DIAGRAMMATIC MULTIPLET-SUM (MS) DENSITY-FUNCTIONAL THEORY (DFT): "SIMPLE" DFT-BASED APPROACH(ES) TO MULTI-DETERMINANTAL (MD) PROBLEMS

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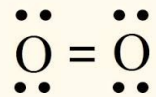*38058 Grenoble cedex 9*
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ASESMA
Kigali, Rwanda
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60 min

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OXYGEN PHOTOCHEMISTRY AS AN EXAMPLE PROBLEM

Oxygen is inescapable in chemistry, biology, and materials science. It makes up 20% of our atmosphere.

The Lewis dot structure of O_2 is famously misleading because the ground state of O_2 is a paramagnetic triplet state with unpaired spins.

Reaction of O_2 with many substances is thermodynamically favored, which accounts for the presence of oxides just about everywhere.
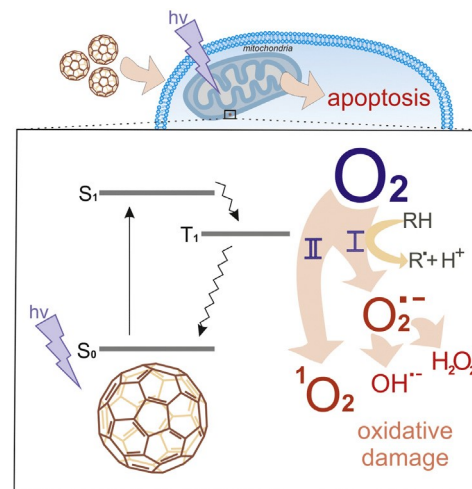
But we do not spontaneously combust (!!) because we are kinetically stable with respect to reacting with O_2, until you add enzymes and then we have respiration.

Singlet oxygen is another story. It can be created in many different ways, including photosensitization.

From an article in
Free radical biology & medicine
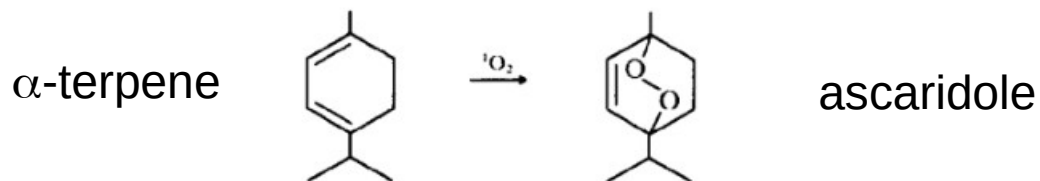124. 10.1016/j.freeradbiomed.2018.06.022.

OXYGEN PHOTOCHEMISTRY AS AN EXAMPLE PROBLEM

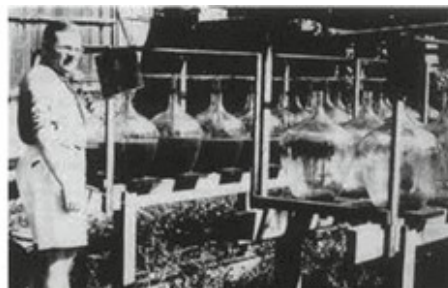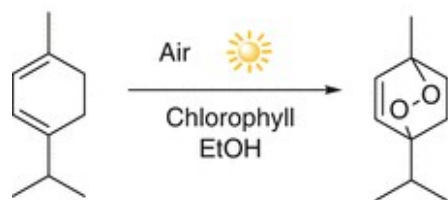Singlet oxygen can also do useful photochemistry.

One of the earliest examples of a photochemical reaction in nature.

α-terpene   ascaridole

Ascaridole is used as an anthelmintic drug that expels parasitic worms from plants, domestic animals and the human body.
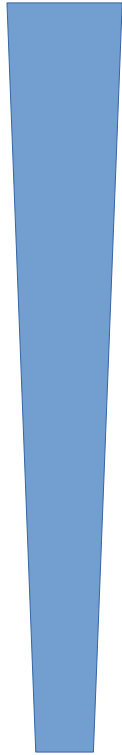

Schenck at his ascaridol pilot plant in 1952.

Abraham Ponra, Anne Justine Etindele, Ousmanou Motapon, and Mark E. Casida, Theo. Chem. Acc. 140, 154 (2021). DOI: 10.1007/s00214-021-02852-8. "Practical Treatment of Singlet Oxygen with Density-Functional Theory and the Multiplet-Sum Method" **AN ASESMA SUCCESS STORY!**
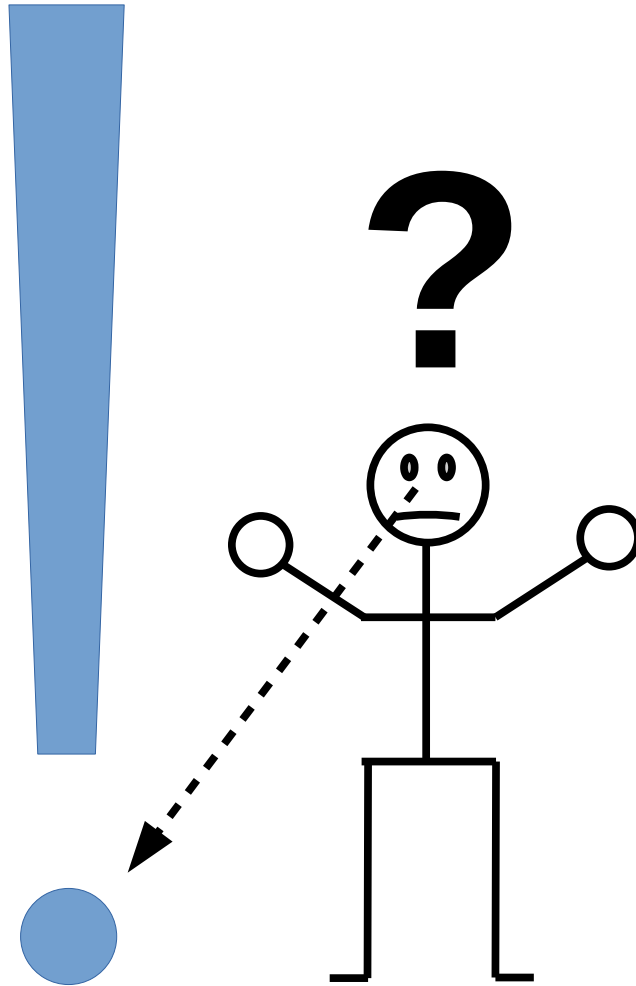
Applied Science

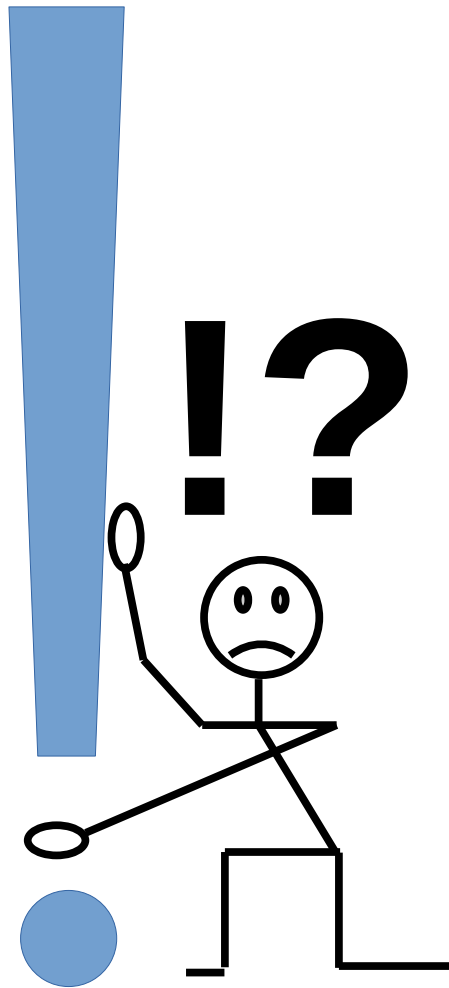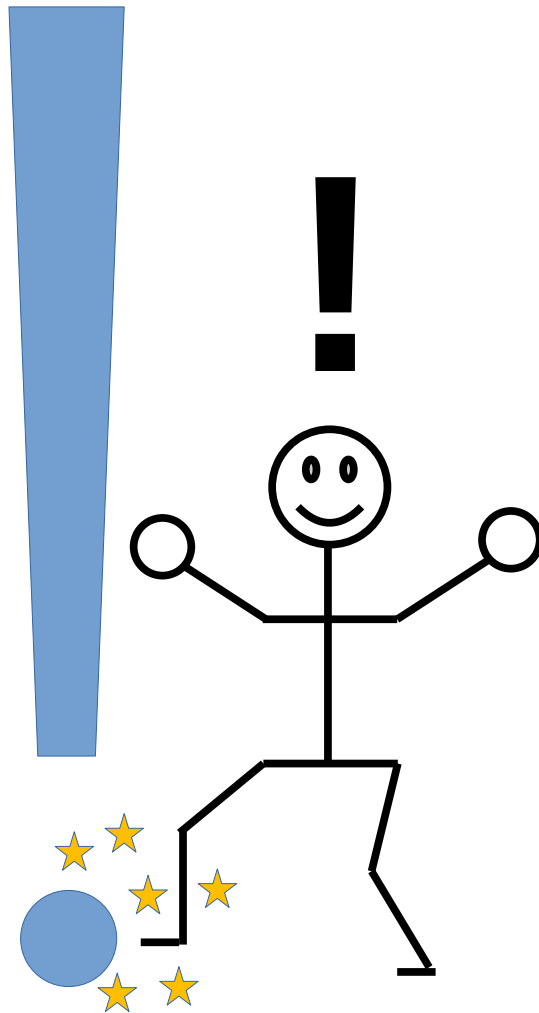Basic Science

Applied Science

Basic Science

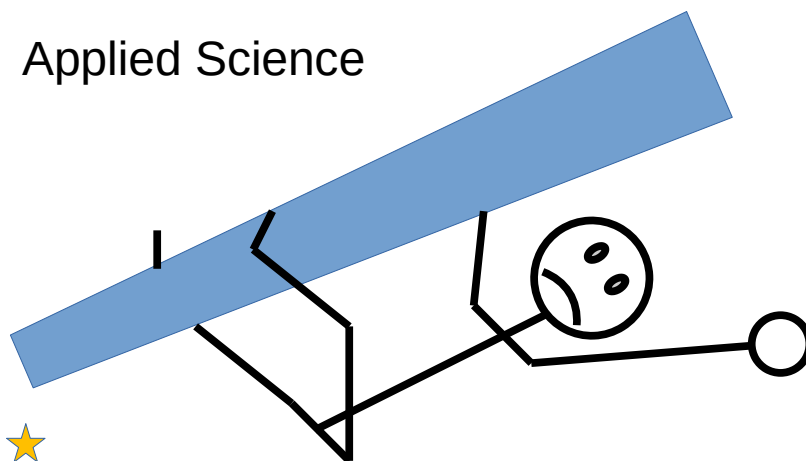Applied Science

!?

