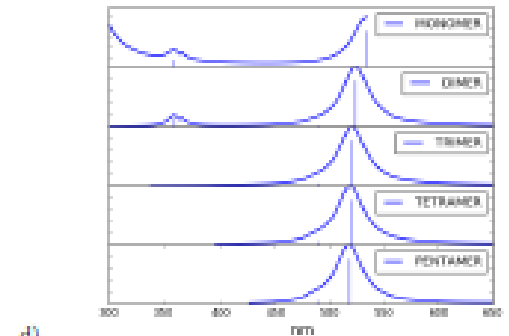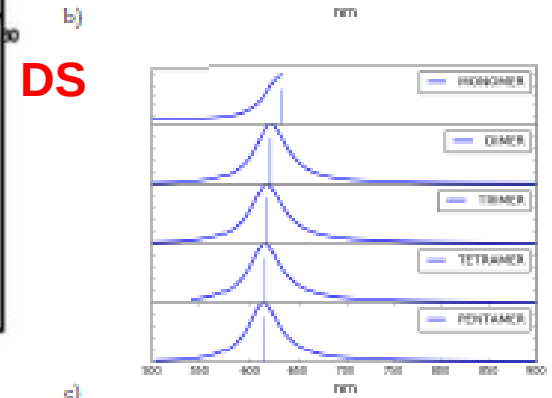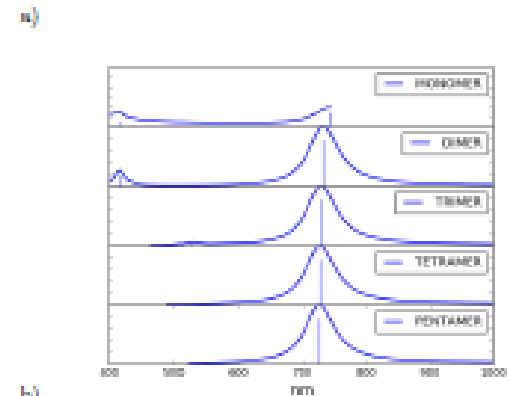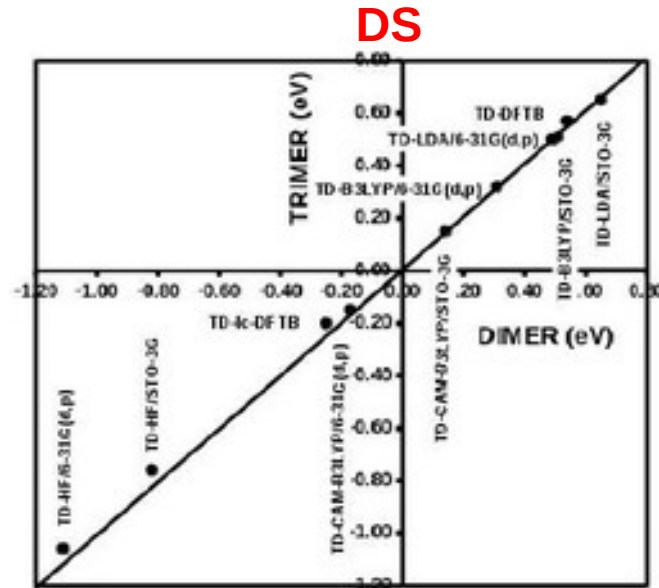