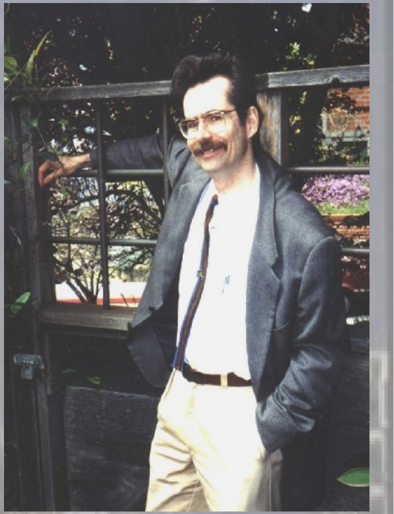
nanostar

An Overview of the RPA From the Quantum Chemistry Perspective

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

RPA workshop
Paris, France
40 min.
Tuesday 26 January 2010



ETSF
European Theoretical Spectroscopy Facility
Rhône-Alpes Associated Node

I. What is Chemistry All About?

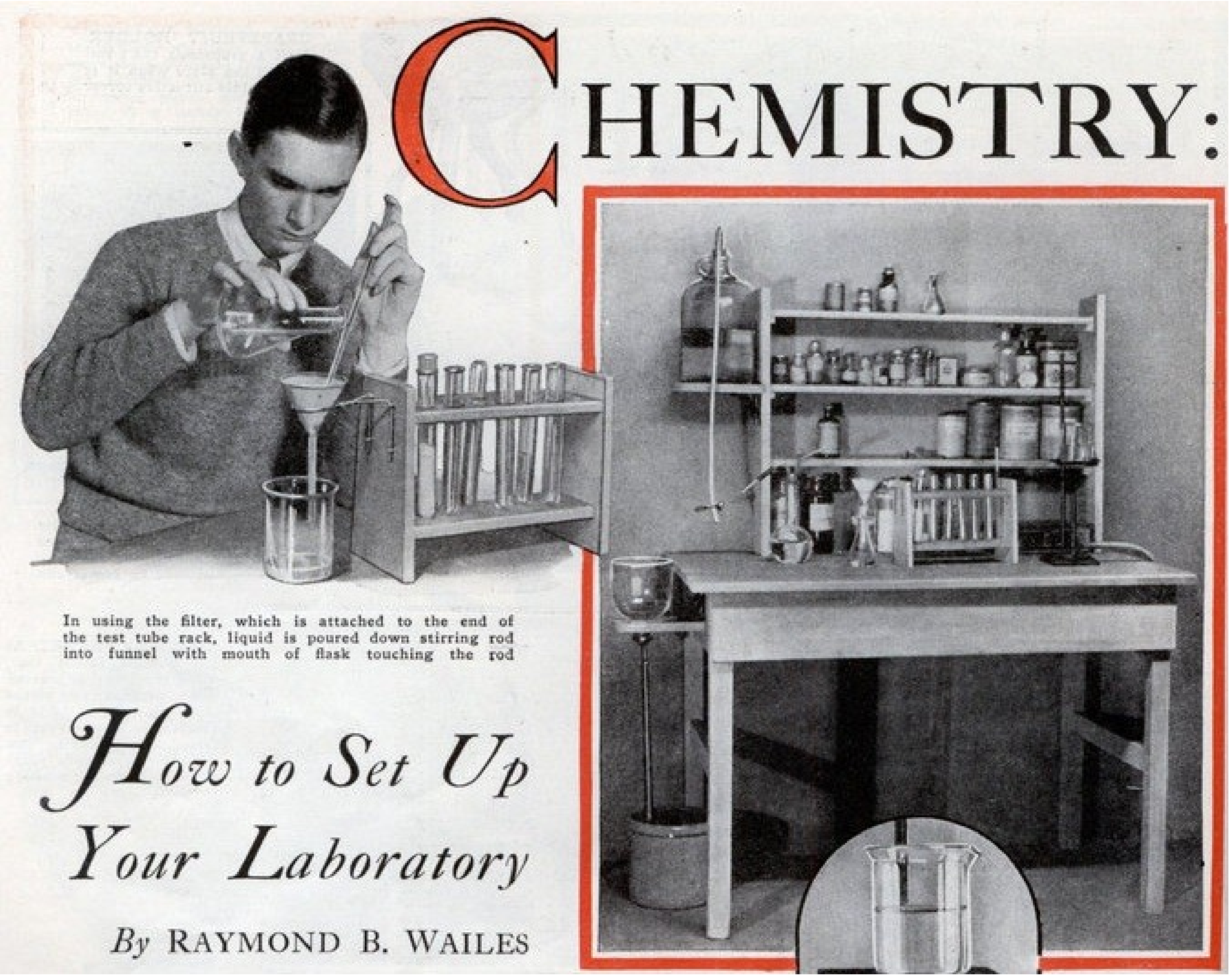
II. The Quantum Chemistry Paradigm

III. Sources of the RPA in Chemistry

IV. Cross-Fertilization

V. (NanoStar)

Bench Chemistry



CHEMISTRY:

In using the filter, which is attached to the end of the test tube rack, liquid is poured down stirring rod into funnel with mouth of flask touching the rod

How to Set Up Your Laboratory

By RAYMOND B. WAILES

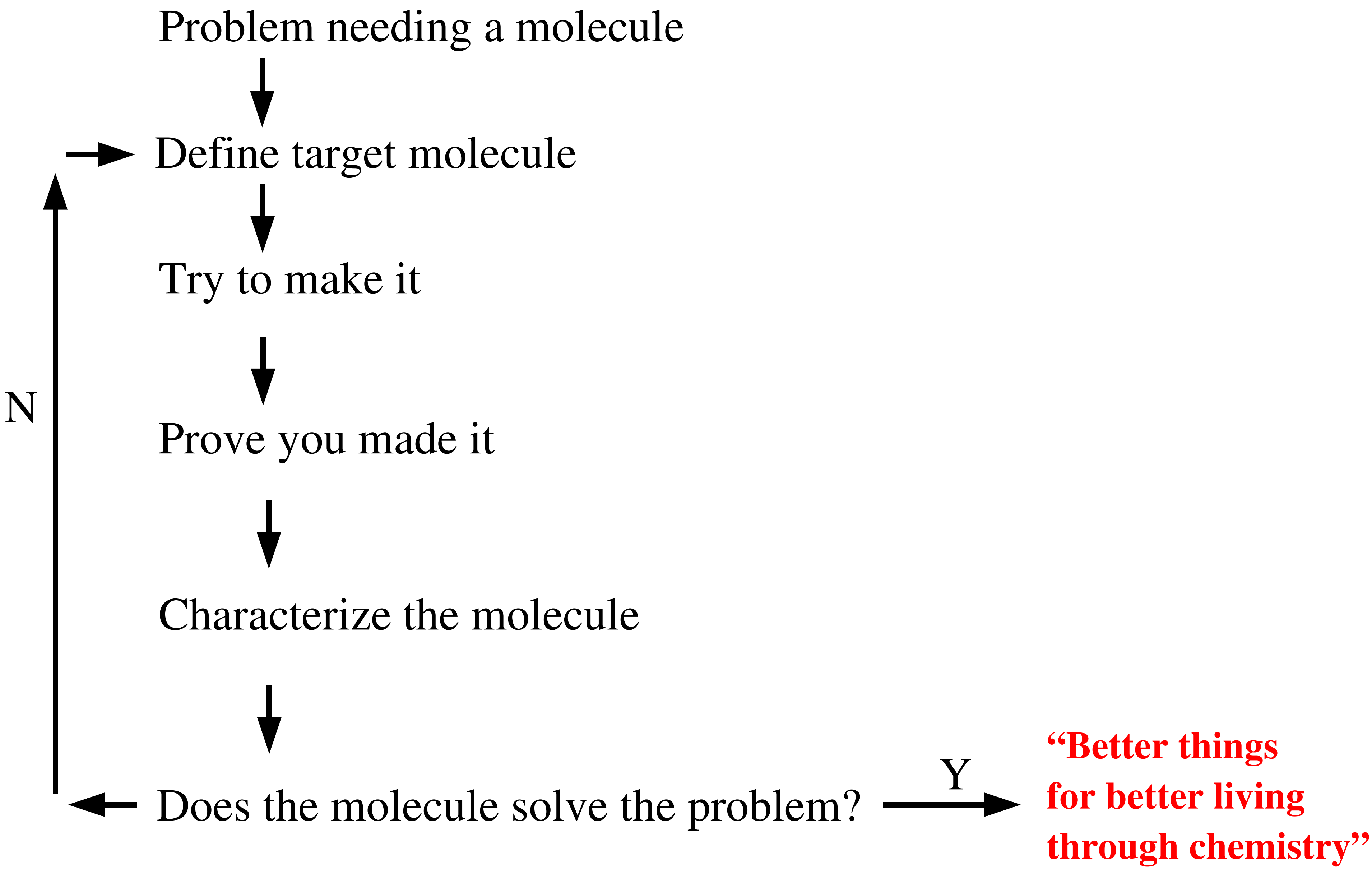
DuPont Chemical Company Motto

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

1982
“Better things for better living.”

1999
“The miracles of science.”

Bench Chemist's Perspective (?)



Problem needing a molecule

Define target molecule

Try to make it

Prove you made it

Characterize the molecule

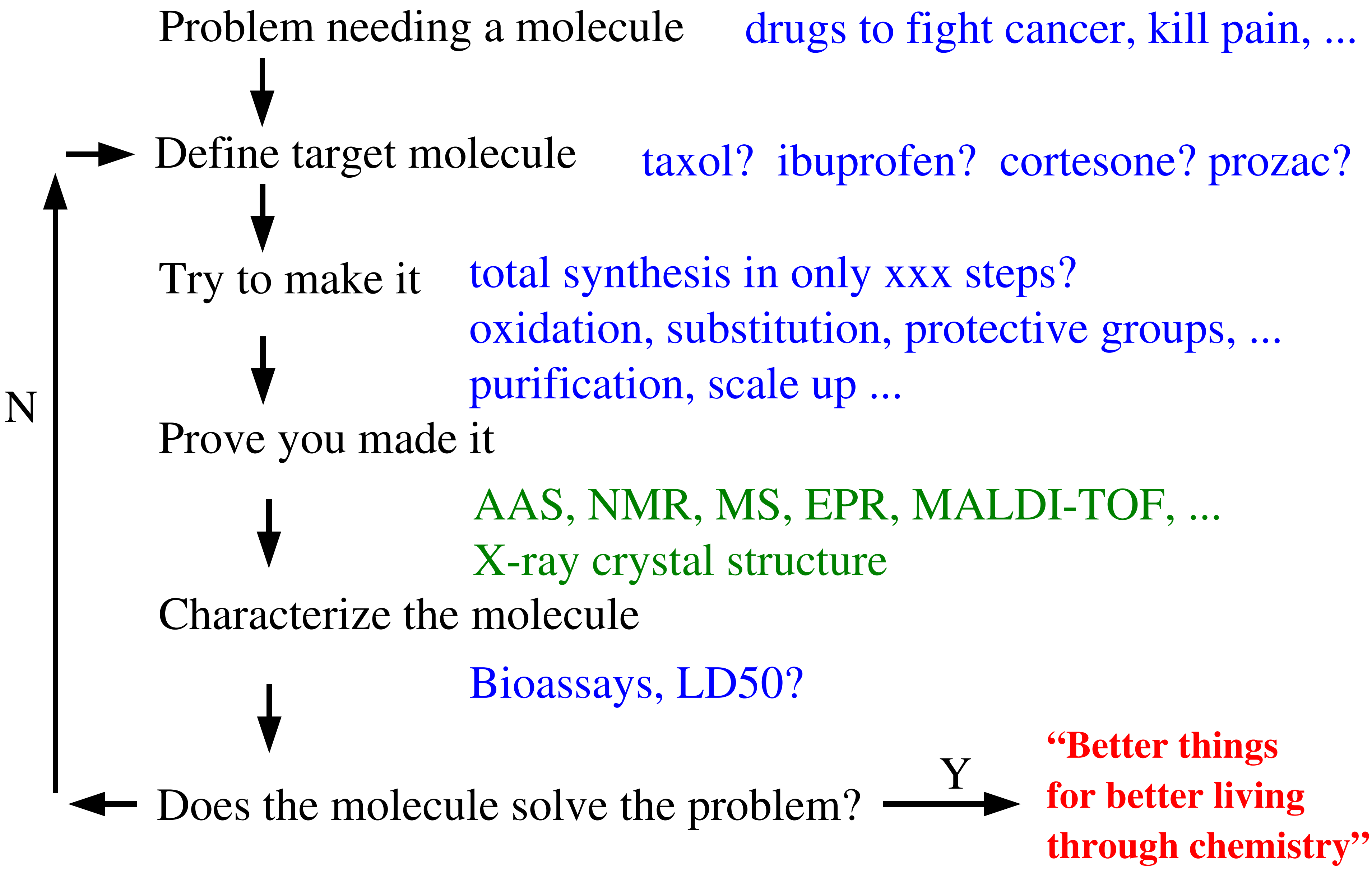
Does the molecule solve the problem?

N

Y

“Better things for better living through chemistry”

Example: Medicinal Chemistry



Problem needing a molecule

drugs to fight cancer, kill pain, ...

Define target molecule

taxol? ibuprofen? cortesone? prozac?

Try to make it

total synthesis in only xxx steps?
oxidation, substitution, protective groups, ...
purification, scale up ...

Prove you made it

AAS, NMR, MS, EPR, MALDI-TOF, ...
X-ray crystal structure

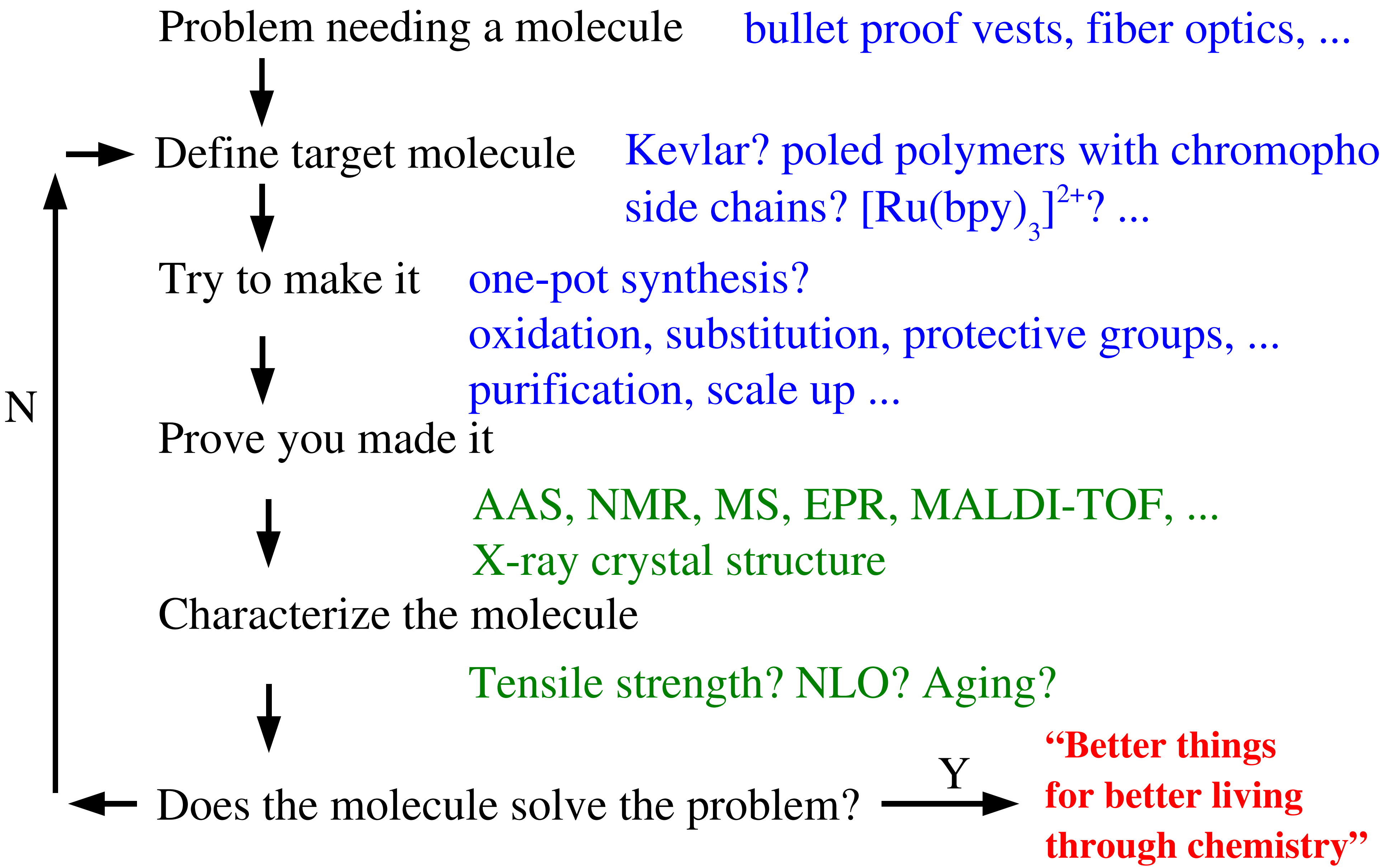
Characterize the molecule

Bioassays, LD50?

