

Time-Dependent Density-Functional Theory

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ASESMA
Addis Ababa, Ethiopia
26 October 2018
1 hour 45 minutes



Rhône-Alpes Associated Node

OUTLINE

I. PRE-AMBLE

II. THIS COURSE

III. QUANTUM CHEMISTRY FOR EXCITED STATES

IV. TD-DFT FOR EXCITED STATES

V. CONCLUSION

O'Caiside (Irish Gaelic *casadh* twist --- reference to curly hair?)

Cassidy



Frangas non flectas.
(You may break me but never bend me.)

Cassiday
Cassidy
Casada
Casida
etc. etc.

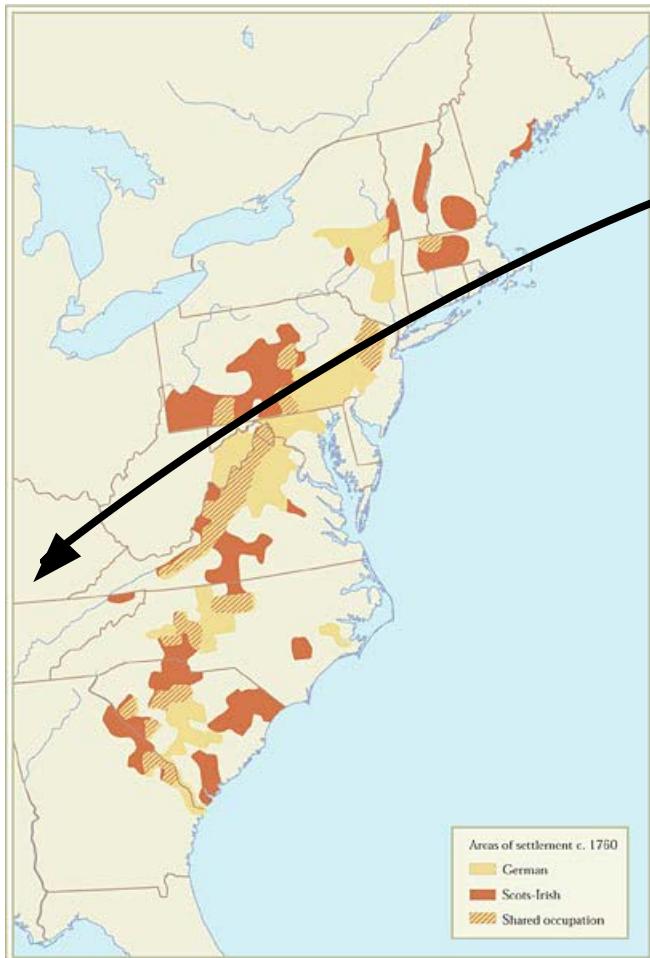
*But they are
all pronounced
similarly!*



County Fermanagh

WHAT GENEALOGY TELLS US

Scotch-Irish Immigration



Scotch-Irish
settlements
ca. 1760

Abraham Casada
+
Rhoda Hall
1774 Kentucky

Children:
John Casada (Cherokee)
Elizabeth Cassday
Issac Newton Cassday
Reuben Casada
Pheobe Cassday
Martin Casada
Nancy Cassday
Mary Cassday



County Fermanagh

INTEGRATION OF THE BERKELEY SCHOOL SYSTEM (10 September 1968)

Berkeley's School Integration Program Proceeds Smoothly

City Will Become First in Nation to Fully Desegregate by Using Buses to Change Unusual Sociogeographic Patterns

City Will Become First in Nation to Fully Desegregate by Using **Buses** To Change its Unusual Sociogeographic Patterns

BY JACK MCCLURE
Times-Mirror Staff

One of the things about Berkeley which brings word spreading is that the sociogeographic status of residence can be placed on a sliding scale which corresponds almost exactly to the elevation along the East San Francisco Bay Hillsides.

The poorest live near the sea level along the bay shore, with income levels rising gradually as elevation increases up the Berkeley Hills to

Berkeley schools through an age which have been experiencing desegregation and integration and creation of the nation of the United States finally the door to desegregation.

Total integration planned by



Martin Luther King Jr. even testified that, when it came to the project of school desegregation, it was only through the example of Berkeley that "Hope returned to my soul and spirit."

ASESMA 2018, Addis Ababa

<http://revolution.berkeley.edu/projects/public-schools/>

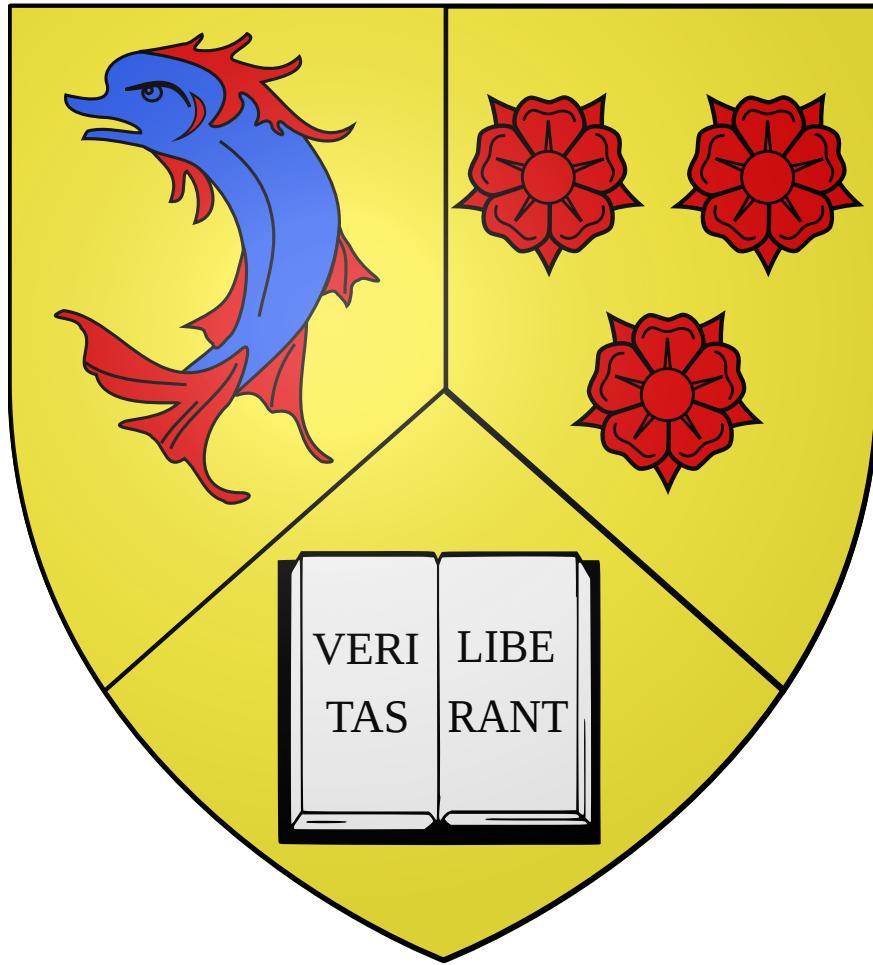
FRANCE (aka* “the hexagon”)



PARIS,
center of
the world
(or at least
of France)



* aka = also known as

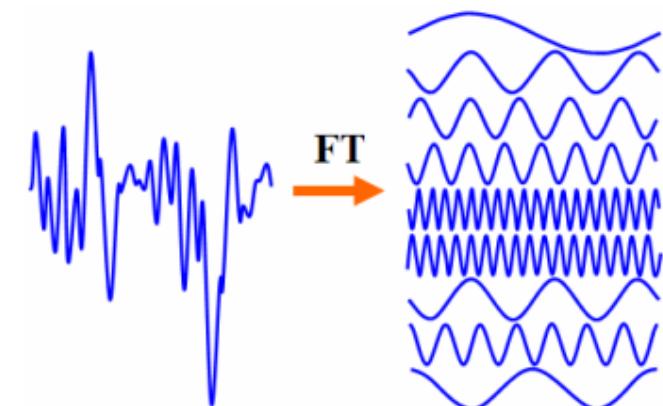


“The truth will set you free”

Université de Grenoble

Established: 1339

Recreated: 1809 Napolean appointed
Joseph Fourier rector of the university.



Dissolved: during the reorganization
of 1970 to create Grenoble I, II, III,
and the INPG.

Currently:

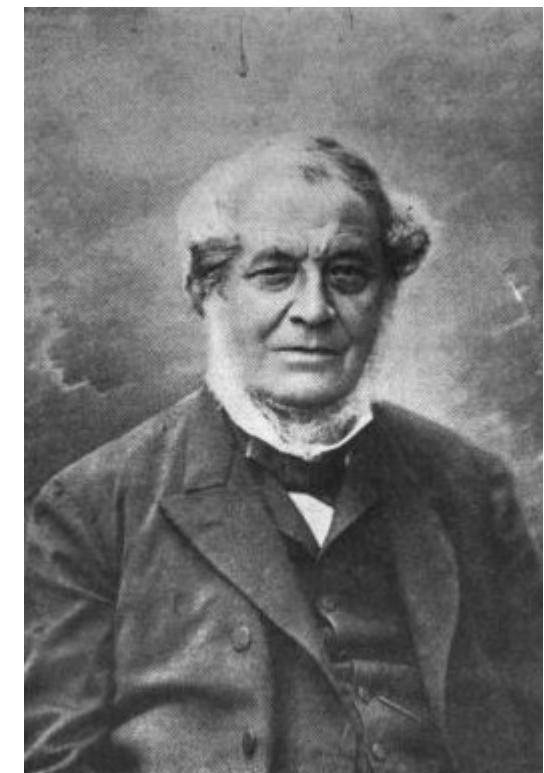
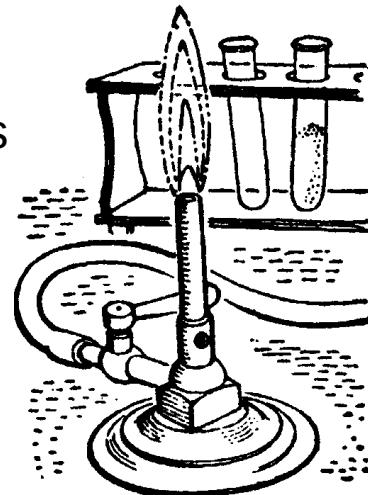


I AM A CHEMIST ON THE BORDER-LINE WITH PHYSICS

*“Ein Chemiker, der nicht gleichzeitig Physiker ist,
ist gar nichts.”**

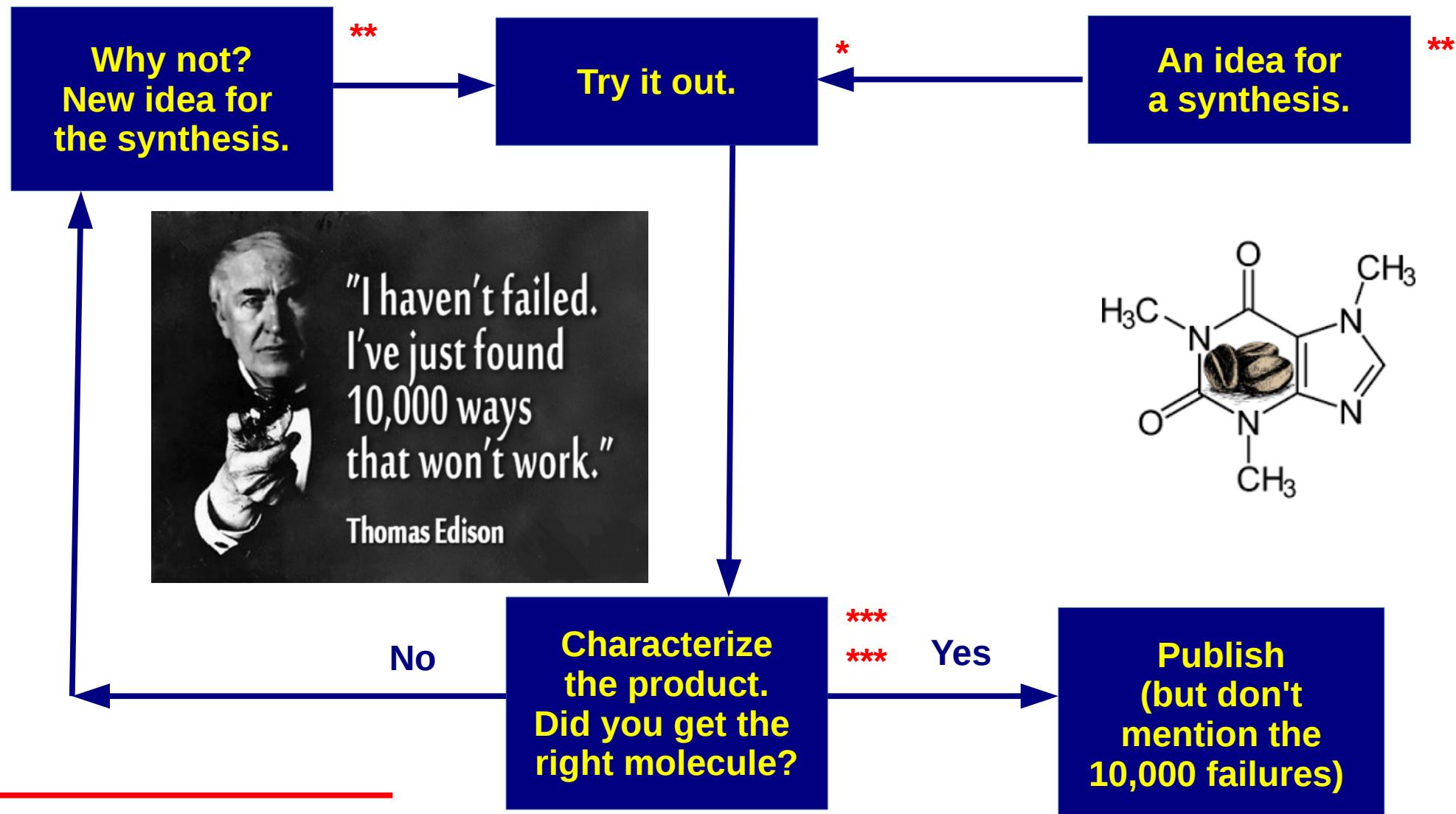
Robert Eberhard Wilhelm Bunsen (1811-1899)

- 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.”

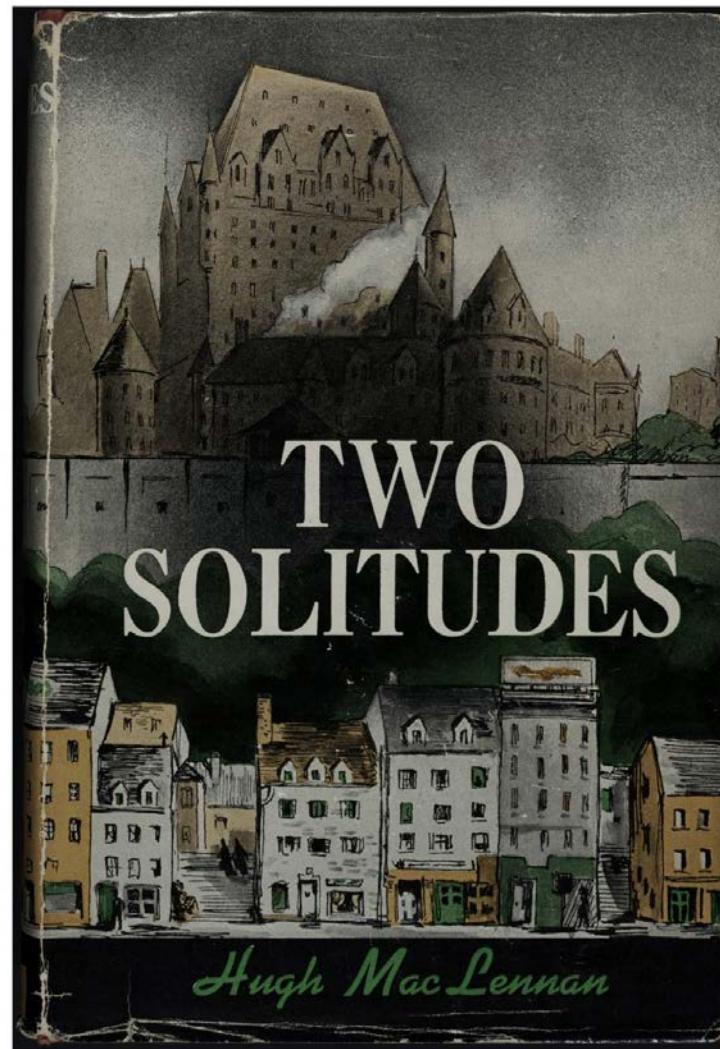
CHEMISTRY: “Better things for better living through chemistry”
Dupont Chemical Motto: 1935-1982



* Physical chemistry and theoretical chemistry are here.

The Canadian Experience

French

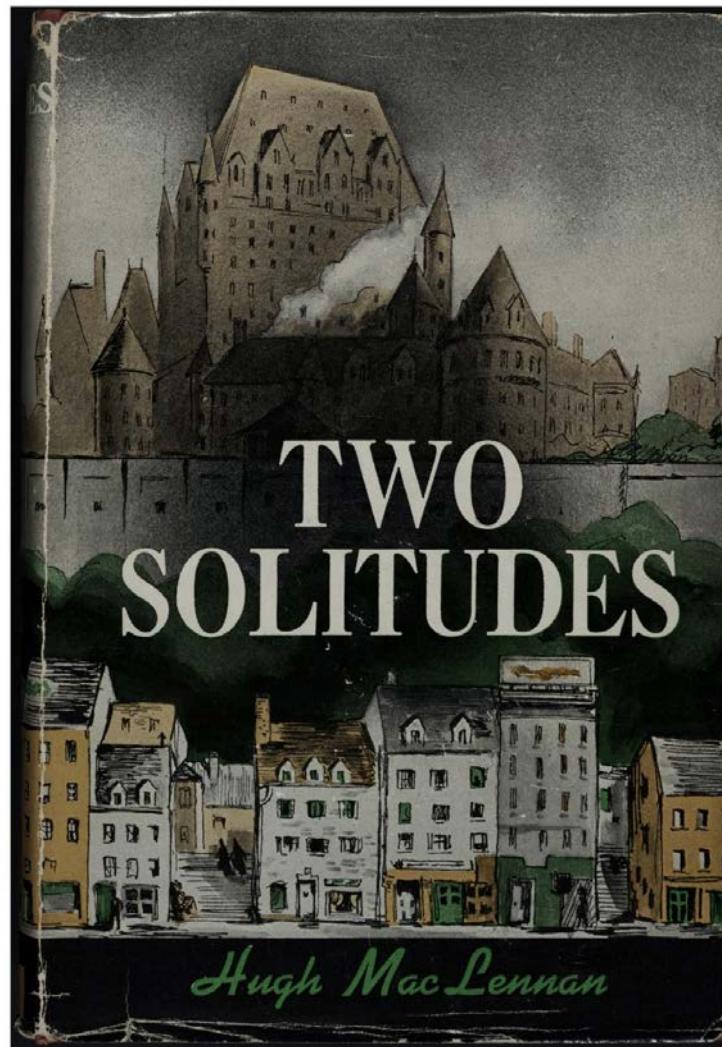


English

The Physical Chemist/Chemical Physicist Experience

Quantum Chemistry

Condensed Matter Physics



When a Quantum Chemist says, then he or she means ...

***Ab initio* theory** – We are going to solve everything from the beginning. This is Supposed to be a first principles theory with a hierarchy of increasingly accurate approximate solutions to Schrödinger's equation usually beginning with the Hartree-Fock approximation. The only empirical parameters allowed are:

$$\hbar, m_e, e$$

Alphabet soup: HF, CI, MPn, MBPT, GF, ADC, CC, ...

Density-functional theory (DFT) – Formally exact. In practice, DFT is less systematic than *ab initio* theory, but seeks *ab initio* accuracy. A handful of empirical parameters suffice for the whole periodic table. (Often called *ab initio* by physicists.)

Alphabet soup: LDA, BLYP, B3LYP, CAM-B3LYP, ...

Semi-empirical theory – Most approximate of the three approaches. Typically there Are several parameters per atom in the periodic table and even per pair of atoms.

Alphabet soup: ZINDO, DFTB

**CHEMISTRY
SPOKEN
HERE**

**PHYSICS
SPOKEN
HERE**

**PHYSICAL CHEMISTRY/CHEMICAL PHYSICS
SPOKEN
HERE**

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I want to give you an understanding of the mathematics and the physics behind the programs that do TD-DFT.

Goals :

- coffee beans icon Keep this presentation as simple as possible (Masters level).
- coffee beans icon Just talk about calculating spectra.
- coffee beans icon But never be afraid to do something hard if it is also useful.

“WHY DO WE NEED TO STUDY MORE THAN DFT?”

- coffee beans icon Because DFT is intended to extend *ab initio* accuracy to larger systems than can normally be treated by *ab initio* methods. “Know the enemy.”
- coffee beans icon Because DFT and *ab initio* theory share many common algorithms. e.g., double hybrid density functionals such as B2PLYP
- coffee beans icon Because DFT is limited to the ground stationary state and TD-DFT looks a whole lot like a the BSE.
- coffee beans icon Because sometimes DFT is not enough and you really must add a semi-empirical component (e.g., DFT-U, Grimme's vdw correction) or do *ab initio* calculations.

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DIRAC'S FAMOUS CHALLENGE

“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, No. 792 (6 April 1929)

THE PART OF THE QUOTATION WHICH IS RARELY SEEN

“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.”

BORN-OPPENHEIMER APPROXIMATION

$$\left(\hat{T}_n + V_I(\mathbf{R}) \right) \Psi_{I,v}^n(\mathbf{R}, t) = i \frac{\partial}{\partial t} \Psi_{I,v}^n(\mathbf{R}, t) \quad (1)$$

$$V_I(\mathbf{R}) = E_I^e(\mathbf{R}) + V_{nn}(\mathbf{R}) \quad (2)$$

$$\hat{H}_e(\mathbf{r}; \mathbf{R}) \Psi_I^e(\mathbf{x}; \mathbf{R}) = E_I^e(\mathbf{R}) \Psi_I^e(\mathbf{x}; \mathbf{R}) \quad (3)$$

$$\hat{H}_e(\mathbf{r}; \mathbf{R}) = \hat{T}_e(\mathbf{r}) + V_{ne}(\mathbf{r}; \mathbf{R}) + V_{ee}(\mathbf{r}) \quad (4)$$

$$\Psi_{I,v}^{ne}(\mathbf{x}, \mathbf{R}, t) = \Psi_I^e(\mathbf{x}; \mathbf{R}) \Psi_{I,v}^n(\mathbf{R}, t) \quad (5)$$

Let us concentrate on the electronic problem!

$$\hat{H}_e(\mathbf{r}; \mathbf{R}) \Psi_I^e(\mathbf{x}; \mathbf{R}) = E_I^e(\mathbf{R}) \Psi_I^e(\mathbf{x}; \mathbf{R}) \quad \text{(1)}$$

$$\hat{H} \Psi_I(\mathbf{x}) = E_I \Psi_I(\mathbf{x}) \quad \text{(2)}$$

THE VARIATIONAL PRINCIPLE*

We want to solve

$$\hat{H}\Psi_I = E_I \Psi_I; E_0 \leq E_1 \leq E_2 \leq \dots \quad (1)$$

We will use the variational principle

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

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

* Quantum Chemistry 101 ?