Basic Science

Applied Science

Basic Science

Applied Science

Basic Science

MORAL OF THE STORY:

Applied Science relies on Basic Science even if we do not always understand how.
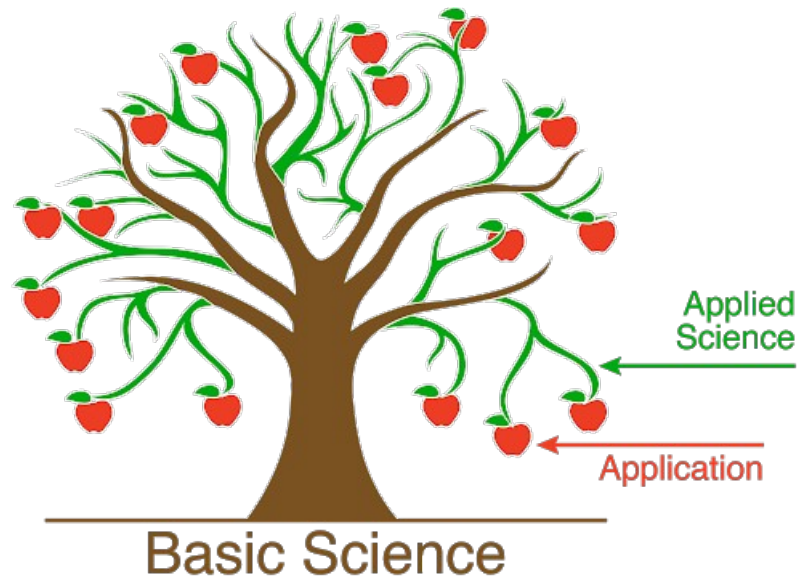
I. INTRODUCTION
II. SECOND QUANTIZATION
III. SPIN COUPLING
IV. DISSOCIATION
V. DYNAMIC AND STATIC CORRELATION
VI. MS-DFT
VII. TD-DFT
VIII. UNIFYING MS- AND TD-DFT
IX. CONCLUSION

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same ground-state electron density

$$\rho(\vec{r}) \text{ or } n(\vec{r})$$

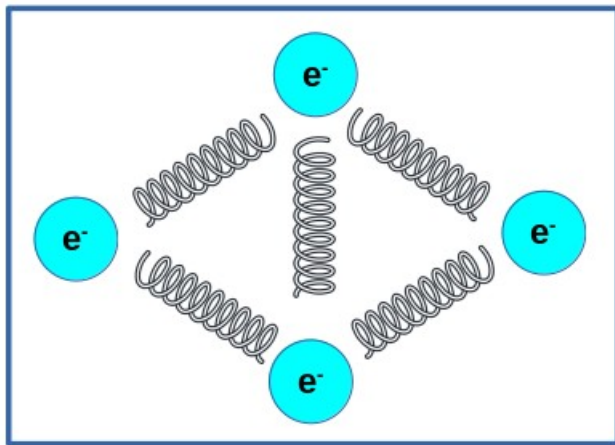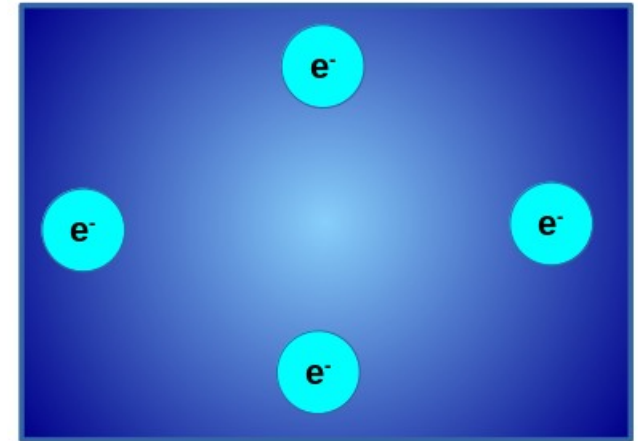real system of interacting electrons

fictious system of noninteracting electrons

$$V=\sum_{i=1,N} v_{\text{ext}}(i)+\sum_{i,j=1,N}^{i<j} \frac{e^2}{r_{i,j}}$$

$$\Psi=\Phi C_0+\sum_{i,a} \Phi_i^a C_i^a+\sum_{i<j}^{a<b} \Phi_{i,j}^{a,b} C_{i,j}^{a,b}+\cdots$$

$$v_s(i)=v_{\text{ext}}(i)+v_H[\rho](i)+v_{xc}[\rho](i)$$

$$\Phi=\left| i_1, i_2, \ldots, i_N \right|$$

$$=\frac{1}{\sqrt{N!}} det \begin{vmatrix} i_1(1) & i_1(2) & \cdots & i_1(N) \\ i_2(1) & i_2(2) & \cdots & i_2(N) \\ \vdots & \vdots & \ddots & \vdots \\ i_N(1) & i_N(2) & \cdots & i_N(N) \end{vmatrix}$$

REPRESENTABILITY QUESTIONS

<u>*N*-representability</u> : Can we always find a Ψ that will give us any given (reasonable) ρ ?

The answer turns out to be yes.
J.E. Harriman, *Phys. Rev. A* **24**, 680 (1981).

(equidensity orbitals)

<u>v-representability</u> : Can we always find a ground-state external potential which will give us any given (reasonable) ρ ?

Some external potentials are ensemble v-representable but not pure-state v-representable.
M. Levy, *Phys. Rev. A* **26**, 1200 (1982)
E. Lieb, *Int. J. Quant. Chem.* **24**, 243 (1983).

Even for N=1 and 1D some densities fail to be v-representable in the strict sense.
H. Englisch and R. Englisch, *Physica* **121A**, 253 (1983).

$$\rho(x) = \left(a + b|x|^{\alpha + 1/2}\right)^2 \quad ; \quad a, b > 0 \quad ; \quad 0 \le \alpha \le 1/2$$

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

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

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

Proof (Levy-Lieb*)

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

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

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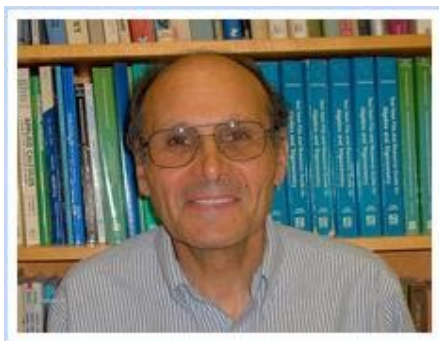 M. Levy, *Phys. Rev. A* **26**, 1200 (1982).

Mel LEVY

Elliott LIEB

BUT WE STILL NEED
NON-INTERACTING v-REPRESENTABILITY

<u>Non-interacting v-representability</u> (NIVR): Can we always find a ground-state external potential of a non-interacting system of which will give us any given (reasonable) ρ ?

Mel LEVY

We can always find an external potential whose ground *or excited-state* gives ρ .

Effective NIVR means a "hole below the Fermi level."

HS d^6
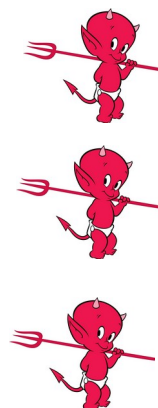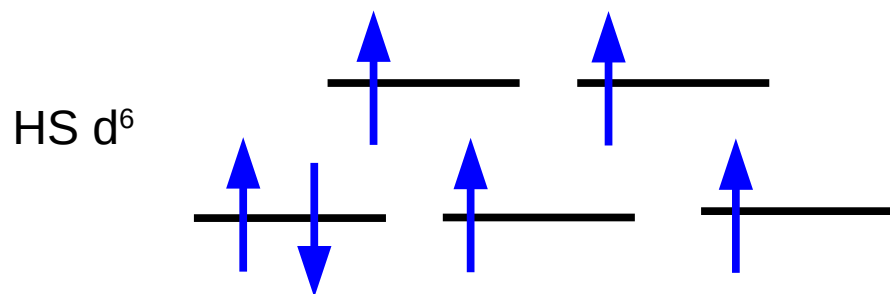
NOT RARE!

Common for open-shell systems.

Common when making and breaking bonds.