Does the molecule solve the problem?

“Better things for better living through chemistry”

Example: Materials Chemistry



Problem needing a molecule — bullet proof vests, fiber optics, ...

Define target molecule — Kevlar? poled polymers with chromophore side chains? $[Ru(bpy)_3]^{2+}$? ...

Try to make it — one-pot synthesis?
oxidation, substitution, protective groups, ...
purification, scale up ...

Prove you made it

AAS, NMR, MS, EPR, MALDI-TOF, ...
X-ray crystal structure

Characterize the molecule

Tensile strength? NLO? Aging?

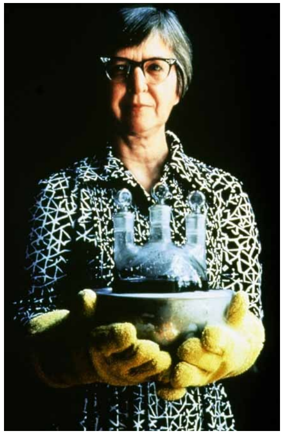
Does the molecule solve the problem?

“Better things for better living through chemistry”

Some Bench Chemists

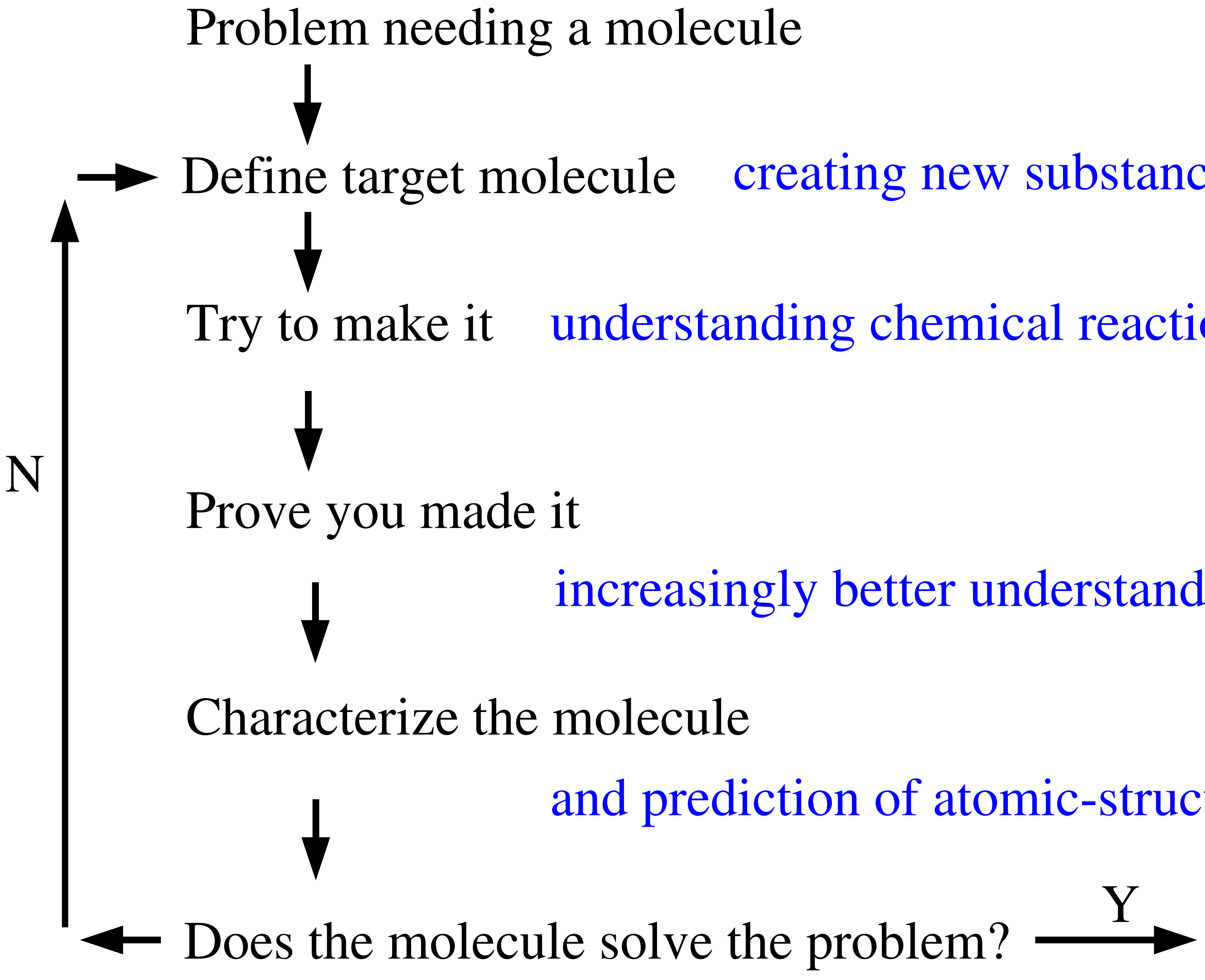
George Washington Carver
(~100 uses of peanuts)

Marie Curie



Stephanie Kwolek
(Kevlar)

From the CNRS Institut de Chimie Web Page*:
“The fundamental missions of chemistry are ...



Problem needing a molecule

Define target molecule

Try to make it

Prove you made it

Characterize the molecule

Does the molecule solve the problem?

creating new substances,

understanding chemical reactions,

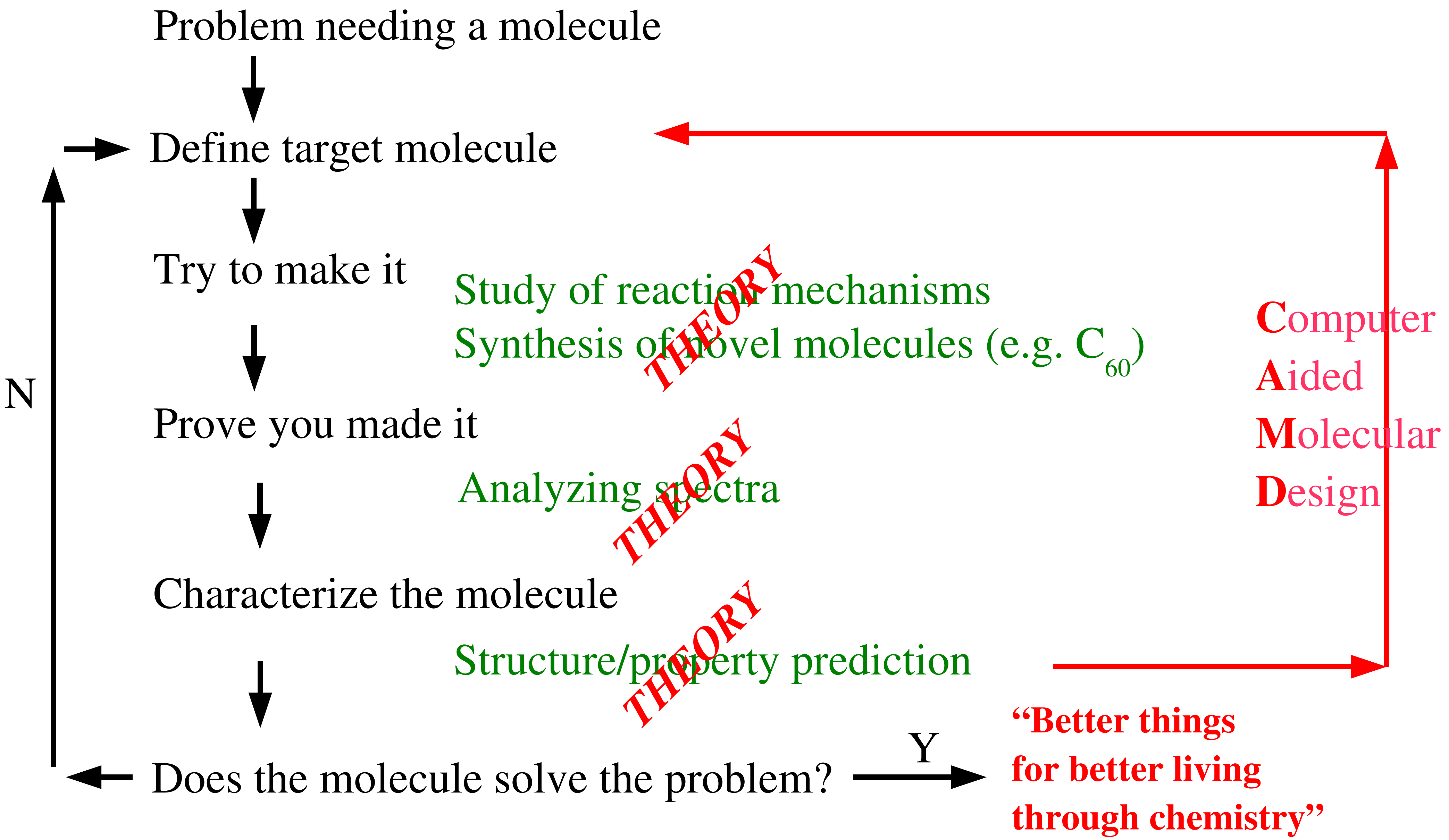
increasingly better understanding of

and prediction of atomic-structure/property relations.”

“Better things
for better living
through chemistry”

*translation MEC

Where is Physical Chemistry? Where is Theoretical Chemistry?



Problem needing a molecule

Define target molecule

Try to make it

Study of reaction mechanisms

Synthesis of novel molecules (e.g. C_{60})

THEORY

Prove you made it

Analyzing spectra

THEORY

Characterize the molecule

Structure/property prediction

THEORY

Does the molecule solve the problem?

Computer
Aided
Molecular
Design

"Better things for better living through chemistry"

“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.”

Also Chemistry

Yuan T. Lee

Traditional Areas of Theoretical Chemistry

Electronic Structure Theory

Quantum chemistry:

- Molecular geometries
- Electronic spectra **RPA**
- Chemical reactivity

Dynamics

- Vibrational/rotational spectra
- Reaction mechanisms
- Reaction rates

Statistical Mechanics

- Crystal structure
- Thermodynamics
- Mechanical strength

What Is Wanted From Quantum Chemistry?

- **“Chemical properties”:**
  - Molecular geometries (bonding)
  - Bond energies
  - Reaction paths
  - Barrier heights
  - etc.
- **“Physical properties”:**
  - UV-Vis
  - EPR
  - ESCA
  - PES
  - NMR
  - NLO
  - etc.

We will understand this distinction between “chemical” and “physical” better later.

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ENVIRONMENTAL EFFECTS

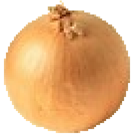
Typical places to find molecules:

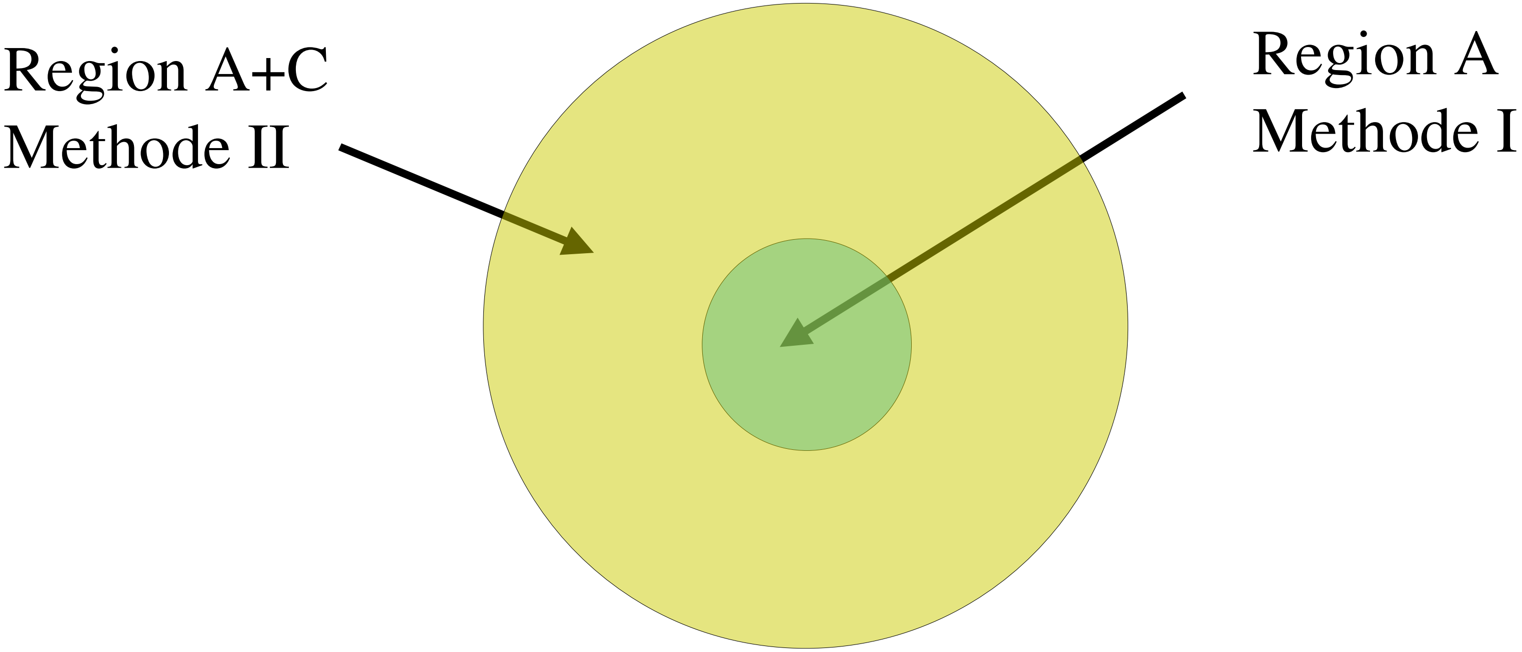
- Gas phase (*rare!*)
- Crystallized in molecular solids
- In solution
- At interfaces (e.g. electrodes, heterogeneous catalysis)

Environmental effects:

- Nonexistent – weak : neglect
- Weak – medium : dielectric continuum
- Medium to strong : semi-empirical force fields and classical mechanics
- Strong : Embedding in a lower-level model (e.g. ONIOM)

ONIOM: Extrapolating Higher-Order Results to Regions Described by Lower-Order Methods





Region A+C
Methode II

Region A
Methode I

$$E^{I}_{A+C} \approx E^{ONIOM}_{A+C} = E^{I}_{A} + \underbrace{\left(E^{II}_{A+C} - E^{II}_{A}\right)}_{scale\,up} = E^{II}_{A+C} + \left(E^{I}_{A} - E^{II}_{A}\right)$$

S. Dapprich, I. Komaromi, K.S. Byun, K. Morokuma et M.J. Frisch, *J. Mol. Struct. (Theochem)* **461-462**, 1 (1999).

Born-Oppenheimer Approximation

Electrons move in field of clamped nuclei

$$\hat{H}_{elec}(\boldsymbol{r};\boldsymbol{R})\Psi_I(\boldsymbol{r};\boldsymbol{R})=E_I^{elec}(\boldsymbol{R})\Psi_I(\boldsymbol{r};\boldsymbol{R})$$