THE PAULI PRINCIPLE

Electrons are fermions:

$$\Psi(1, 2, \dots, j, \dots, i, \dots, N) = -\Psi(1, 2, \dots, i, \dots, j, \dots, N) \quad (1)$$

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

The simplest function satisfying equation (1) is a **Slater determinant**:

$$\Phi = |\Psi_1, \Psi_2, \dots, \Psi_N| = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \Psi_1(1) & \Psi_2(1) & \cdots & \Psi_N(1) \\ \Psi_1(2) & \Psi_2(2) & \cdots & \Psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \Psi_1(N) & \Psi_2(N) & \cdots & \Psi_N(N) \end{bmatrix} \quad (3)$$

where $\langle \Psi_i | \Psi_j \rangle = \delta_{i,j}$ (4)

FOR A (FICTITIOUS) SYSTEM OF NONINTERACTING ELECTRONS

$$\hat{h}^0 \psi_i = \epsilon_i^0 \psi_i ; \quad \epsilon_1^0 \leq \epsilon_2^0 \leq \epsilon_3^0 \leq \dots \quad (1)$$

$$\hat{H}^0 = \sum_{i=1,N} \hat{h}^0(i) \quad (2)$$

$$\hat{H}^0 \Psi_0 = E_0 \Psi_0 \quad (3)$$

$$E_0^0 = \sum_{i=1,N} \epsilon_i^0 \quad (4)$$

$$\Psi_0 = |\psi_1, \psi_2, \dots, \psi_N| \quad (5)$$

ROGUES GALLERY



Wolfgang
PAULI



John C. SLATER



Douglas Rayner
HARTREE



Vladimir
FOCK



Charlotte FROESE FISCHER*
(applied mathematician and computer scientist
who worked on multiconfigurational Hartree-Fock)

The test function is a Slater determinant.

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

$$\hat{f} \psi_i = \epsilon_i \psi_i \quad (1)$$

The Fock operator:

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

Self-consistent field (SCF) :

$$\hat{v}_{SCF} = \underbrace{\nu_H + \hat{\Sigma}_x}_{\substack{\text{Physics notation}}} = \underbrace{\hat{J} - \hat{K}}_{\substack{\text{Chemistry notation}}} \quad (3)$$

Physics notation

Chemistry notation

THE SELF-CONSISTENT FIELD

Density matrix

$$\gamma(1,2) = \sum_i n_i \psi_i(1) \psi_i^*(2) \quad (1)$$

Density

$$\rho(1) = \sum_i n_i |\psi_i(1)|^2 \quad (2)$$

The Hartree (or Coulomb) potential

$$v_H(1) = \int \frac{\rho(2)}{r_{12}} d2 \quad (3)$$

The exchange self-energy (or exchange operator)

$$\hat{\Sigma}_x \varphi(1) = - \int \frac{\gamma(1,2)}{r_{12}} \varphi(2) d2 \quad (4)$$

HARTREE-FOCK (HF) ENERGY

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

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

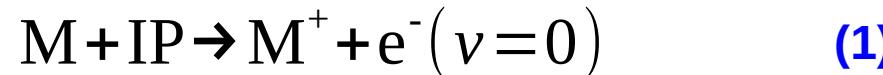
$$E_H = \frac{1}{2} \int \int \frac{\rho(1)\rho(2)}{r_{12}} d1 d2 \quad (3)$$

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

KOOPMANS' THEOREM*

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

Ionization potential (IP)



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

The occupied orbitals “see” N-1 electrons.

Electron affinity (EA)



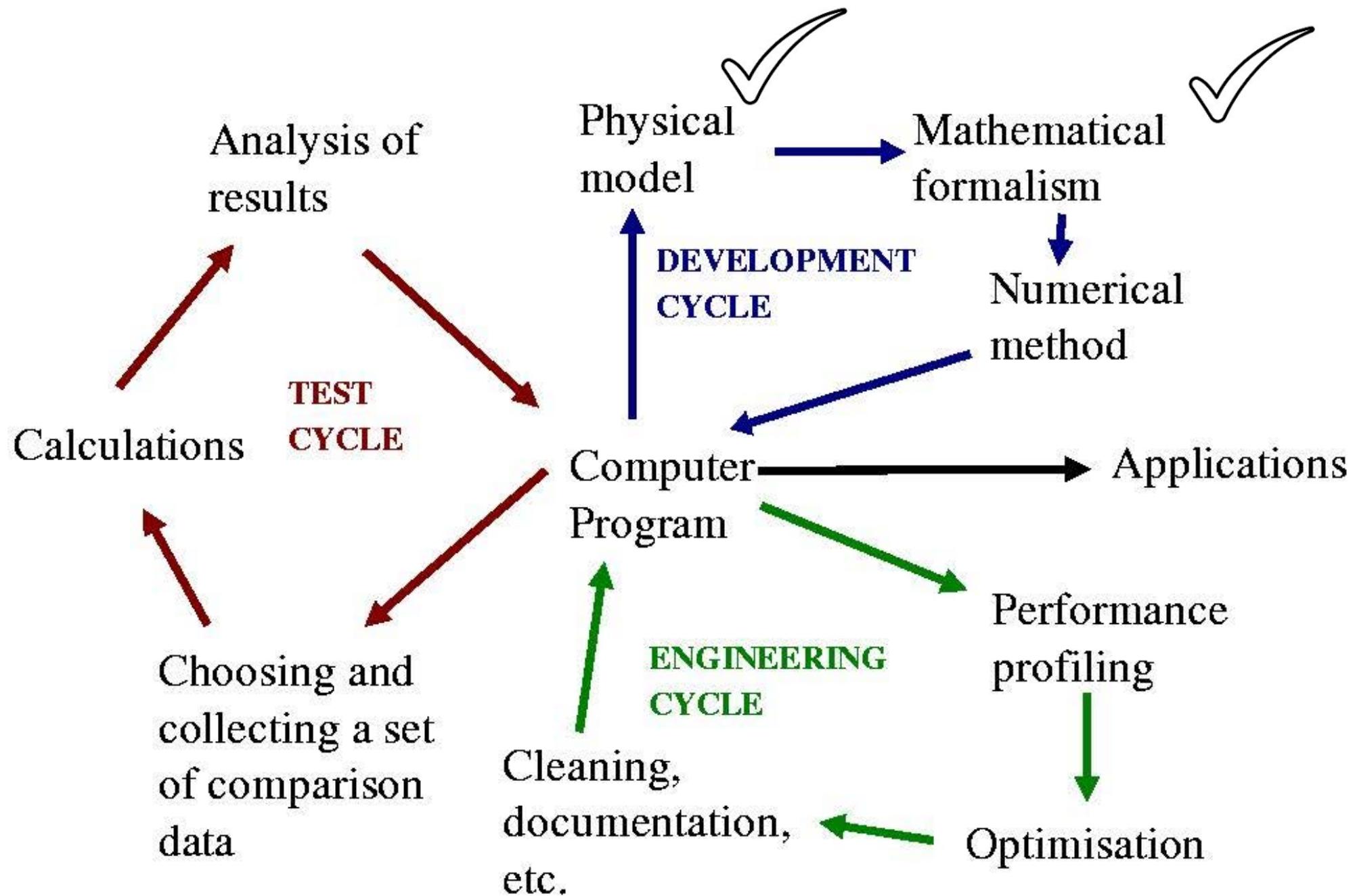
$$-EA_a = E_{N+1} (a^{+1}) - E_N = \epsilon_a \quad (4)$$

The unoccupied orbitals “see” N electrons.



Tjalling Charles
KOOPMANS

* T. Koopmans, "Über die Zuordnung von Wellenfunktionen und Eigenwerten zu den Einzelnen Elektronen Eines Atomes", *Physica* **1**, 104 (1934).



Linear Combination of Atomic Orbitals (LCAO) Theory

Want to solve the molecular orbital (MO) equation,

$$\hat{f} \psi_i = \epsilon_i \psi_i \quad (1)$$

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

$$\psi_i = \sum_v \chi_v c_{v,i} \quad (2)$$

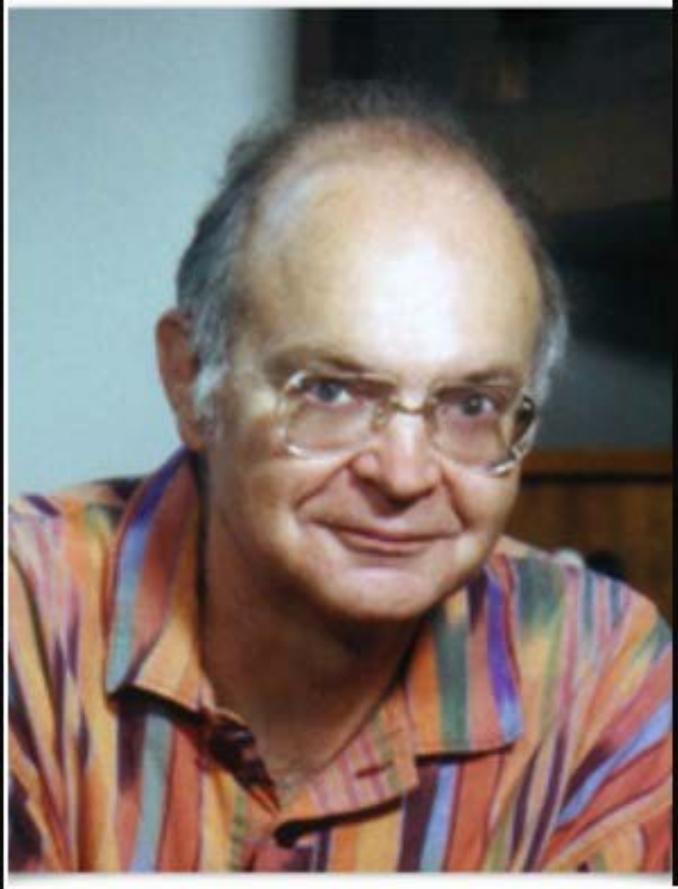
Either (i) rigorously by finding the MO coefficients $c_{v,i}$ by doing a variational minimization of the energy or (ii) heuristically by inserting Eq. (2) in Eq. (1) and projecting:

$$\sum_v \hat{f} \chi_v c_{v,i} \approx \epsilon_i \sum_v \chi_v c_{v,i} \quad (3)$$

$$\sum_v \langle \chi_u | \hat{f} | \chi_v \rangle c_{v,i} = \epsilon_i \sum_v \langle \chi_u | \chi_v \rangle c_{v,i} \quad (4a)$$

N equations in
N unknowns

$$f \vec{c}_i = \epsilon_i s \vec{c}_i \quad (4b)$$

A portrait photograph of Donald Knuth, an elderly man with glasses and a striped shirt.

An algorithm must be seen to be
believed.

— *Donald Knuth* —

AZ QUOTES

Per-Olov Löwdin's Solution

Solve $\mathbf{s} \vec{v}_i = \lambda_i \vec{v}_i$ (1) with $\vec{v}_i^+ \vec{v}_j = \delta_{i,j}$ (2)

Construct $\mathbf{s}^{-1/2} = \sum_i \vec{v}_i^+ \lambda_i^{-1/2} \vec{v}_i$ (3) and $\tilde{\mathbf{f}} = \mathbf{s}^{-1/2} \mathbf{f} \mathbf{s}^{-1/2}$ (4)

Then $\vec{c}_i = \mathbf{s}^{-1/2} \vec{d}_i$ (5) may be obtained by solving $\tilde{\mathbf{f}} \vec{d}_i = \epsilon_i \vec{d}_i$ (6)

because
$$\underbrace{(\mathbf{s}^{-1/2} \mathbf{f} \mathbf{s}^{-1/2})}_{\tilde{\mathbf{f}}} \underbrace{(\mathbf{s}^{+1/2} \vec{c}_i)}_{\vec{d}_i} = \epsilon_i \underbrace{(\mathbf{s}^{+1/2} \vec{c}_i)}_{\vec{d}_i}$$
 (7)



Upsala,
Sweden

Gainsville,
Florida,
USA ASEMSA 2018, Addis Ababa



28 OCTOBER 1916 - 6 OCTOBER 2000

CONFIGURATION INTERACTION (CI)

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!

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

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*”.

$$\Psi_{\text{test}} = \text{truncated CI} \quad (1)$$

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

$$\mathbf{H} \vec{C}_I = E_I \vec{C}_I \quad (2)$$

$$H = \begin{bmatrix} H_{0,0} & \vec{H}_{0,1}^+ & \cdots \\ \vec{H}_{0,1} & \mathbf{H}_{1,1} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} \quad (3a)$$

$$\vec{C}_I = \begin{pmatrix} C_0 \\ \vec{C}_2 \\ \vdots \end{pmatrix} \quad (4a)$$

$$H_{0,0} = \langle \Phi | \hat{H} | \Phi \rangle = E_{\text{HF}} \quad (3b)$$

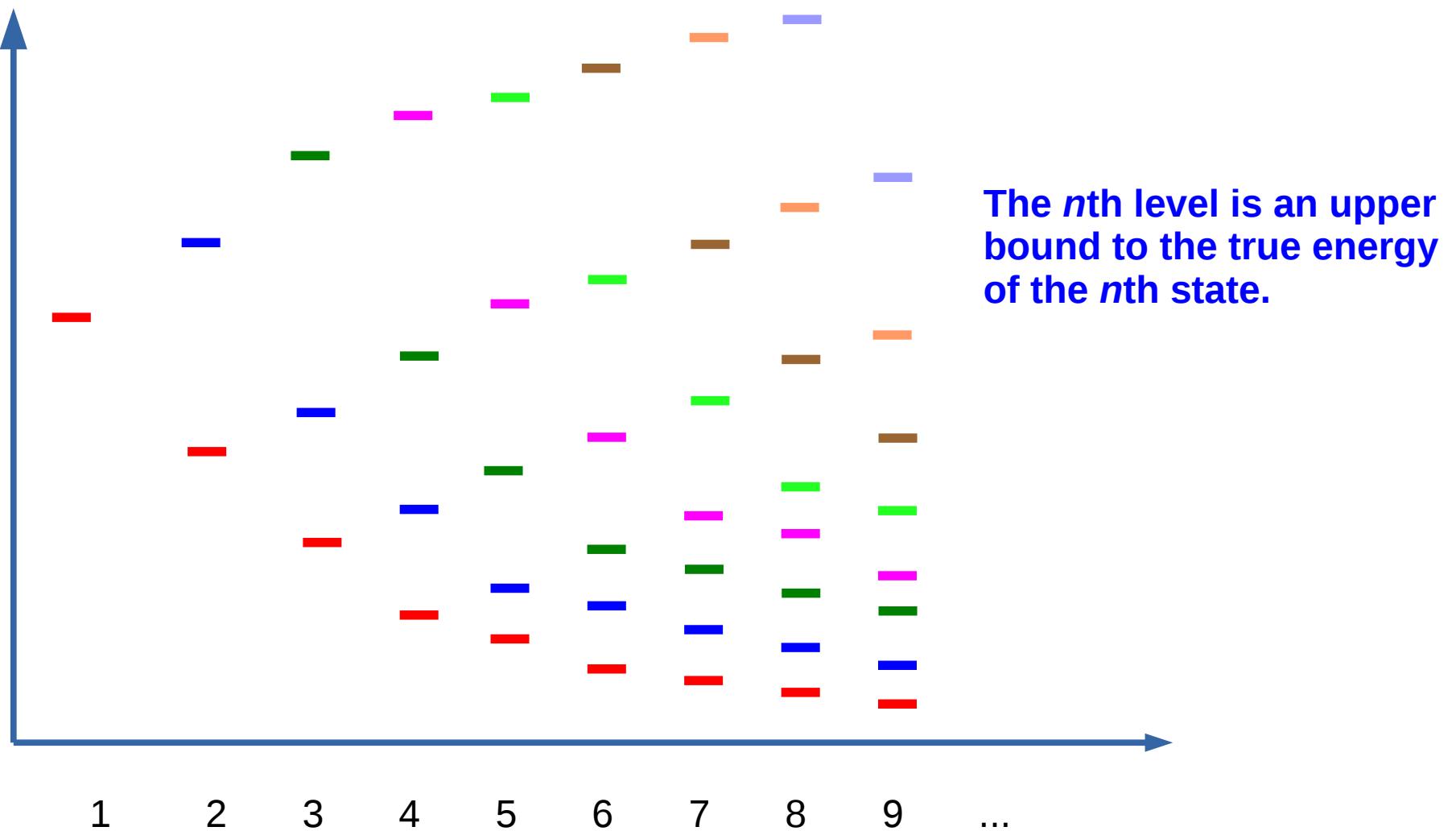
$$(\vec{C}_1)_{ai} = C_{ai} \quad (4b)$$

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

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

THE HYLLERAAS-UNDHEIM-MACDONALD or CAUCHY'S INTERLEAVING THEOREM

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



CONFIGURATION INTERACTION SINGLES (CIS)

$$\begin{bmatrix} H_{0,0} & \vec{H}_{0,1}^+ \\ \vec{H}_{0,1} & \mathbf{H}_{1,1} \end{bmatrix} \begin{pmatrix} \vec{C}_0 \\ \vec{C}_1 \end{pmatrix} = E \begin{pmatrix} \vec{C}_0 \\ \vec{C}_1 \end{pmatrix} \quad (1)$$

$$\begin{bmatrix} E_{HF} & \vec{0}^+ \\ \vec{0} & \mathbf{A} + E_{HF} \end{bmatrix} \begin{pmatrix} \vec{C}_0 \\ \vec{C}_1 \end{pmatrix} = E \begin{pmatrix} \vec{C}_0 \\ \vec{C}_1 \end{pmatrix} \quad (2)$$

$$\mathbf{A} \vec{C}_1 = (E - E_{HF}) \vec{C}_1 = \omega \vec{C}_1 \quad (3)$$

How do we solve such a big eigenvalue equation?

Block Davidson Diagonalsation



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 $A \vec{x} = a \vec{x}$

1) guess \vec{x}_0

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

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

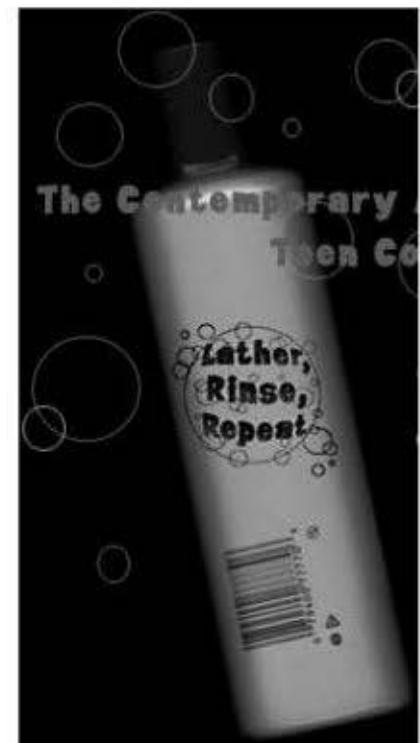
4) orthonormalize with respect to \vec{x}_0 to obtain \vec{x}_1

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

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

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

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					

Exact up to numerical convergence.
Not an approximation!

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

ALTERNATIVE KRYLOV-SPACE METHOD: LANCZOS ALGORITHM

Want to solve

$$\mathbf{A} \vec{x} = a \vec{x}$$

Orthonormalize a special basis set by Gramm-Schmidt orthogonalization

$$\vec{x}_0 \quad (\text{initial guess})$$

$$\vec{x}_1 = \mathbf{A} \vec{x}_0$$

$$\vec{x}_2 = \mathbf{A} \vec{x}_1 = \mathbf{A}^2 \vec{x}_0$$

Etc.

This gives a tridiagonal matrix whose eigenvalue problem is much easier to solve.

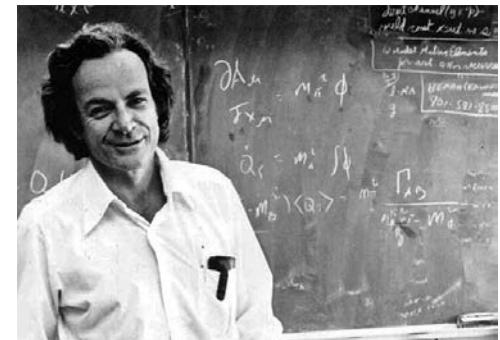
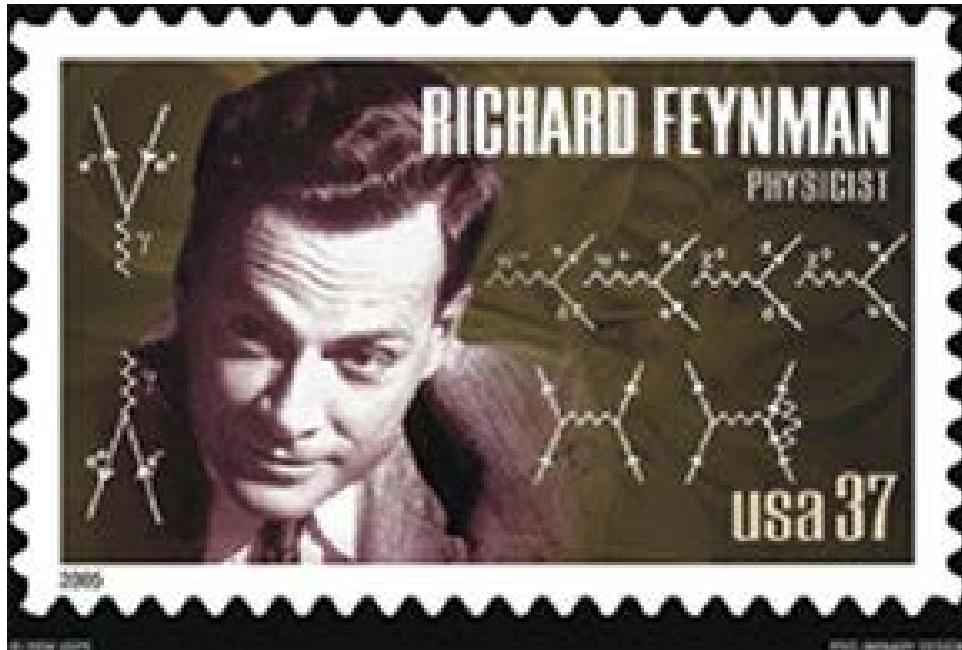
HOW TO FIND A FORMULA FOR THE A MATRIX?

$$(\mathbf{H}_{1,1})_{ai,bj} = \delta_{i,j} \delta_{a,b} E_{\text{HF}} + A_{ai,bj} \quad (1)$$

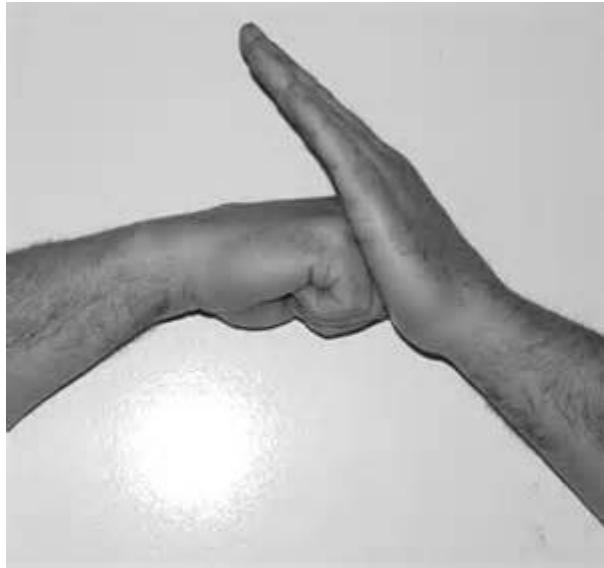
It is “easy” with **Second Quantization**.