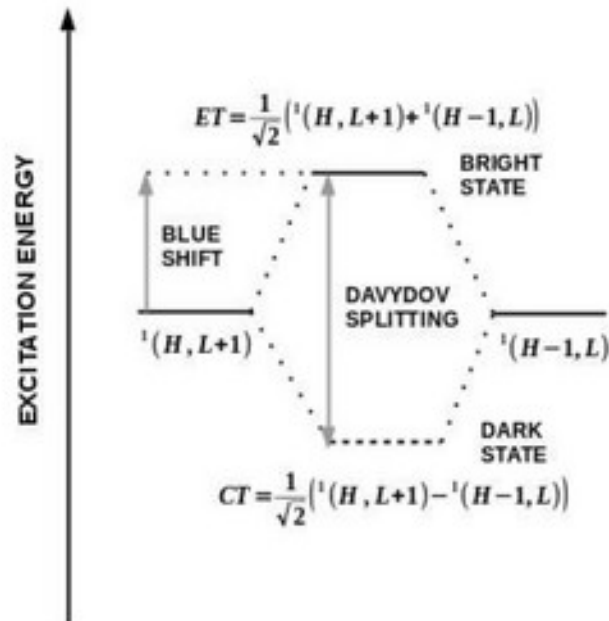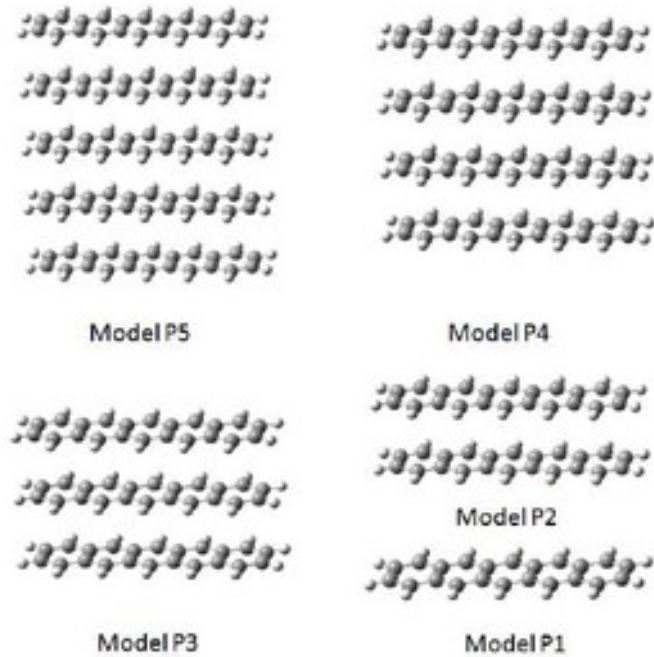
Reality Check: Herringbone Pentacene
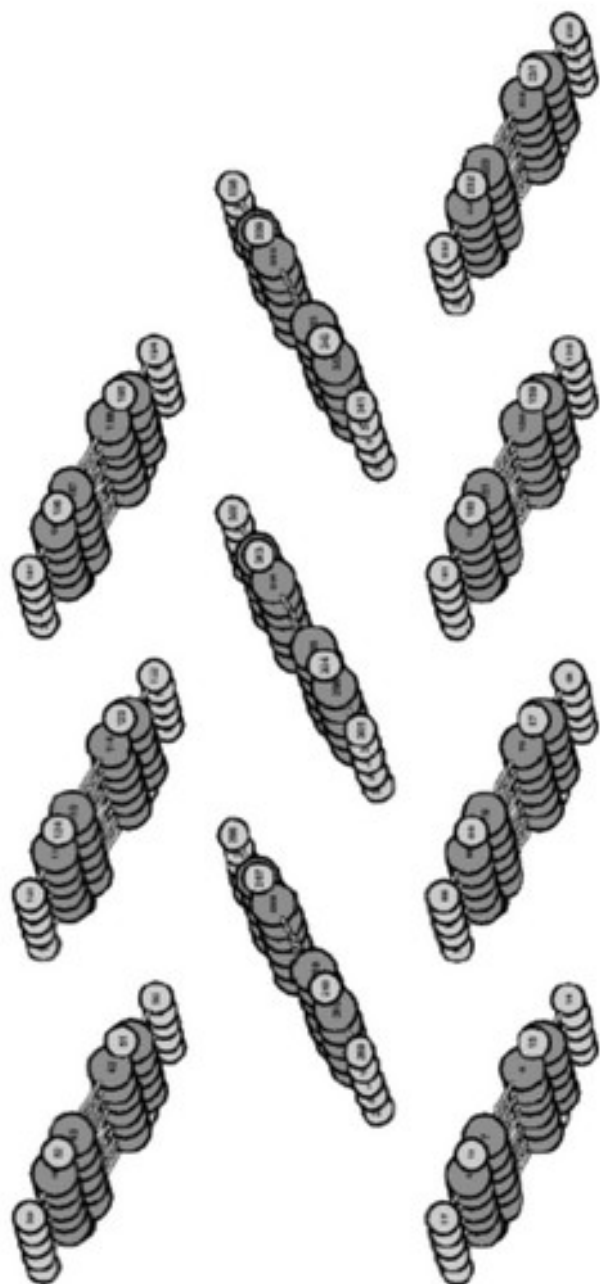
TD-B3LYP/6-31G(d,p)