Nuclei move on potential energy surfaces (PESs)

$$\left(\hat{T}(\boldsymbol{R})+V_I(\boldsymbol{R})\right)X_{I,\nu}(\boldsymbol{R})=E_{I,\nu}X_{I,\nu}(\boldsymbol{R})$$

$$V_I(\boldsymbol{R})=E_I^{elec}(\boldsymbol{R})+V_{N,N}(\boldsymbol{R})$$

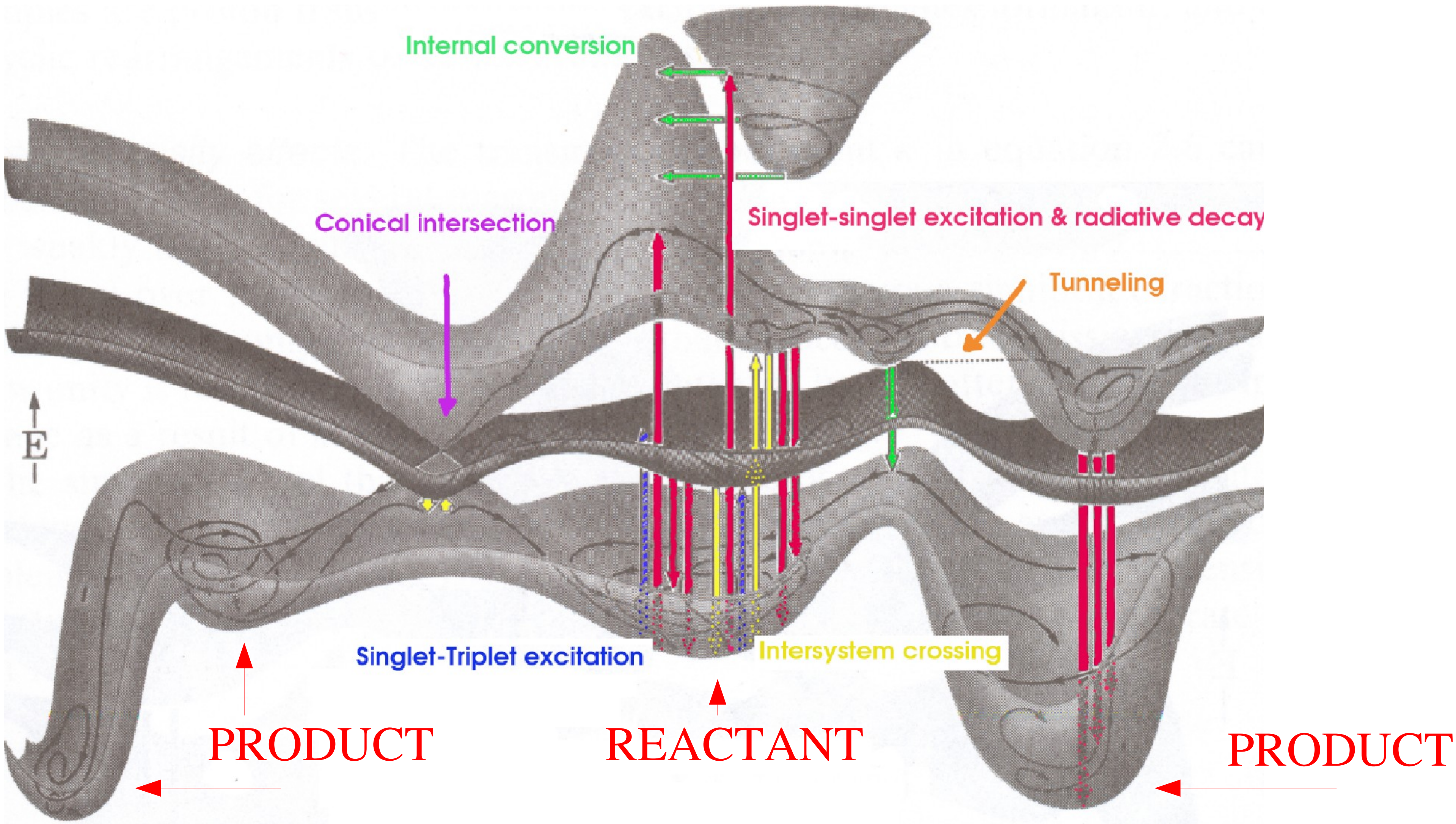
Number of internal degrees of freedom

3N-5 linear molecule
3N-6 otherwise

Classical approximation

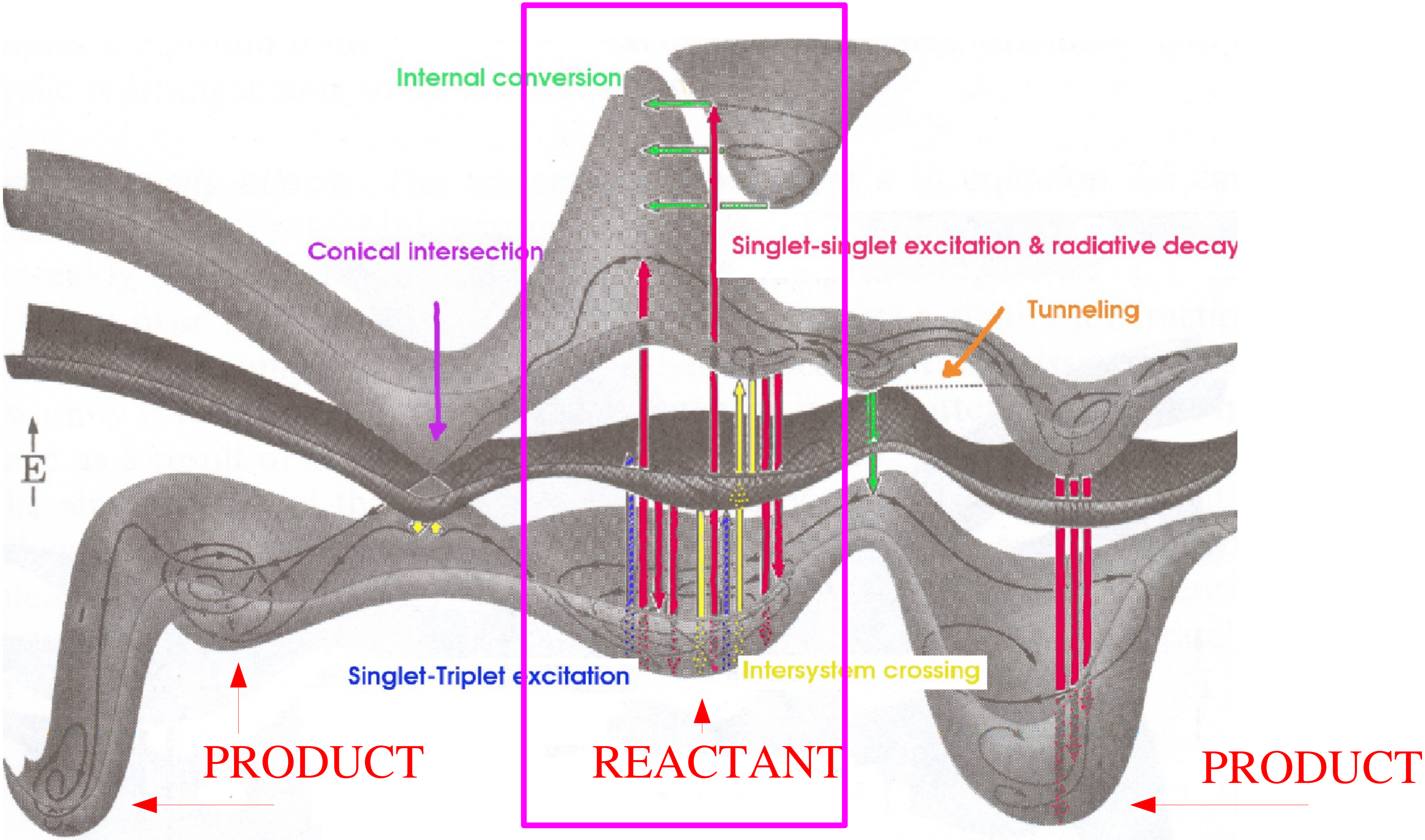
$$M\ddot{\boldsymbol{R}}=\boldsymbol{F}_I=-\nabla\boldsymbol{V}_I(\boldsymbol{R})$$

THERMAL AND PHOTOCHEMICAL POTENTIAL ENERGY SURFACES



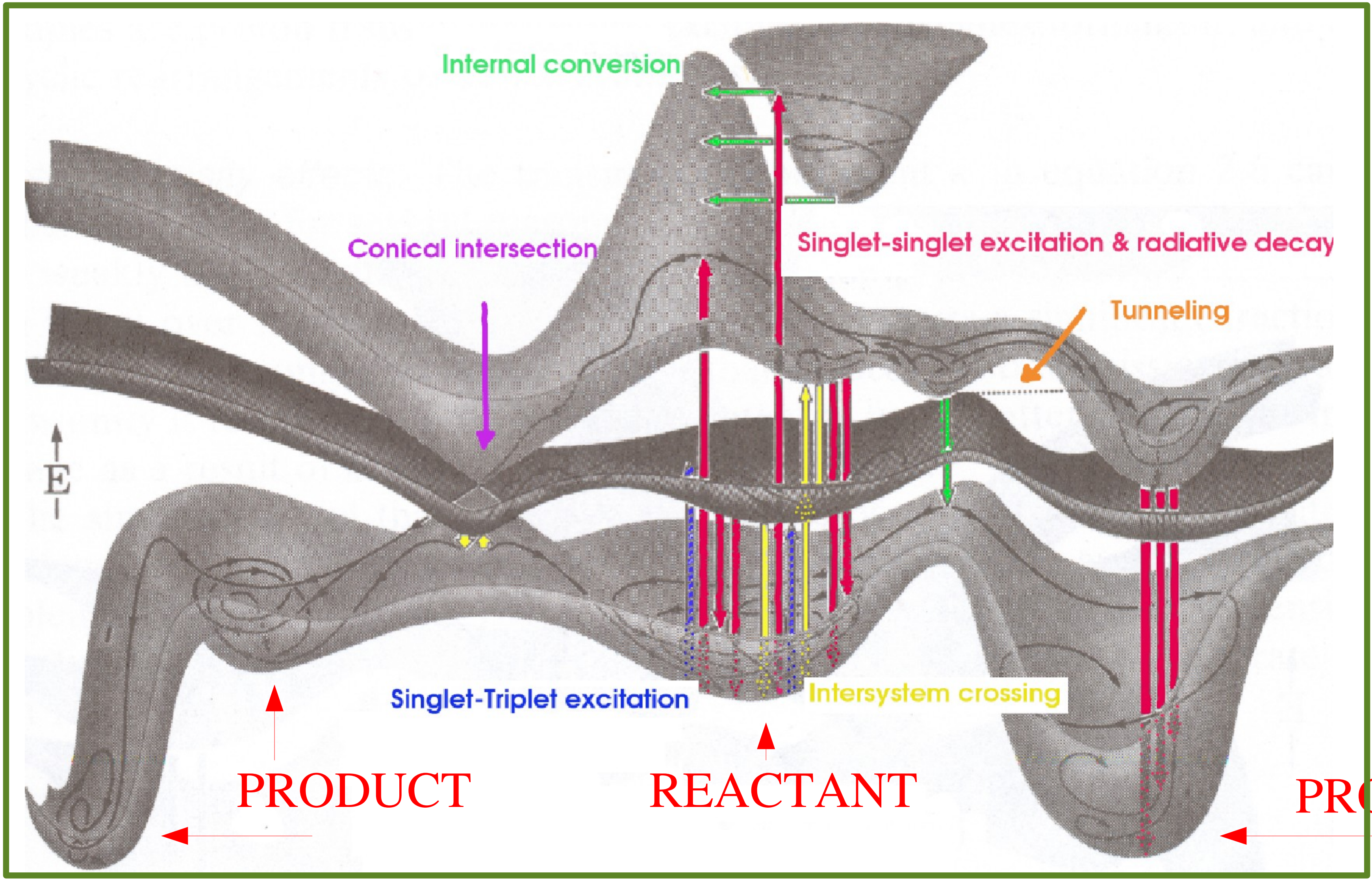
Original image: J. Michl and V. Bonacic-Koutecky, *Electronic Aspects of Organic Photochemistry* (Wiley: New York, 1990), p. 71. Embellishment: E. Tapvicza.

PHOTOPHYSICS



Original image: J. Michl and V. Bonacic-Koutecky, *Electronic Aspects of Organic Photochemistry* (Wiley: New York, 1990), p. 71. Embellishment: E. Tapvicza.

PHOTOCHEMISTRY



PRODUCT

REACTANT

PRODUCT

Original image: J. Michl and V. Bonacic-Koutecky, *Electronic Aspects of Organic Photochemistry* (Wiley: New York, 1990), p. 71. Embellishment: E. Tapvicza.

Ab Initio Solutions of the Electronic Problem

Variational principle

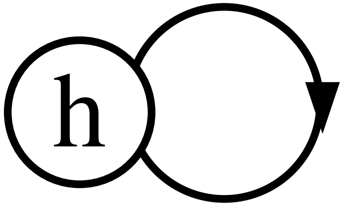
$$E \leq \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

Slater determinant

$$\Phi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \cdots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \cdots & \psi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(N) & \psi_2(N) & \cdots & \psi_N(N) \end{vmatrix} = |\psi_1 \psi_2 \cdots \psi_N|$$

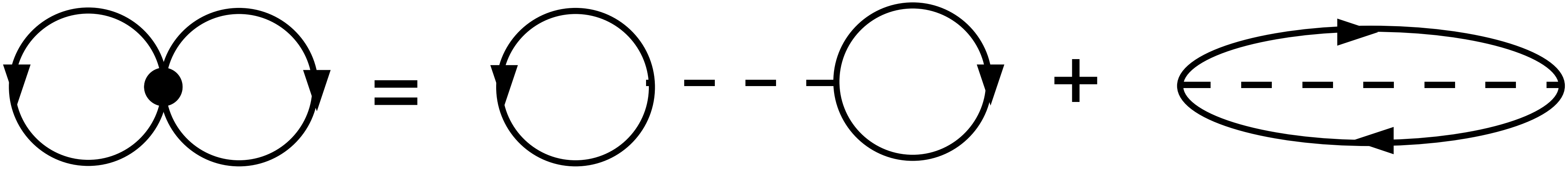
Hartree-Fock Energy

1-electron part



$$E(1)=\sum_i h_{i,i}$$

2-electron part



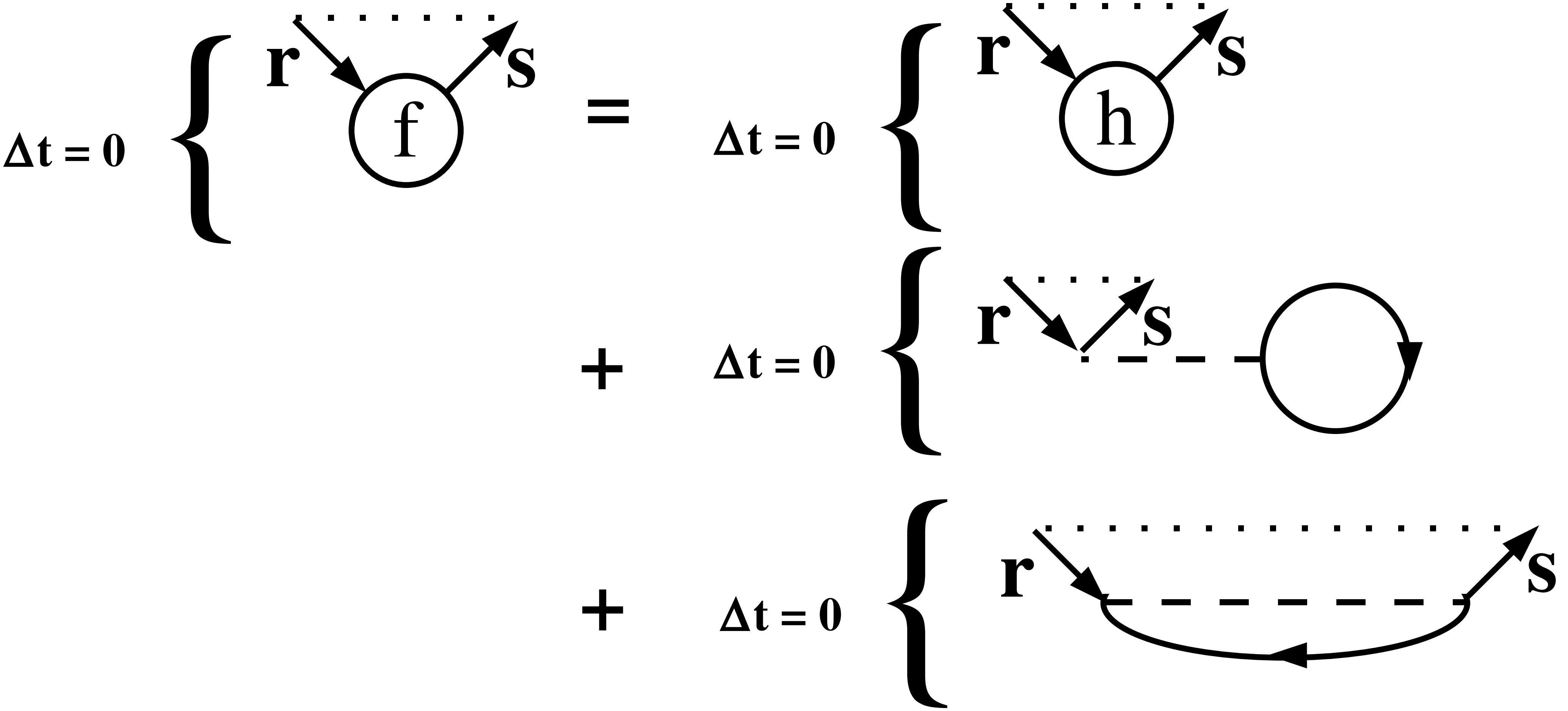
Hugenholtz

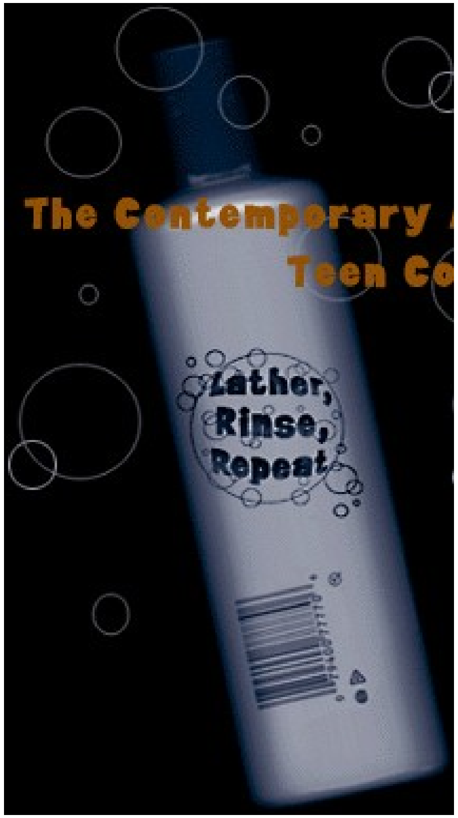
Goldstone

$$E(2)=\frac{1}{4}\sum_{i,j}\langle ij||ij\rangle=\frac{1}{2}\sum_{i,j}(ii||jj)-\frac{1}{2}\sum_{i,j}(ij||ji)$$

Hartree-Fock Equation

Minimizing E_{HF} subject to orbital orthnormality gives $\hat{f}\,\psi_i = \epsilon_i \psi_i$





Of course you solve the HF equations self-consistently!