Answer:

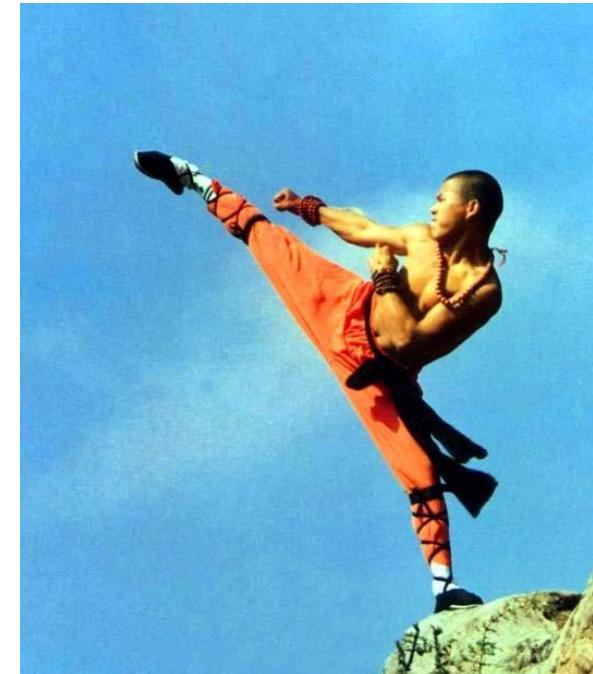
$$A_{ai,bj} = \delta_{i,j} \delta_{a,b} (\epsilon_a - \epsilon_i) + [ai|jb] - [ab|ji] \quad (2)$$



His car from the 1970s.



Only for Shaolin masters!?
(I don't think so.)



For us, this is just a way to make it easier to do the algebra needed when working with antisymmetric wave functions.

FUNDAMENTAL IDEAS

The physical vacuum $\Phi = |\psi_1, \psi_2, \dots, \psi_N|$ (1)

Creation operator $\hat{a}_r^+ \Phi = |\psi_r, \psi_1, \psi_2, \dots, \psi_N|$ (2)

Annihilation operator

$$\hat{a}_r \hat{a}_r^+ \Phi = \hat{a}_r |\psi_r, \psi_1, \psi_2, \dots, \psi_N| = |\psi_1, \psi_2, \dots, \psi_N| = \Phi \quad (3)$$

Lazy notation:

$$r = \hat{a}_r \quad (4) \qquad r^+ = \hat{a}_r^+ \quad (5)$$

Anticommutation rules:

$$[r, s]_+ = rs + sr = 0 \quad (6) \qquad [r^+, s^+]_+ = r^+ s^+ + s^+ r^+ = 0 \quad (7)$$

$$[r, s^+] = rs^+ + s^+ r = \delta_{r,s} \quad (8)$$

SECOND-QUANTIZED OPERATORS

$$\hat{H} = \sum_{r,s} h_{r,s} r^+ s + \frac{1}{2} \sum_{p,q,r,s} [pr|qs] p^+ q^+ s r \quad (1)$$

$$h_{r,s} = \langle \psi_r | \hat{h} | \psi_s \rangle \quad (2)$$



Mullikan “charge cloud” notation:

$$[pq|r s] = \int \int \psi_p^*(1) \psi_q(1) \frac{1}{r_{12}} \psi_r^*(2) \psi_s(2) d1 d2 \quad (3)$$

WICK'S THEOREM (I)

“FORTRAN index” notation

$a b c \cdots g h i j k l m n o p q \cdots y z$

unoccupied occupied free

Normal order: A product of creation and annihilation operators is in normal order when

- (1) *For occupied orbitals*, all the creation operators are to the right of all of the annihilation operators ($i j k \dots m^+ n^+ \dots$)
- (2) *For unoccupied orbitals*, all the annihilation operators are to the right of all the creation operators ($a^+ b^+ c^+ \dots d e \dots$)

Nonzero contractions:



$$i^+ j = \delta_{i,j} \quad (\text{occupied})$$



$$ab^+ = \delta_{a,b} \quad (\text{unoccupied})$$

or

$$r^+ s = n_s \delta_{r,s}$$



$$s r^+ = (1 - n_r) \delta_{r,s} = \bar{n}_r \delta_{r,s}$$

WICK'S THEOREM (II)

Wick's Theorem (simplified) :

The expectation value with respect to the physical vacuum is just the sum of all possible fully-contracted products multiplied by +1 (-1) if the number of intersections of the contraction lines is even (odd).

Example :

$$\begin{aligned}\langle \Phi | v_{ee} | \Phi \rangle &= \frac{1}{2} \sum_{p,q,r,s} [pr|qs] \langle \Phi | p^+ q^+ s r | \Phi \rangle \\ &= \frac{1}{2} \sum_{p,q,r,s} [pr|qs] \left[\overbrace{p^+ q^+ s r}^{\text{even}} + \overbrace{p^+ q^+ s r}^{\text{odd}} \right] \\ &= \frac{1}{2} \sum_{p,q,r,s} [pr|qs] \left[n_p n_q \delta_{p,r} \delta_{q,s} - n_p n_q \delta_{p,s} \delta_{q,r} \right] \\ &= \frac{1}{2} \sum_{i,j \in occ} ([ii|jj] - [ij|ji])\end{aligned}$$

HARTREE-FOCK (HF)

$$E_{\text{HF}} = \sum_i h_{i,i} + \frac{1}{2} \sum_{i,j} ([ii|jj] - [ij|ji]) \quad (1)$$

$$\hat{f} = \sum_{r,s} f_{r,s} r^+ s \quad (2) \qquad f_{r,s} = h_{r,s} + \sum_i ([rs|ii] - [ri|is]) \quad (3)$$

If the orbital basis consists of HF orbitals, then

$$f_{r,s} = \epsilon_r \delta_{r,s} \quad (4)$$

$$\hat{f} = \sum_r \epsilon_r r^+ r \quad (5)$$

EVALUATION OF $H_{ia,jb}$

One-electron part

$$h_{ai,bj} = \langle \Phi_i^a | \hat{h} | \Phi_j^b \rangle = \sum_{p,q} h_{p,q} \langle \Phi | i^+ a p^+ q b^+ j | \Phi \rangle \quad (1)$$

$$= \sum_{p,q} h_{p,q} (i^+ a p^+ q b^+ j + i^+ a p^+ q b^+ j + i^+ a p^+ q b^+ j) \quad (2)$$

$$= \sum_{p,q} h_{p,q} (\delta_{i,j} \delta_{a,p} \delta_{b,q} - \delta_{a,b} \delta_{i,q} \delta_{j,p} + \delta_{i,j} \delta_{a,b} \delta_{p,q} n_p) \quad (3)$$

$$= \delta_{i,j} h_{a,b} - \delta_{a,b} h_{j,i} + \delta_{i,j} \delta_{a,b} \sum_k h_{k,k} \quad (4)$$

$$= \delta_{i,j} h_{a,b} - \delta_{a,b} h_{j,i} + \delta_{i,j} \delta_{a,b} \langle \Phi | \hat{h} | \Phi \rangle \quad (5)$$

EVALUATION OF $H_{ia,jb}$

Two-electron part

$$v_{ai,bj} = \langle \Phi_i^a | \hat{v}_{ee} | \Phi_j^b \rangle = \sum_{p,q,r,s} [pr|qs] \langle \Phi | i^+ a p^+ q^+ s r b^+ j | \Phi \rangle \quad (1)$$

$$= \sum_{p,q,r,s} [pr|qs] i^+ a p^+ q^+ s r b^+ j + \sum_{p,q,r,s} [pr|qs] i^+ a p^+ q^+ s r b^+ j \quad (2)$$

(Term A)
(Term B)

Two-electron part (continued)

EVALUATION OF $H_{ia,jb}$

Two-electron part (continued)

$$+ \sum_{p,q,r,s} [pr|qs] i^+ a p^+ q^+ s r b^+ j + \sum_{p,q,r,s} [pr|qs] i^+ a p^+ q^+ s r b^+ j$$

(Term G) **(Term H)** (1)

EVALUATION OF $H_{ia,jb}$

Two-electron part (continued)

$$+ \sum_{p,q,r,s} [pr|qs] i^+ a p^+ q^+ s r b^+ j + \sum_{p,q,r,s} [pr|qs] i^+ a p^+ q^+ s r b^+ j \quad (1)$$

(Term K) **(Term L)**

EVALUATION OF $H_{ia,jb}$

Two-electron part

$$v_{ai,bj} = \langle \Phi_i^a | \hat{v}_{ee} | \Phi_j^b \rangle = \sum_{p,q,r,s} [pr|qs] \langle \Phi | i^+ a p^+ q^+ s r b^+ j | \Phi \rangle \quad (1)$$

$$= \delta_{i,j} \delta_{a,b} \sum_{k,l} [kk|ll] - \delta_{i,j} \delta_{a,b} [kl|lk] \quad (2)$$

(Term A) (Term B)

which is simply $\delta_{i,j} \delta_{a,b} \langle \Phi | \hat{v}_{ee} | \Phi \rangle$

EVALUATION OF $H_{ia,jb}$

Two-electron part (continued)

$$+\delta_{i,j} \sum_k [ab|kk] - \delta_{i,j} \sum_k [ak|kb] \quad (1)$$

(Terms C+E) (Terms D+F)

which is simply $+\delta_{i,j} v_{a,b}^{\text{SCF}}$

$$-\delta_{a,b} \sum_k [ji|kk] + \delta_{i,j} \sum_k [jk|ki] \quad (2)$$

(Terms H+I) (Terms G+J)

which is simply $-\delta_{a,b} v_{j,i}^{\text{SCF}}$

Two-electron part (continued)

$$+[ai|jb] - [ab|ji] \quad (1)$$

(Terms L+M) (Terms K+N)

Putting it all together gives:

$$H_{ai,bj} = A_{ai,bj} + \delta_{i,j} \delta_{a,b} E_{HF} \quad (2)$$

where

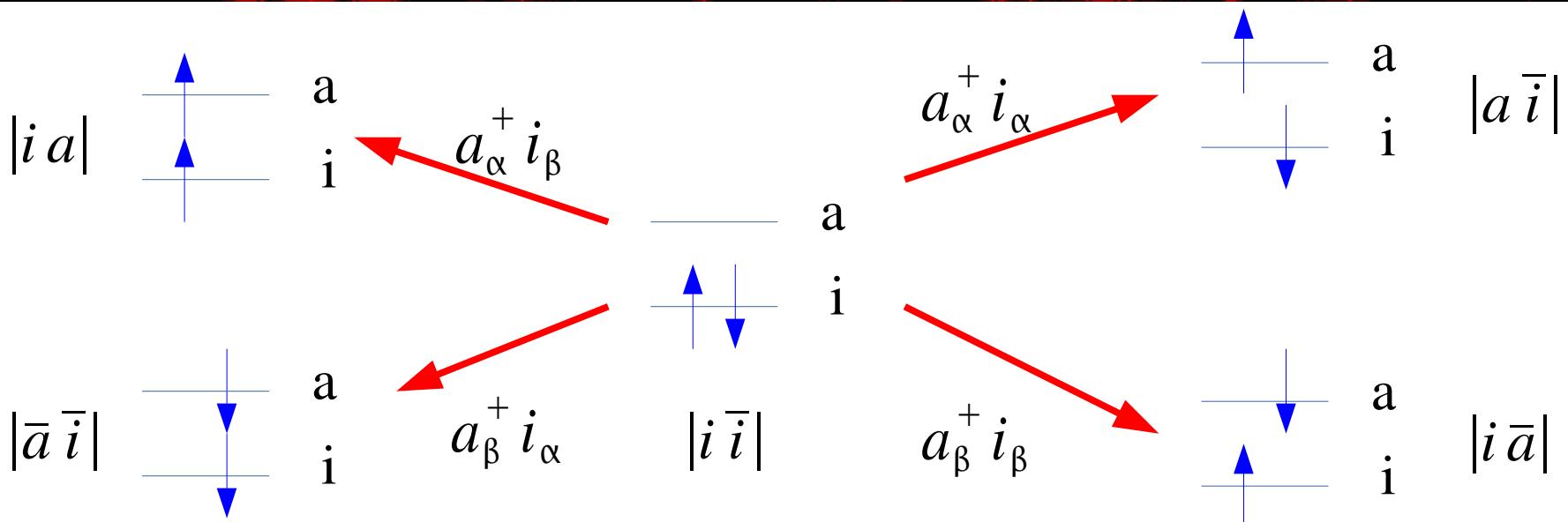
$$A_{ai,bj} = \delta_{i,j} f_{a,b} - \delta_{a,b} f_{j,i} + [ai|jb] - [ab|ji] \quad (3)$$

or

$$A_{ai,bj} = \delta_{i,j} \delta_{a,b} (\epsilon_a - \epsilon_i) + [ai|jb] - [ab|ji] \quad (4)$$

in terms of HF MOs.

TWO-ORBITAL TWO-ELECTRON MODEL (TOTEM)*



	Ψ_{S, M_s}
Singlet	$\Psi_{0,0} = \frac{1}{\sqrt{2}}(a \bar{i} + i \bar{a})$
Triplets	$\Psi_{1,0} = i a $ $\Psi_{1,0} = \frac{1}{\sqrt{2}}(a \bar{i} - i \bar{a})$ $\Psi_{1,-1} = \bar{a} \bar{i} $

* two-orbital two-electron model.

TOTEM CIS

$$\begin{bmatrix} \epsilon_a - \epsilon_i + [ai|ia] - [aa|ii] & [ai|ia] \\ [ai|ia] & \epsilon_a - \epsilon_i + [ai|ia] - [aa|ii] \end{bmatrix} \begin{pmatrix} X_{ai\alpha} \\ X_{ai\beta} \end{pmatrix} = \omega \begin{pmatrix} X_{ai\alpha} \\ X_{ai\beta} \end{pmatrix}$$

Singlet type excitation

$$\begin{pmatrix} X_{ai\alpha} \\ X_{ai\beta} \end{pmatrix} = \begin{pmatrix} 1 \\ 1 \end{pmatrix} \Rightarrow \omega = \epsilon_a - \epsilon_i + 2[ai|ia] - [aa|ii]$$

Triplet type excitation

$$\begin{pmatrix} X_{ai\alpha} \\ X_{ai\beta} \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix} \Rightarrow \omega = \epsilon_a - \epsilon_i - [aa|ii]$$



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

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

	Ψ_{S, M_S}
Singlet	$\Psi_{0,0} = \frac{1}{\sqrt{2}}(a\bar{i} + i\bar{a})$
Triplets	$\Psi_{1,0} = ia $ $\Psi_{1,0} = \frac{1}{\sqrt{2}}(a\bar{i} - i\bar{a})$ $\Psi_{1,-1} = \bar{a}\bar{i} $

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

\Rightarrow

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

\Rightarrow

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

because

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

* 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

EQUATION-OF-MOTION/SUPEROPERATOR APPROACH

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.



EQUATION-OF-MOTION (EOM)

The EOM

$$\check{H} \hat{O}^+ = [\hat{H}, \hat{O}^+] = \omega \hat{O}^+ \quad (1)$$

has excitation-type solutions

$$[\hat{H}, |I\rangle\langle 0|] = (E_I - E_0) |I\rangle\langle 0| \quad (2)$$

and de-excitation-type solutions

$$[\hat{H}, |0\rangle\langle I|] = (E_0 - E_I) |0\rangle\langle I| \quad (3)$$

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

Let us seek a solution of the form

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

$$\check{H} \hat{O}^+ = [\hat{H}, \hat{O}^+] = \omega \hat{O}^+ \quad (1)$$

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

Inserting (2) into (1) and using the “metric”

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

gives us

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

with

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

$$B_{ai,bj} = [ib|ja] - [jb|ia] \quad (6)$$

excitation

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

corresponding de-excitation

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

THE TAMM-DANCOFF APPROXIMATION

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

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

This is the same as CIS !!

triplet

$$\omega_T = \sqrt{[\epsilon_a - \epsilon_i + (ia|f_H|ai) - (ii|f_H|aa)][\epsilon_a - \epsilon_i - (ia|f_H|ai) - (ii|f_H|aa)]} \quad (1a)$$

$$\approx \epsilon_a - \epsilon_i - (ii|f_H|aa) \quad (1b)$$

singlet

$$\omega_S = \sqrt{[\epsilon_a - \epsilon_i + (ia|f_H|ai) - (ii|f_H|aa)][\epsilon_a - \epsilon_i + 3(ia|f_H|ai) - (ii|f_H|aa)]} \quad (2a)$$

$$\approx \epsilon_a - \epsilon_i + 2(ia|f_H|ai) - (ii|f_H|aa) \quad (2b)$$

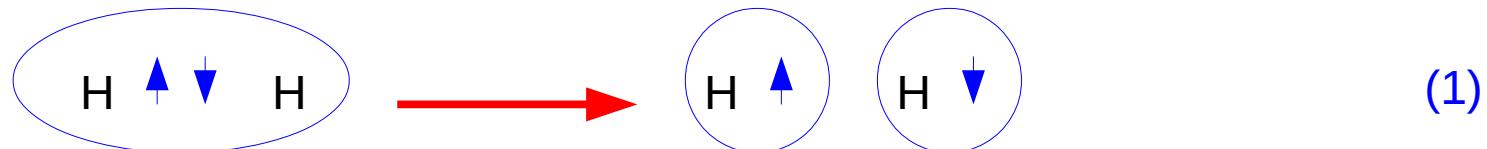
Triplet-type instability!

ω_T will be *imaginary* when

$$(ia|f_H|ai) + (ii|f_H|aa) > \epsilon_a - \epsilon_i \quad (3)$$

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?



Look at an arbitrary unitary transformation of the orbitals:

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

We find

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

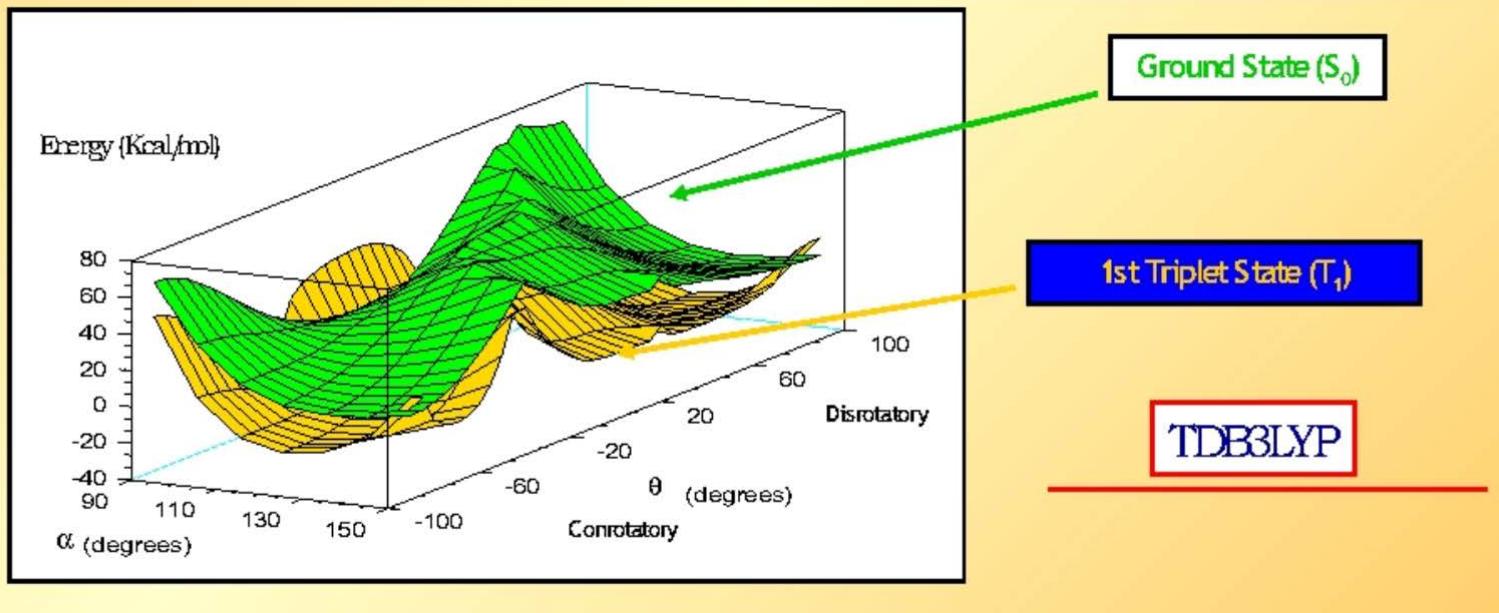
But another way to write the EOM matrix equation is

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

Conclusion :

Symmetry breaking will occur if there are imaginary excitation energies.

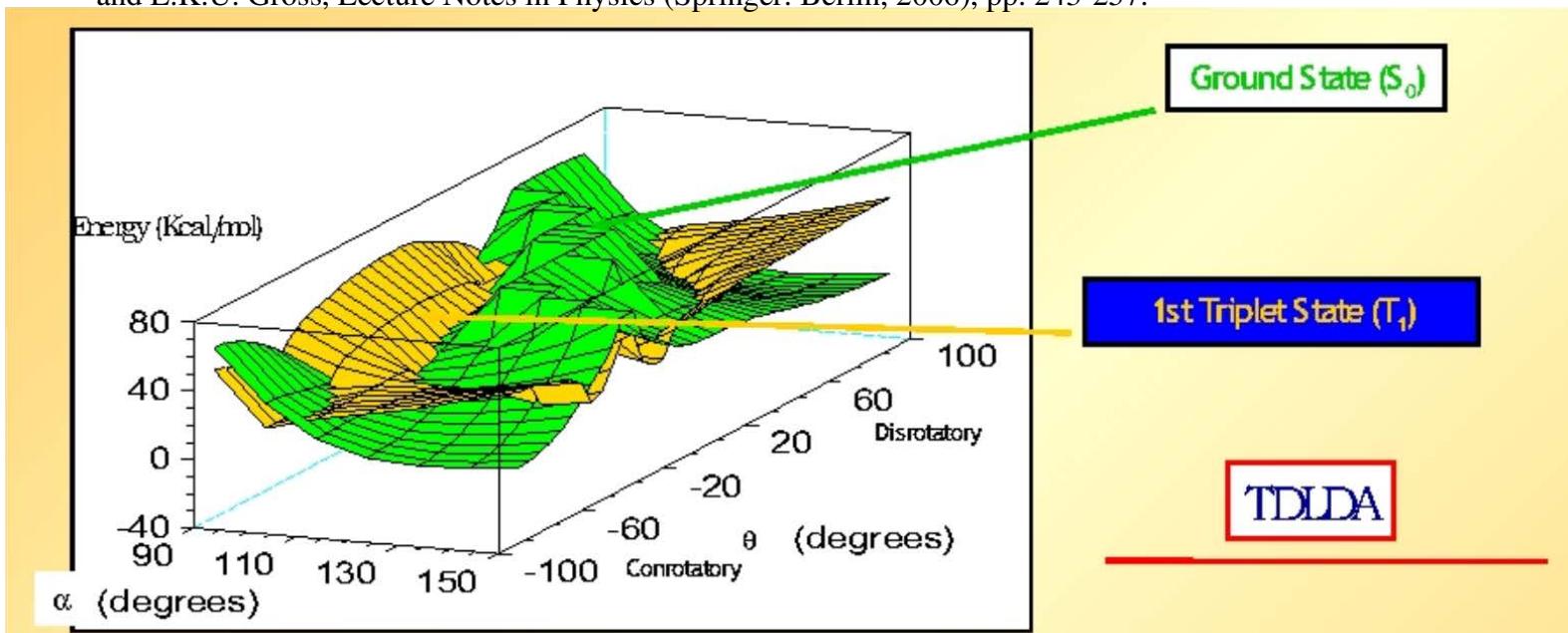
* J. Cizek and J. Paldus, *J. Chem. Phys.* **47**, 3976 (1967).