ENERGY
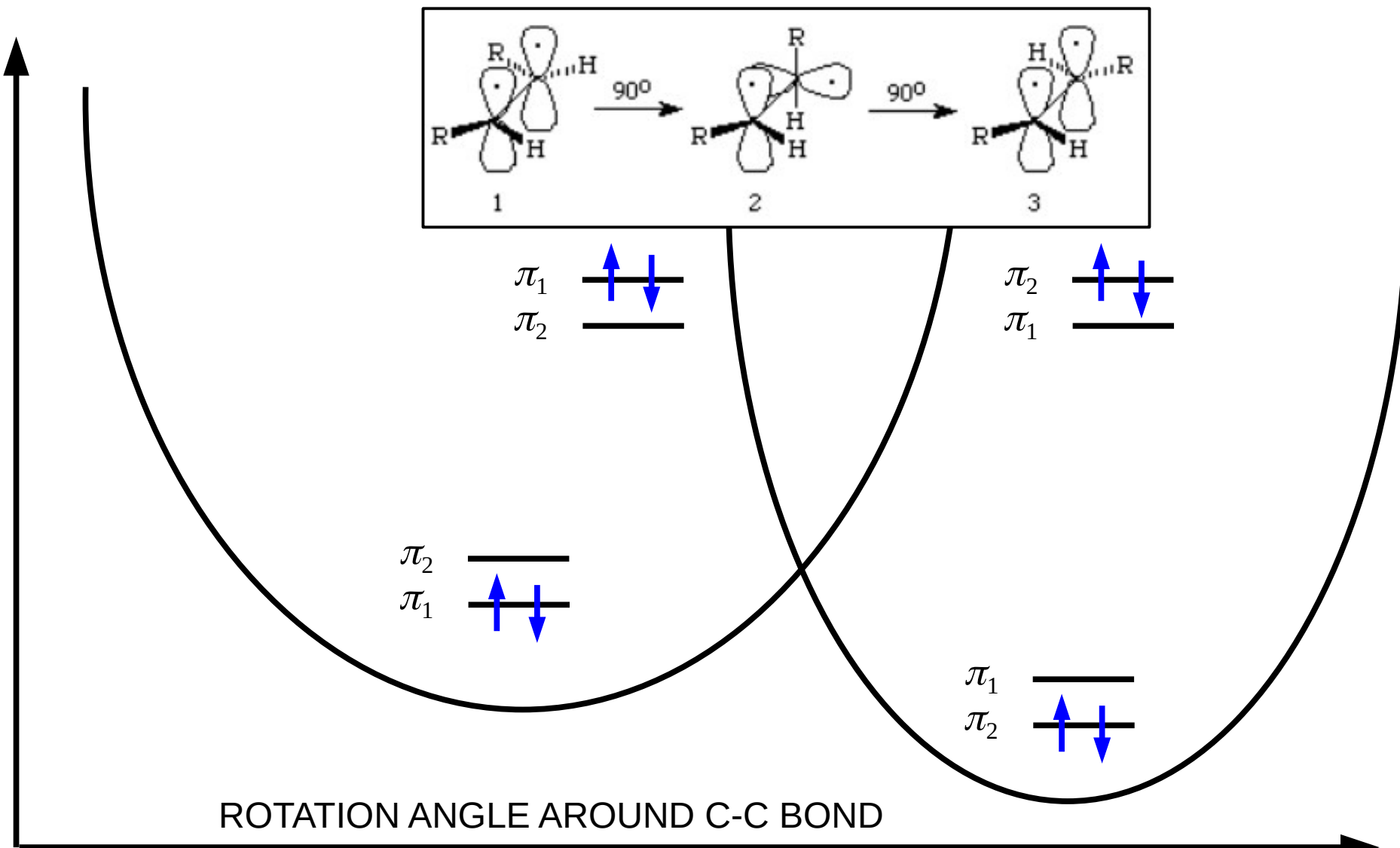
ROTATION ANGLE AROUND C-C BOND

ENERGY

$$\Psi = \Psi_R C_R + \Psi_P C_P$$

configuration mixing

avoided crossing

π_1 π_2 Ψ_R

π_1 π_2 Ψ_P
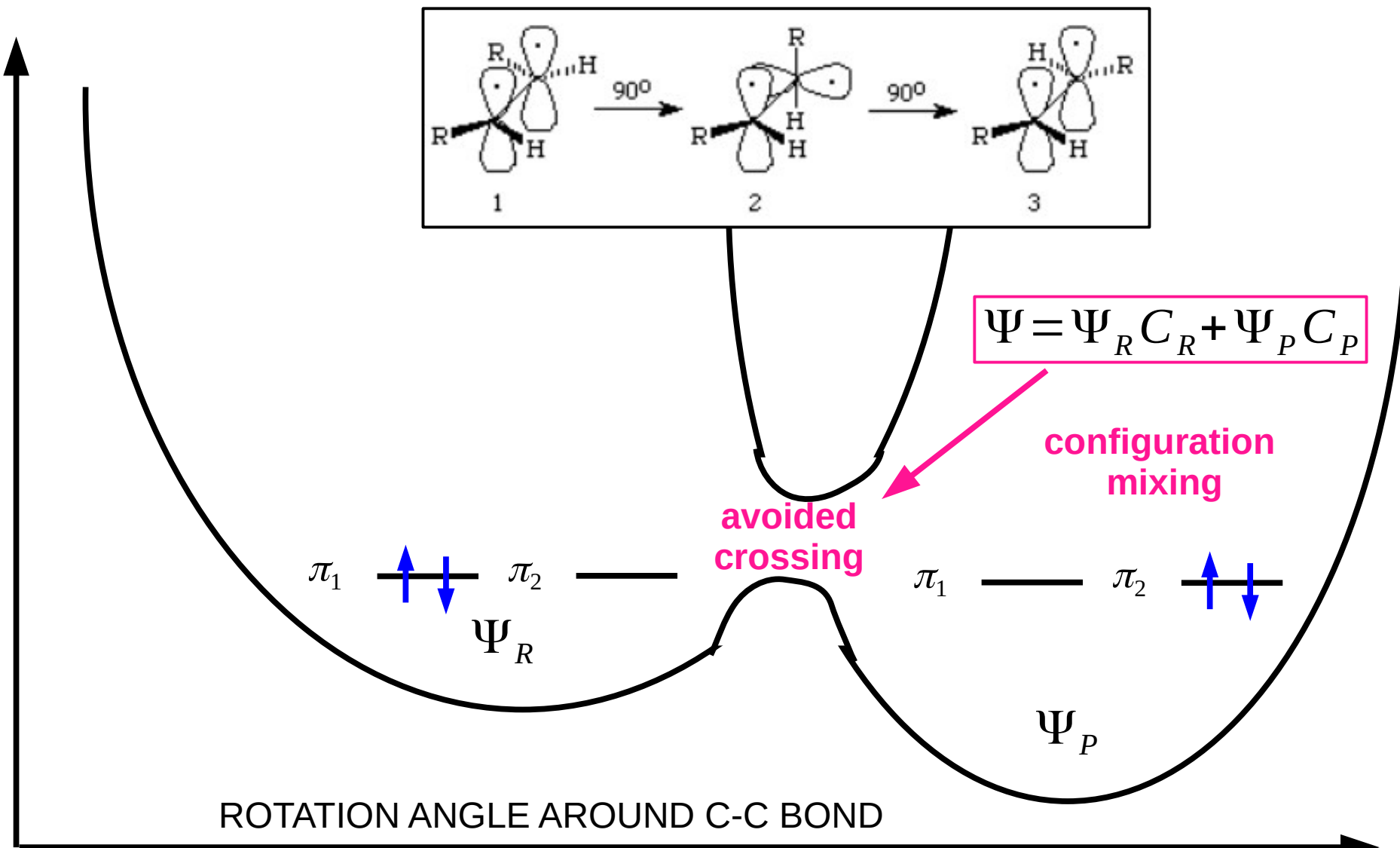
ROTATION ANGLE AROUND C-C BOND

ENERGY
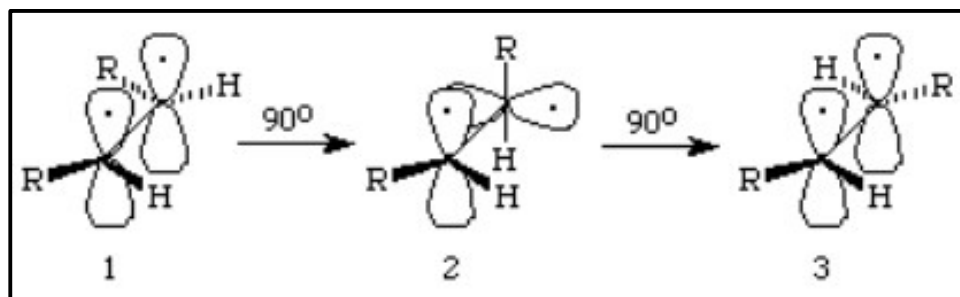
Photochemistry is plagued
with effective NIVR:

open-shell states

quasi-degenerate sates

$$\Psi = \Psi_R C_R + \Psi_P C_P$$

**configuration
mixing**

**avoided
crossing**

Ψ_R

Ψ_P

ROTATION ANGLE AROUND C-C BOND

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Tux, the Linux mascot

3,4,4,5-tetramethylcyclohexa-2,5-dien-1-one
alias
penguinone
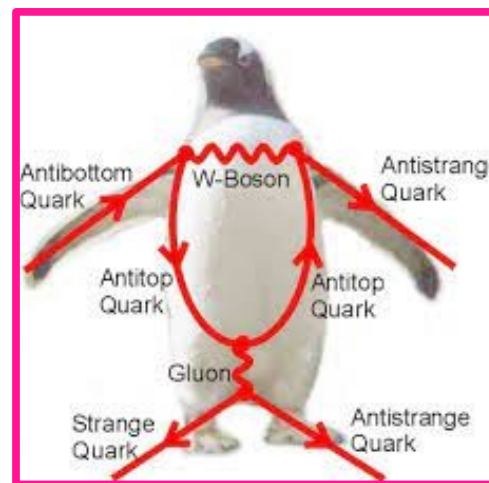
Penguin Feynman diagram
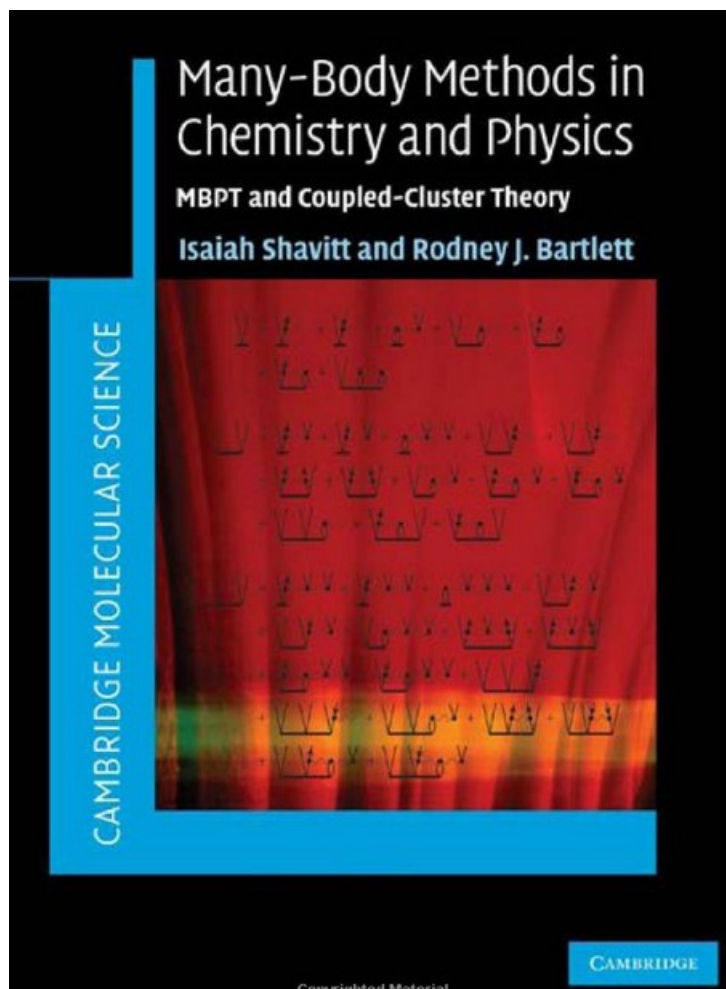
[SB09]

Divide orbitals into occupied and unoccupied.

"FORTRAN index convention": $\underbrace{a,b,\cdots,h}_{virtual},\underbrace{i,j,\cdots,n}_{occupied},\underbrace{o,p,q,\cdots,z}_{free}$ (1)
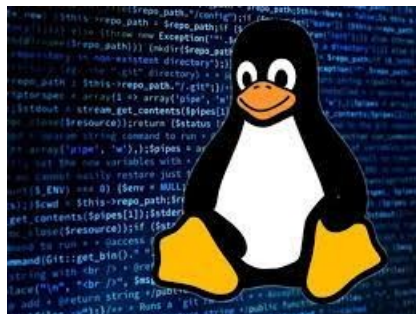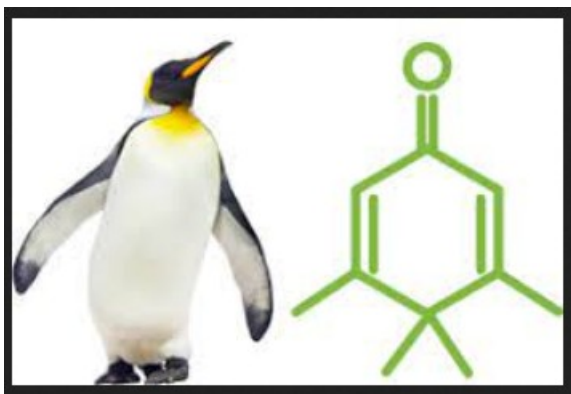
Creation operators

$$\hat{a}_b^+ \left| i\,j\,k\cdots \right| = b^+ \left| i\,j\,k\cdots \right| = \left| b\,i\,j\,k\cdots \right| \tag{2a}$$

$$b^+ \left| b\,i\,j\,k\cdots \right| = \left| b\,b\,i\,j\,k\cdots \right| = 0 \tag{2b}$$

Annihiliation operators

$$\hat{a}_b \left| b\,i\,j\,k\cdots \right| = b \left| b\,i\,j\,k\cdots \right| = \left| i\,j\,k\cdots \right| \tag{3a}$$

$$b \left| i\,b\,j\,k\cdots \right| = -b \left| b\,i\,j\,k\cdots \right| = -\left| i\,j\,k\cdots \right| \tag{3b}$$

$$b \left| i\,j\,k\cdots \right| = 0 \qquad \text{if} \qquad i \notin i,j,k,\cdots \tag{3c}$$

The vacuum state has no electrons. $\quad | \, >$

We can add electrons into orbitals until all the occupied orbitals are present.

$$i_N^+ | \, > = |i_N>$$

$$i_{N-1}^+ |i_N> = |i_{N-1} \, i_N>$$

$$...$$

$$i_1^+ |i_2, \cdots, i_{N-1}, i_N> = |i_1, i_2, \cdots, i_{N-1}, i_N> = |\Phi>$$

This defines the physical vacuum. We can now define excitations in terms of the creation of holes (removal of orbitals *i* and *j*) and the creation of particles (addition of orbitals *a* and *b*).

$$|\Phi>$$
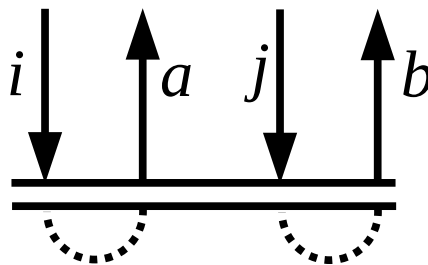
$$b^+ j \, a^+ i |\Phi> = |\Phi_{i,j}^{a,b}>$$
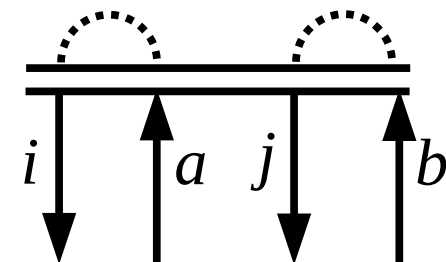
$$<\Phi|i^+ a \, j^+ b = <\Phi_{i,j}^{a,b}|$$

$$\hat{H}=\sum_{r,s} h_{r,s}\, r^{+} s+\frac{1}{2}\sum_{p,q,r,s} (pq|f_H|rs)\, p^{+} r^{+} s q \qquad (1)$$

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

(The number of particles no longer appears ... nice for infinite systems.)