1960s : Developing Techniques to Solve Hartree-Fock Equation

Molecular Orbitals (MOs) treated as
Linear Combinations of Atomic Orbitals (LCAOs)

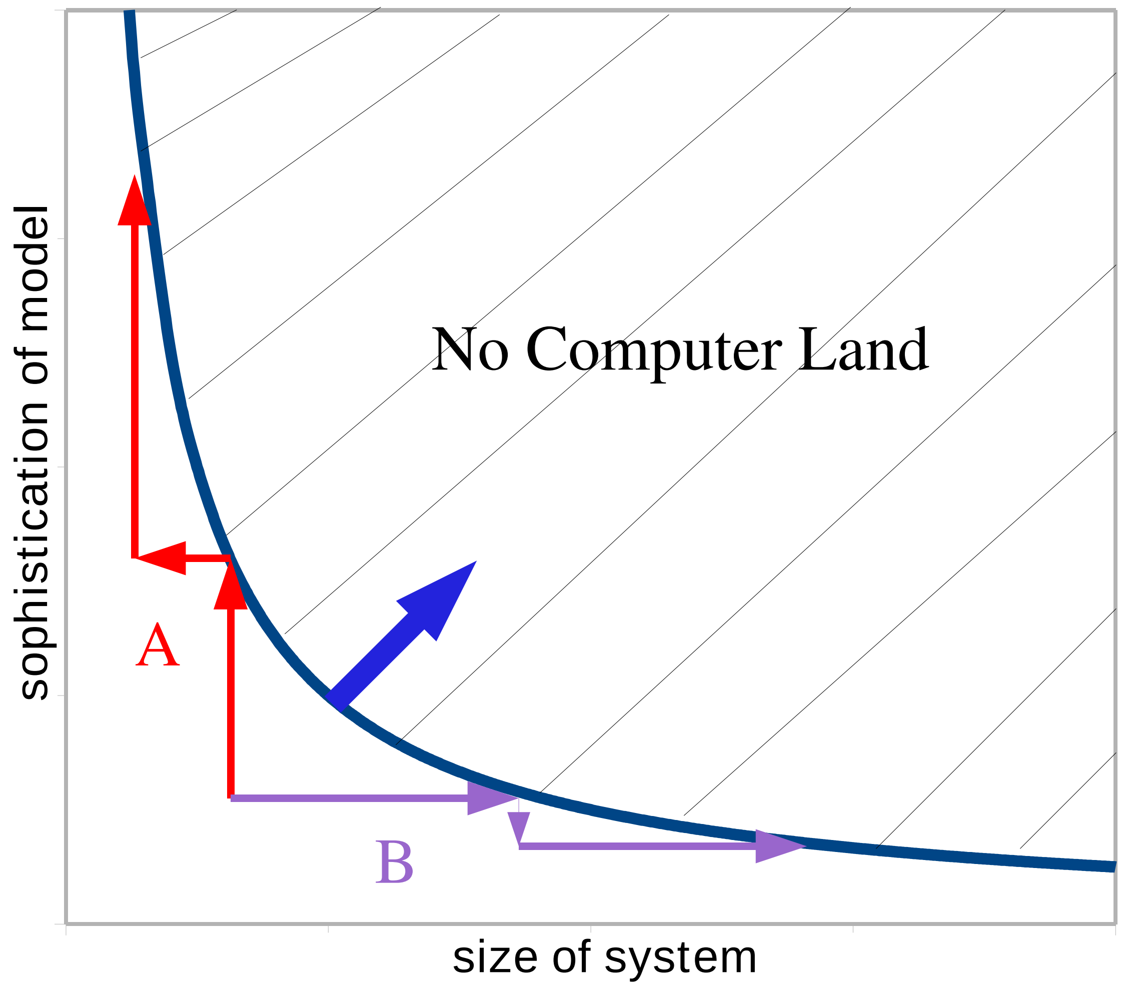
$$\psi_i(1)=\sum_{\mu}\chi_{\mu}(1)\,c_{\mu,i}$$

MO AO

AOs are Atomic Orbitals except

- Usually they are represented as fixed linear combinations of cartesian Gaussian basis functions. $CGTO(\mathbf{r}_A;k,l,m)=x_A^k\,y_A^l\,z_A^m\sum e^{-\alpha_i r_A^2}C_i$
- Even a minimal set of AOs doesn't look like real AOs until it is orthonormalized.
- Extra basis functions are added to allow flexibility for describing bond polarization, lone pair electrons, electron correlation, etc.
- Integrals are analytic => All *ab initio* codes should give identical results to machine precision. (Historically very important!!)

John Pople's Diagram
(Explains Coulson Type A and Type B)



Moving boundary :
computer advances (50%)
theory advances (50%)

C.A. Coulson, "Present status of molecular structure calculations," *Rev. Mod. Phys.* **32**, 170 (1960).
J.A. Pople, "A two dimensional chart of quantum chemistry," *J. Chem. Phys.* **43**, S229 (1965).
M. Karplus, "Three-dimensional `Pople diagram'," *J. Phys. Chem.* **94**, 5435 (1990).

1970s : The Correlation Energy Problem

Typical energy needed to break a chemical bond: 50-100 kcal/mol, but optimizing geometries and finding barrier heights requires greater accuracy.

Bad news: Hartree-Fock is often not quantitative

$$\Delta E_{corr} = E - E_{HF} \leq 0$$

Chemical accuracy = 1 kcal/mol = 0.043363 eV = 1.5936 mH

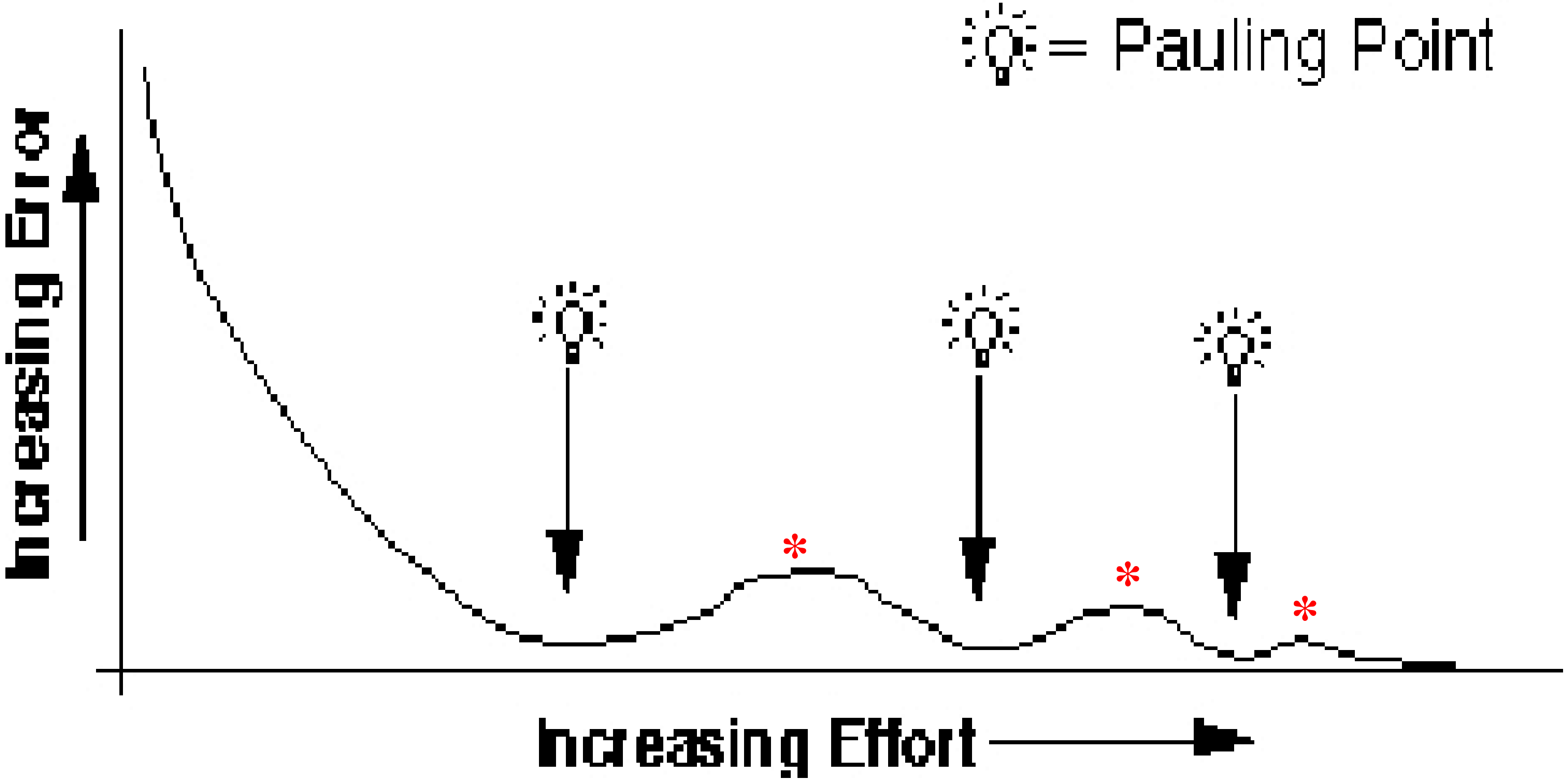
~ ΔE_{corr} for an electron pair in a molecule

C_6H_6 : 42 electrons => 861 pairs => should try to get ΔE_{corr} right!

Good news: Energy differences =>

Quantum Chemistry can often rely on error cancellation

Linus Pauling was good at knowing when to stop



* PhD point

See e.g., Udo Anders, “Interview with Professor Roy McWeeny”, Pisa University, 9 Sept. 1993 http://www.quantum-chemistry-history.com/McWee1.htm

Configuration Interaction

Warning: This is *not* what nuclear physicists mean by configuration interaction!

$$\Psi = \left(\hat{1} + \sum a^+ i C_i^a + \sum b^+ j a^+ i C_{i,j}^{a,b} + \sum c^+ k b^+ j a^+ i C_{i,j,k}^{a,b,c} + \cdots \right) \Phi_{HF}$$

Lazy notation for second quantization: $r^+ = \hat{a}_r^+ \qquad r = \hat{a}_r$

“FORTRAN” index convention:

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

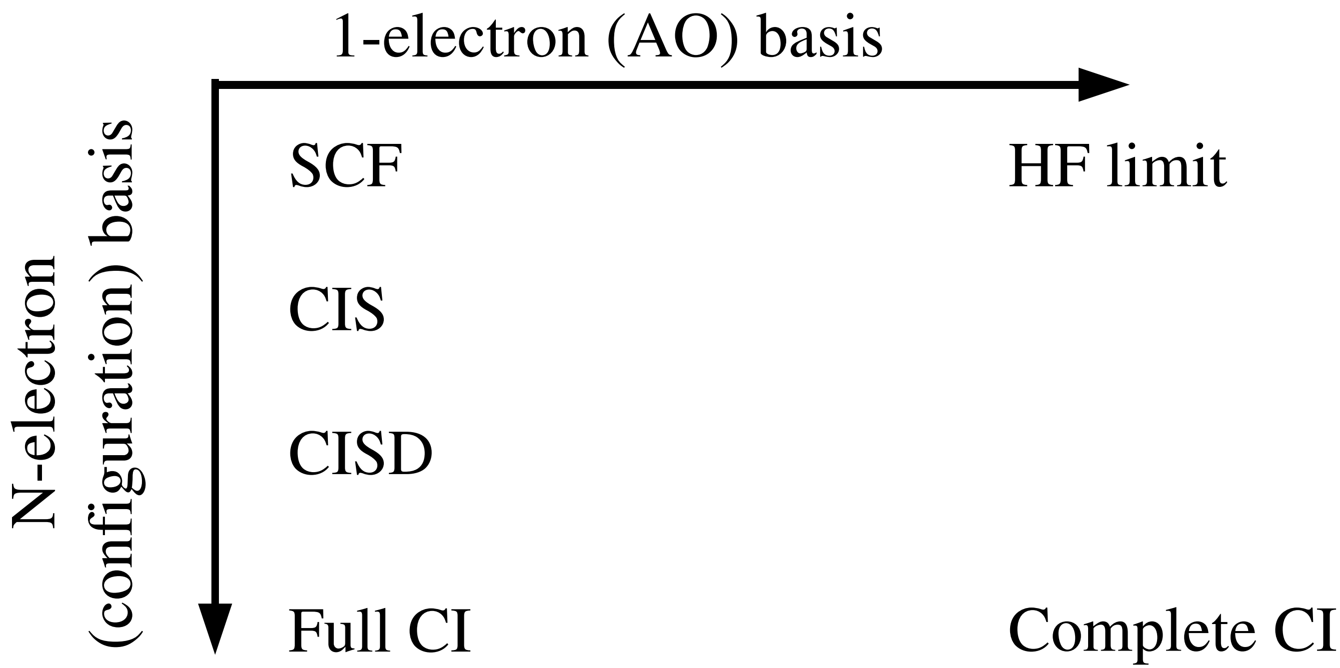
Variational principle

$$E \leq \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

Configuration Interaction

Brillouin's theorem

$$\begin{array}{c|cccc|} & R & S & D & \\ R & E_{HF} & 0 & \boldsymbol{H}_{R,D} & \cdots \\ S & 0 & \boldsymbol{H}_{S,S} & \boldsymbol{H}_{S,D} & \cdots \\ D & \boldsymbol{H}_{D,R} & \boldsymbol{H}_{D,S} & \boldsymbol{H}_{D,D} & \cdots \\ & \vdots & \vdots & \vdots & \cdots \end{array} \begin{pmatrix} 1 \\ \vec{C}_S \\ \vec{C}_D \\ \vdots \end{pmatrix} = E_{CI} \begin{pmatrix} 1 \\ \vec{C}_S \\ \vec{C}_D \\ \vdots \end{pmatrix}$$



1-electron (AO) basis

N-electron (configuration) basis

SCF

HF limit

CIS

CISD

Full CI

Complete CI

Problems with truncated CI

- Must diagonalize very large matrices
- Single-reference CI may not be chemically sensible
- Not size-consistent (also not size-extensive)

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**"

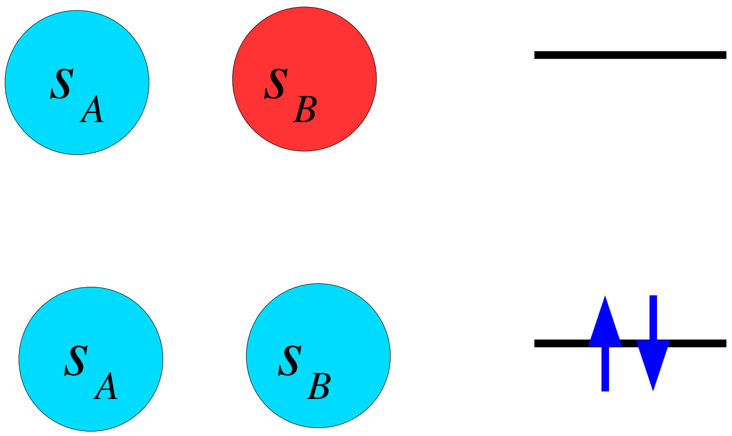
Ernest R. Davidson, *Comp. Phys. Comm.* **53**, 49 (1989).
"**Super-matrix methods**"

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**"

NOTION OF A CONFIGURATION

A configuration is a space and spin symmetry adapted linear combination of Slater determinants.