93% of the surface shows symmetry breaking

Which would you use?

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.



50% of the surface shows symmetry breaking

A COMMON PROBLEM: INFORMATION OVERLOAD



ETHIOPIA – THE HOLY LAND?



Picture of the Queen of Sheba (Makeda)
Bellifortis by Conrad Kyeser
ca. 1405



King Ezana of Axum,
first Christian King



First Hegira

PAN-AFRICANISM – THE HOLY LAND?

"The Blood,
My Black People
Shed For Their Land."



"Every time you see another nation on the African continent become independent you know that Marcus Garvey is alive...had it not been for Marcus Garvey and the foundations laid by him, you would find no independent nations in the Caribbean today..All of the freedom movement that is taking place right here in America today was initiated by the work and teachings of Marcus Garvey."

Malcolm X

ASESMA 2018, Addis Ababa

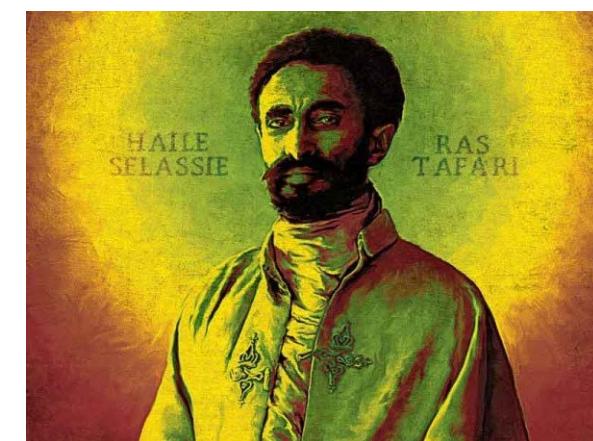


Marcus Garvey

LOOK TO AFRICA,
FOR THERE A KING
WILL BE CROWNED.

QUOTEHD.COM

Marcus Garvey
Jamaican Publisher

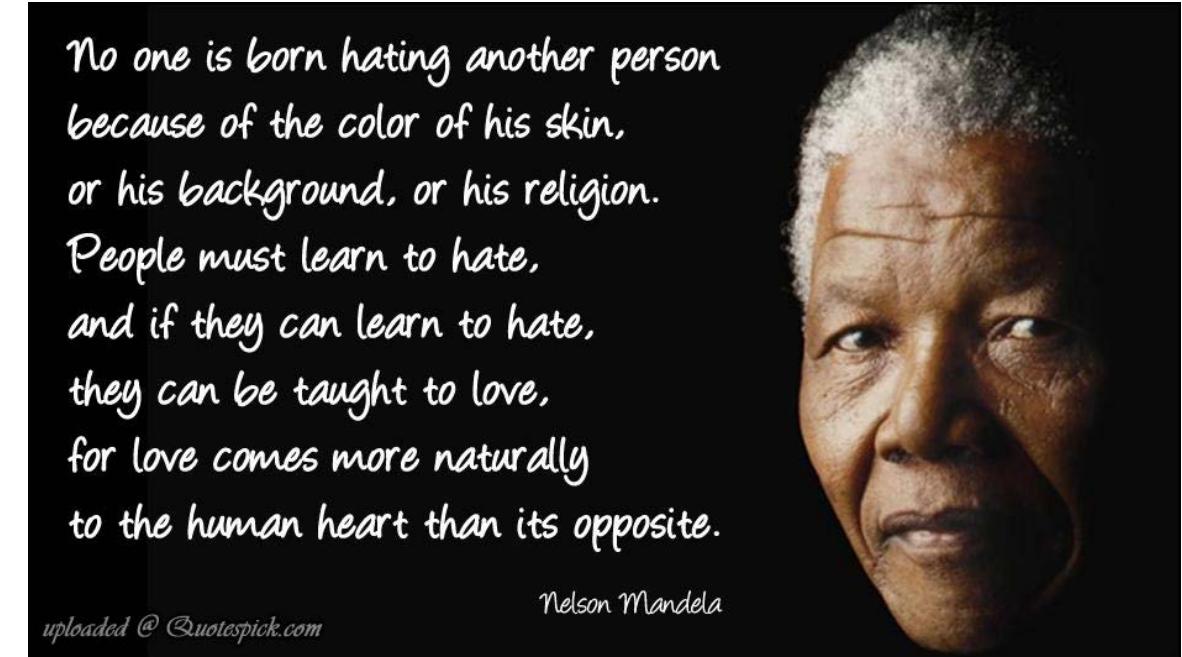
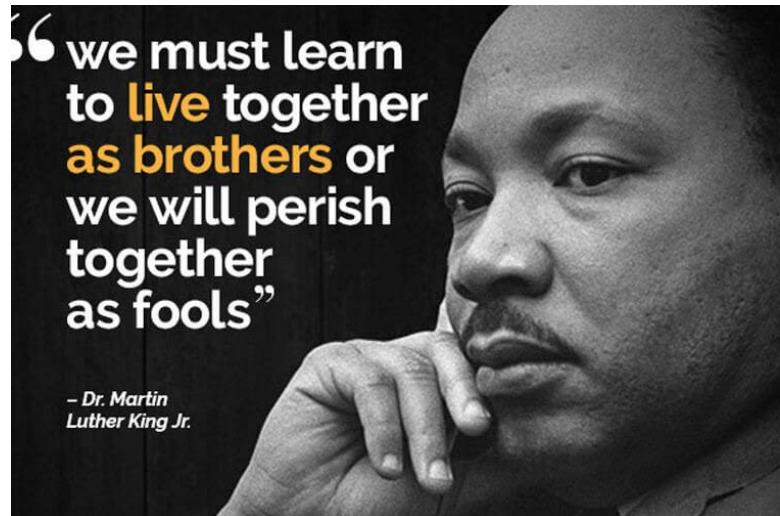


Hailie Salassie/Ras Tafari



Bob Marley

PAN-AFRICANISM TODAY



African Union (55 states)



ASESMA 2018, Addis Ababa

STUDENTS FINANCED THROUGH THE FRENCH EMBASSY IN KENYA



Cleophas Muhavini Wawire, PhD Chemistry, Université de Grenoble, 18 June 2012



Denis Magero, PhD Chemistry, Université Grenoble Alpes, 14 December 2017



**Valid Mwatati Mwalukuku, Masters Nanochemistry,
Université Grenoble Alpes, 2017-2019**

OUTLINE

I. PRE-AMBLE

II. THIS COURSE

III. QUANTUM CHEMISTRY FOR EXCITED STATES

IV. TD-DFT FOR EXCITED STATES

V. CONCLUSION





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

The Two Hohenberg-Kohn (HK) 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:

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

2nd HK Theorem: The ground-state energy and charge density may be obtained by minimizing the variational expression

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

The functional $F[\rho]$ is "universal" in the sense of being independent of v_{ext} .

The Levy-Lieb Constrained Search Formalism

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

Avoids the ν -representability problem.

It assumes that the density is N -representable (and it really is!)

The exact functional is actually known! (but it is not practical!)

Ensemble formulation:

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

$$\hat{D} = \sum_I p_I |\Psi_I\rangle \langle \Psi_I| \quad (3)$$

p_I is the probability of observing the state Ψ_I .

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

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

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

where

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

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

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

where the exchange-correlation (xc) potential is

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

Functional Derivatives

Definition

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

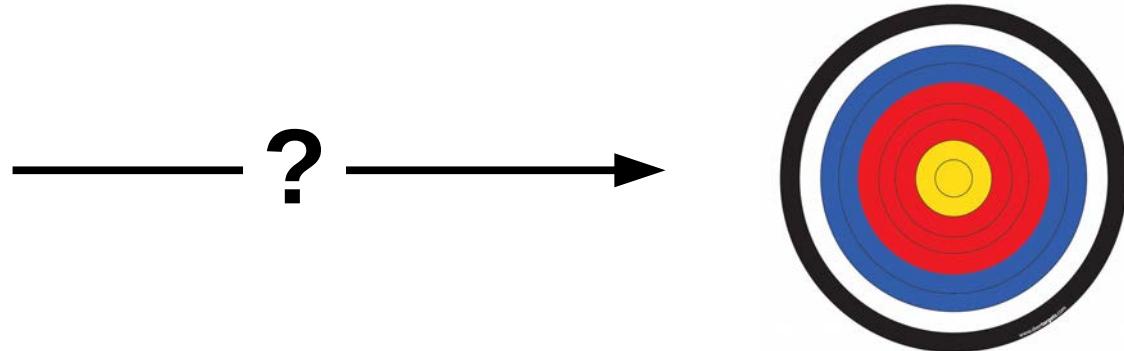
We need ...

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

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

and sometimes also

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



« *Le but n'est pas toujours placé pour être atteint, mais pour servir de point de mire ou de direction.* »*

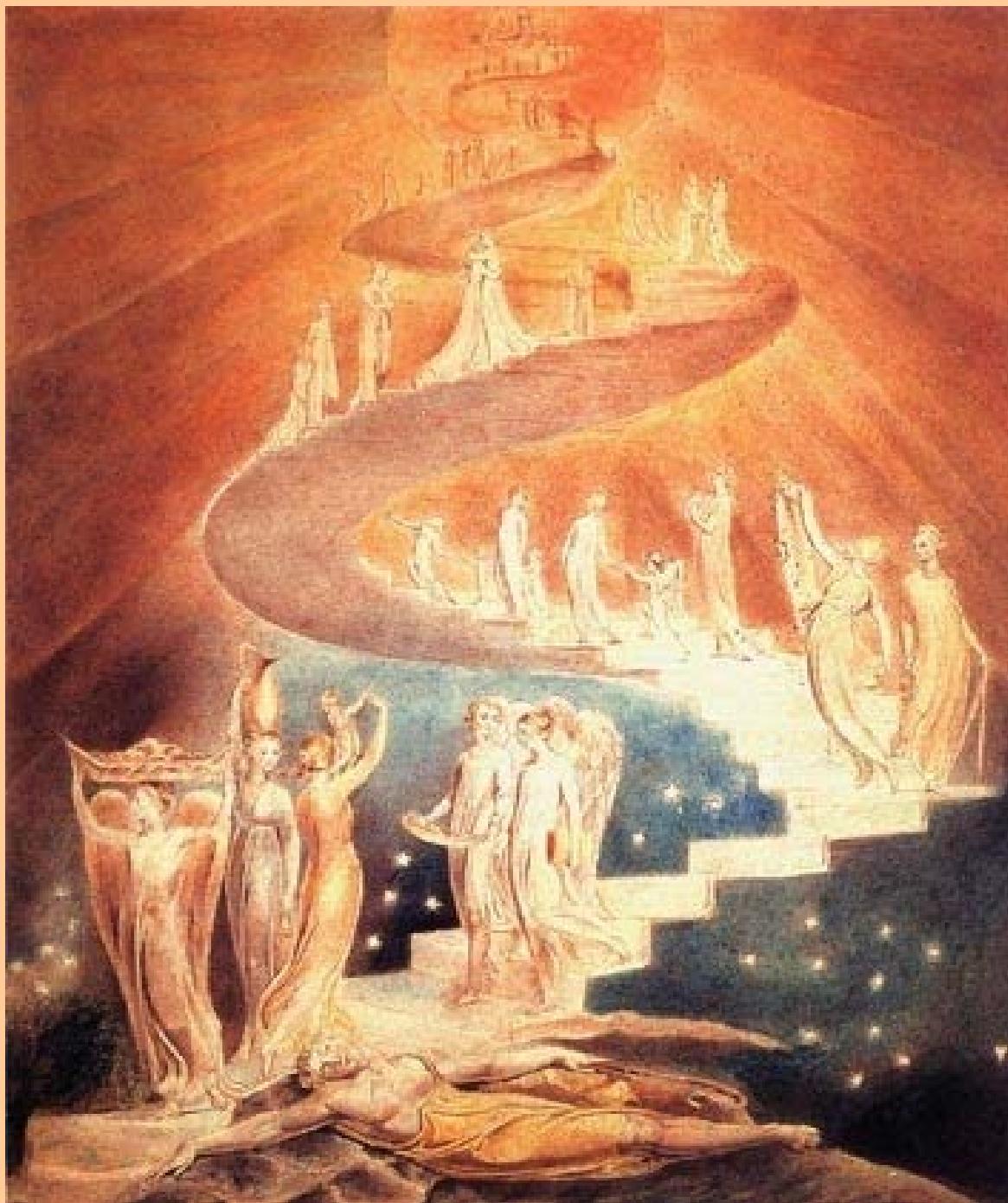
--- Joseph Joubert (p. 221 of *Receuil des pensées de M. Joubert* by F.-R. De Chateaubriand, 1838)

* 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

THEORETICAL
CHEMISTRY
HEAVEN**

MBPT *ab initio* DFT

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

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

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

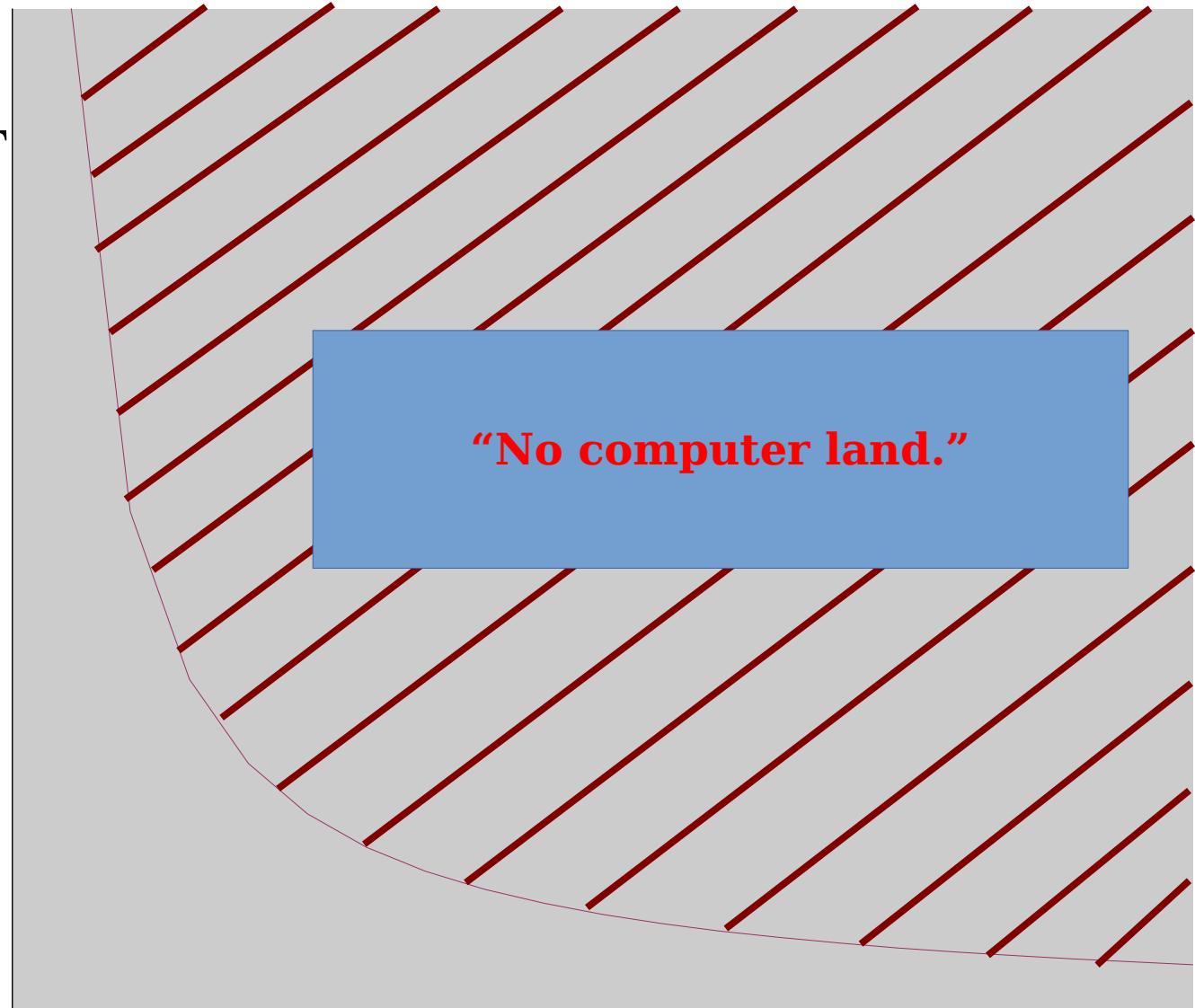
pure DFT

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

HARTREE WORLD

* or include $\nabla^2 \rho$

Jacob's Ladder



Size of the molecule →

ASESMA 2018, Addis Ababa

85

** 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.

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

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. Tellgren, 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 DISPERSION CORRECTION*

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".

$$E_{\text{disp}} = \sum_{A,B} \sum_{n=6,8,10,\dots} S_n \frac{C_n^{A,B}}{R_{A,B}^n \left[1 + 6 \left(\frac{R_{AB}}{S_{r,n} R_0^{A,B}} \right)^{-\alpha_n} \right]} - \sum_{A,B,C} \frac{\sqrt{C_6^{AB} C_6^{AC} C_6^{BC}} (3 \cos \theta_a \cos \theta_b \cos \theta_c + 1)}{(R_{AB} R_{BC} R_{CA})^3 \left[1 + 6 \left(\frac{\bar{R}_{ABC}}{S_{r,3} R_0^{A,B}} \right)^{-\alpha_3} \right]}$$

* 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”

TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY (TD-DFT)

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

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

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

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

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

[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)]

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

where $\rho(\mathbf{r} t) = \sum_{i\sigma} n_{i\sigma} |\Psi_{i\sigma}(\mathbf{r} t)|^2$ (2)

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

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

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

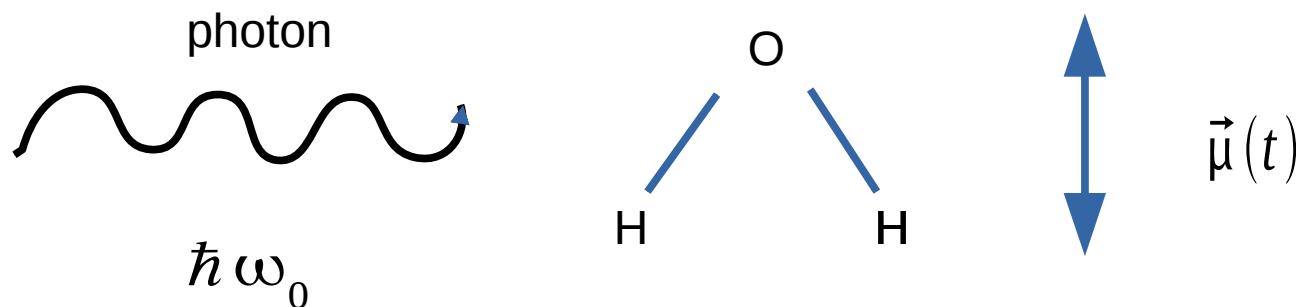
TD-DFT ADIABATIC APPROXIMATION (AA)

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

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

This defines “conventional TD-DFT”.

ELECTRONIC POLARIZATION INDUCED BY THE APPLICATION OF A TIME-DEPENDENT ELECTRIC FIELD



Classical model of a photon

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

$$v(\vec{r} t) = e \vec{\varepsilon}(t) \cdot \vec{r} \quad (2)$$

Induced dipole moment

$$\delta \vec{\mu}(t) = -e (\langle \Psi_0 | \vec{r} | \delta \Psi_0(t) \rangle + \langle \delta \Psi_0(t) | \vec{r} | \Psi_0 \rangle) \quad (3)$$

REONSE THEORY FOR CHEMISTS ...

The linear response for a property a $\delta \langle \hat{a} \rangle(t)$

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

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

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

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

which allows us to deduce the 1st order equation

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

ENERGY REPRESENTATION

Fourier transforms

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

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

Transform the 1st order equation

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

$$\hat{b}(\omega)\Psi_0 = (\hbar\omega - \hat{H} + E_0) \delta\Psi_0(\omega) \quad (4)$$

Solve by Rayleigh-Schrödinger perturbation theory!