TD-DFTB

TD-CAM-B3LYP/6-31G(d,p)

TD-lc-DFTB
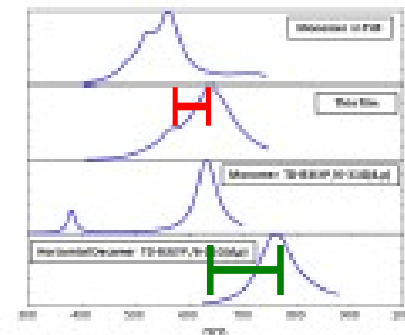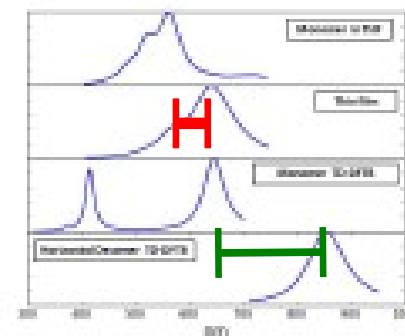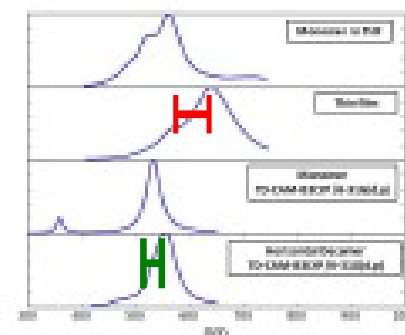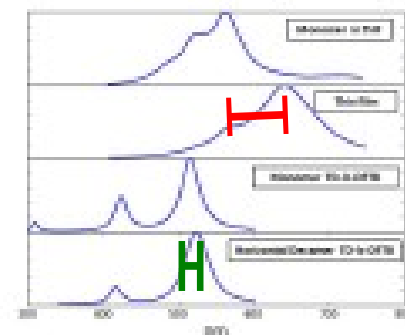
I. MOTIVATION
II. GROUND-STATE THEORY
III. QUANTUM CHEMISTRY FOR EXCITED STATES
IV. TD-DFT
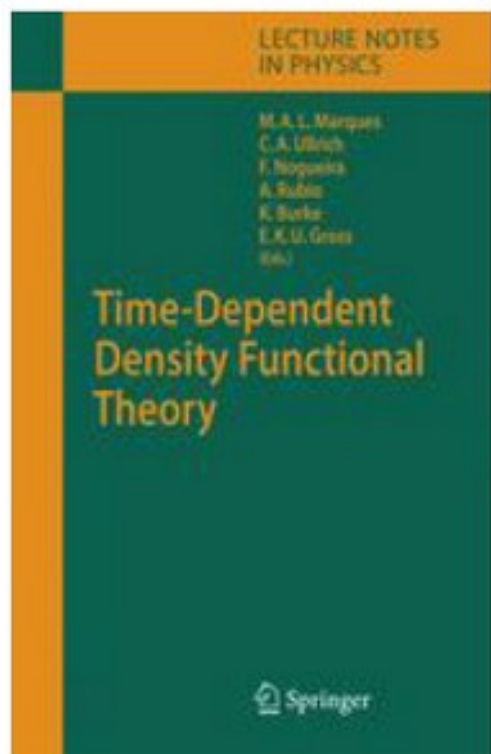V. HOW WELL DOES IT WORK IN PRACTICE?
VI. CONCLUSION