The Hartree kernel and Mulliken charge cloud notation

$$(pq|f_H|rs)=\int\int\; \psi_p^{*}(1)\,\psi_q(1)\frac{1}{r_{1,2}}\,\psi_r^{*}(2)\,\psi_s(2)\,d1\,d2 \qquad (2)$$

$$[r,s]_+ = rs + sr = 0 \qquad (1)$$

$$[r^+, s^+]_+ = r^+ s^+ + s^+ r^+ = 0 \qquad (2)$$

$$[r^+, s]_+ = r^+ s + sr^+ = \delta_{r,s} \qquad (3)$$

Take all possible nonzero contractions, namely

$$\overbracket{r^+ s} = n_r \delta_{r,s}$$

$$\overbracket{r s^+} = \bar{n}_r \delta_{r,s}$$

between holes   between particles

The sign of the integral is obtained by counting loops and hole lines.

$$\boxed{\text{sign} = (-1)^{h+l}}$$

Examples:

$$\langle \Phi | \hat{h} | \Phi_i^a \rangle = \langle \Phi | \hat{h} \, a^+ i | \Phi \rangle = \sum_{r,s} h_{r,s} \langle \Phi | r^+ s \, a^+ i | \Phi \rangle$$

$$= \sum_{r,s} h_{r,s} \, \overbracket{r^+ \underbracket{s \, a^+} i} = \sum_{r,s} h_{r,s} \, \delta_{i,r} \delta_{a,s} = h_{i,a}$$

$$\langle \Phi | \hat{h} | \Phi \rangle = \sum_{r,s} h_{r,s} \langle \Phi | r^+ s | \Phi \rangle = \sum_{r,s} h_{r,s} \, \overbracket{r^+ s}$$

$$= \sum_{r,s} h_{r,s} \, n_r \delta_{r,s} = \sum_k h_{k,k} = \sum_k \epsilon_k^0$$
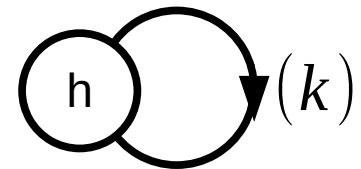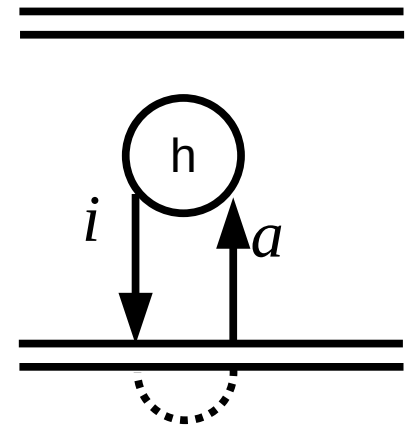
$$\langle \Phi | v_{e,e} | \Phi_i^a \rangle = \langle \Phi | v_{e,e} a^+ i | \Phi \rangle = \frac{1}{2} \sum_{p,q,r,s} (pq|f_H|rs) \langle \Phi | p^+ r^+ s q a^+ i | \Phi \rangle$$

$$= \frac{1}{2} \sum_{p,q,r,s} (pq|f_H|rs) \left(p^+ r^+ s q a^+ i + p^+ r^+ s q a^+ i + p^+ r^+ s q a^+ i + p^+ r^+ s q a^+ i \right)$$

The sign is determined by the parity of the number of contraction line crossings.

$$= \frac{1}{2} \sum_{p,q,r,s} (pq|f_H|rs) \left(-n_p \delta_{p,s} \delta_{r,i} \delta_{q,a} - n_r \delta_{r,q} \delta_{p,i} \delta_{s,a} + n_r \delta_{r,s} \delta_{q,a} \delta_{p,i} + n_p \delta_{p,q} \delta_{r,i} \delta_{s,a} \right)$$

$$= \frac{1}{2} \left[-\sum_k (ka|f_H|ik) - \sum_k (ik|f_H|ka) + \sum_k (ia|f_H|kk) + \sum_k (kk|f_H|ia) \right]$$

$$= \sum_k (ia|f_H|kk) - \sum_k (ik|f_H|ka)$$
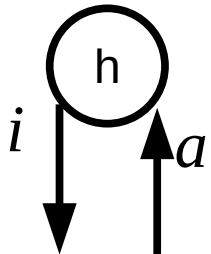
Four terms become two diagrams. The diagrams also help us keep track of terms more easily.
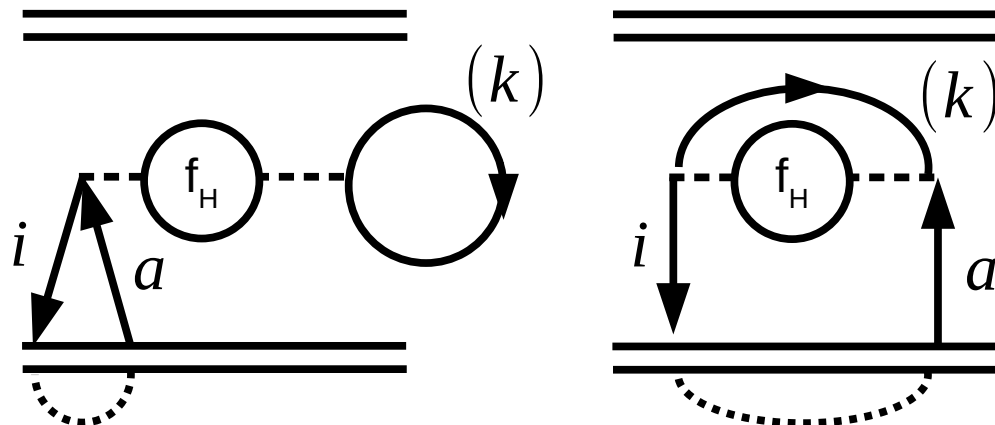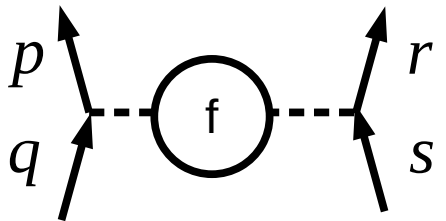
incoming line	$\leftrightarrow$	annihilation operator	$\leftrightarrow$	ket state (IAK)
outgoing line	$\leftrightarrow$	creation operator	$\leftrightarrow$	bra state (OCB)

[SB09] p. 98

$$= \langle \text{out} | \hat{h} | \text{in} \rangle = \langle i | \hat{h} | a \rangle = h_{i,a}$$

$$= \left(\text{left out, left in} | f | \text{right out, right in} \right) = \left(p\,q | f | r\,s \right)$$
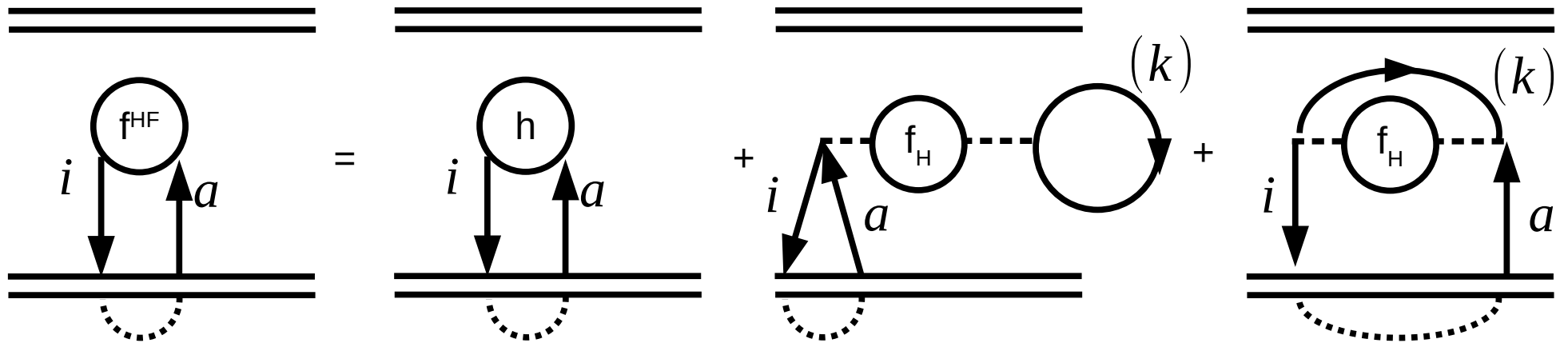
$$f_{i,a}^{\mathrm{HF}} = h_{i,a} + \sum_k \left(ia|f_H|kk\right) - \sum_k \left(ik|f_H|ka\right) = 0$$

(Hartree-)Fock operator
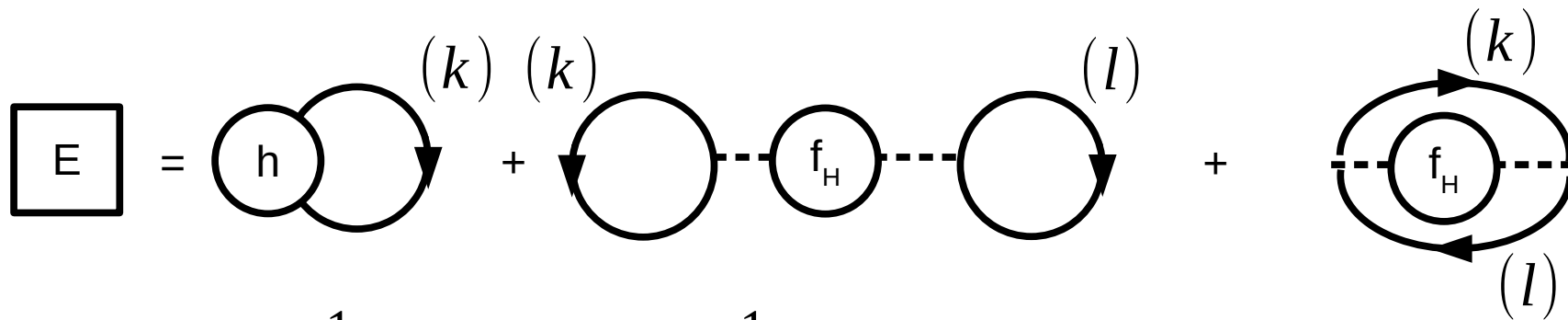
$$E = \sum_k \epsilon_k^0 + \frac{1}{2}\sum_{k,l}\left(kk|f_H|ll\right) - \frac{1}{2}\sum_k \left(kl|f_H|lk\right)$$

Left-right symmetry => Factor 1/2

PECs of H$_2$ molecule by Kolos, Wolniewicz and collaborators

$X\,^2\Sigma_g^+$ (H$_2^+$)

$D\,^1\Pi_u$

$B''\,^1\Sigma_u^+$

$i\,^3\Pi_g$

$B'\,^1\Sigma_u^+$ $C\,^1\Pi$ $c\,^3\Pi_u$

$EF\,^1\Sigma_g^+$

$\left[:\text{H}^-\ \text{H}^+ \leftarrow\rightarrow \text{H}^+\ \text{H}:^-\right]$

$B\,^1\Sigma_u^+$

$b\,^3\Sigma_u^+$

$\left[\uparrow\text{H}\ \text{H}\downarrow \leftarrow\rightarrow \downarrow\text{H}\ \text{H}\uparrow\right]$

$X\,^1\Sigma_g^+$

Potential energy curve (a. u.)

Internuclear distance R (a. u.)