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



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



TIME REPRESENTATION

Since

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

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

we find

$$\begin{aligned} \delta \Psi_0(t) &= \left(\sum_{I \neq 0} \Psi_I \frac{\omega_I \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega_0^2 - \omega_I^2} \right) \cos \omega_0 t \\ &\quad - i \left(\sum_{I \neq 0} \Psi_I \frac{\omega_0 \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega_0^2 - \omega_I^2} \right) \sin \omega_0 t \end{aligned} \quad (3)$$

RESPONSE OF AN ARBITRARY PROPERTY

$$\delta \langle \hat{a} \rangle(t) = \langle \Psi_0 | \hat{a} | \delta \Psi_0(t) \rangle + \langle \delta \Psi_0(t) | \hat{a} | \Psi_0 \rangle \quad (1)$$

Electronic polarizabilities, NMR chemical shifts

$$\begin{aligned} \delta \langle \hat{a} \rangle(t) &= \left(\sum_{I \neq 0} \frac{2 \omega_I \Re e \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega_0^2 - \omega_I^2} \right) \cos \omega_0 t \\ &\quad + \sum_{I \neq 0} \left(\frac{2 \omega_0 \Im m \langle \Psi_0 | \hat{a} | \Psi_I \rangle \langle \Psi_I | \hat{b} | \Psi_0 \rangle}{\omega_I^2 - \omega_0^2} \right) \sin \omega_0 t \end{aligned} \quad (2)$$

Circular dichroïsme

THE DYNAMIC POLARIZABILITY

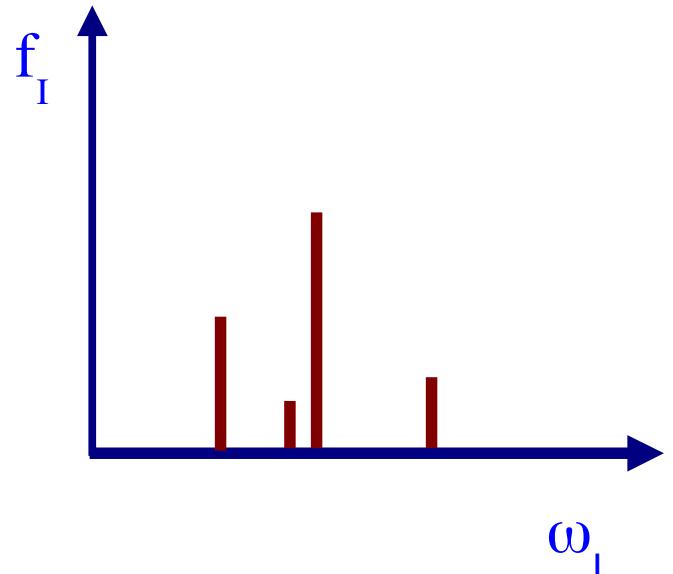
$$\mu_i(t) = \mu_i + \sum_j \alpha_{i,j}(\omega) \varepsilon_j \cos \omega t + \dots \quad (1)$$

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

Sum-over-states (SOS*)

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

$$f_I = \frac{2}{3} \omega_I (| \langle \Psi_0 | x | \Psi_I \rangle |^2 + | \langle \Psi_0 | y | \Psi_I \rangle |^2 + | \langle \Psi_0 | z | \Psi_I \rangle |^2) \quad (4)$$



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

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

or

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

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

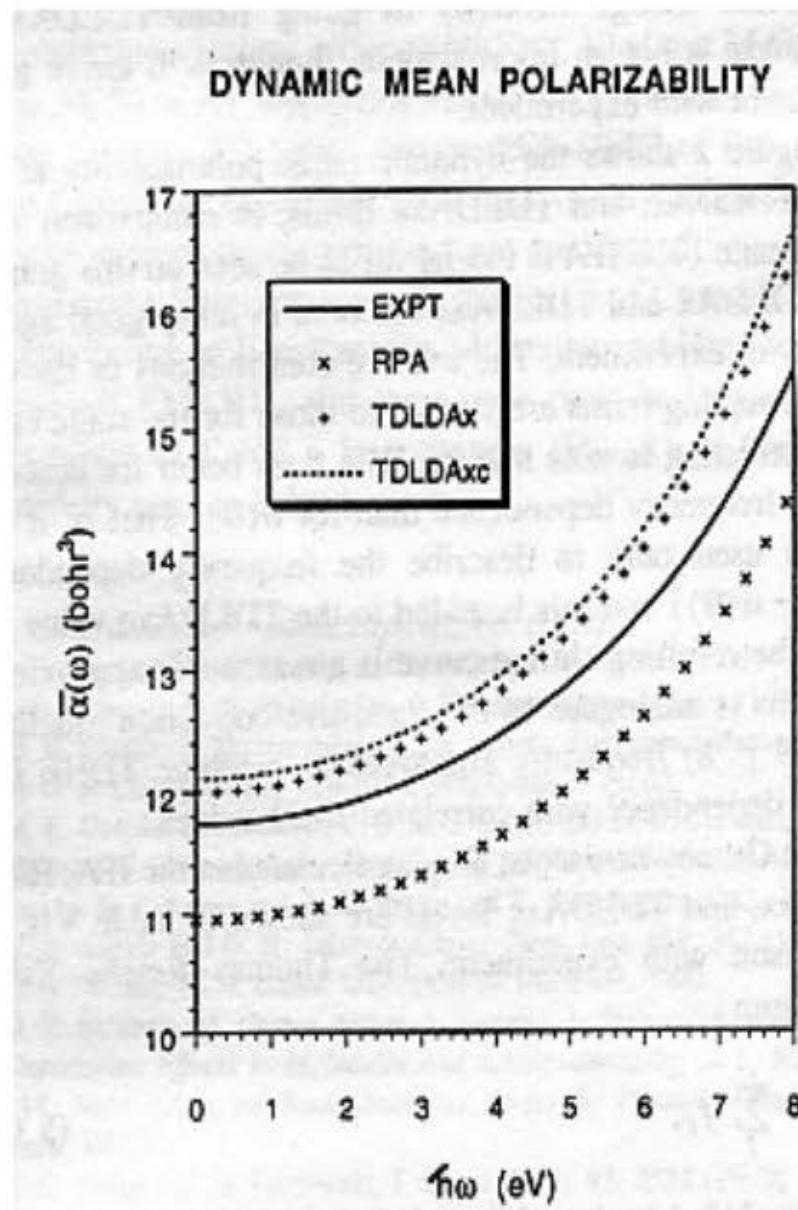
Coupling matrix

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

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

The Dynamic Polarizability of the Nitrogen Molecule

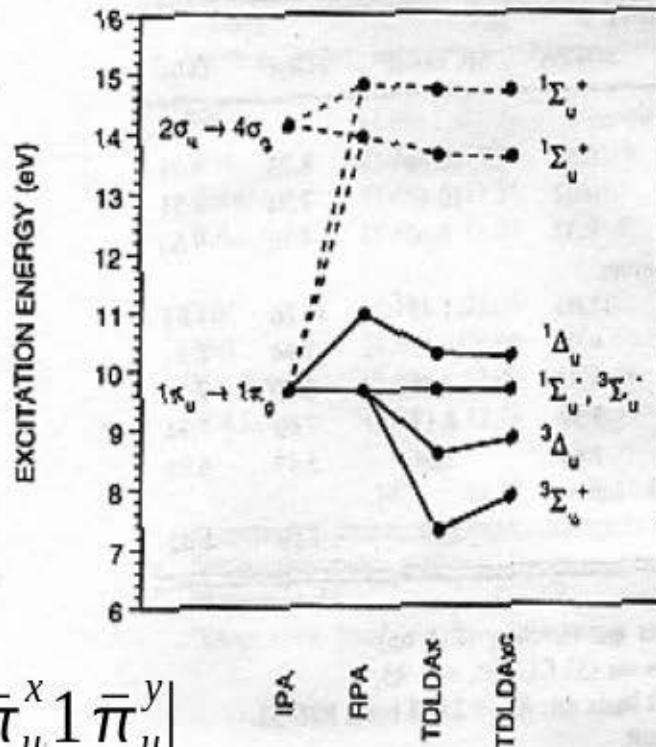
C. Jamorski, M.E. Casida, and
D.R. Salahub, J. Chem. Phys.
104, 5134 (1996).



$N_2 \pi \rightarrow \pi^*$ Excitations

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

CORRELATION BETWEEN COUPLED AND UNCOUPLED STATES FOR THE $\pi \rightarrow \pi^*$ TRANSITIONS IN NITROGEN



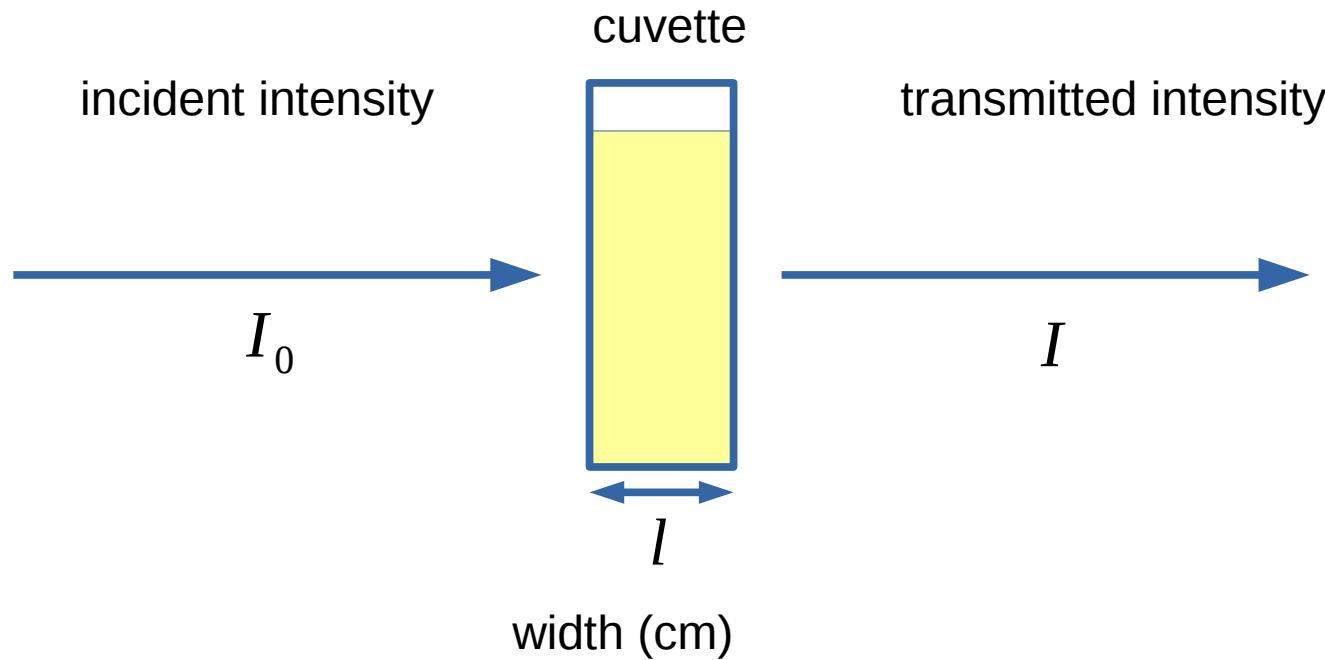
$$\Sigma_u^+ \Rightarrow |1\pi_g^x 1\pi_u^y 1\bar{\pi}_u^x 1\bar{\pi}_u^y| + |1\pi_u^x 1\pi_g^y 1\bar{\pi}_u^x 1\bar{\pi}_u^y|$$

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

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

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

BEER'S LAW*

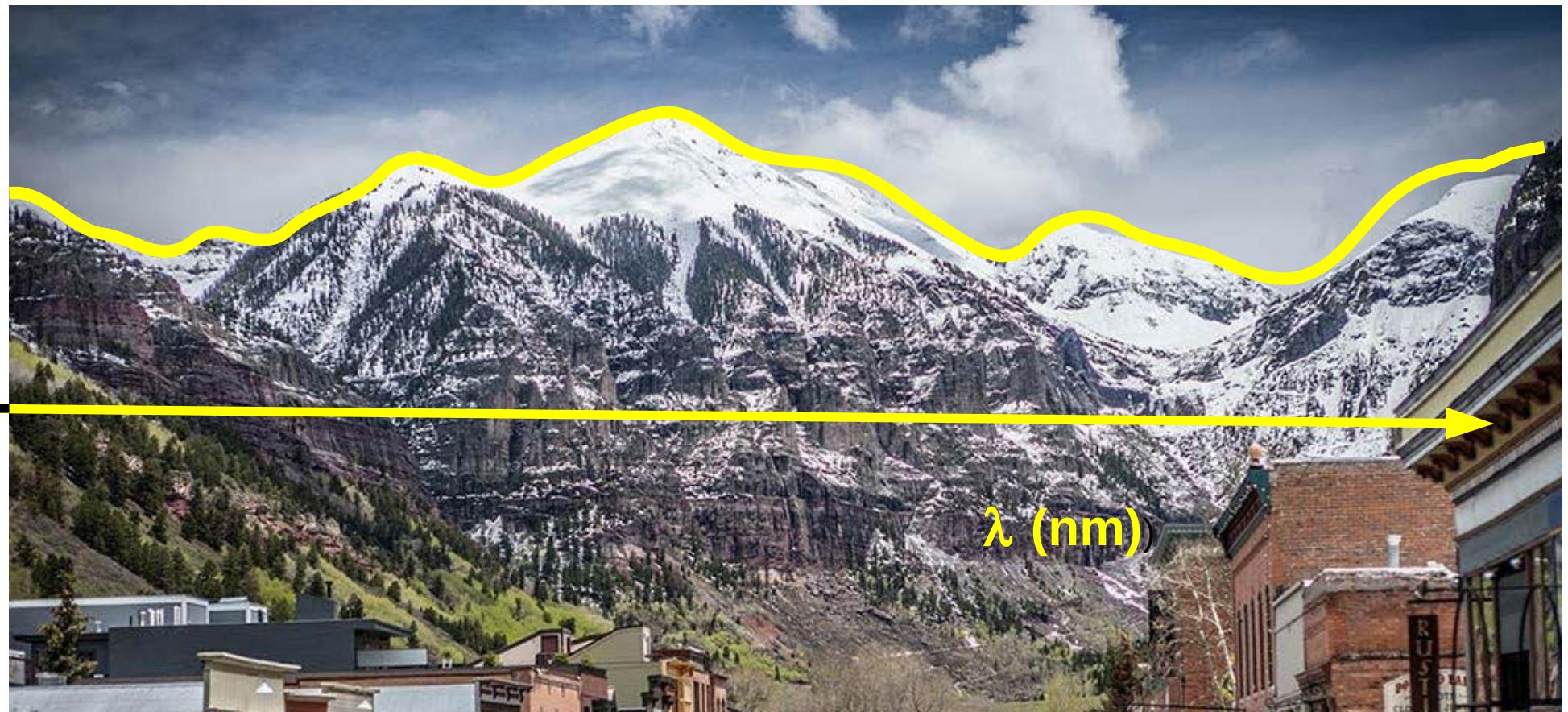


Absorbance (unitless) $A = \log_{10} \frac{I_0}{I}$ (1) Concentration (mol/L) C

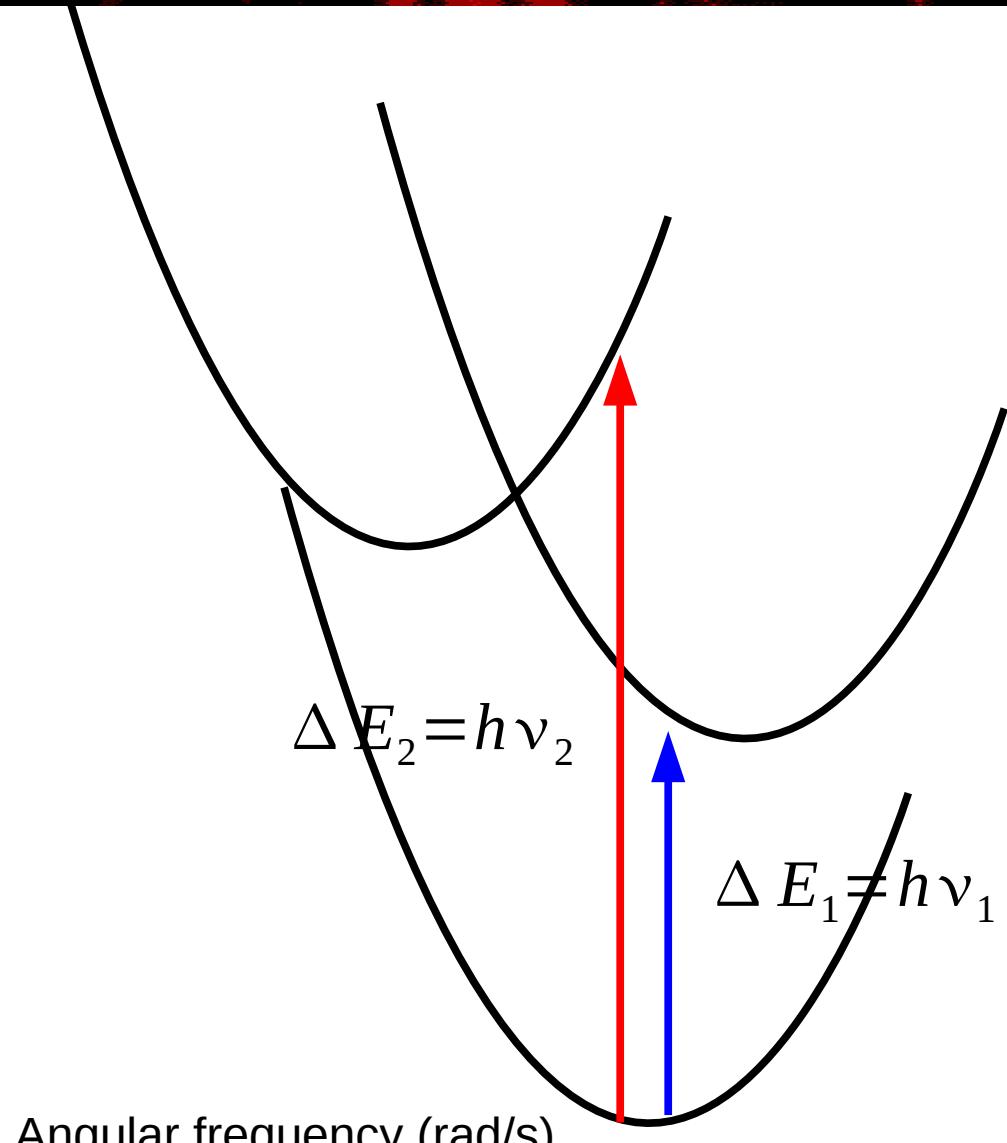
Beer's law $A = \epsilon C l$ (2) Molar extinction coefficient (L/mol.cm) ϵ

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

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



STICK SPECTRUM



$$\omega = 2\pi \nu \quad (3)$$

$$h\nu = \hbar\omega \quad (4)$$

- 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

Spectral function (units: cm)

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

Oscillator strength (unitless)

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

More about oscillator strengths ...

If $[\hat{x}, \hat{p}_x] = +i\hbar$ (1)

Plane-wave basis or any sufficiently complete basis set ...

Then the following are equivalent:

$$f_I = \frac{2\omega_I m_e}{3\hbar} |\langle \Psi_0 | \mathbf{r} | \Psi_I \rangle|^2 \quad (2) \quad \text{Length form}$$

$$f_I = \frac{2}{3\hbar\omega_I m_e} |\langle \Psi_0 | \hat{\mathbf{p}} | \Psi_I \rangle|^2 \quad (3) \quad \text{Momentum form}$$

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

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)

N₂**TRK f-sum**

TABLE VIII. Comparison of TDLDAnC 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_{-1}	S_{-4}	S_{-6}
TD-DPRT Calculations					
TDLDAnC	TZVPP+	11.48	11.92	32.71	114.5
	BK90	12.96	10.36	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

^aMean static polarizability.

^bReference 66.

^cExact value equals number of electrons.

^dTime-dependent Hartree-Fock calculation of Ref. 46.

^eTime-dependent Hartree-Fock calculation of Ref. 67.

^fTime-dependent Hartree-Fock calculation of Ref. 44.

^gMulticonfigurational time-dependent Hartree-Fock calculation of Ref. 46. Six orbital active space.

^hMulticonfigurational time-dependent Hartree-Fock calculation of Ref. 60. Twelve orbital active space.

ⁱSecond-order polarization propagator approximation calculation of Ref. 44.

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

EXPERIMENTAL OSCILLATOR STRENGTHS

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



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

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

In SI units, this becomes

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

which makes

$$f_I = (1.44 \times 10^{-19} \text{ mol.cm.s/L}) \int \epsilon(\nu) d\nu \quad (3)$$

* It Can Be Shown That

THEORETICAL CALCULATION OF THE MOLAR EXTINCTION COEFFICIENT

For a single transition,

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

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

For several transitions,

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

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

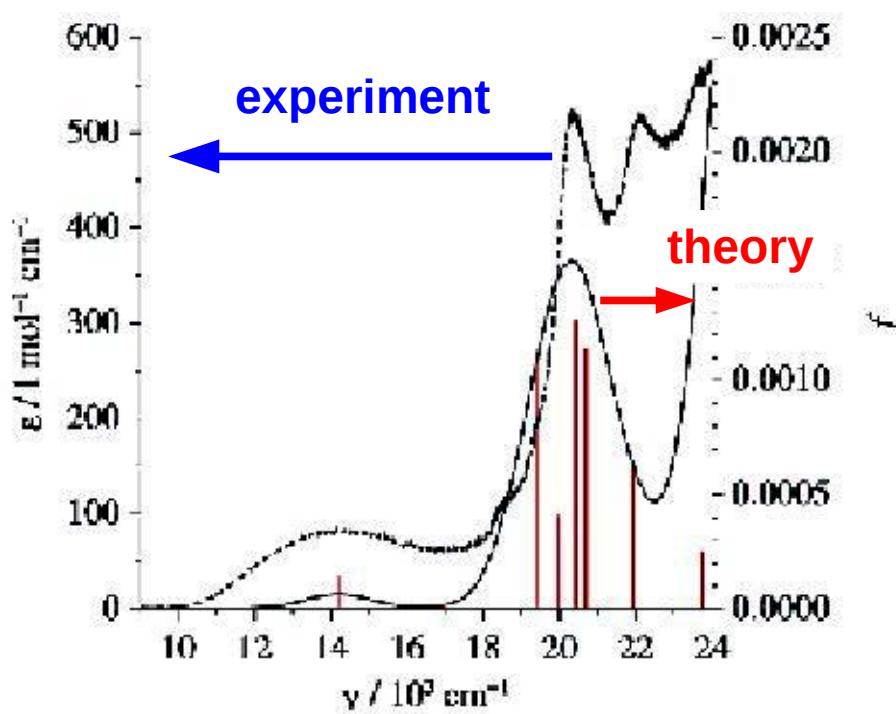
GAUSSIAN CONVOLUTION

Normalized gaussian function

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

Full width at half maximum (FWHM)

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



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

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:

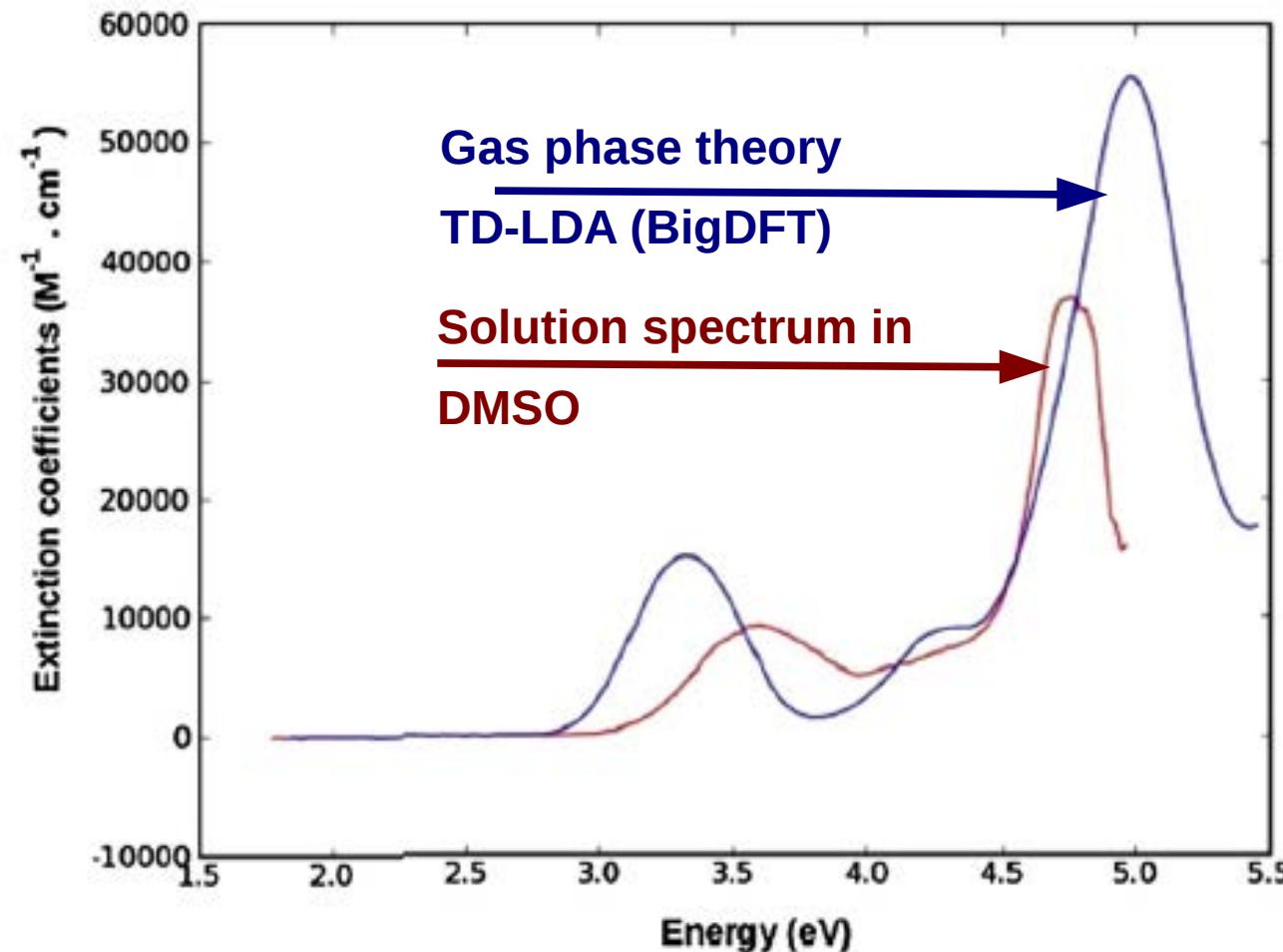
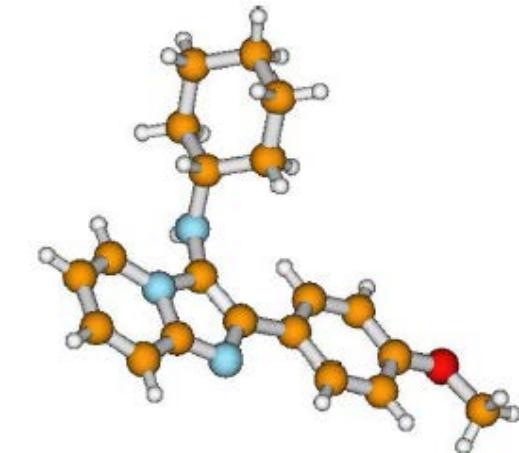
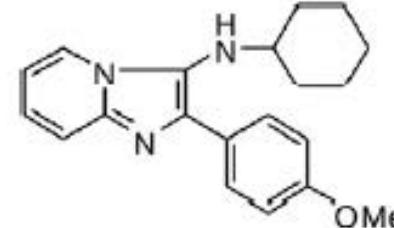
- Imperfect spectrometers
- Neglect of vibrational coupling
- Neglect of solvent
- ???