There is no shortage of quantum chemistry and quantum physics programs which allow you to perform TD-DFT calculations. Why not try it out for yourself?
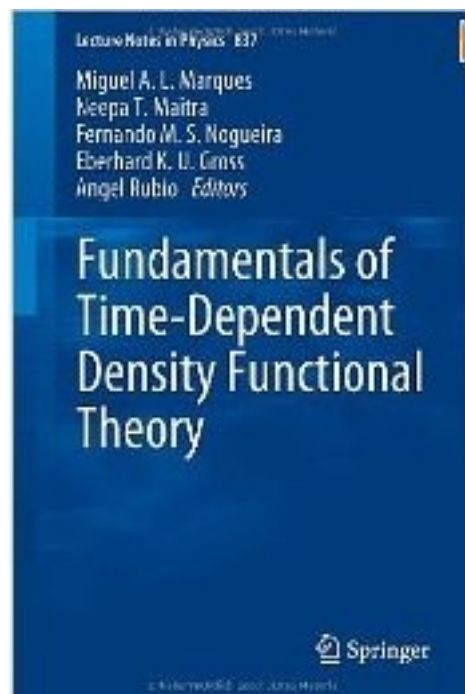

师傅领进门，修行在个人 [師傅領進門，修行在個人]
Shī fu lǐng jìn mén, xiū xíng zài gè rén.
Teachers open the door. You enter by yourself.
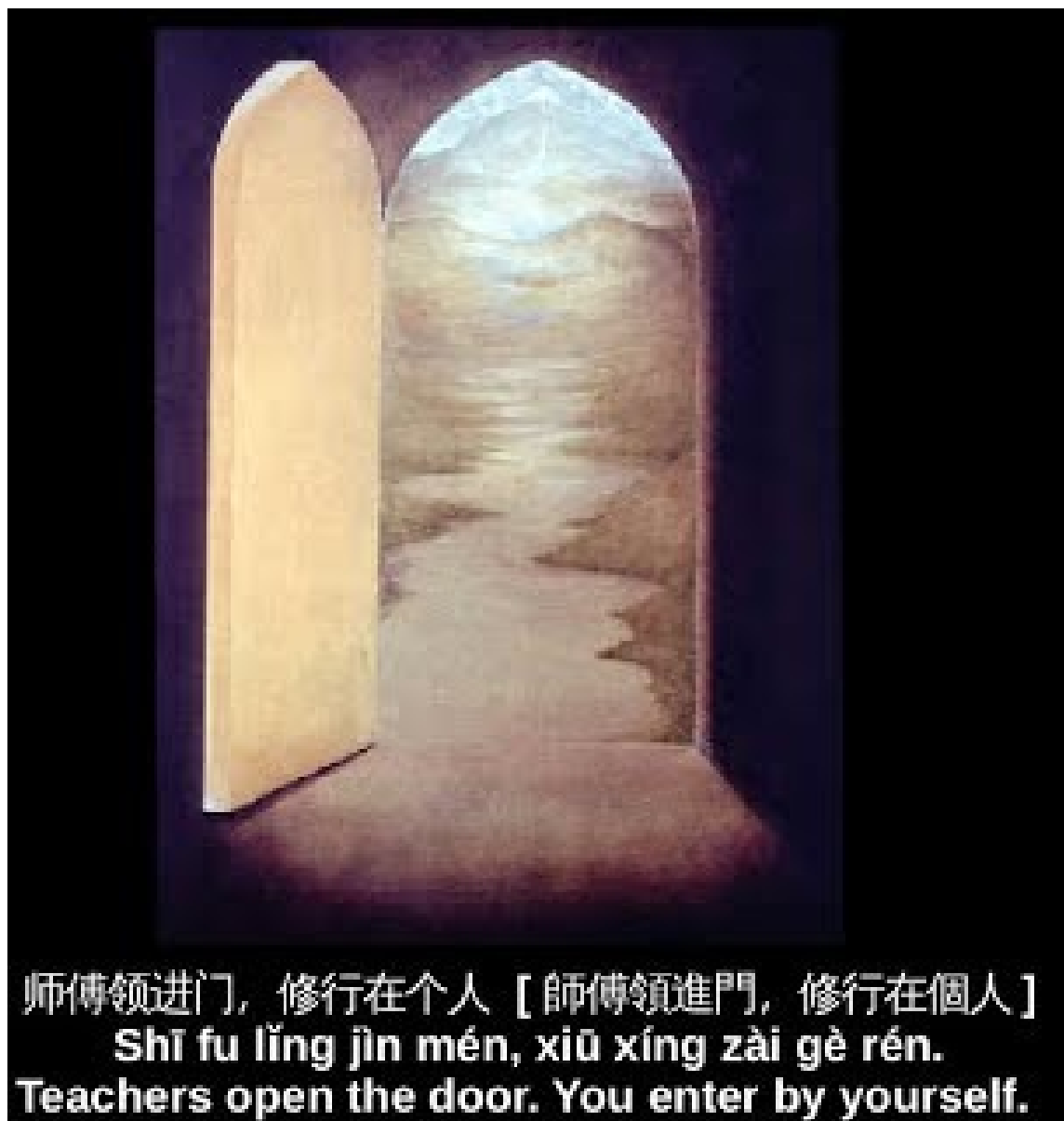
To learn more about TD-DFT ...