Figure 1. Potential energy curves of H$_2$ obtained by Kolos

H — H

$$u = \sigma_u = \frac{1}{\sqrt{2(1-S)}}\left(s_A - s_B\right)$$

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

ASESMA, Kigali, 2023.06.21

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Lee, Chun-woo *et al*. "Calculation of Potential Energy Curves of Excited States of Molecular Hydrogen by Multi-Reference Configuration-interaction Method." Bulletin of The Korean Chemical Society 34 (2013): 1771-1778.
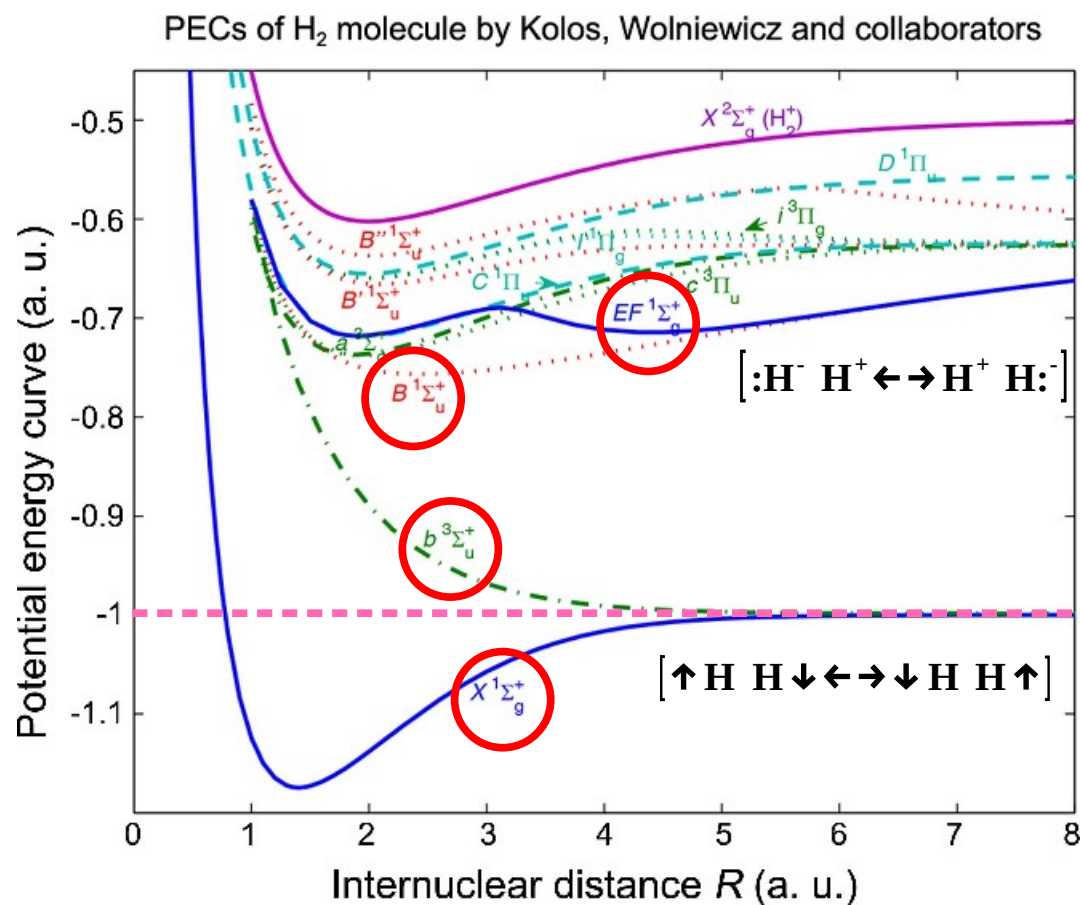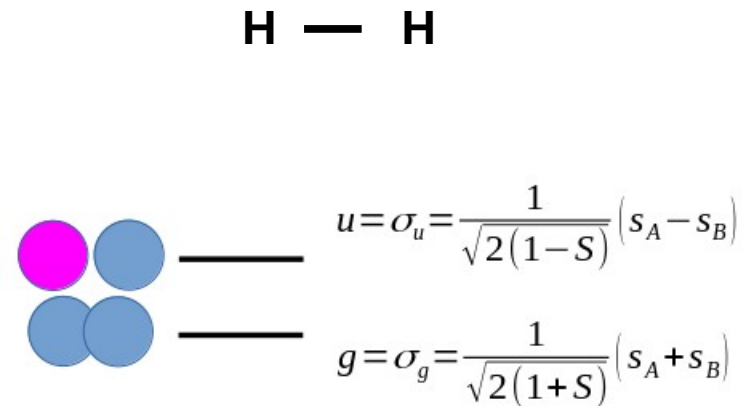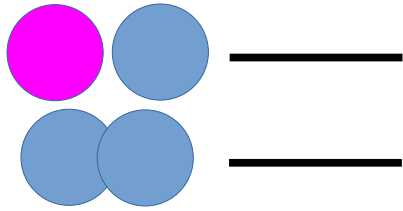
$$u = \sigma_u = \frac{1}{\sqrt{2(1-S)}}(s_A - s_B)$$

The overlap matrix $S = \langle s_A | s_B \rangle$

is used by chemists as one measure of bonding.

$$g = \sigma_g = \frac{1}{\sqrt{2(1+S)}}(s_A + s_B)$$

H — H

Possible fillings:

$^1\Sigma_g$

$|u\bar{u}|$

$^1\Sigma_g$

$|g\bar{g}|$

$^3\Sigma_u$

$|\bar{u}\bar{g}|$

$^3\Sigma_u$

$|gu|$

$^?\Sigma_u$

$|g\bar{u}|$

We need to mix these.

$^?\Sigma_u$

$|u\bar{g}|$

The N-electron wave function should be simultaneously an eigenfunction of

$$\hat{H} \text{ and } \hat{S}^2 \text{ and } \hat{S}_z$$

$$\hat{S}^2|S,M> = \hbar^2 S(S+1)|S,M>$$

$$\hat{S}_z|S,M> = \hbar M|S,M>$$

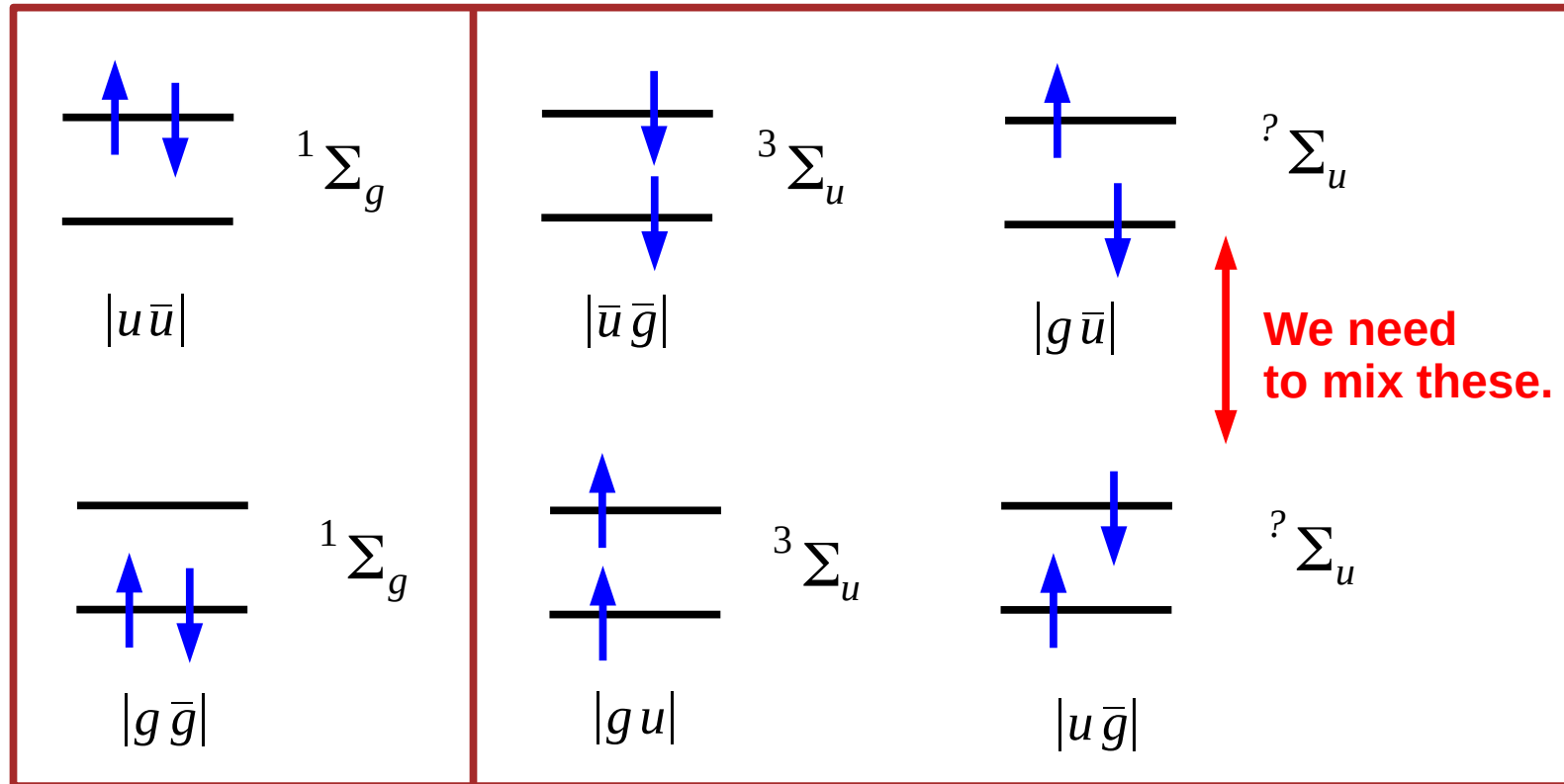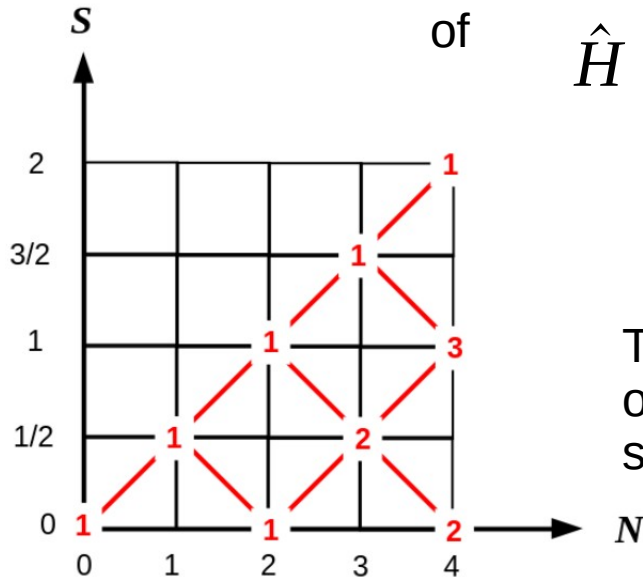The spin-coupling diagram tells us that we should have one triply degenerate triplet state (S = 1) and one singly degenerate singlet state (S = 0).

Answer:
$$\Psi_{1,+1} = |g\,u| = \left[\frac{1}{\sqrt{2}}\big(g(1)u(2)-u(1)g(2)\big)\right]\big(\alpha(1)\alpha(2)\big)$$

The three triplets must all have the same energy.
$$\Psi_{1,0} = \frac{1}{\sqrt{2}}\big(|g\,\bar{u}| - |u\,\bar{g}|\big) = \left[\frac{1}{\sqrt{2}}\big(g(1)u(2)-u(1)g(2)\big)\right]\frac{1}{\sqrt{2}}\big(\alpha(1)\beta(2)+\beta(1)\alpha(2)\big)$$

$$\Psi_{1,-1} = |\bar{u}\,\bar{g}| = \left[\frac{1}{\sqrt{2}}\big(g(1)u(2)-u(1)g(2)\big)\right]\big(\beta(1)\beta(2)\big)$$

$$\Psi_{0,0} = \frac{1}{\sqrt{2}}\big(|g\,\bar{u}| + |u\,\bar{g}|\big) = \left[\frac{1}{\sqrt{2}}\big(g(1)u(2)+u(1)g(2)\big)\right]\left[\frac{1}{\sqrt{2}}\big(\alpha(1)\beta(2)-\beta(1)\alpha(2)\big)\right]$$