B. Natarajan, L. Genovese, M.E. Casida, T. Deutsch, O.N. Burchak,
C. Philouze, and M. Y. Balakirev, *Chem. Phys.* **402**, 29 (2012);
corrigendum *Chem. Phys.* **436-437**, 63 (2014) "Wavelet-Based
Linear-Response Time-Dependent Density-Functional Theory"

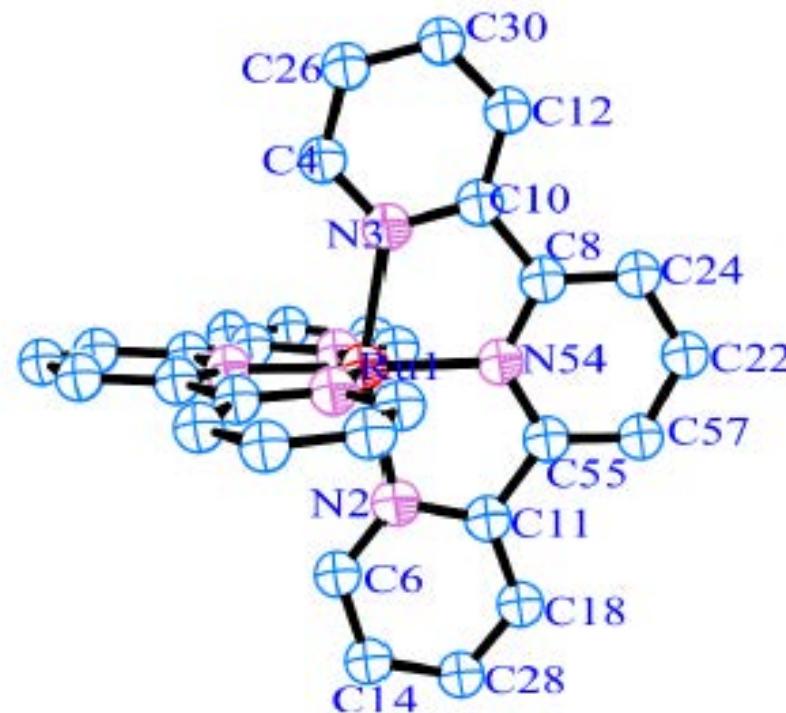
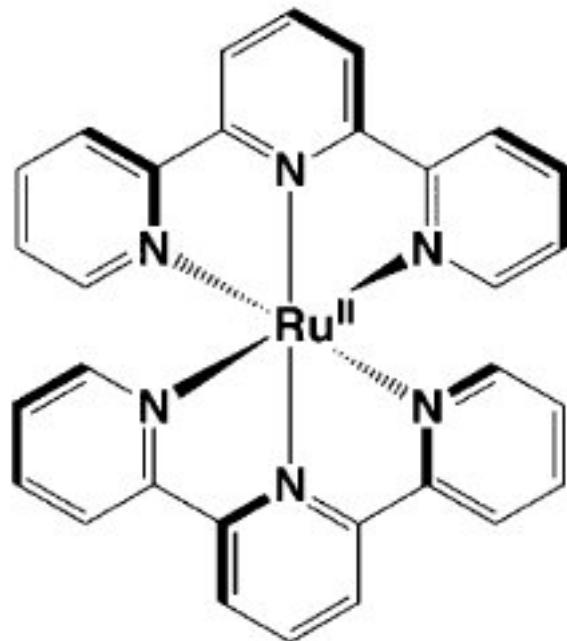


Bhaarathi Natarajan

N-cyclohexyl-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-amine



CALCULATION OF THE ABSORPTION SPECTRUM OF $[\text{Ru}(\text{trpy})_3]^{2+}$



Optimisation
beginning with the
X-ray structure.

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



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

HOW GOOD IS THE GEOMETRY?

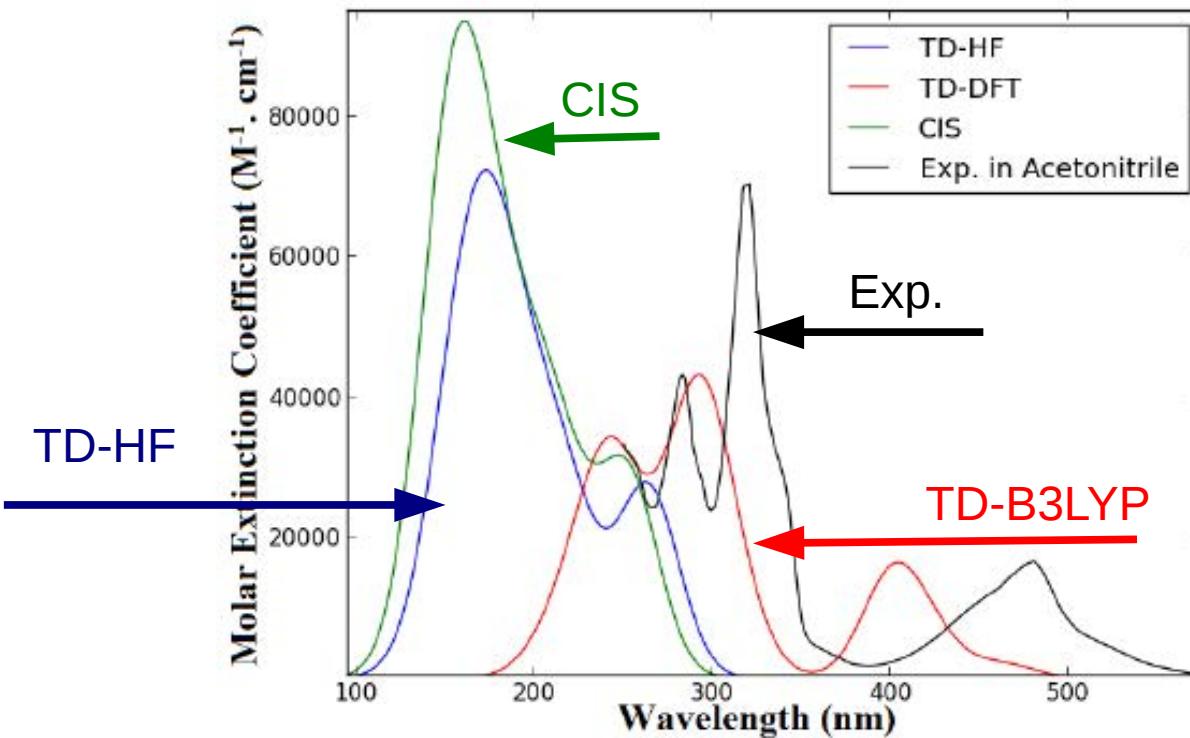
Table 5. Comparison of parameters for geometries optimized at HF and DFT. Bond lengths are in (Å) and bond angles are in degrees.

	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 ₂ C ₁₁	1.353	1.382	1.374	1.38
C ₁₁ C ₅₅	1.489	1.474	1.466	1.47
N ₂ C ₆	1.33	1.354	1.35	1.36
RuN ₅₄ C ₅₅	118.132	118.784	119.4	118.8
RuN ₂ C ₁₁	112.473	113.477	113.4	113.8
RuN ₂ C ₆	127.502	127.336	127.5	126.6
N ₅₄ RuN ₂	77.002	78.456	78.6	78.9



Gas phase B3LYP calculations give a geometry close to the one measured in the crystal.

CALCULATION OF THE ABSORPTION SPECTRUM OF $[\text{Ru}(\text{trpy})_3]^{2+}$



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 $[\text{Ru}(\text{trpy})_2]^{2+}$. Calculated spectra has been done with 100 singlet states and 6-31G(d) basis set. Experimental spectra; measured at room temperature in acetonitrile [99].

Literally introduce

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

$$\mathbf{v}_{appl}(\mathbf{r}t) = \boldsymbol{\varepsilon}(t) \cdot \mathbf{r} \quad (2)$$

Propagate in time :

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

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

Basic Time-Dependent (TD) Theory

May solve the time-dependent Schrödinger equation (TDSE), $\hat{H}(t)\Psi(t)=i\frac{\partial}{\partial t}\Psi(t)$ (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 $\Psi(t_{i+1}) = \Psi(t_i) - i(\Delta t) \hat{H}(t_i) \Psi(t_i)$ (1)

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

Calculate

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

Dynamic polarizability

$$\Delta \mu(t) = \int \alpha(t-t') \epsilon_{appl}(t') dt' + HOT \quad (2)$$

Convolution theorem

$$\Delta \mu(\omega) = \alpha(\omega) \epsilon_{appl}(\omega) + HOT \quad (3a)$$

$$\alpha(\omega) = \frac{\Delta \mu(\omega)}{\epsilon_{appl}(\omega)} \quad (3b)$$

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

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

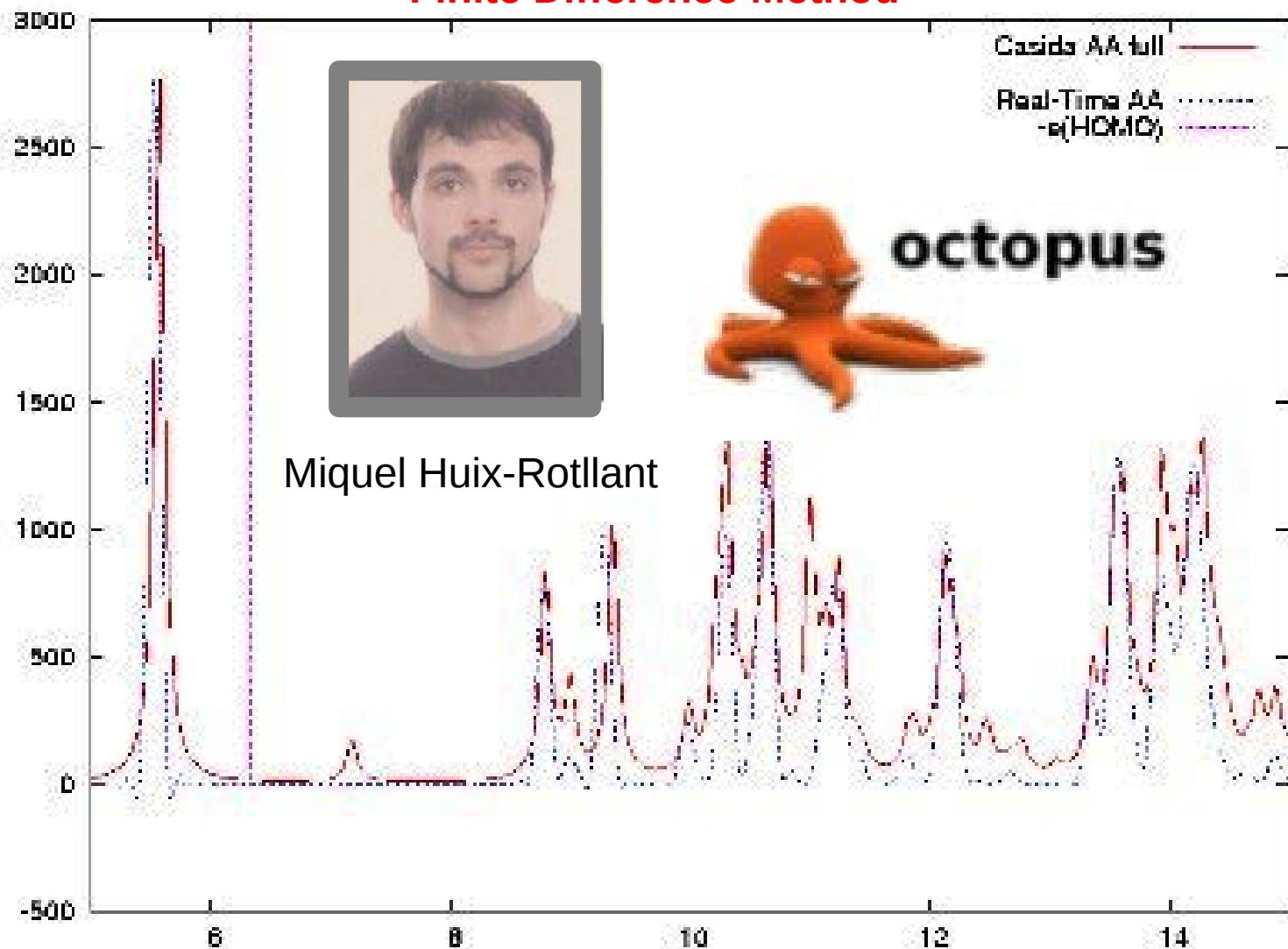
$$S(\omega) = \frac{2\omega}{\pi} \Im \alpha(\omega + i\eta) \quad (3)$$

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

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

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

Finite Difference Method



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).

Extrapolation of Lanczos coefficients

In the Liouville-Lanczos approach, the absorption coefficient is computed as:

$$\alpha(\omega) = (\zeta_N, (\omega - \hat{T}_N)^{-1} \cdot \mathbf{e}_1^N)$$

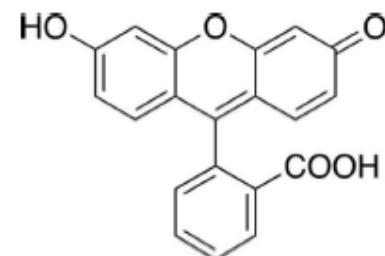
where \hat{T}_N is the tridiagonal matrix composed of the Lanczos coefficients.

$$\hat{T}_N = \begin{pmatrix} 0 & \gamma_2 & 0 & \cdots & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & \gamma_N \\ 0 & \cdots & 0 & \beta_N & 0 \end{pmatrix} \xrightarrow{\text{Extrapolation}} \hat{T}_{N'} = \begin{pmatrix} 0 & \gamma_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \beta_2 & 0 & \gamma_3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \beta_3 & 0 & \ddots & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \ddots & \ddots & \gamma_N & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \beta_N & 0 & \langle \gamma \rangle & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \langle \beta \rangle & 0 & \langle \gamma \rangle & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \ddots & 0 & \ddots & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \langle \beta \rangle & 0 & \langle \gamma \rangle \end{pmatrix}$$

$$\langle \beta \rangle = \frac{\beta_1 + \beta_2 + \dots + \beta_N}{N} \quad \langle \gamma \rangle = \frac{\gamma_1 + \gamma_2 + \dots + \gamma_N}{N} \quad N = \text{itermax0}, \quad N' = \text{itermax}$$

From an ICTP talk by Iurii Timrov, Trieste, Italy, 23 January 2017

turbo_lanczos.x => turbo_spectrum.x



FLUORECEIN

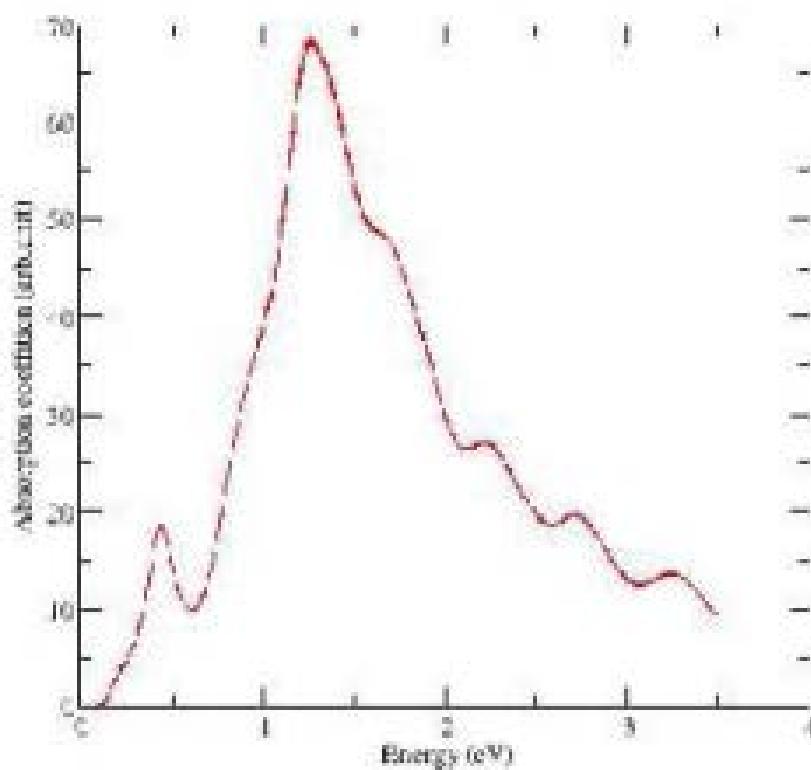


FIG. 8: Results obtained with QUANTUM ESPRESSO at ASEESMA in Accra.

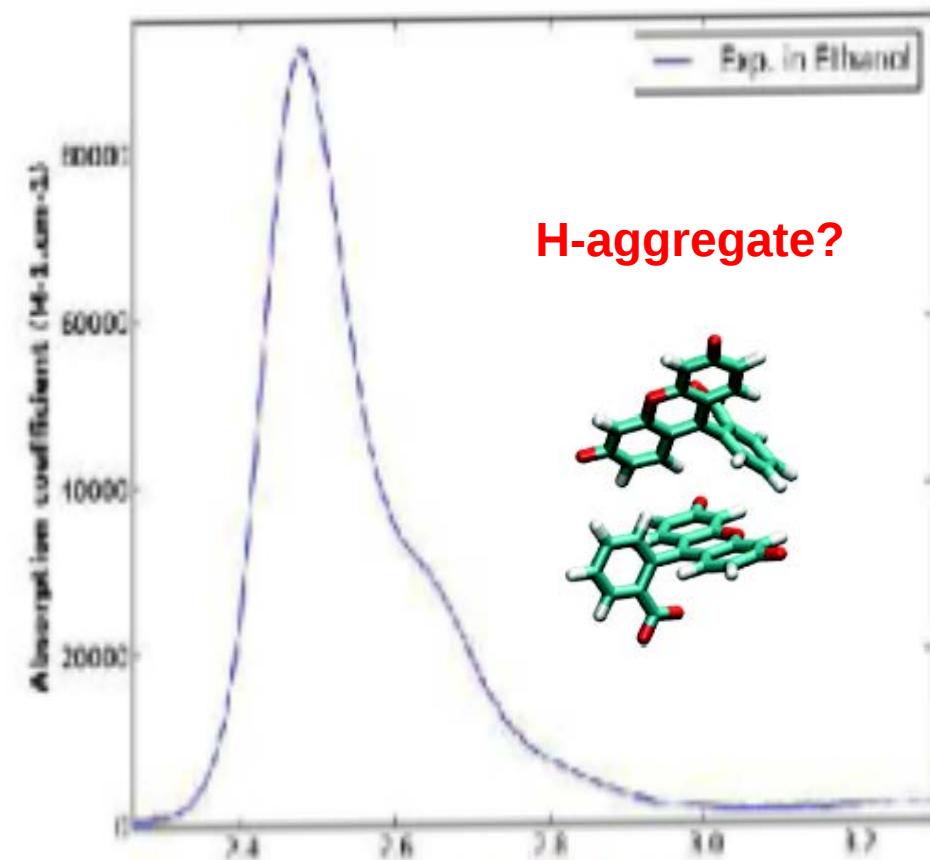


FIG. 5: Absorption spectrum of fluorecein in ethanol.