RECENT BOOKS ON TD-DFT

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).

Book:
Fundamentals of Time-Dependent Density-
Functional Theory, edited by M. Marques,
N. Maitra, F. Noguiera, E.K.U. Gross, and
A. Rubio, *Lecture Notes in Physics*, Vol. 837
(Springer: Berlin, 2011)
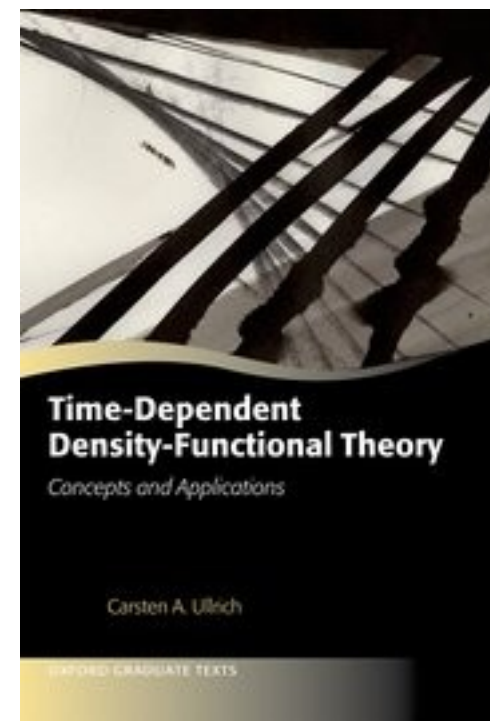
Book:
Time-Dependent Density Functional Theory,
C.A. Ullrich (Oxford: 2012)

Review

Time-dependent density-functional theory for molecules and molecular solids

Mark E. Casida [*]

Laboratoire de Chimie Théorique, Département de Chimie Moléculaire (DCM, UMR CNRS/UJF 5250), Institut de Chimie Moléculaire de Grenoble (ICMG, FR2607), Université Joseph Fourier (Grenoble I), 301 rue de la Chimie, BP 53, F-38041 Grenoble Cedex 9, France

Progress in Time-Dependent Density-Functional Theory

M.E. Casida and M. Huix-Rotllant

Laboratoire de Chimie Théorique, Département de Chimie Moléculaire, Institut de Chimie Moléculaire de Grenoble, Université Joseph Fourier, BP 53, F-38041 Grenoble Cedex 9, France; email: mark.casida@ujf-grenoble.fr, miquel.huix@ujf-grenoble.fr

THANK YOU

ASANTE

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شكرا

MERCI