Expanding
$$\Psi = \left|i\,\bar{i}\right| C_0 + \left|a\,\bar{i}\right| C_i^a + \left|i\,\bar{a}\right| C_{\bar{i}}^{\bar{a}} + \left|i\,a\right| C_{\bar{i}}^a + \left|a\,\bar{i}\right| C_i^{\bar{a}} + \left|a\,\bar{i}\right| C_{i\bar{i}}^{a\bar{a}}$$

and using the variational principle, leads to the classic configuration interaction (CI) eigenvalue problem,

$$i = g$$
$$a = u$$

$$\begin{vmatrix} E[i\,\bar{i}] & 0 & 0 & 0 & 0 & B \\ 0 & E[a\,\bar{i}] & A & 0 & 0 & 0 \\ 0 & A & E[i\,\bar{a}] & 0 & 0 & 0 \\ 0 & 0 & 0 & E[i\,a] & 0 & 0 \\ 0 & 0 & 0 & 0 & E[\bar{a}\,\bar{i}] & 0 \\ B & 0 & 0 & 0 & 0 & E[a\,\bar{a}] \end{vmatrix} \begin{vmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{\bar{i}}^a \\ C_i^{\bar{a}} \\ C_{i\bar{i}}^{a\bar{a}} \end{vmatrix} = E \begin{vmatrix} C_0 \\ C_i^a \\ C_{\bar{i}}^{\bar{a}} \\ C_{\bar{i}}^a \\ C_i^{\bar{a}} \\ C_{i\bar{i}}^{a\bar{a}} \end{vmatrix}$$
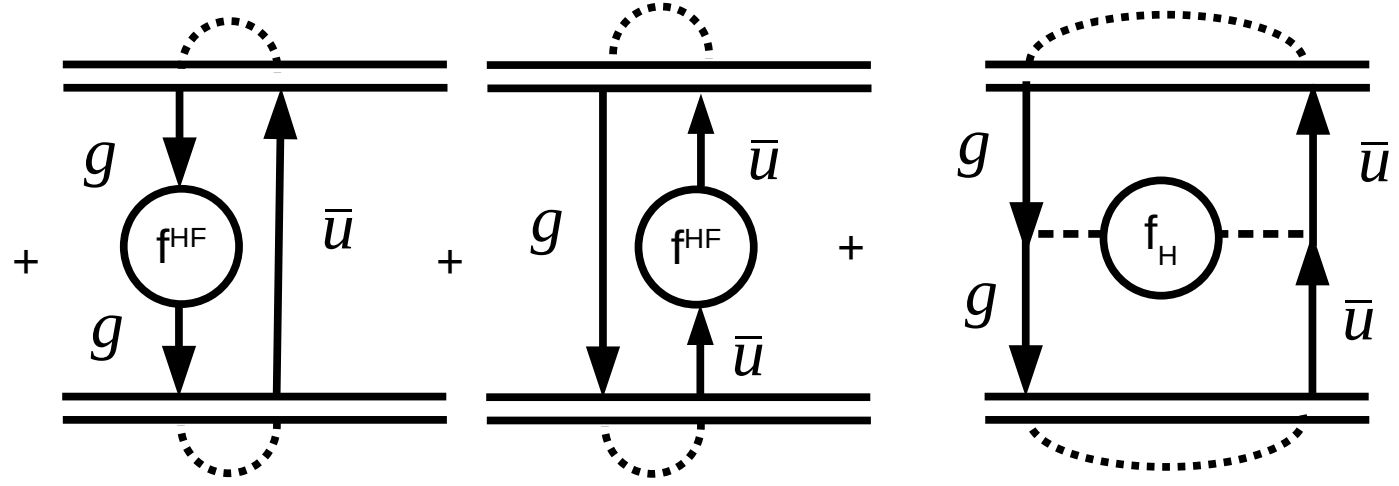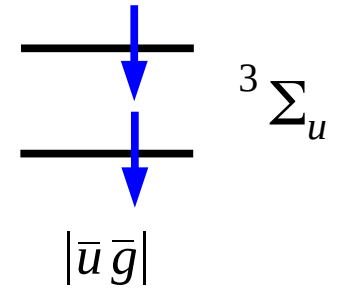
There are a lot of zeros because there is both spin and spatial symmetry in this problem.

As $E[i\,\bar{a}] = E[a\,\bar{i}]$, then it is easy to see that the block indicated in red diagonalizes

to give $E_{\pm} = E[a\,\bar{i}] \pm A$
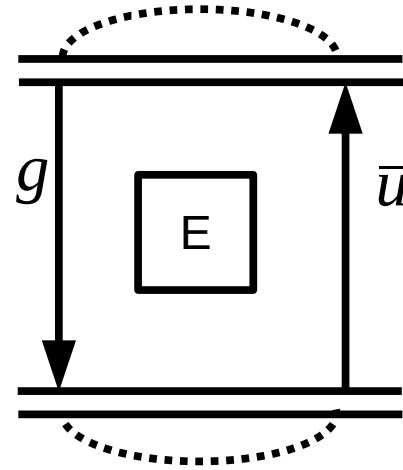
$$E[\bar{u}\,\bar{g}] = \langle g\,\bar{g}|g^+\bar{u}\,\hat{H}\,\bar{u}^+g|g\,\bar{g}\rangle =$$

$$E[\bar{u}\,\bar{g}] = E + \epsilon_u - \epsilon_g - (g\,g|f_H|u\,u)$$

$$E[g\,u] = E + \epsilon_u - \epsilon_g - (g\,g|f_H|u\,u)$$

$$E[u\bar{g}]=\langle g\bar{g}|g^+u\hat{H}u^+g|g\bar{g}\rangle =$$

$$E[u\bar{g}]=E+\epsilon_u-\epsilon_g-(gg|f_H|uu)+(gu|f_H|ug)$$

$$E[g\bar{u}]=E+\epsilon_u-\epsilon_g-(gg|f_H|uu)+(gu|f_H|ug)$$

$$A = \langle g\bar{u}|\hat{H}|u\bar{g}\rangle = \langle g\bar{g}|\bar{u}^+\bar{g}\hat{H}u^+g|g\bar{g}\rangle =$$
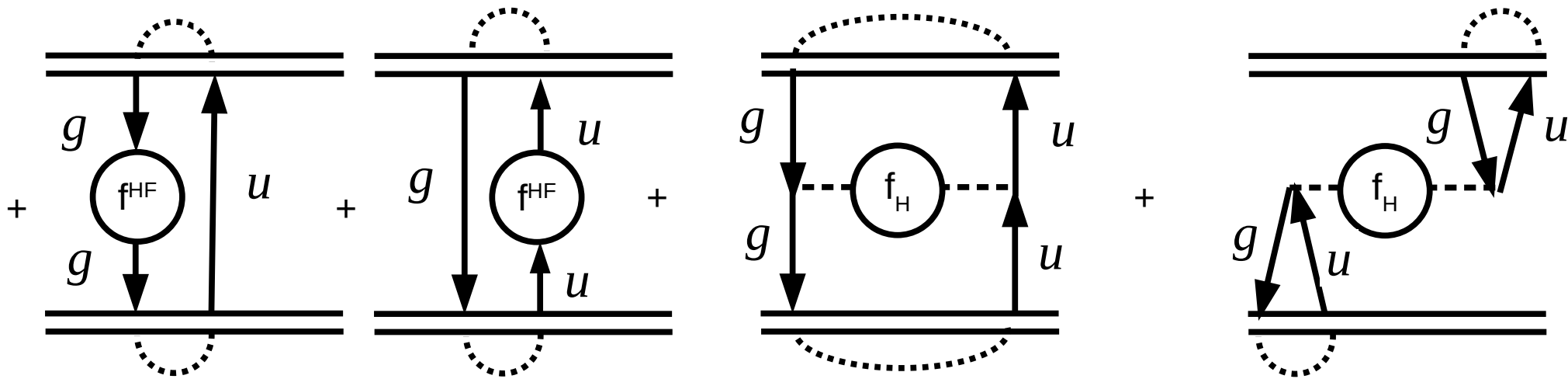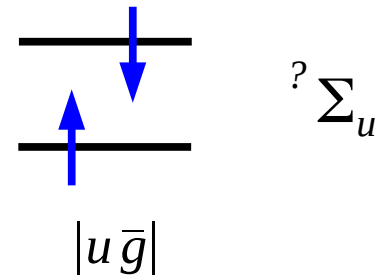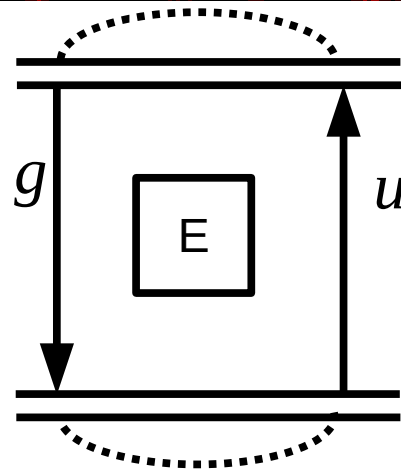
$$A = (gu|f_H|ug)$$
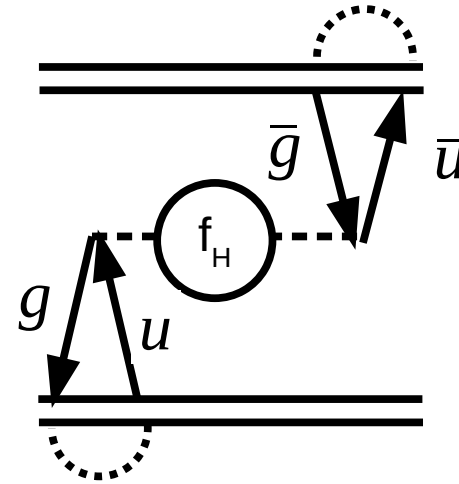
Triplet Energies

$$E[\bar{u}\bar{g}] = E + \epsilon_u - \epsilon_g - (gg|f_H|uu)$$

$$E[gu] = E + \epsilon_u - \epsilon_g - (gg|f_H|uu)$$

$$E[u\bar{g}] - A = E + \epsilon_u - \epsilon_g - (gg|f_H|uu)$$

$$^3\Sigma_u$$

Mixed Symmetry SD Energy

$$E[u\bar{g}] = E + \epsilon_u - \epsilon_g - (gg|f_H|uu) + (gu|f_H|ug)$$

$$^?\Sigma_u$$

Singlet Energy

$$E[u\bar{g}] + A = E + \epsilon_u - \epsilon_g - (gg|f_H|uu) + 2(gu|f_H|ug)$$

$$^1\Sigma_u$$

The mathematician's patterns, like the painter's or the poet's must be beautiful; the ideas, like the colours or the words must fit together in a harmonious way. Beauty is the first test: there is no permanent place in the world for ugly mathematics.

— G. H. Hardy —

AZ QUOTES

I. INTRODUCTION
II. SECOND QUANTIZATION
III. SPIN COUPLING
IV. DISSOCIATION
V. DYNAMIC AND STATIC CORRELATION
VI. MS-DFT
VII. TD-DFT
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IX. CONCLUSION