Take a minimal orbital basis description of H_2 as an illustration.



$$\sigma^* = \frac{1}{\sqrt{2}}\left(s_A - s_B\right)$$

$$\sigma = \frac{1}{\sqrt{2}}\left(s_A + s_B\right)$$

Before dissociation, $\Psi_{react} = |\sigma, \bar{\sigma}|$

After dissociation,

$$\Psi_{prod} = \frac{1}{\sqrt{2}}\left(|s_A, \bar{s}_B| + |s_B, \bar{s}_A|\right) = \frac{1}{2}\left(|\sigma, \bar{\sigma}| - |\sigma^*, \bar{\sigma}^*|\right)$$

NOTION OF *COMPLETE ACTIVE SPACE SELF-CONSISTANT FIELD* (CASSCF)

The minimal model needed to describe the dissocation of H_2 is

$$\Psi = C_{react} \Psi_{react} + C_{prod} \Psi_{prod}$$

or a linear combination of two determinants,

$$\Psi = c_1 |\sigma, \bar{\sigma}| + c_2 |\sigma^*, \bar{\sigma}^*|$$

Minimize the variational energy

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

with respect to the CI coefficients and with respect to the MOs.

MBPT in Quantum Chemistry

Richard Feynman's van ca. 1975.
Licence plate: QANTUM

Moller-Plesset Perturbation Theory

C. Moller and M.S. Plesset, *Phys. Rev.* **46**, 618 (1934)

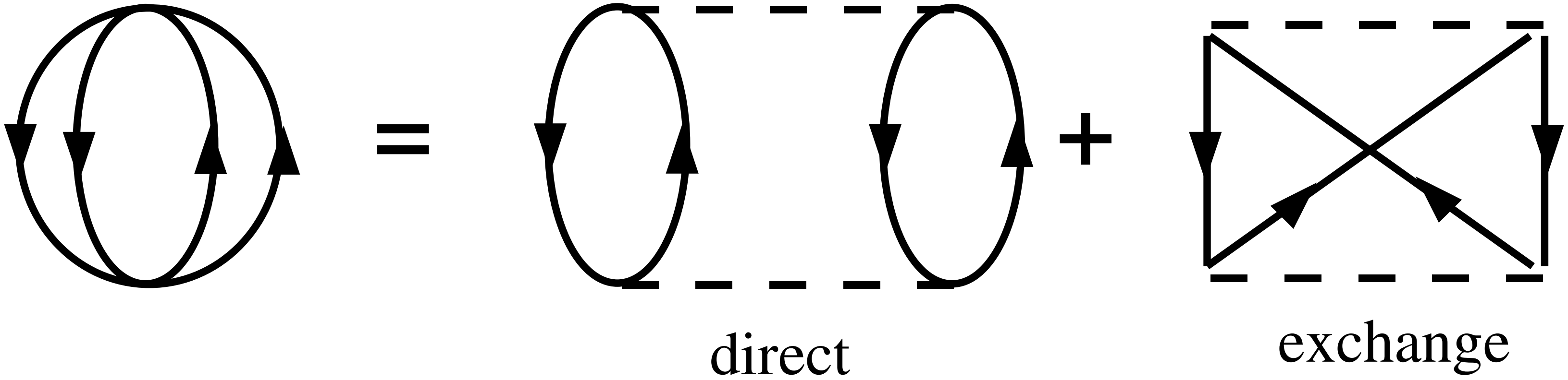
$\hat{H}^{(0)} = \hat{f} = \hat{h} + \hat{v}_{SCF}$ Fock operator

$\hat{V} = \hat{v}_{e,e} - \hat{v}_{SCF}$ fluctuation potential

J. Goldstone, *Proc. Roy. Soc. (London)* **A239**, 267 (1957): Linked cluster theorem.

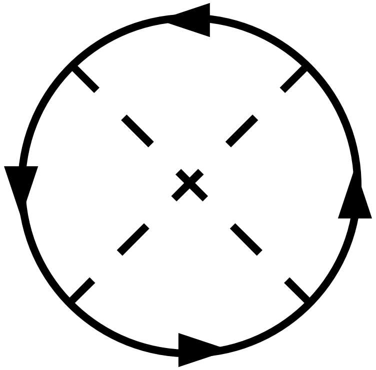
H.P. Kelly, *Phys. Rev.* **131**, 684 (1963): MP2 for atoms, EPV diagrams.

MP2



Things that may bother quantum chemists:

- Diagrams ;-)
- Diagrams with time-going horizontally
- Diagrams disregarding time (Feynman-type) :



Coupled Cluster Theory

$$\Psi = e^{\hat{T}} \Phi \qquad \hat{T} = \sum a^{+} i\, t_{i}^{a} + \sum b^{+} j\, a^{+} i\, t_{i,j}^{a,b} + \cdots$$

Solve projected equations

$$\hat{H}\, e^{\hat{T}} \Phi = E\, e^{\hat{T}} \Phi$$ Schrödinger equation

$$\langle \Phi | \hat{H} | e^{\hat{T}} \Phi \rangle = E \langle \Phi | e^{\hat{T}} \Phi \rangle$$

$$\langle a^{+} i \Phi | \hat{H} | e^{\hat{T}} \Phi \rangle = E \langle a^{+} i \Phi | e^{\hat{T}} \Phi \rangle$$

$$\langle b^{+} j\, a^{+} i \Phi | \hat{H} | e^{\hat{T}} \Phi \rangle = E \langle b^{+} j\, a^{+} i \Phi | e^{\hat{T}} \Phi \rangle$$

etc

Heavy use of diagrams. Conventions may differ.

Pros and Cons of MBPT

Pros

- Size-consistent
- Size-extensive
- Can go systematically to higher order

Cons

- Only single-reference
- Diagrammatic methods are too limiting

Ideally want

- Multireference
- Variational
- Expandable in diagrams
- Possibility to include environmental effects

Density-Functional Theory (DFT)

P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A1133 (9165).

Energy

$$E = T_s + \int \rho \, v_{ext} + \frac{1}{2} \int \int \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}} + E_{xc}[\rho]$$

MO equation

$$\left(\hat{t}_s + v_{ext} + \int \frac{\rho(\boldsymbol{r}_2)}{r_{12}} + v_{xc} \right) \psi_i = \epsilon_i \psi_i \qquad v_{xc}[\rho](1) = \frac{\delta E_{xc}[\rho]}{\delta \rho(1)}$$

Time-dependent DFT (TD-DFT)

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

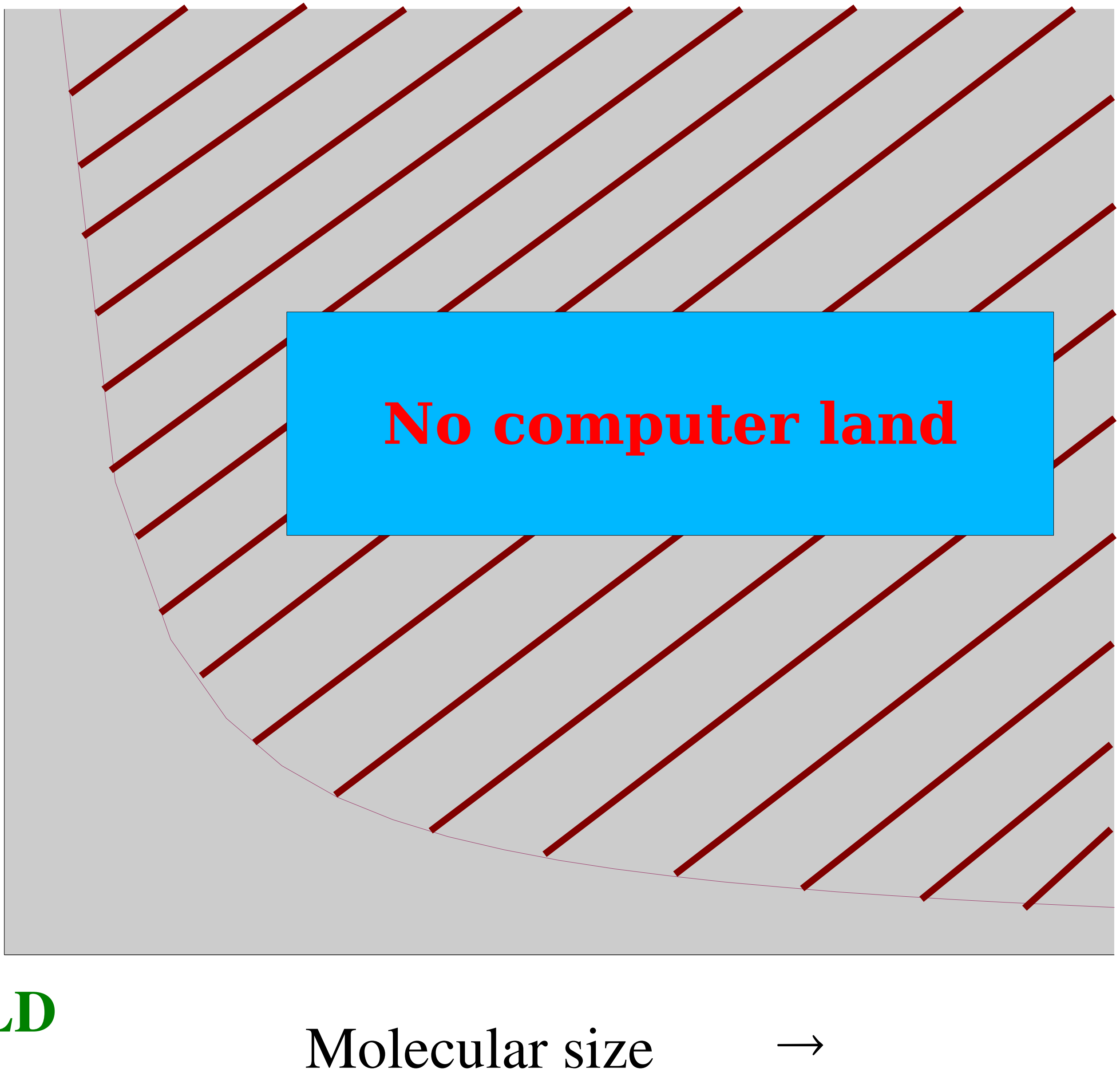
$$\left(\hat{t}_s + v_{ext}(t) + \int \frac{\rho(\boldsymbol{r}_2 t)}{r_{12}} + v_{xc}(t) \right) \psi_i(t) = i \frac{\partial}{\partial t} \psi_i(t) \qquad v_{xc}^{AA}[\rho](\boldsymbol{r}_1 t) = \frac{\delta E_{xc}[\rho_t]}{\delta \rho_t(\boldsymbol{r}_1)}$$

Jacob's ladder

THEORETICAL CHEMISTRY HEAVEN

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

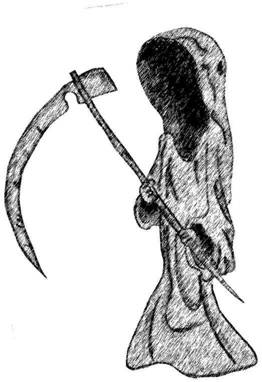
HARTREE WORLD



J.P. Perdew and K. Schmidt, "Jacob's ladder of density functional approximations for the exchange-correlation energy," in *Density Functional Theory and Its Applications*, edited by V.E. Van Doren, K. Van Alseoy, and P. Geerlings (American Institute of Physics, Melville, New York. 2001)

Born as Thomas-Fermi theory

Peter M. W. Gill, “Obituary: Density-Functional Theory (1927-1993)”, *Aust. J. Chem.* **54**, 661-662 (2001).



Died when Axel Becke introduced hybrid functionals

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V. (NanoStar)

1970s: The Era of Photoionization Spectra

Introduction of Green's functions/propagators into Quantum Chemistry

Functional Derivative Approach (Schwinger, Hedin)

- G.Y. Csanak, H.S. Taylor, and R. Yaris, *Adv. At. Mol. Phys.* **17**, 287 (1971)

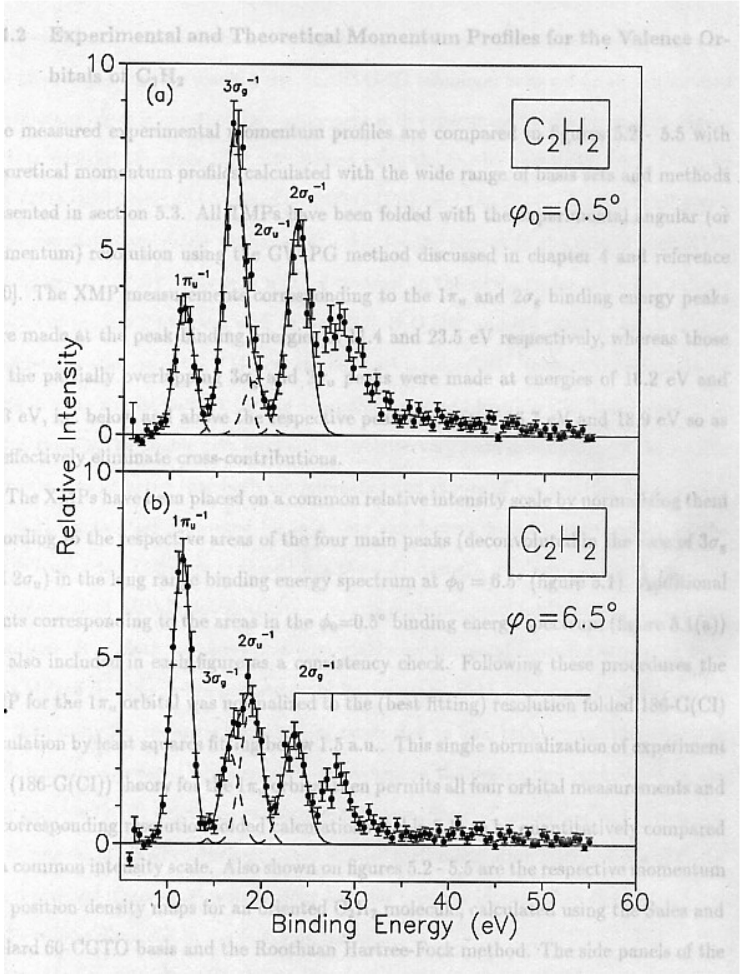
Diagrammatic MBPT (Feynman, Dyson)

- L.S. Cederbaum, *J. Phys. B* **8**, 290 (1975)
- L.S. Cederbaum and W. Domcke, *Adv. Chem. Phys.* **36**, 205 (1977)

Equation-of-Motion (EOM)/Superoperator

(Rowe, Linderberg and Öhrn, Simons and Yeager)

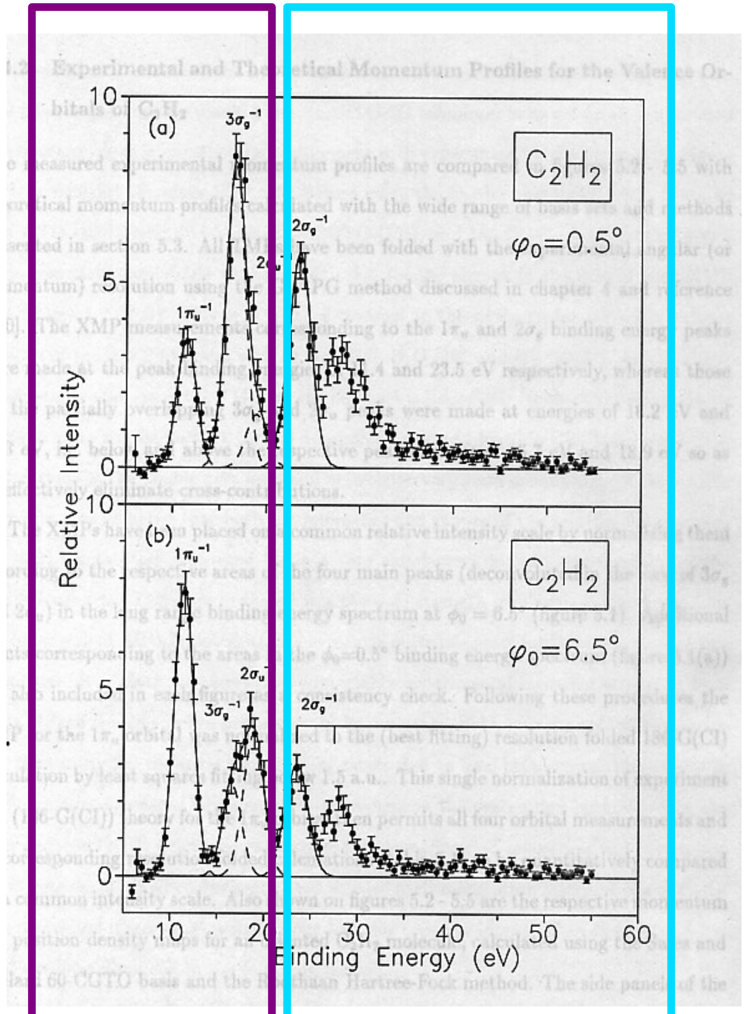
- J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry* (Academic Press : New York, 1973).
- P. Jorgensen and J. Simons, *Second Quantization-Based Methods in Quantum Chemistry* (Academic Press : New York, 1981). Chapter 6 : “Green's Functions”
- M.F. Herman, K.F. Freed, and D.L. Yeager, *Adv. Quant. Chem.* **13**, 1 (1981)



P. Duffy *et al.*, *Chem. Phys.* **165**, 183 (1992)

Things Learned During This Era

- Exchange diagrams are necessary in finite systems! (One reason is to remove EPV terms which correspond to unphysical self-polarization.)
- Outer valence (quasiparticle) spectra converge in an oscillatory manner with respect to order of perturbation.
- Inner valence (satellite) spectra require some mixture of MBPT and variational methods.