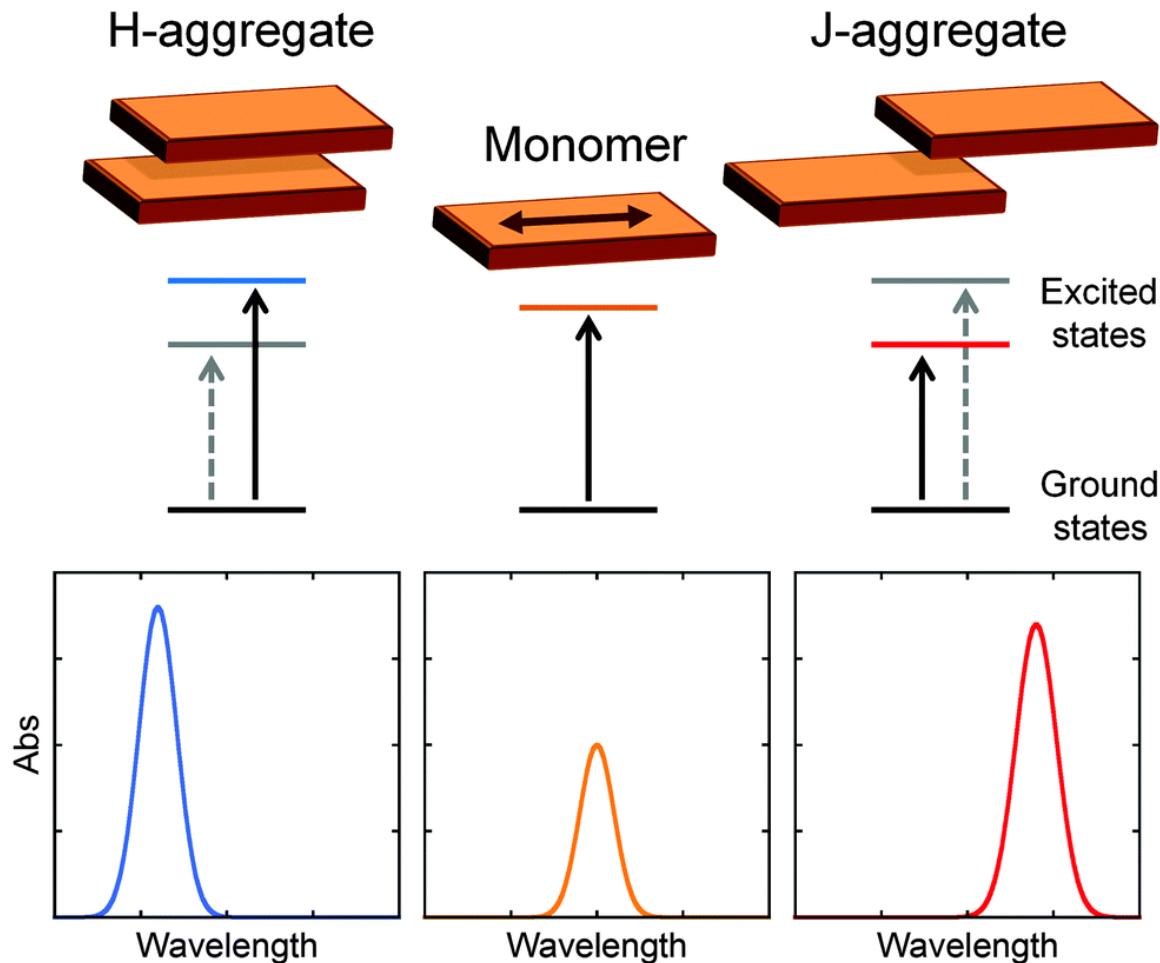


A.A.M.H.M. Darghouth, G.C. Correa, S. Juillard, M.E. Casida, A. Humeniuk, and R. Mitrić,
"Davydov-Type Excitonic Effects on the Absorption Spectra of Parallel-Stacked and Herringbone
Aggregates of Pentacene: Time-Dependent Density-Functional Theory and Time-Dependent
Density-Functional Tight Binding",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

Spectral effects seen in dye aggregates:

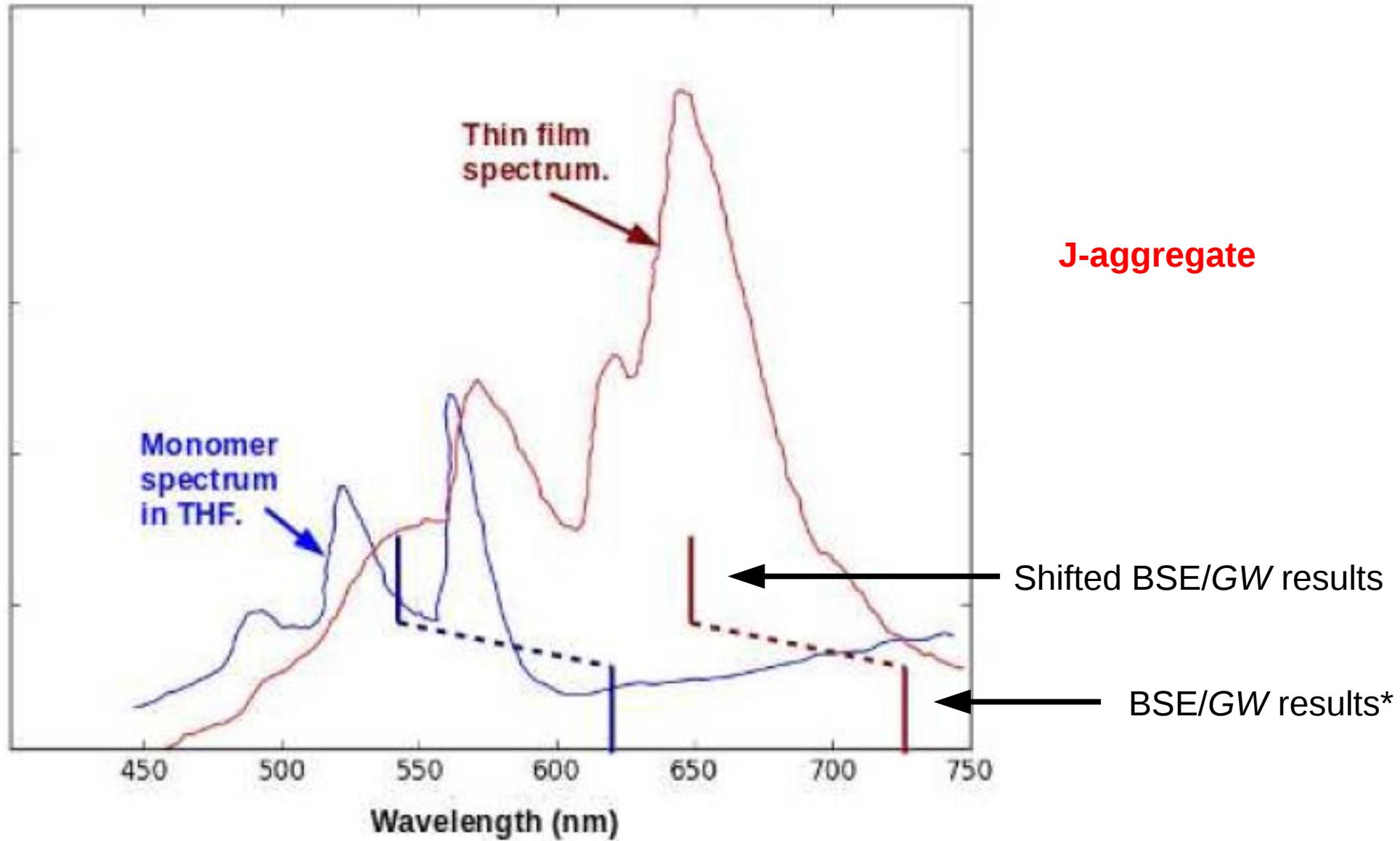
J-aggregates (Jelly/Scheibe) spectrum shifts to lower energies and new narrow peaks appear.

H-aggregates (hypsochromic) spectrum shifts to higher energies.



Davydov Splitting in Pentacene

Absorbance (arbitrary units)

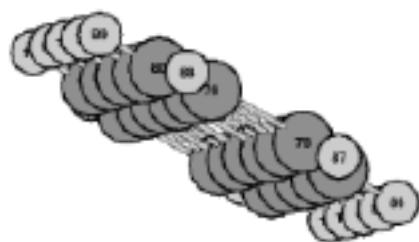


* P. Cudazzo, F. Sottile, A. Rubio, and M. Gatti, "Topical Review: Exciton dispersion in molecular Solids," *J. Phys. Condens. Matter* **27**, 113204 (2015).

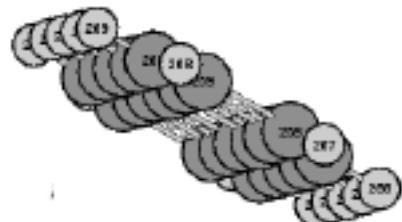
Kasha's Exciton Model*



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.



$$\Psi_1^0 \rightarrow \Psi_1^I \quad (1)$$



$$\Psi_2^0 \rightarrow \Psi_2^I \quad (3)$$

Michael Kasha (1920-2013)

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

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

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

* [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

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

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

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

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

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

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

Excited-State Energy

$$\Psi_I = C_1 \Psi_1^I \Psi_2^0 + C_2 \Psi_1^0 \Psi_2^I \quad (1)$$

$$\begin{bmatrix} A & B \\ B & A \end{bmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E^I \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} \quad (2)$$

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

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

$$\Psi_{\pm}^I = \frac{1}{\sqrt{2}} (\Psi_1^I \Psi_2^0 \pm \Psi_1^0 \Psi_2^I) \quad (5)$$

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

Exciton Splitting

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

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

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

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

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

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

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

Transition Moments

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

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

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

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

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

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

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

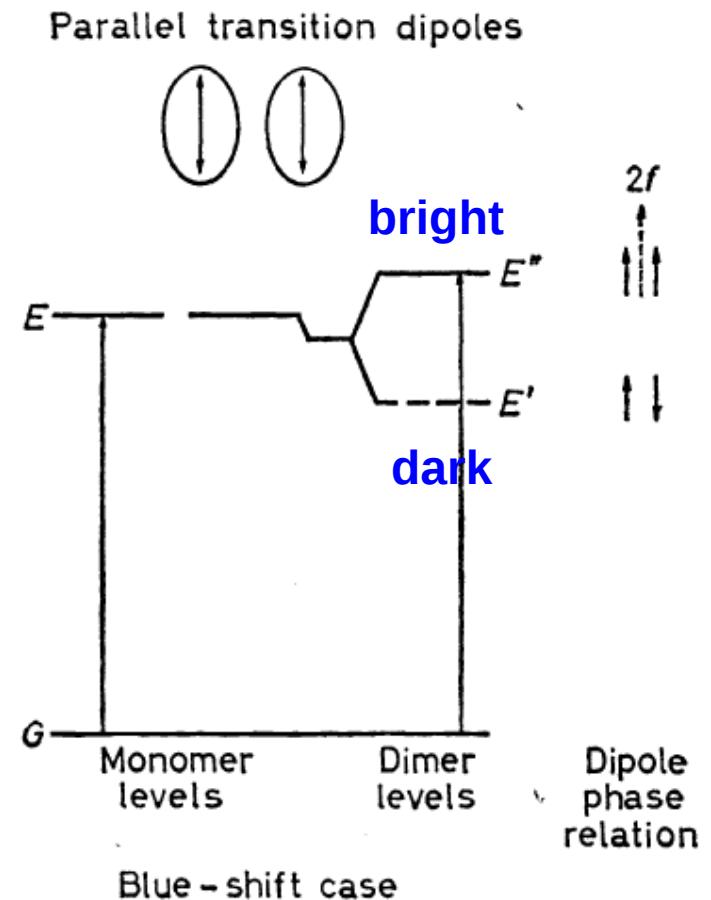
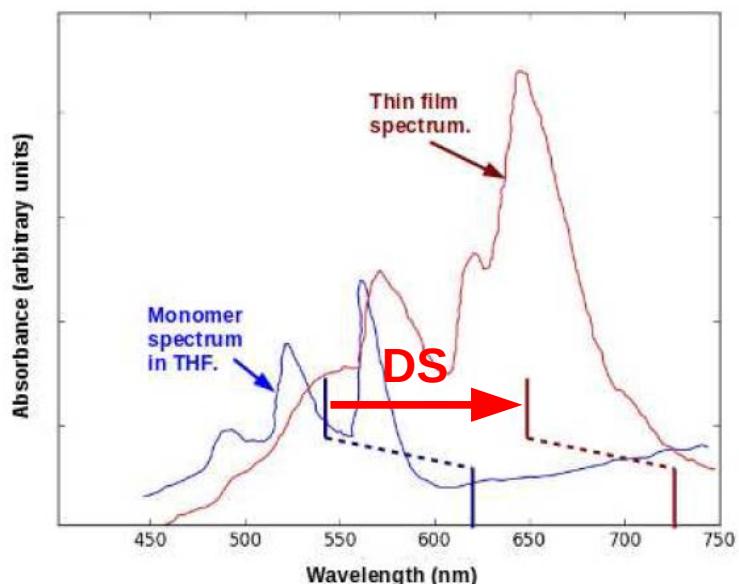


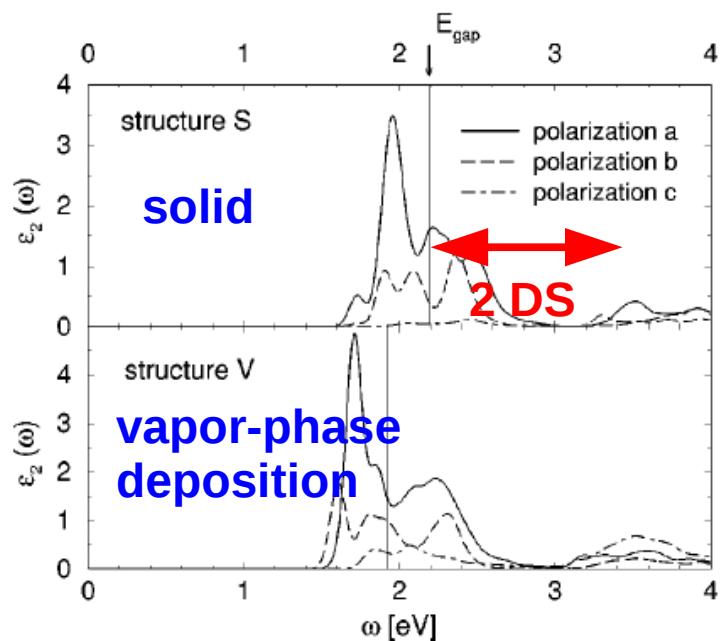
Fig. 1. Ref. [KRE65]

Two Ways to Get the Davydov Splitting (DS)



Shift upon aggregation.

$$\omega_{\pm}^I - \omega_1^0 = (E_{vdW}^I - E_{vdW}^0) \pm E_{\text{exciton splitting}} \approx \pm DS \quad (1)$$

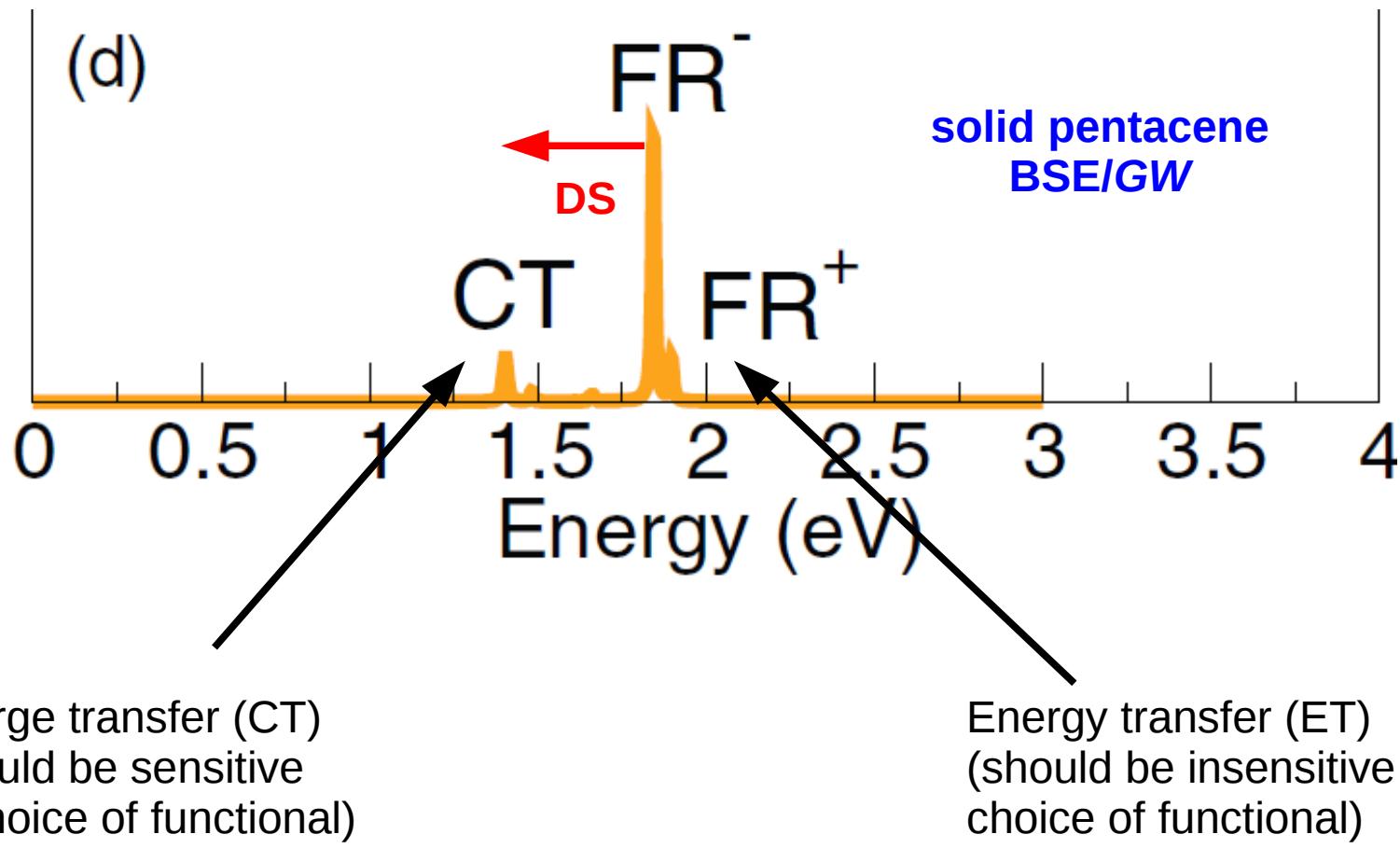


Intensities as a function of light polarization direction.

$${}^q f_{\pm}^I = \frac{\omega_{\pm}^I}{3} |{}^q \mu_1^{I0} \pm {}^q \mu_2^{I0}|^2 \quad (2)$$

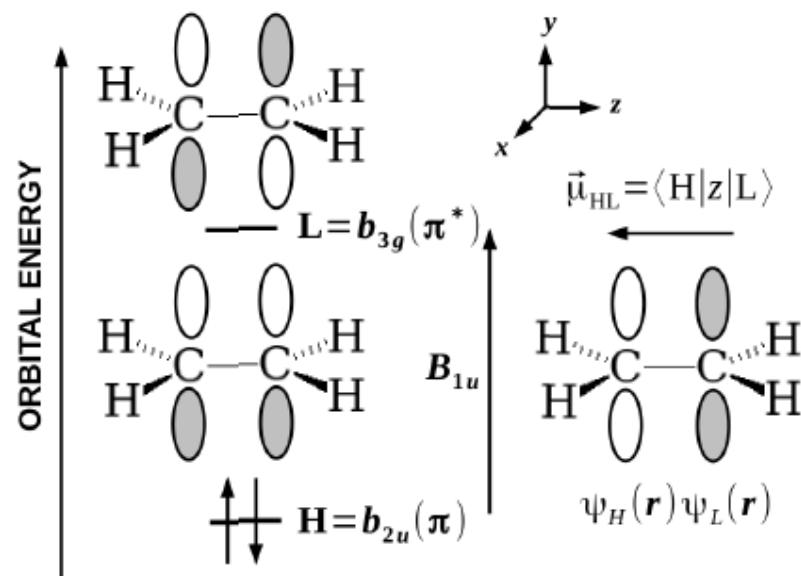
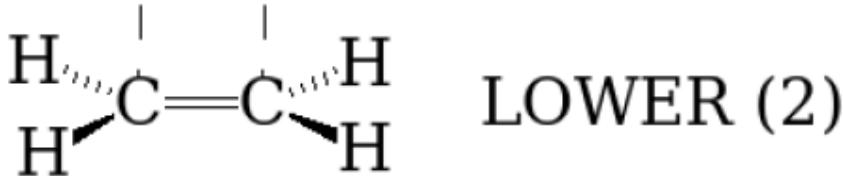
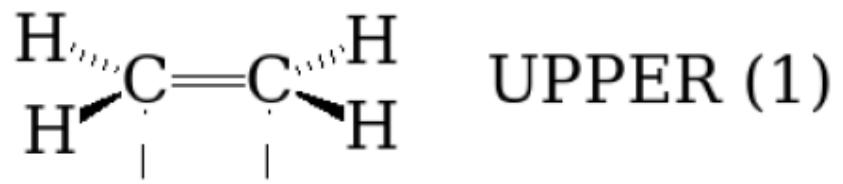
M.L. Tiago, J.E. Northrup, and S.G. Louie, "Ab initio Calculation of the electronic and optical properties of Solid pentacene", *Phys. Rev. B* **67**, 115212 (2003).

But Kasha's Model Neglects Charge Transfer!

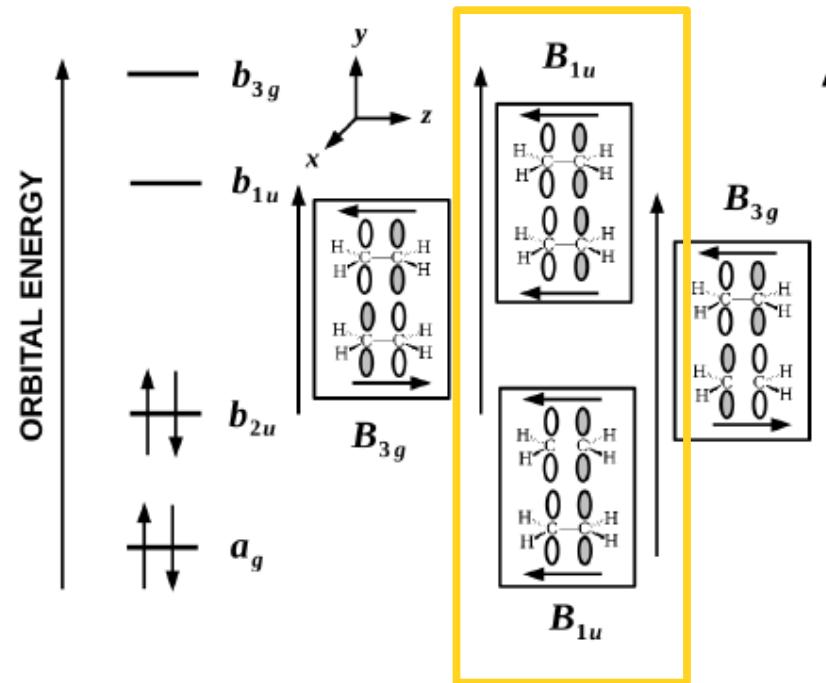
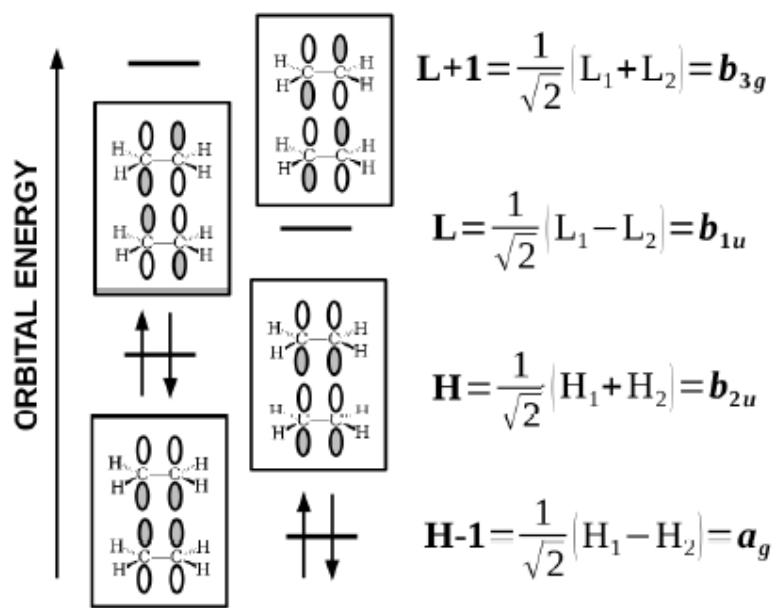


* P. Cudazzo, F. Sottile, A. Rubio, and M. Gatti, "Topical Review: Exciton dispersion in molecular Solids," *J. Phys. Condens. Matter* **27**, 113204 (2015); P. Cudazzo, M. Gatti, A. Rubio, and M. Gatti, "Frenkel versus charge-transfer exciton dispersion in molecular crystals", *Phys Rev. B* **88**,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

Let's try to understand how this works ... "simply"!