PECs of H_2 molecule by Kolos, Wolniewicz and collaborators

Figure 1. Potential energy curves of H_2 obtained by Kolos

H — H

$$u = \sigma_u = \frac{1}{\sqrt{2(1-S)}}\left(s_A - s_B\right)$$

$$g = \sigma_g = \frac{1}{\sqrt{2(1+S)}}\left(s_A + s_B\right)$$
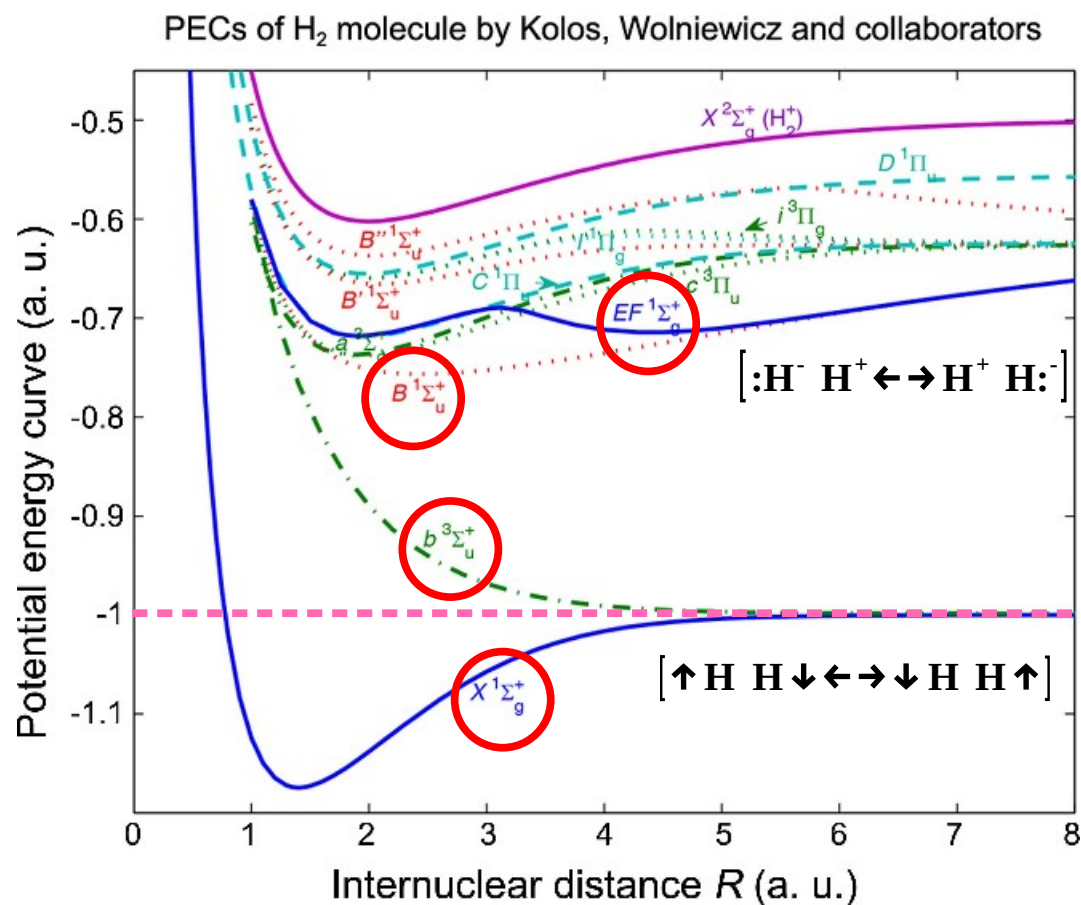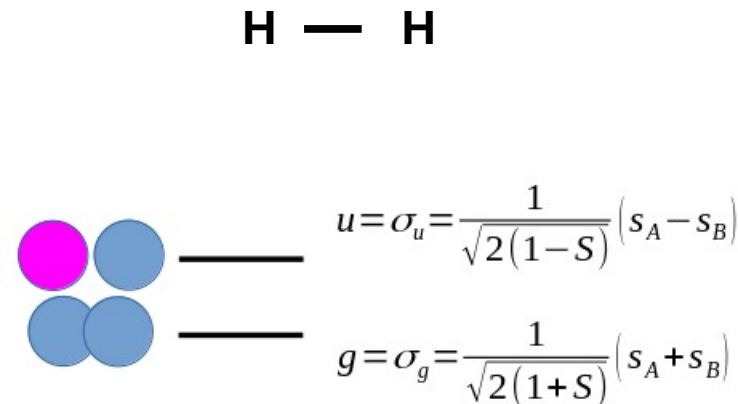
How to make and break bonds?

Lee, Chun-woo *et al*. "Calculation of Potential Energy Curves of Excited States of Molecular Hydrogen by Multi-Reference Configuration-interaction Method." Bulletin of The Korean Chemical Society 34 (2013): 1771-1778.

Molecular orbital (MO) theory

Angel (you!) in the spherical approximation

Valence-bond (VB) theory

Lewis dot structures (LDS) &
Valence Shell Electron Pair Repulsion (VSEPR)

$$g = \frac{1}{\sqrt{2}}(s_A + s_B) \qquad\qquad u = \frac{1}{\sqrt{2}}(s_A - s_B)$$

$$\Psi_{1,+1} = |g, u| = \frac{1}{2}|s_A + s_B, s_A - s_B|$$

$$= \frac{1}{2}\left(|s_A, s_A| - |s_B, s_B| + |s_B, s_A| - |s_A, s_B| \right) = -|s_A, s_B|$$

$$\text{H}\uparrow \quad \text{H}\uparrow$$

$$\Psi_{1,0} = \frac{1}{\sqrt{2}}\left(|g, \bar{u}| - |u, \bar{g}| \right) = -\frac{1}{\sqrt{2}}\left(|s_A, \bar{s}_B| - |s_B, \bar{s}_A| \right)$$

$$\left[\text{H}\uparrow \quad \text{H}\downarrow \leftarrow \rightarrow \text{H}\downarrow \quad \text{H}\uparrow \right]$$

$$\Psi_{1,+1} = |\bar{u}, \bar{g}| = +|\bar{s}_A, \bar{s}_B|$$

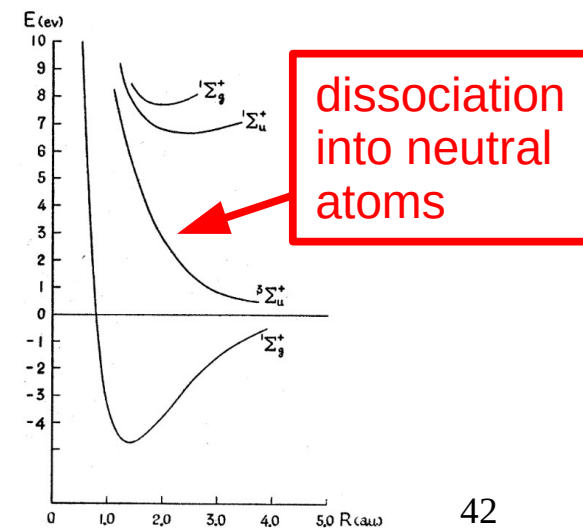$$\text{H}\downarrow \quad \text{H}\downarrow$$

FIG. 2. Computed potential energy curves for H₂.

dissociation into neutral atoms

ASESMA, Kigali, 2023.06.21

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$$\Psi_{0,0}=\frac{1}{\sqrt{2}}\left(\left|g,\bar{u}\right|+\left|u,\bar{g}\right|\right)=\frac{1}{\sqrt{2}}\left(\left|s_A,\bar{s}_A\right|-\left|s_B,\bar{s}_B\right|\right)$$

$$\left[\mathrm{H:^-}\quad\mathrm{H^+}\longleftrightarrow\mathrm{H^+}\quad\mathrm{H:^-}\right]$$

dissociation into ions

dissociation into neutral atoms

FIG. 2. Computed potential energy curves for H_2.

W. Kołos and C. C. J. Roothaan, "Accurate electronic wave functions for the H_2 molecule", *Rev. Mod. Phys.* **32**, 219 (1960).
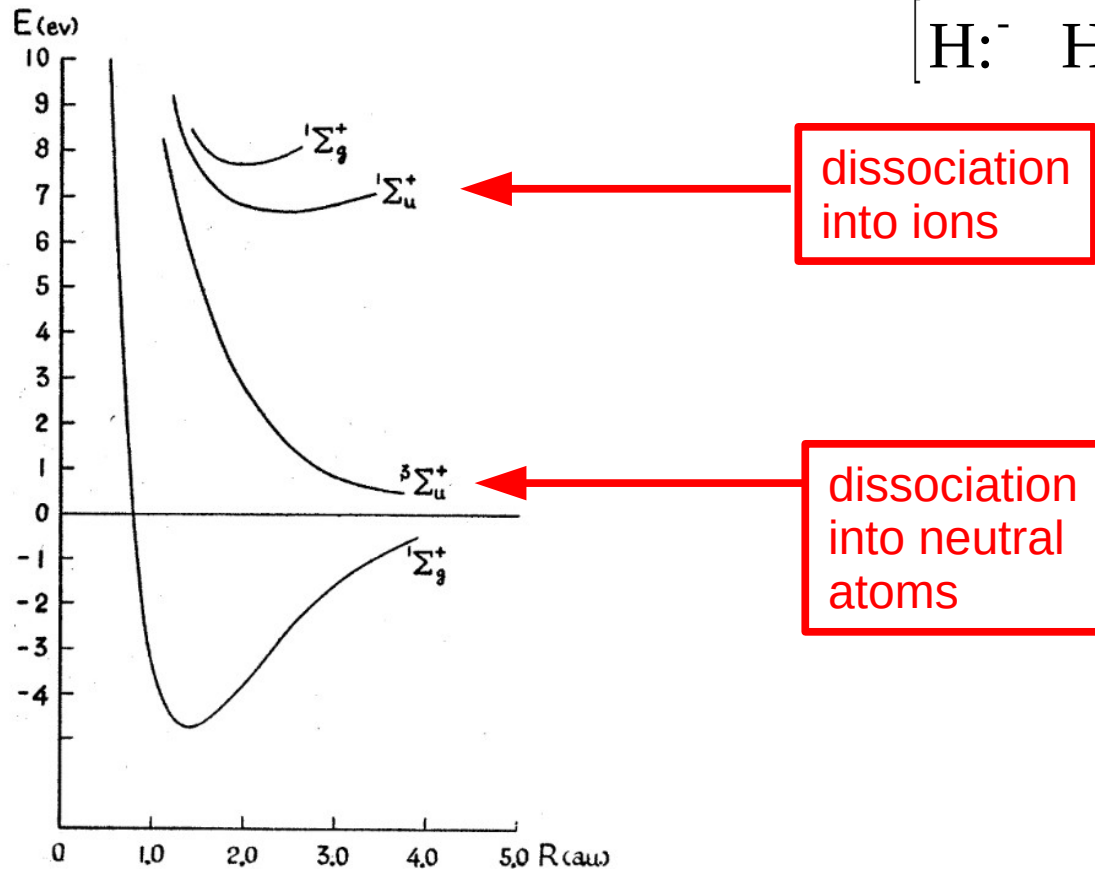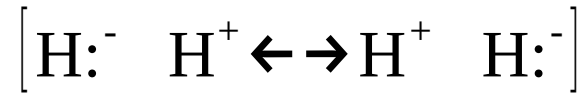
$$|u, \bar{u}| = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(|s_A, \bar{s}_A| + |s_B, \bar{s}_B|\right) - \frac{1}{\sqrt{2}}\left(|s_A, \bar{s}_B| + |s_B, \bar{s}_A|\right)\right]$$

$$\left[\text{H:}^-\quad \text{H}^+ \longleftrightarrow \text{H}^+ \quad \text{H:}^-\right] \quad \left[\text{H}\uparrow\quad \text{H}\downarrow \longleftrightarrow \text{H}\downarrow \quad \text{H}\uparrow\right]$$

$$|g, \bar{g}| = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\left(|s_A, \bar{s}_A| + |s_B, \bar{s}_B|\right) + \frac{1}{\sqrt{2}}\left(|s_A, \bar{s}_B| + |s_B, \bar{s}_A|\right)\right]$$

$$\left[\text{H:}^-\quad \text{H}^+ \longleftrightarrow \text{H}^+ \quad \text{H:}^-\right] \quad \frac{1}{\sqrt{2}}\left(|g, \bar{g}| + |u, \bar{u}|\right) = \frac{1}{\sqrt{2}}\left(|s_A, \bar{s}_A| + |s_B, \bar{s}_B|\right)$$

$$\left[\text{H}\uparrow\quad \text{H}\downarrow \longleftrightarrow \text{H}\downarrow \quad \text{H}\uparrow\right] \quad \frac{1}{\sqrt{2}}\left(|g, \bar{g}| - |u, \bar{u}|\right) = \frac{1}{\sqrt{2}}\left(|s_A, \bar{s}_B| + |s_B, \bar{s}_A|\right)$$