P. Duffy *et al.*, *Chem. Phys.* **165**, 183 (1992)

Electron Excitations: CIS (LR-TDHF TDA)

$$\begin{array}{ccc} & \mathrm{R} & \mathrm{S} \\ \mathrm{R} & E_{HF} & 0 \\ \mathrm{S} & 0 & \boldsymbol{H}_{S,S} \end{array} \begin{pmatrix} 1 \\ \vec{C}_S \end{pmatrix} = E_{CI} \begin{pmatrix} 1 \\ \vec{C}_S \end{pmatrix} \qquad \Rightarrow \underbrace{\left(\boldsymbol{H}_{S,S} - E_{HF}\right)}_{\boldsymbol{A}} \vec{C}_S = \underbrace{\left(E_{CIS} - E_{HF}\right)}_{\omega} \vec{C}_S$$

Same as

$$\sum \langle \Phi | [i^+ a, [\hat{H}, b^+ j]] | \Phi \rangle C_i^a = \omega \sum \langle \Phi | [i^+ a, b^+ j] | \Phi \rangle C_i^a$$

Compactly

$$\sum \left(a^+ i | \breve{H} | b^+ j \right) C_i^a = \omega \sum \left(a^+ i | b^+ j \right) C_i^a$$

Method is “very old.” Resurrected by M. Head-Gordon *et al.* Who developed especially efficient algorithms

Liouvillian superoperator $\breve{H} \hat{A} = [\hat{H}, \hat{A}]$

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

Electron Excitations: LR-TDDFT (à la Rowe)

$$\hat{O}^{+} = |\Psi_I> <\Psi_0| \qquad \hat{O} = |\Psi_0> <\Psi_I|$$

$$\breve{H}\hat{O}^{+} = [\hat{H},\hat{O}^{+}] = \omega_I \hat{O}^{+} \qquad \breve{H}\hat{O} = [\hat{H},\hat{O}] = -\omega_I \hat{O}$$

Expand in a basis

$$\hat{O}^{+},\hat{O} \approx \sum b^{+} j X_{jb} + \sum j^{+} b Y_{bj}$$

Project

$$\begin{bmatrix} (a^{+} i|\breve{H}|b^{+} j) & (a^{+} i|\breve{H}|j^{+} b) \\ (i^{+} a|\breve{H}|b^{+} j) & (i^{+} a|\breve{H}|j^{+} b) \end{bmatrix} \begin{pmatrix} X_{jb} \\ Y_{bj} \end{pmatrix} = \omega \begin{bmatrix} (a^{+} i|b^{+} j) & (a^{+} i|j^{+} b) \\ (i^{+} a|b^{+} j) & (i^{+} a|j^{+} b) \end{bmatrix} \begin{pmatrix} X_{jb} \\ Y_{bj} \end{pmatrix}$$

I.e.

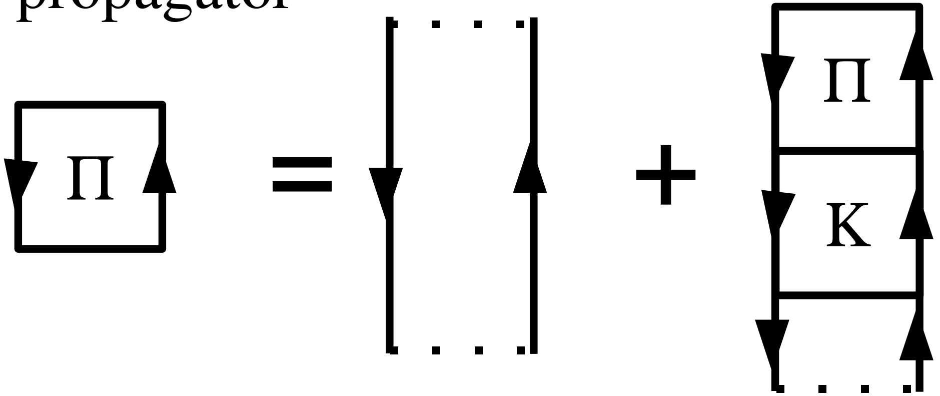
$$\begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B}^{*} & \boldsymbol{A}^{*} \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \vec{X} \\ \vec{Y} \end{pmatrix}$$

TDA

$$\Rightarrow \boldsymbol{A}\vec{X} = \omega \vec{X}$$

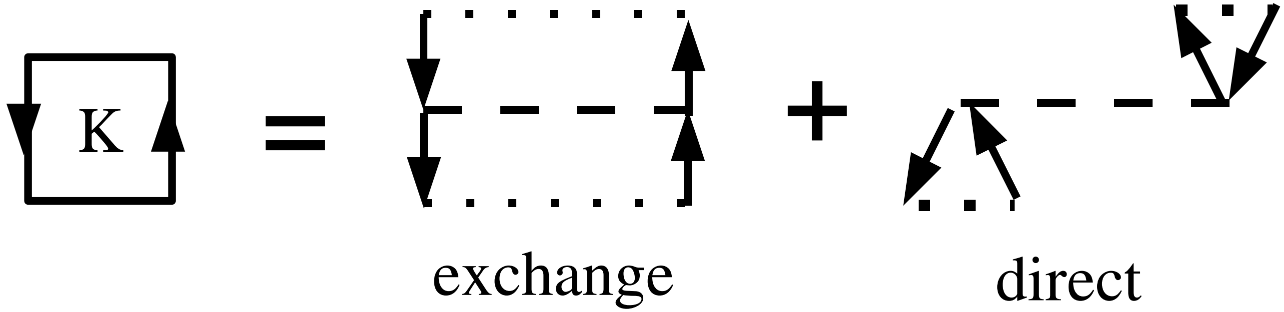
Electron Excitations: LR-TDHF Diagrams

Polarization propagator



(similarly for ph)

Coupling matrix



$$A_{ia,jb} = \delta_{i,j}\delta_{a,b}\left(\epsilon_a - \epsilon_i\right) + K_{ia,jb}$$

$$B_{ia,bj} = K_{ia,bj}$$

RPA, dRPA = direct
RPAE, RPAX, RPA = direct+exchange

LR-TDDFT

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

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

where

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

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

Coupling matrix

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

BETHE-SALPETER EQUATION

BSE is an equation for a 4-spatial, 4-time coordinate quantity

$$\boldsymbol{L}=\boldsymbol{L}_s+\boldsymbol{L}_s\boldsymbol{\Xi}_{Hxc}\boldsymbol{L} \qquad (1)$$

Resembles TDDFT equation which is for a 2-spatial, 2-time quantity

$$\boldsymbol{\chi}=\boldsymbol{\chi}_s+\boldsymbol{\chi}_s\boldsymbol{f}_{Hxc}\boldsymbol{\chi} \qquad (2)$$

Polarization propagator is a 4-spatial, 2-time coordinate quantity

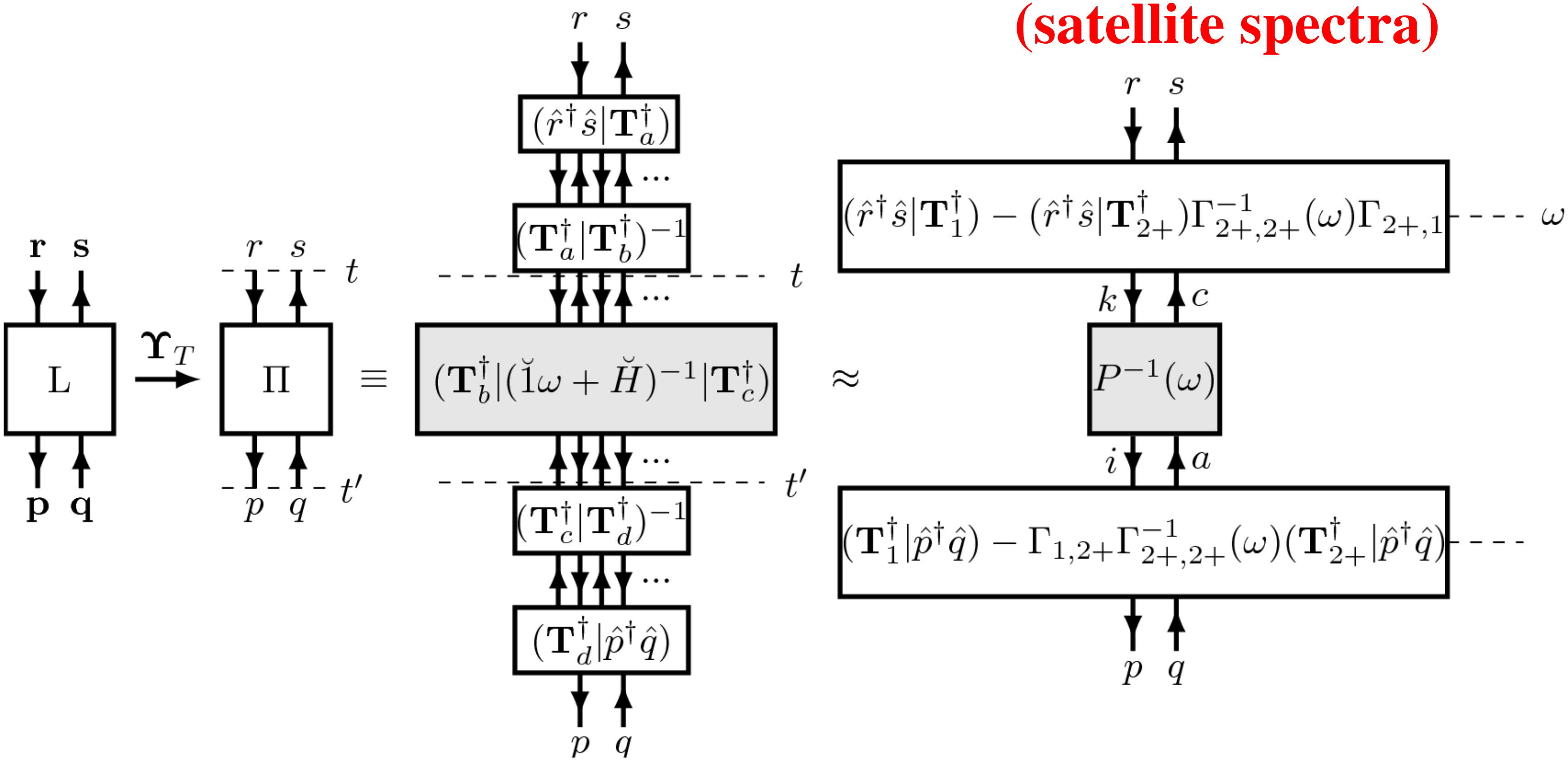
$$\Pi(1,2,3,4;t-t')=L(1\mathrm{t},2\mathrm{t};3\mathrm{t}',4\mathrm{t}') \qquad (3)$$

$$\boldsymbol{\Pi}=\boldsymbol{\Pi}_s+\boldsymbol{\Pi}_s\left(\boldsymbol{\Pi}_s^{-1}-\boldsymbol{\Pi}^{-1}\right)\boldsymbol{\Pi} \qquad (4)$$

GET $\Pi_s^{-1}(\omega)-\Pi^{-1}(\omega)$ FROM SOPPA OR ADC(2)

SOPPA: J. Oddershede and P. Jorgensen, *J. Chem. Phys.* **66**, 1541 (1977); E.S. Nielsen, P. Jorgensen, and J. Oddershede, *J. Chem. Phys.* **73**, 6238 (1980).
ADC(2): J. Schirmer, *Phys. Rev. A* **26**, 2395 (1982).

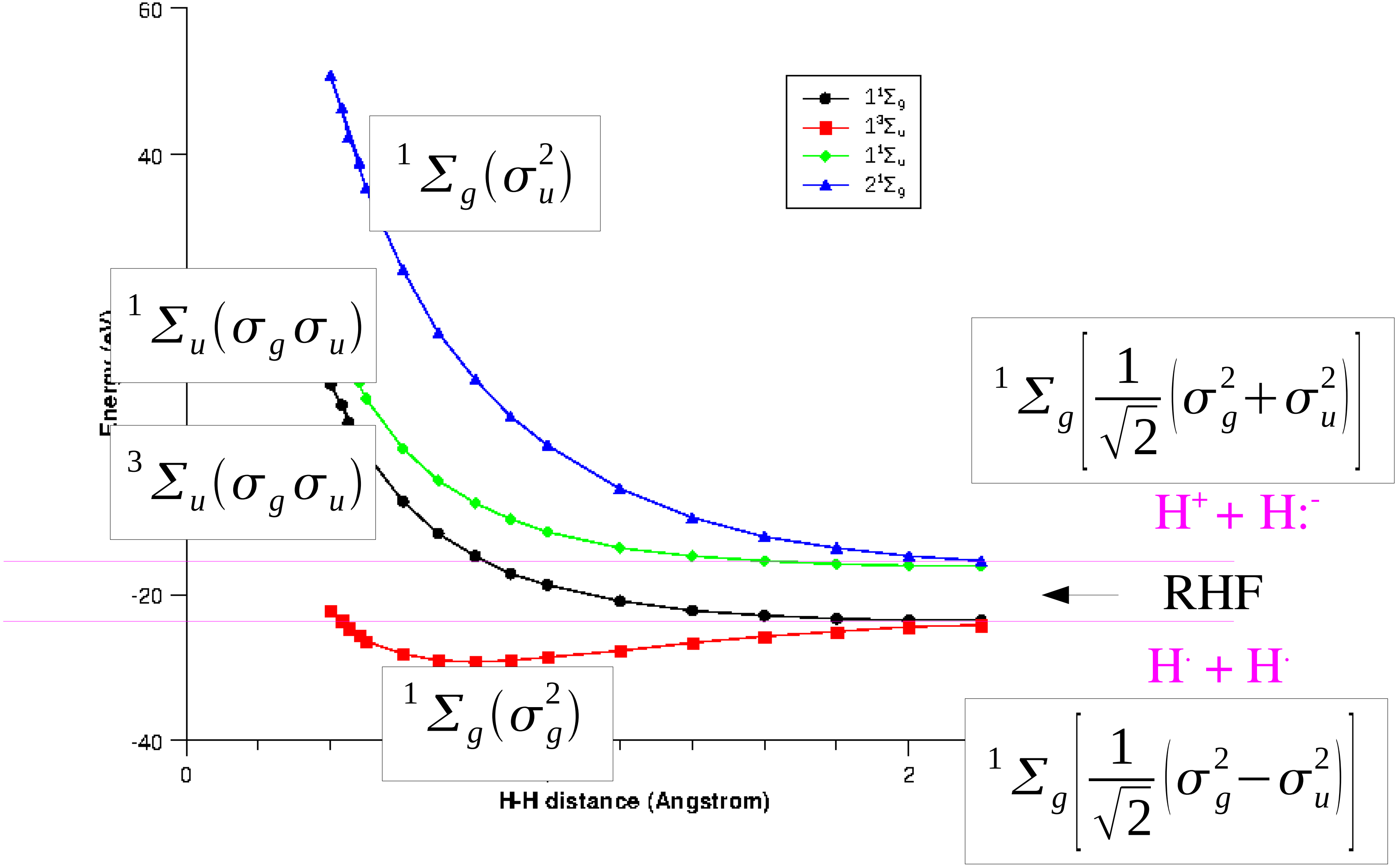
Explicit double excitations (satellite spectra)