Let's try to understand how this works ... "simply"!



$$\Psi = c_1^1(H, L+1) + c_2^1(H-1, L) \quad (1)$$

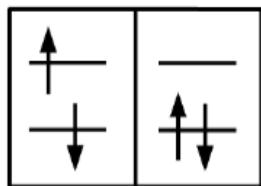
$$\Psi = \frac{c_1 + c_2}{\sqrt{2}} ET_{12} + \frac{c_1 - c_2}{\sqrt{2}} CT_{12} \quad (2)$$

$$ET_{12} = \frac{1}{\sqrt{2}} [{}^1(H_1, L_1) + {}^1(H_2, L_2)] \quad (3)$$

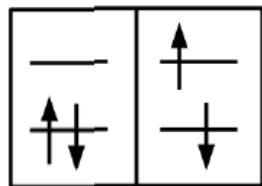
$$CT_{12} = \frac{1}{\sqrt{2}} [{}^1(H_1, L_2) + {}^1(H_2, L_1)] \quad (4)$$

Let's try to understand how this works ... "simply"!

ENERGY TRANSFER (ET)

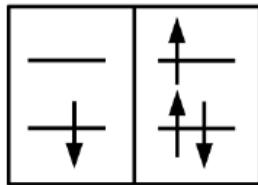


$$^1(H_1, L_1)$$

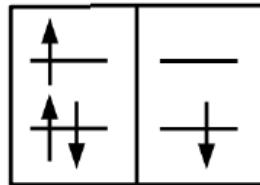


$$^1(H_2, L_2)$$

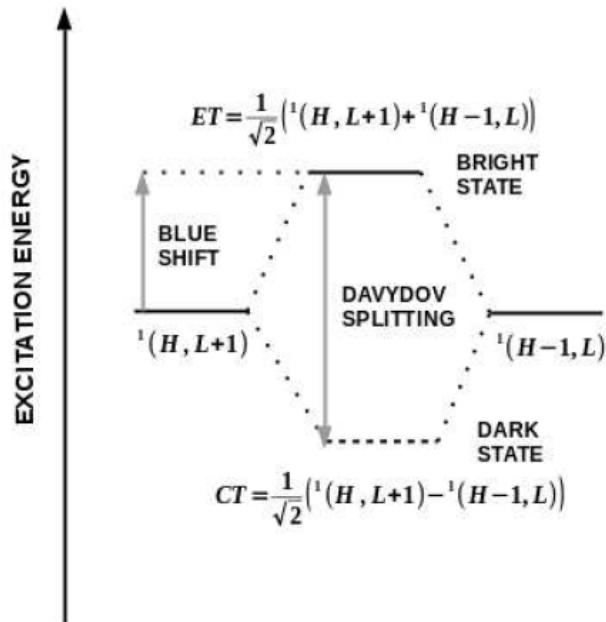
CHARGE TRANSFER (CT)



$$^1(H_1, L_2)$$



$$^1(H_2, L_1)$$



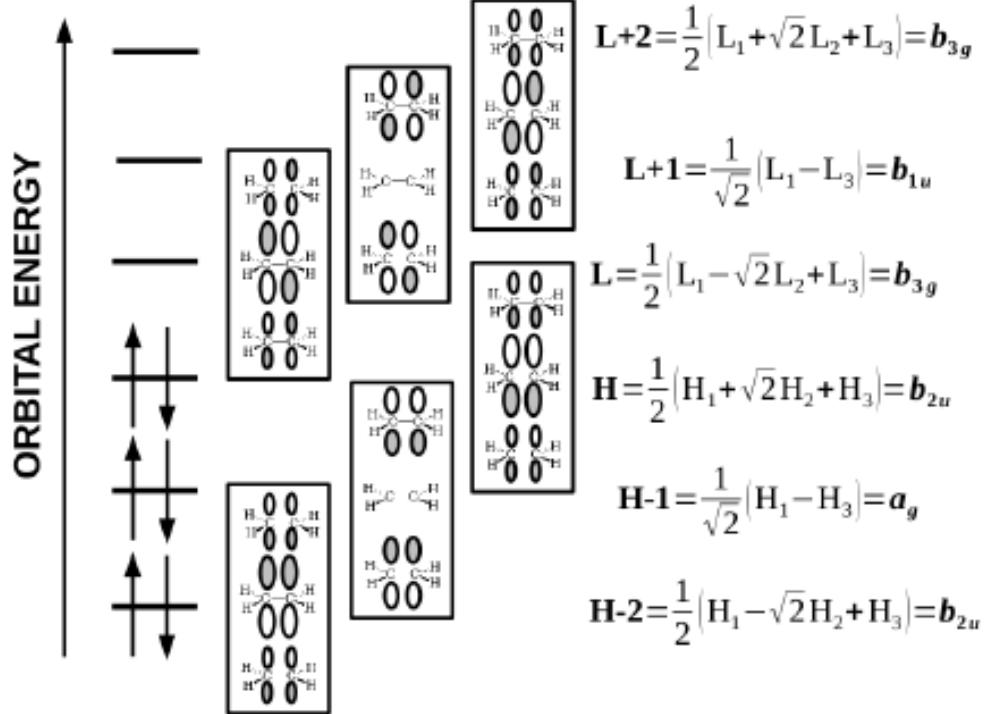
$$\Psi = c_1 {}^1(H, L+1) + c_2 {}^1(H-1, L) \quad (1)$$

$$\Psi = \frac{c_1 + c_2}{\sqrt{2}} ET_{12} + \frac{c_1 - c_2}{\sqrt{2}} CT_{12} \quad (2)$$

$$ET_{12} = \frac{1}{\sqrt{2}} [{}^1(H_1, L_1) + {}^1(H_2, L_2)] \quad (3)$$

$$CT_{12} = \frac{1}{\sqrt{2}} [{}^1(H_1, L_2) + {}^1(H_2, L_1)] \quad (4)$$

Three Stacked Ethylene Molecules!

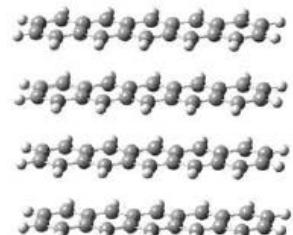


$$\begin{aligned}
 \Psi &= c_1^{-1}(H, L) \\
 &+ \frac{3c_2 + 2c_3 + 3c_4}{2\sqrt{6}} \left(\frac{ET_{12} + ET_{23}}{\sqrt{3}} \right) \\
 &+ \sqrt{\frac{2}{3}}c_3 \left\{ \frac{\sqrt{3}}{2} \left[ET_{13} - \frac{1}{3}(ET_{12} + ET_{23}) \right] \right\} \\
 &+ \frac{c_2 - c_4}{\sqrt{2}} \left(\frac{CT_{12} + CT_{23}}{\sqrt{2}} \right) \\
 &+ \frac{c_2 - 2c_3 + c_4}{2\sqrt{2}} CT_{13} \\
 &+ c_5^{-1}(H - 2, L + 2),
 \end{aligned}$$

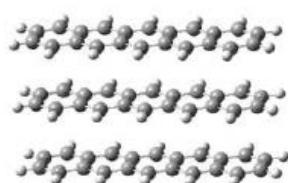
We can apply this to stacked pentacene!!



Model P5

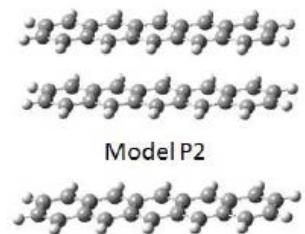


Model P4

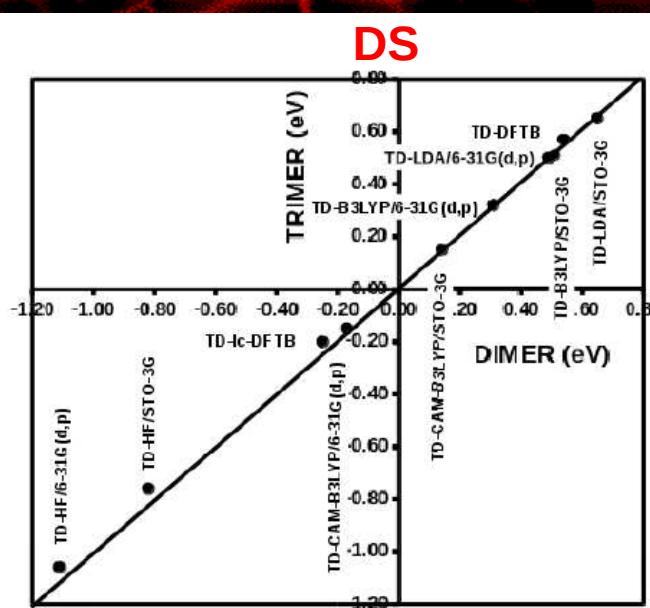
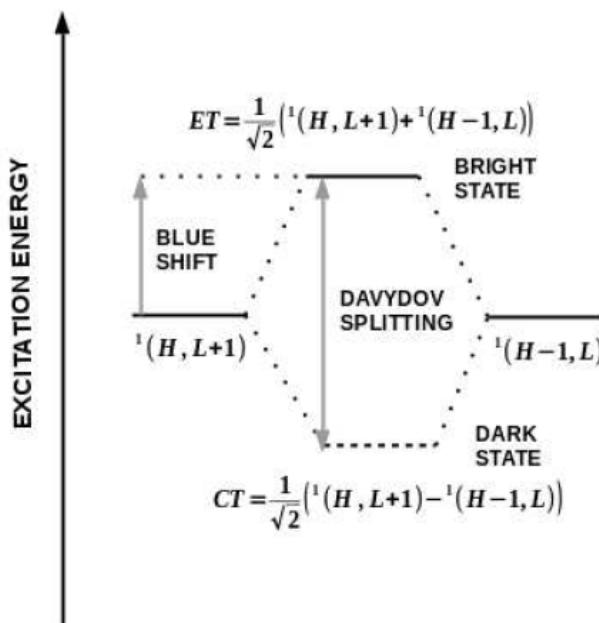


Model P2

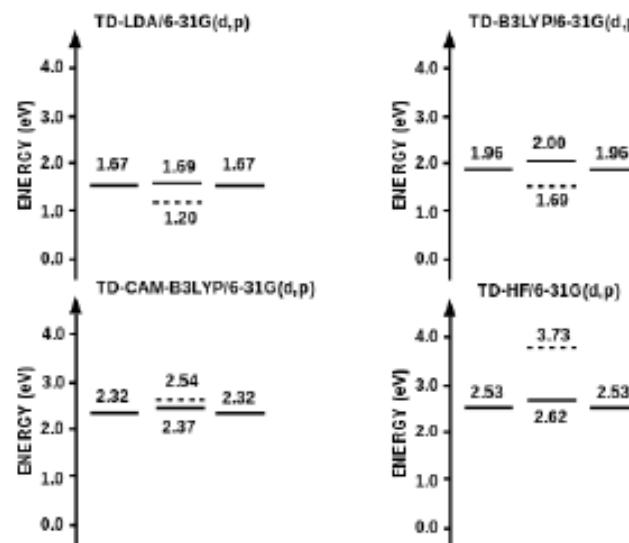
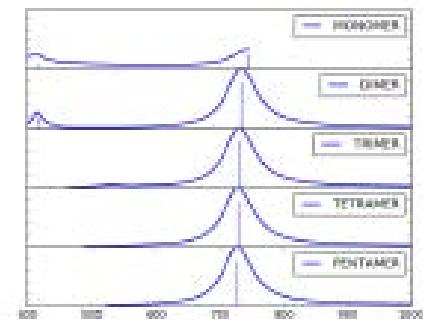
Model P3



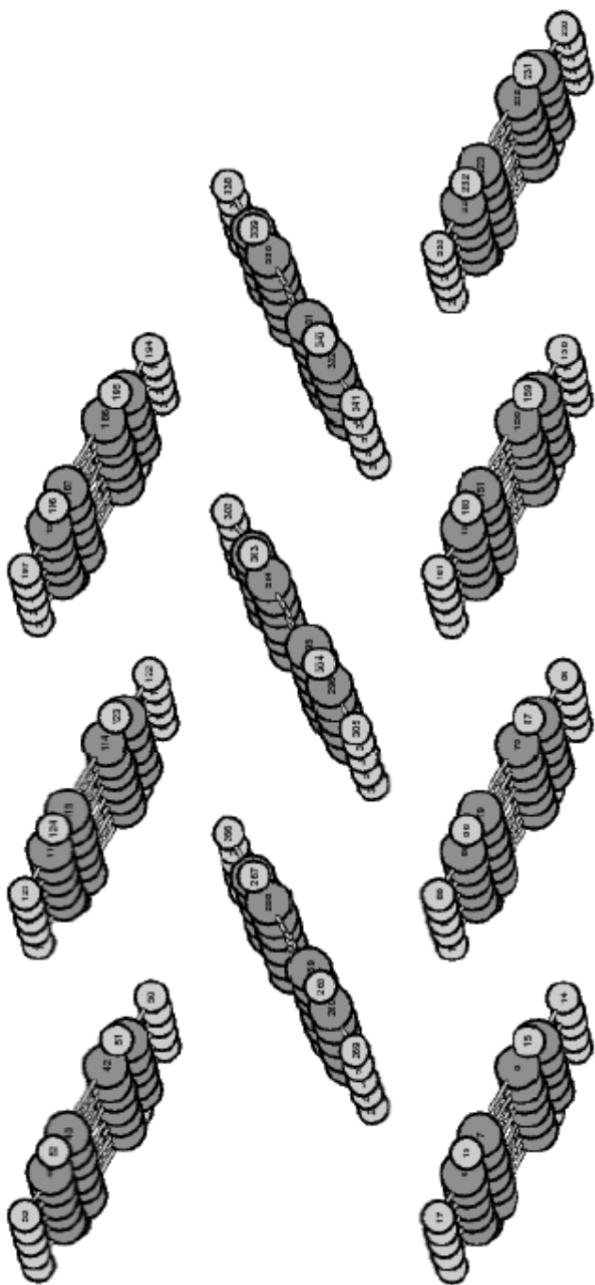
Model P1



DS



Reality Check: Herringbone Pentacene

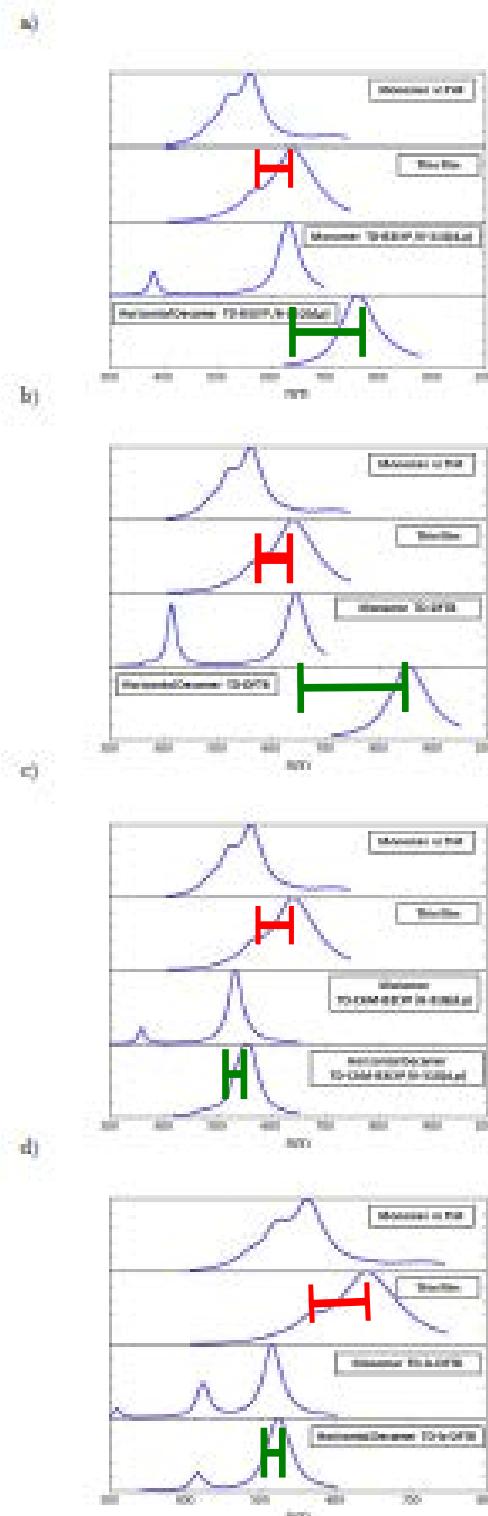


TD-B3LYP/6-31G(d,p)

TD-DFTB

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

TD-Ic-DFTB



OUTLINE

I. PRE-AMBLE

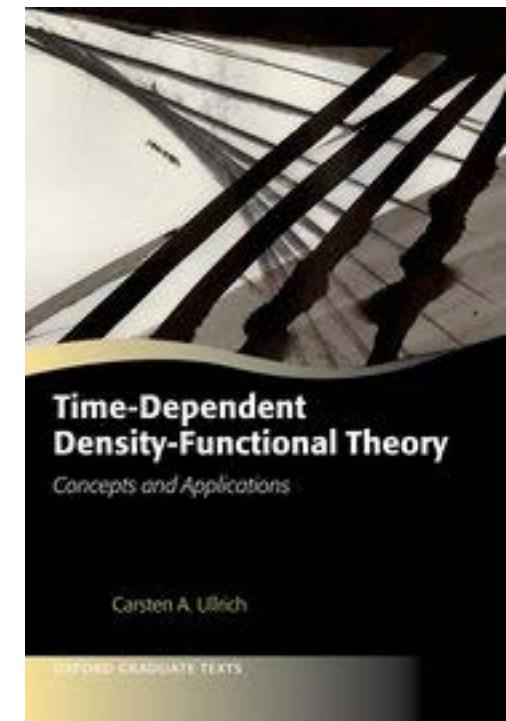
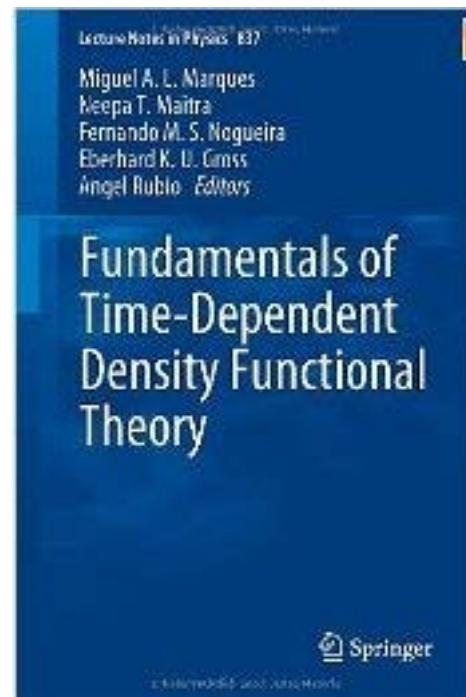
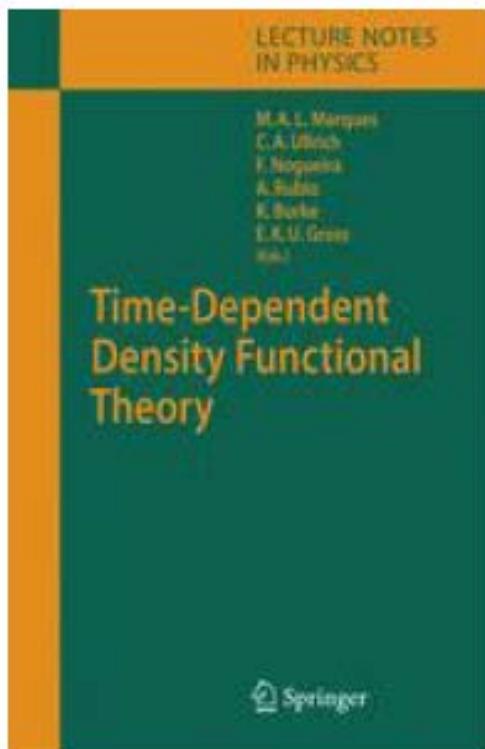
II. THIS COURSE

III. QUANTUM CHEMISTRY FOR EXCITED STATES

IV. TD-DFT FOR EXCITED STATES

V. CONCLUSION

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. Nogueira, E.K.U. Gross, and A. Rubio, *Lecture Notes in Physics*, Vol. 837 (Springer: Berlin, 2011)

Book:

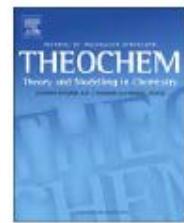
Time-Dependent Density Functional Theory,
C.A. Ullrich (Oxford: 2012)



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Review

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

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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



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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

Annu. Rev. Phys. Chem. 2012. 63:287–323

First published online as a Review in Advance on January 13, 2012

Keywords

adiabatic approximation, memory, electronic excited states, photochemistry, excitons

That's about it ...
... except for a few wise words.

学而不厌

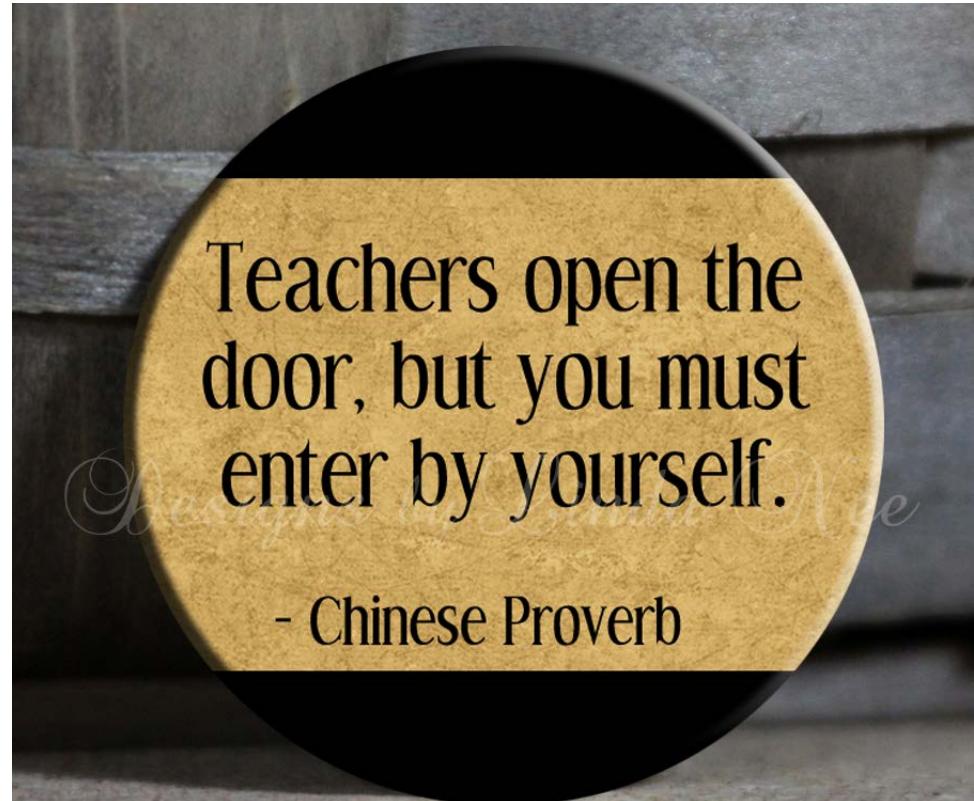
诲人不倦

孔子

Never tire to study -

And to teach others.

Confucius



Teachers open the door, but you must enter by yourself.

- Chinese Proverb

Designs by Linda Nee