See e.g. talk by Miquel HUIX-ROTLLANT

WAVE FUNCTION THEORY

H_2



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

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

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

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

$H^+ + H:^-$

RHF

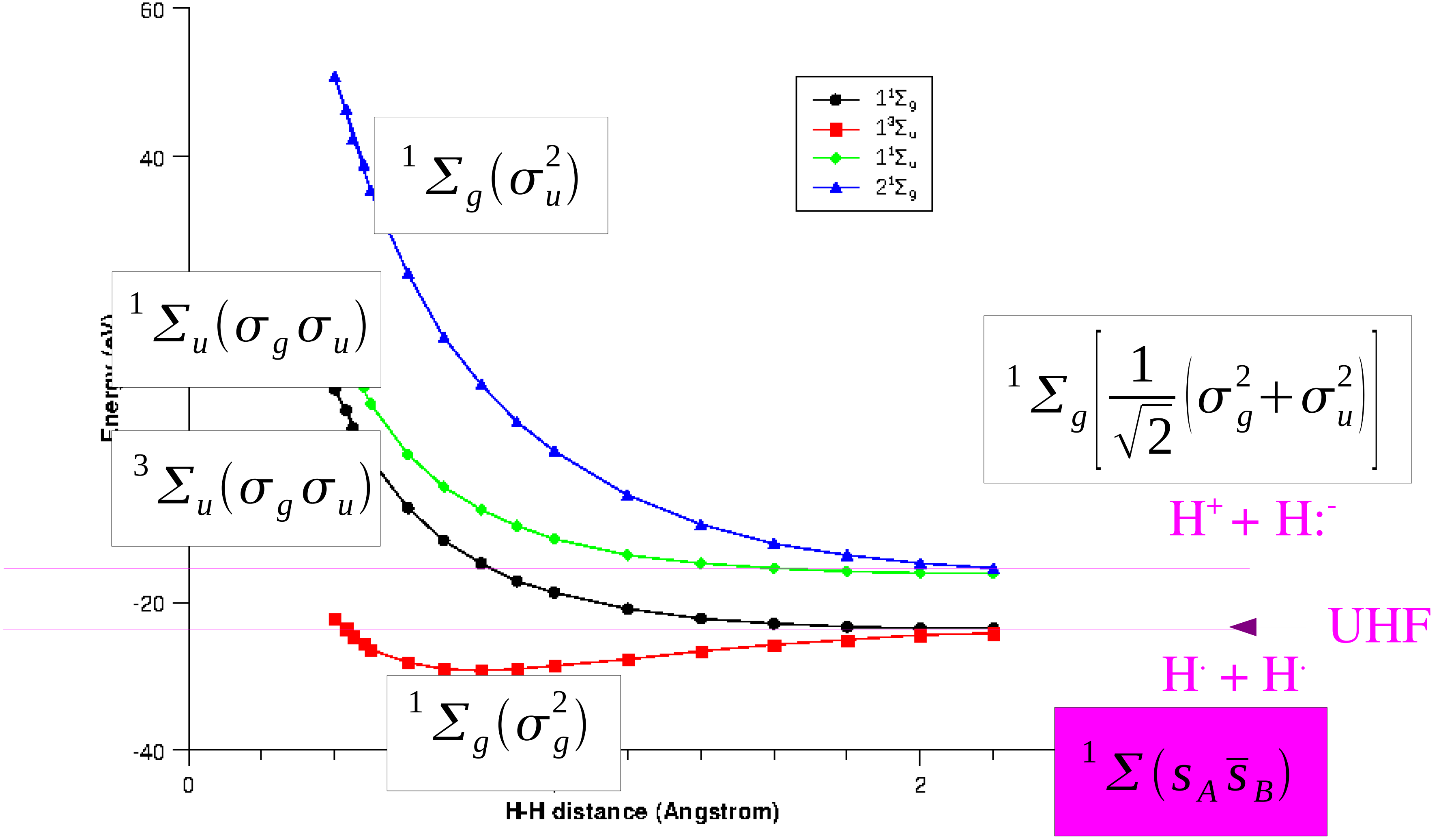
$H^\cdot + H^\cdot$

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

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

WAVE FUNCTION THEORY

H_2



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

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

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

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

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

$H^+ + H:^-$

$H^\cdot + H^\cdot$

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

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

Stability Analysis for Ground State

J. Paldus and others 1960s?

If the energy

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

can be lowered by a unitary transformation

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

then either (**A**-**B**) has a negative eigenvalue (impossible for GGAs if the *Aufbau* principle is obeyed) or (**A+B**) has a negative eigenvalue. Since the THDF and TDDFT eigenvalue problems can be rewritten as

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

this means that ground-state instability translates into imaginary excitation energies.

TAMM-DANCOFF APPROXIMATION (TDA)

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

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

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

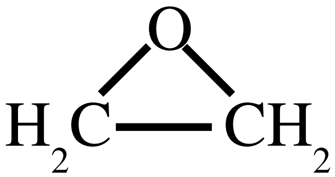
B=0 defines the Tamm-Dancoff approximation

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

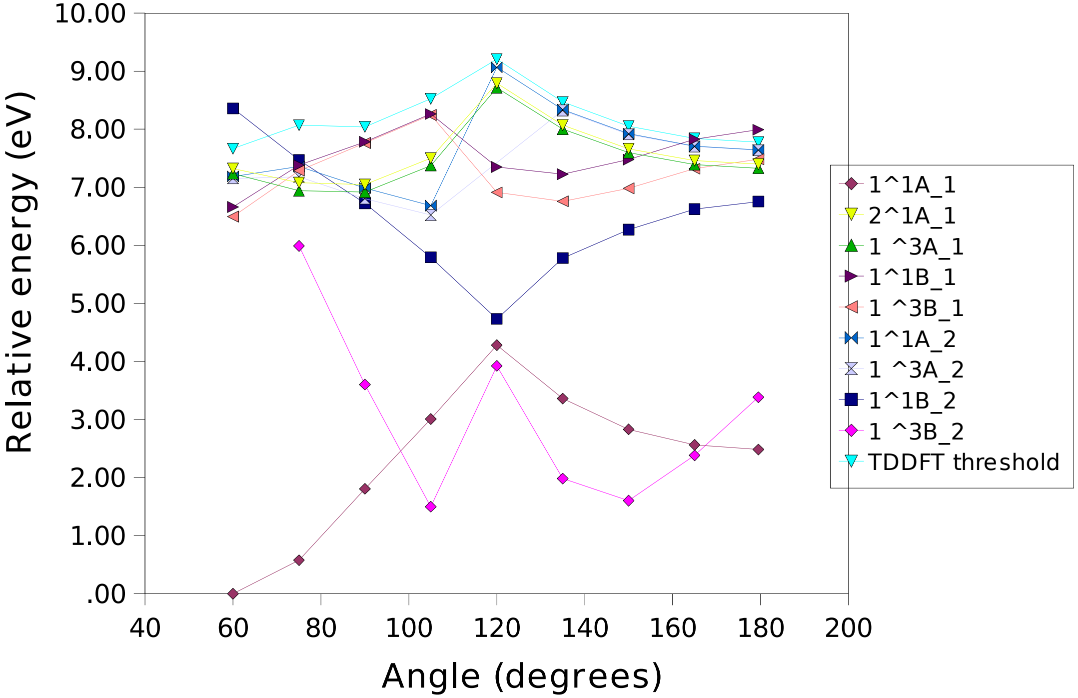
CIS = TDHF + TDA

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

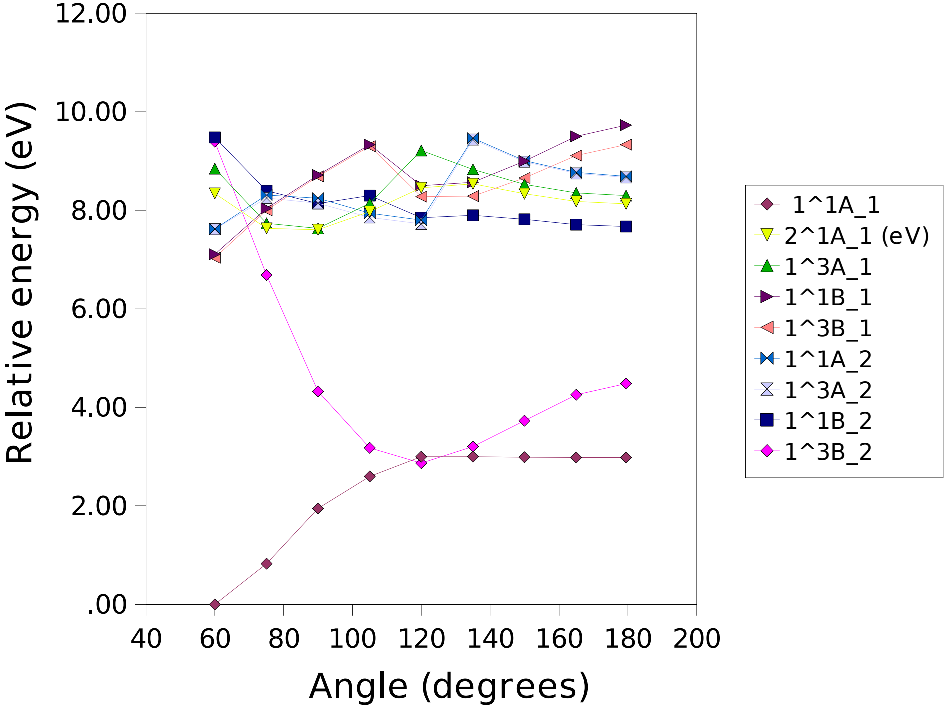
GENERAL COMPARISON OF TDDFT AND *AB INITIO*



TDB3LYP

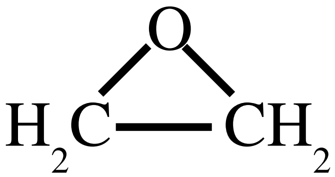


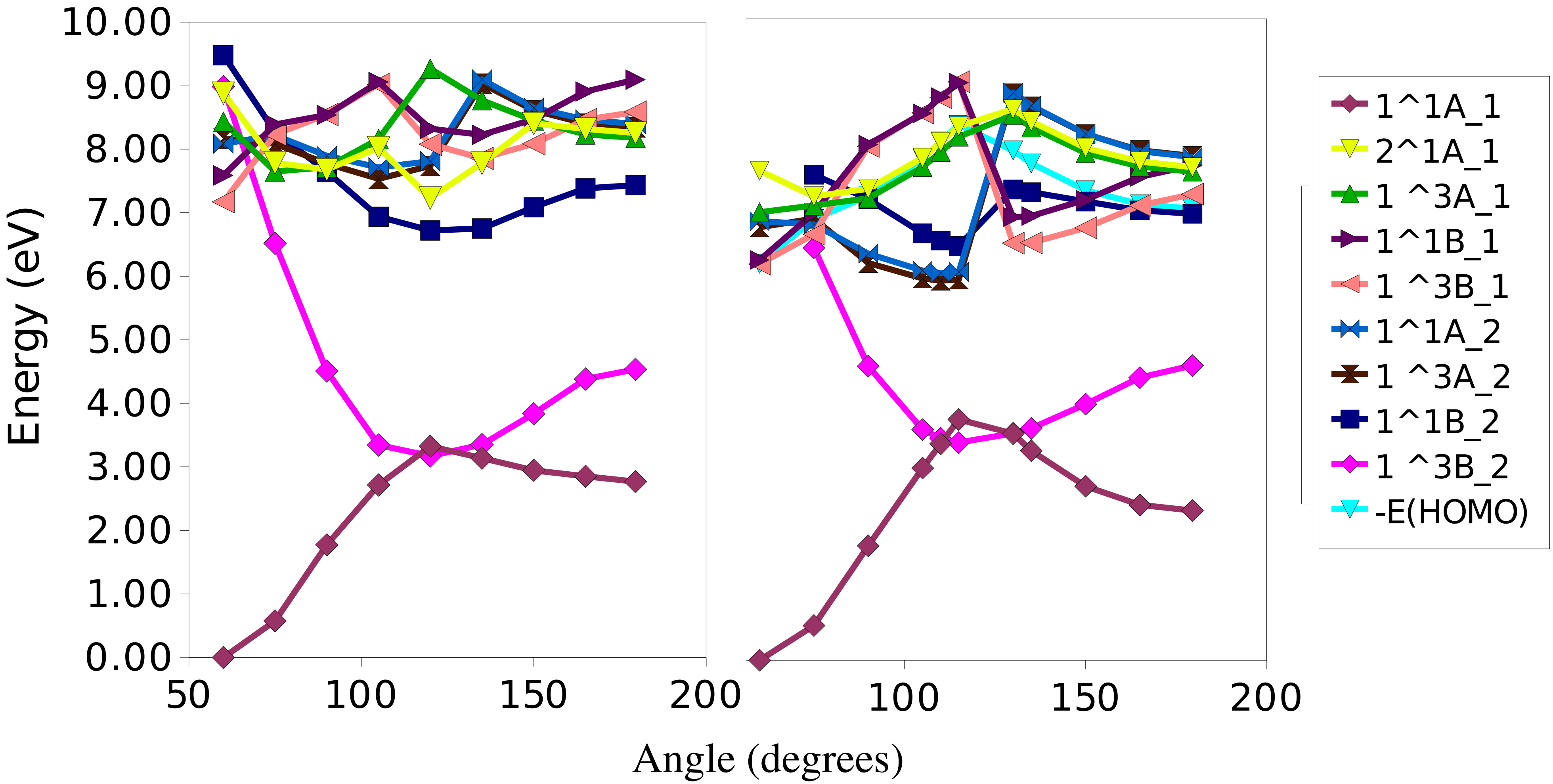
CAS(4,6)



F. Cordova, L. Joubert Doriol, A. Ipatov, MEC, C. Filippi, and A. Vela, *J. Chem. Phys.* **127**, 164111 (2007)

OXIRANE C_{2v} RING OPENING





DMC

TDLDA/TDA

F. Cordova, L. Joubert Doriol, A. Ipatov, MEC, C. Filippi, and A. Vela, *J. Chem. Phys.* **127**, 164111 (2007)

A better solution would be a multireference RPA method
... see e.g. Danny Yeager's work

Analytic Derivatives (i.e. Forces)

1980s

Y. Yamaguchi, Y. Osamura, J.D. Goddard, and H.F. Schaefer III, *A New Dimension to Quantum Chemistry: Analytic Derivative Methods in* Ab Initio *Molecular Electronic Structure Theory* (Oxford University Press, Oxford, 1994)

Vince Ortiz => Analytic derivatives for LR-TDHF (very nice)

Analytic derivatives for LR-TDDFT TDA *without slick tricks* :

Mark E. Casida, *J. Mol. Struct. (Theochem)* **914**, 3 (2009). "Review: Time-Dependent Density-Functional Theory for Molecules and Molecular Solids"

Mark E. Casida, in Computational Methods in Catalysis and Materials Science,
part of the IDECAT Course book series, Philippe Sautet and Rutger A. van Santen, editors

(Wiley-VCH: Weinheim, Germany, 2008), ISBN 978-3-527-32032-5, pp. 33-59. "TDDFT for Excited States"

Coupled Perturbed Coefficients

$$\frac{\partial \psi_s(\mathbf{r})}{\partial \eta} = \psi_s^\eta(\mathbf{r}) + \sum \psi_r(\mathbf{r}) U_{r,s}^\eta$$

$$\sum A_{ai,bj} U_{bj}^\eta = B_{ai}^0$$

Different A and B !

$$A_{ai,bj} = \delta_{i,j}\delta_{a,b}\frac{\epsilon_i - \epsilon_a}{n_i - n_a} - \left(K_{ai,jb} + K_{ai,bj}\right)$$

$$B_{ai}^0 = F_{ai}^\eta \epsilon_i - \sum K_{ai,kj} S_{j,k}^\eta$$

skeleton terms

Excited-State Analytic Derivatives

$$\frac{\partial \omega}{\partial \eta} = \omega^{\eta} - \sum M_{kl} S_{kl}^{\eta} + \sum Z_{ck} B_{ck}^{0}$$

$$M_{kl} = \sum X_{ia}^{*} X_{jb} \left(\delta_{i,j} K_{ab,kl} - \delta_{a,b} K_{ji,kl} - G_{ia,bj,kl} \right)$$

$$G_{pq,p'q',p\ \mathrm{q}} = \frac{\partial K_{pq,p'q'}}{\partial P_{p\ ,\mathrm{q}}}$$

$$\sum A_{ai,bj} Z_{bj} = L_{ai}$$

$$L_{ck} = \sum X_{ia}^{*} X_{jb} \left[\delta_{i,j} \left(K_{ab,kc} + K_{ab,ck} \right) - \delta_{a,b} \left(K_{ji,kc} + K_{ji,ck} \right) + \left(G_{ia,jb,ck} + G_{ia,bj,kc} \right) \right]$$

Calculation of Excited-State Expectation Values
1-Electron Reduced Difference Density Matrix (1-RDDM)

Rowe 1-RDDM:

$$\begin{bmatrix} \boldsymbol{A} & \boldsymbol{B} \\ \boldsymbol{B} & \boldsymbol{A} \end{bmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix} = \omega_I \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{pmatrix} \vec{X}_I \\ \vec{Y}_I \end{pmatrix} \qquad \Delta \boldsymbol{P}_I = \frac{\left(\boldsymbol{X}_I \boldsymbol{X}_I^+ + \boldsymbol{Y}_I \boldsymbol{Y}^+\right) - \left(\boldsymbol{X}_I^+ \boldsymbol{X}_I + \boldsymbol{Y}_I^+ \boldsymbol{Y}_I\right)}{\vec{X}_I^+ \vec{X}_I - \vec{Y}_I^+ \vec{Y}_I}$$

Maurice and Head-Gordon 1-RDDM:

$$\boldsymbol{A} \vec{X}_I = \omega_I \vec{X}_I \qquad \Delta \boldsymbol{P}_I = \frac{\boldsymbol{X}_I^+ \boldsymbol{X}_I - \boldsymbol{X}_I \boldsymbol{X}_I^+}{\vec{X}_I^+ \vec{X}_I}$$

Relaxed 1-RDDM:

$$\boldsymbol{A} \vec{Z} = \vec{L}$$

(different **A**)

$$\Delta P_I = \begin{bmatrix} -\boldsymbol{X}_I \boldsymbol{X}_I^+ & \boldsymbol{Z}^+ \\ \boldsymbol{Z}_I & \boldsymbol{X}_I^+ \boldsymbol{X}_I \end{bmatrix}$$

Fluctuation-Dissipation Theorem

Quantity closely related to xc-hole of DFT

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

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

Electron repulsion energy

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

Correlation energy

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

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

Nonlinear Optics (NLO)

$\chi^{(1)}(-\omega;\omega)$	Dynamic polarizability
$\chi^{(2)}(-2\omega;\omega,\omega)$	Second harmonic generation (SHG)
$\chi^{(2)}(-\omega_1\mp\omega_2;\omega_1,\pm\omega_2)$	Parametric oscillation
$\chi^{(2)}(0;\omega,-\omega)$	Rectification
$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$	Third harmonic generation (THG)
$\chi^{(3)}(-\omega;\omega,-\omega,\omega)$	Nonlinear index (NLO index)
$\chi^{(3)}(-2\omega;\omega,\omega,0)$	Electric field-induced second harmonic generation (EFISH)
$\chi^{(3)}(-\omega;\omega,0,0)$	Quadratic electro-optic effect (QEO)
$\chi^{(3)}(0;-\omega,\omega,0)$	Optical rectification

NLO from TDHF

S. Karna and M. Dupuis, “Frequency dependent nonlinear optical properties of molecules: formulation and implementation in the HONDO program,” *J. Comput. Chem.* **12**, 427 (1991).

H. Sekino and R.J. Bartlett, “New algorithm for high-order time-dependent Hartree-Fock thoery for nonlinear optical properties,” *Int. J. Quant. Chem.* **43**, 119 (1991).

Higher-order response properties are particularly simple within TDHF !

I. What is Chemistry All About?

II. The Quantum Chemistry Paradigm

III. Sources of the RPA in Chemistry

IV. Cross-Fertilization

V. (NanoStar)

RPA Workshop Cross-Fertilization

QUANTUM CHEMISTRY

SOLID-STATE PHYSICS

NUCLEAR PHYSICS

What May We Expect From the "Random People Approximation"?

Tremendous Opportunities

> "If you steal from one author, it is plagiarism; if you steal from many, it's research."
>
> -- Wilson Mizner, US Screenwriter (1987-1933)

Tremendous Challenges

Language: *Les trois solitudes!*

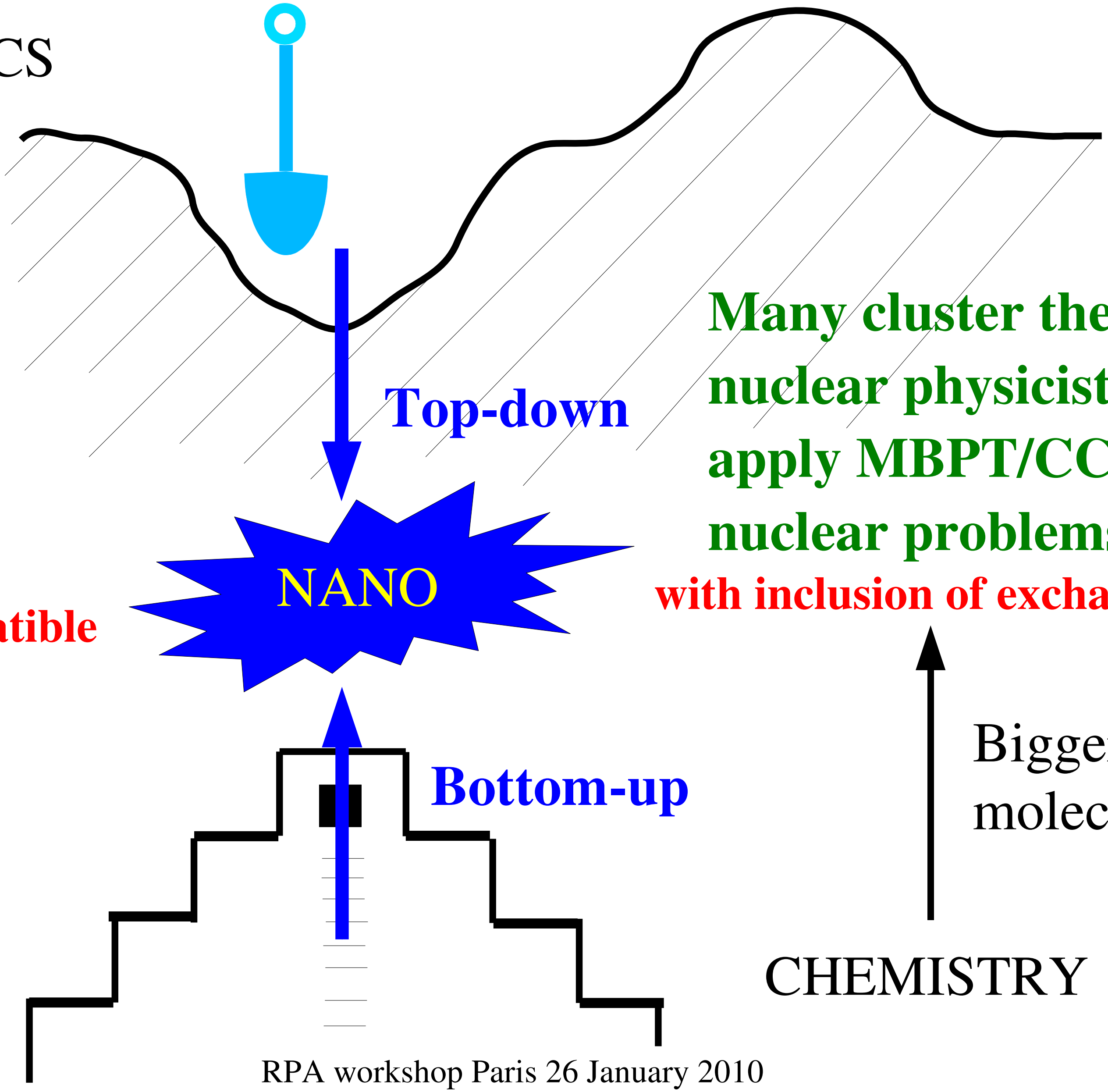
Nuclear Physics | Quantum Chemistry | Solid-State Physics

semiempirical ← CI → *ab initio*
TDHF ↔ TDCDFT
spin-coupling ↔ Kondo effect
Jahn-Teller distortion ↔ Peirls distortion

Different physics leading to different approximations.
Different interests leading to different properties to calculate.

Tremendous Fun!

“Nano” means ...



PHYSICS

Strong correlation

Bigger
unit cells

Top-down

Spherical cows (in a vacuum)

Many cluster theorists were nuclear physicists. Why not apply MBPT/CC/TDDFT to nuclear problems?

with inclusion of exchange diagrams?

NANO

Is screening compatible

Bottom-up

Realistic simulation of complex systems

Bigger
molecules

CHEMISTRY

Bond breaking

I. What is Chemistry All About?

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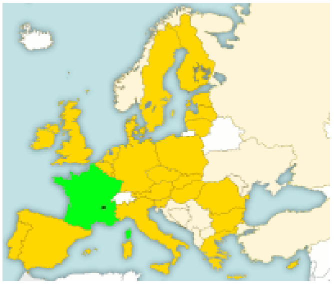
V. (NanoStar)

The **Rhône-Alpes ETSF** associated node:
A new **NanoSTAR** in the **ETSF** constellation

Rhône-Alpes

Rhône-Alpes ETSF - Grenoble

Group Webpage



Team Coordinator

Prof. Alain Pasturel

Topics

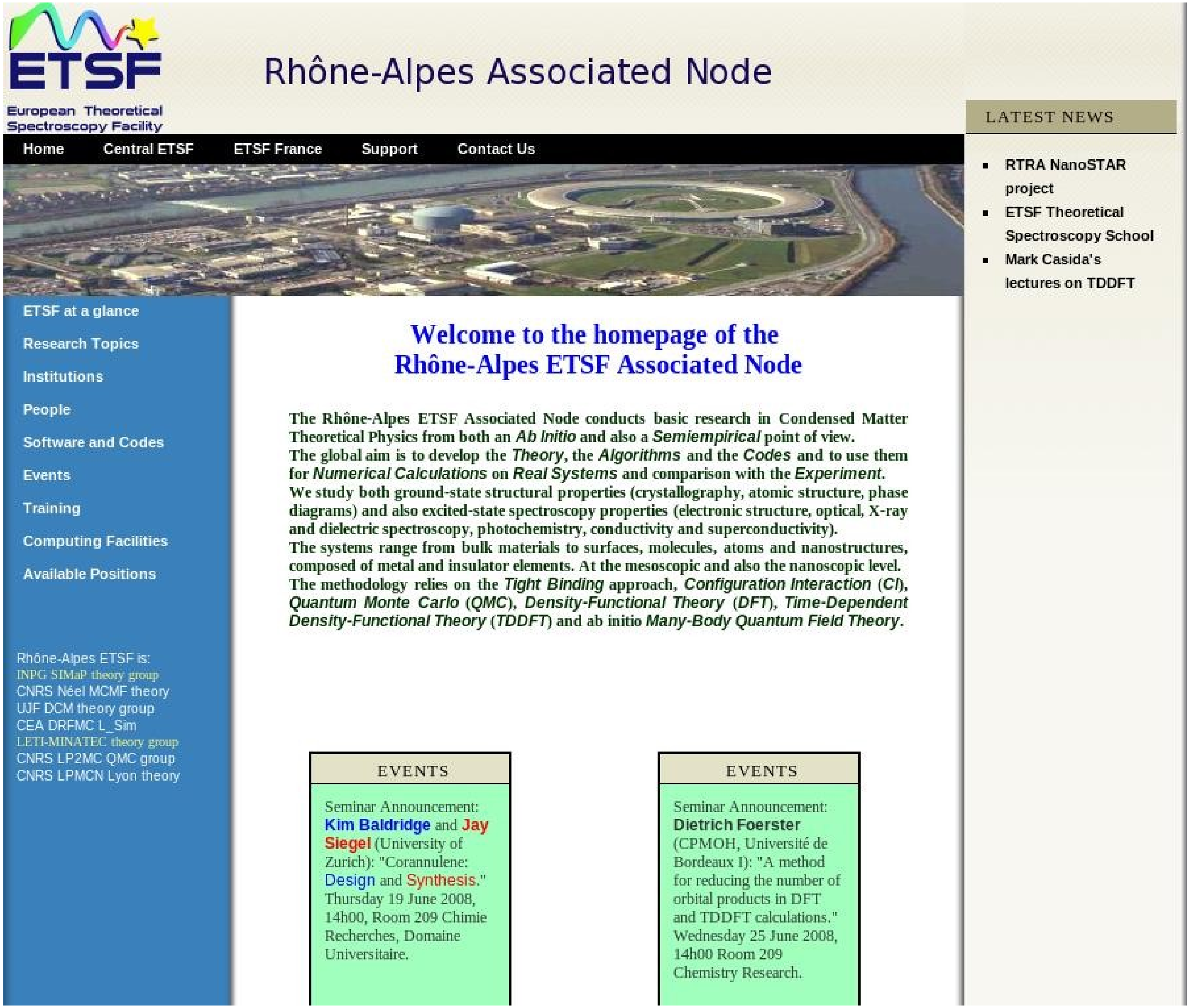
(TD)DFT, MBPT, NEGF and QMC to address Photochemistry, Quantum Transport, BCS-Eliashberg Superconductivity, Magnetic phases and Magnons on Disordered systems, Nanostructures, 2D- and technological systems. O(N) methodological developments.

The ETSF Grenoble is

INPG SIMaP theory group, CNRS Néel MCMF theory, UJF DCM theory group, CEA DRFMC L_Sim LETI-MINATEC theory group, CNRS LP2MC QMC group, CNRS LPMCN Lyon theory.

nanostar

http://etsf.grenoble.cnrs.fr



Rhône-Alpes Associated Node

Rhône-Alpes ETSF is:
INPG SIMaP theory group
CNRS Néel MCMF theory
UJF DCM theory group
CEA DRFMC L_Sim
LETI-MINATEC theory group
CNRS LP2MC QMC group
CNRS LPMCN Lyon theory

Welcome to the homepage of the Rhône-Alpes ETSF Associated Node

The Rhône-Alpes ETSF Associated Node conducts basic research in Condensed Matter Theoretical Physics from both an *Ab Initio* and also a ***Semiempirical*** point of view.
The global aim is to develop the *Theory*, the *Algorithms* and the *Codes* and to use them for *Numerical Calculations* on *Real Systems* and comparison with the *Experiment*.
We study both ground-state structural properties (crystallography, atomic structure, phase diagrams) and also excited-state spectroscopy properties (electronic structure, optical, X-ray and dielectric spectroscopy, photochemistry, conductivity and superconductivity).
The systems range from bulk materials to surfaces, molecules, atoms and nanostructures, composed of metal and insulator elements. At the mesoscopic and also the nanoscopic level.
The methodology relies on the *Tight Binding* approach, *Configuration Interaction* (*CI*), *Quantum Monte Carlo* (*QMC*), *Density-Functional Theory* (*DFT*), *Time-Dependent Density-Functional Theory* (*TDDFT*) and ab initio *Many-Body Quantum Field Theory*.

LATEST NEWS

- RTRA NanoSTAR project
- ETSF Theoretical Spectroscopy School
- Mark Casida's lectures on TDDFT

EVENTS

Seminar Announcement: Kim Baldridge and Jay Siegel (University of Zurich): "Corannulene: Design and Synthesis." Thursday 19 June 2008, 14h00, Room 209 Chimie Recherches, Domaine Universitaire.

EVENTS

Seminar Announcement: **Dietrich Foerster** (CPMOH, Université de Bordeaux I): "A method for reducing the number of orbital products in DFT and TDDFT calculations." Wednesday 25 June 2008, 14h00 Room 209 Chemistry Research.

ETSF Rhône-Alpes - NanoSTAR is:

CNRS Néel MCMF theory group (X. Blase, C. Attaccalite, L. Magaud, D. Mayou, V. Olevano)

CNRS LP2MC QMC group (M. Holzmann)

CEA DSM INAC L_Sim (D. Caliste, T. Deutsch, F. Lancon, Y.M. Niquet, P. Pochet)

CEA DSM SPRAM (S. Roche)

INPG SIMaP theory group (N. Jakse, A. Pasturel)

UJF DCM theory group (M.E. Casida)

LETI-MINATEC theory group (P. Blaise, F. Triozon)

ESRF theory group (L. Genovese)

18 permanents!

ETSF Rhône-Alpes - NanoSTAR

- Expertise in: **CI, DFT, TDDFT, MBPT, NEGF, QMC**
- Important development of **theory** and **codes**: deMon2k, BigDFT, DP, wavelets, O(N), TDDFT, …
- MesoCenter computer facility: Ciment, ~5 TFlop
- Applications to: **Spectroscopy** and **Quantum Transport**, from Nanostructures to Technological Systems
- Training: Casida's lectures on TDDFT
- Local and national financing: RTRA Grenoble Nanoscience foundation and ANR
- Strong **link with industry**:LETI-MINATEC

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