$$\left[H:^- \quad H^+ \longleftrightarrow H^+ \quad H:^- \right]$$

dissociation into ions

dissociation into neutral atoms

$$\left[H\uparrow \quad H\downarrow \longleftrightarrow H\downarrow \quad H\uparrow \right]$$
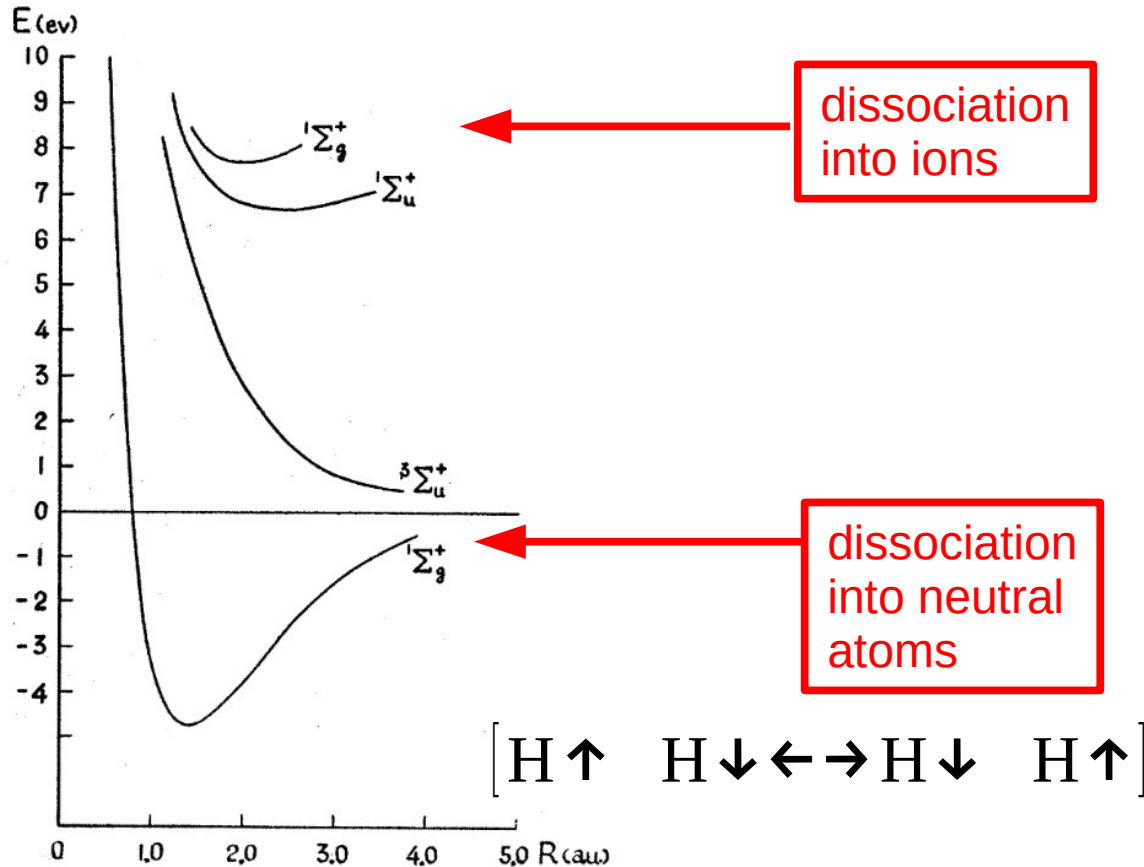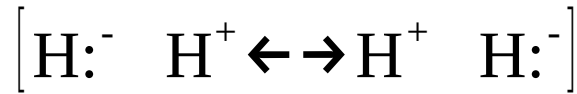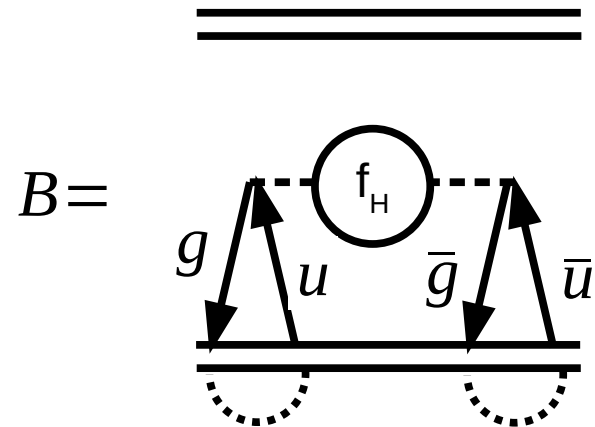

E (ev)

FIG. 2. Computed potential energy curves for H₂.

$$\Psi = |g, \bar{g}| C_0 + |u, \bar{u}| C_D$$

$$\begin{bmatrix} E[g\bar{g}] & B \\ B & E[u\bar{u}] \end{bmatrix} \begin{pmatrix} C_0 \\ C_D \end{pmatrix} = E \begin{pmatrix} C_0 \\ C_D \end{pmatrix}$$
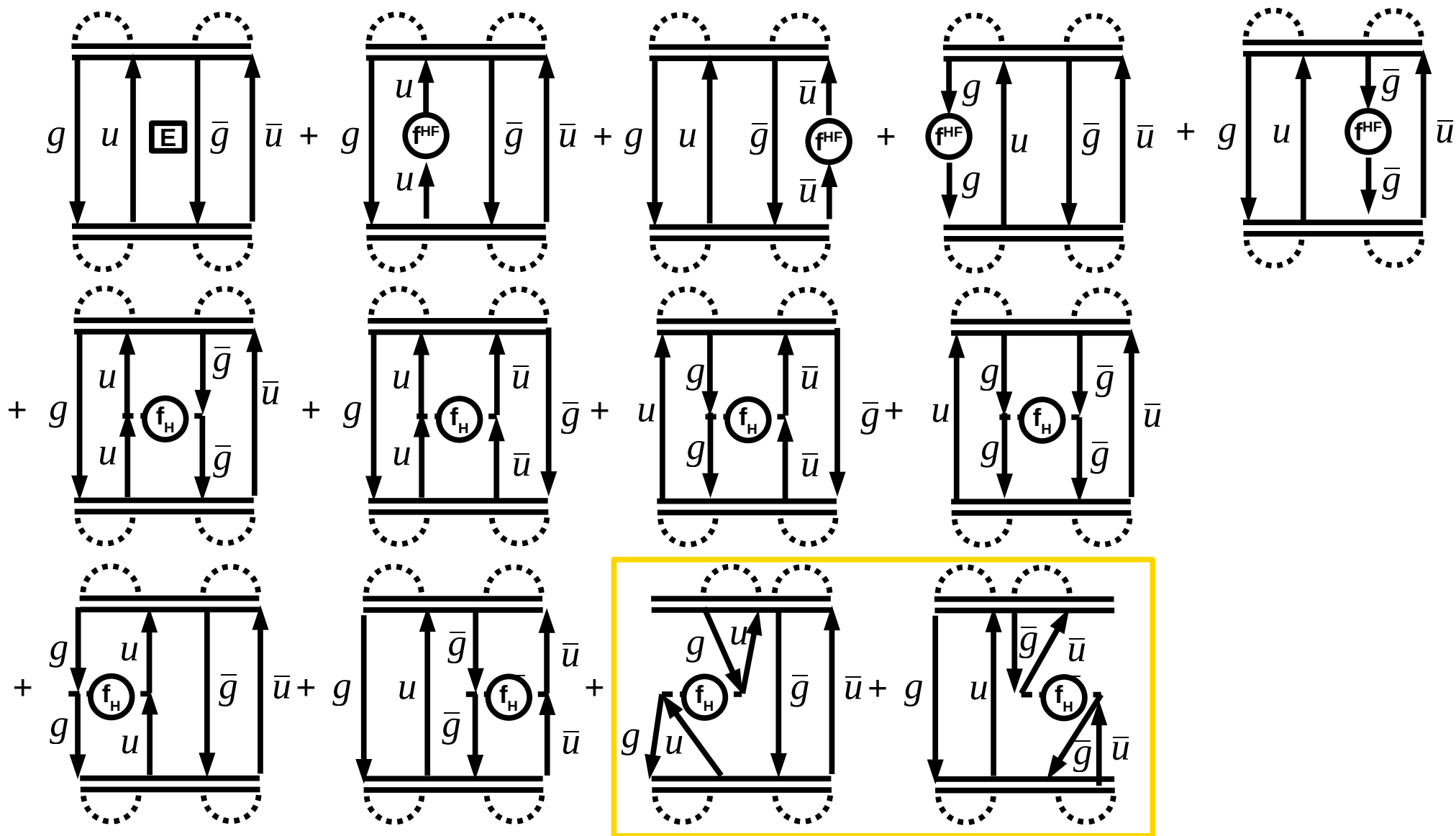
$$B = $$

$$= (g u | f_H | g u) = A$$

only if orbitals are real valued

W. Kołos and C. C. J. Roothaan, "Accurate electronic wave functions for the H₂ molecule", *Rev. Mod. Phys.* **32**, 219 (1960).

$$E[u\bar{u}] = \langle u\bar{u}|\hat{H}|u\bar{u}\rangle = \langle g\bar{g}|g^+ u\bar{g}^+\bar{u}\hat{H}\bar{u}^+\bar{g}u^+g|g\bar{g}\rangle =$$
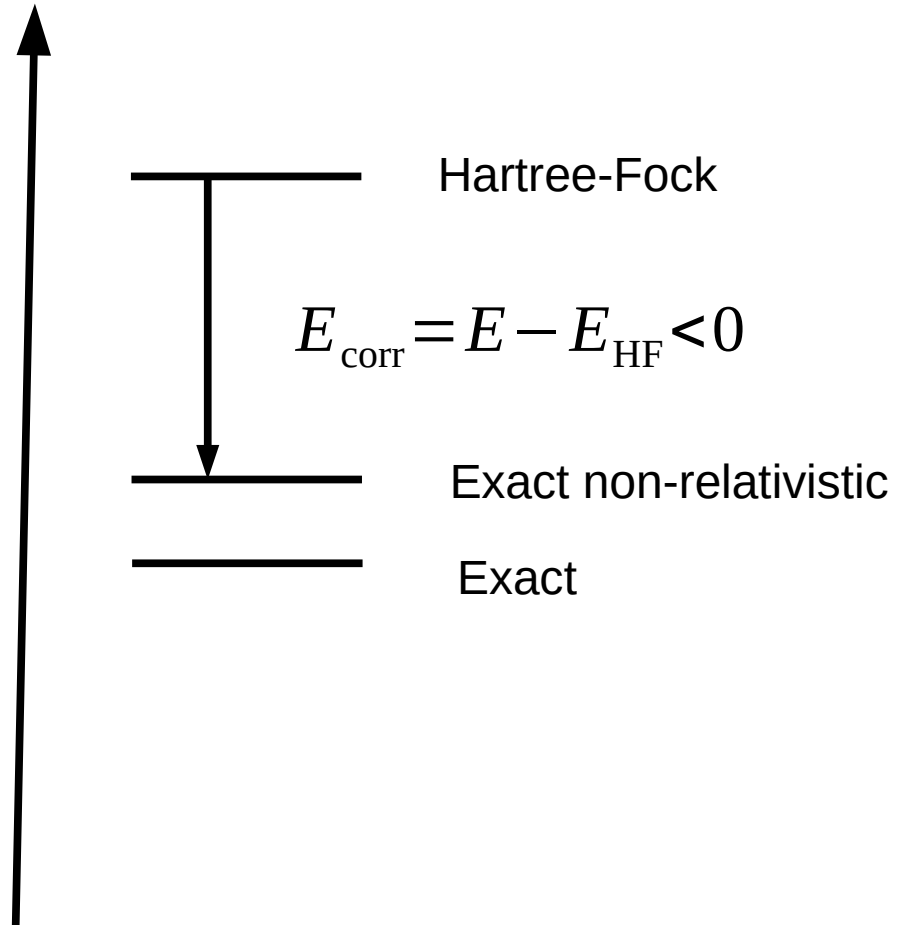
$$E[u\bar{u}] = E + 2\epsilon_u - 2\epsilon_g - 4(uu|f_H|gg) + (uu|f_H|uu) + (gg|f_H|gg) + 2(gu|f_H|gu)$$

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ENERGY

Hartree-Fock

$$E_{\text{corr}} = E - E_{\text{HF}} < 0$$

Exact non-relativistic

Exact

FUZZY TERM

WFT

Can be captured from perturbation theory by summing many many (many!) small terms of a (hopefully) convergent series.

DFT

Atom-like contributions to the correlation energy.

DFT is more efficient than WFT when it comes to including dynamic correlation in calculations.

FUZZY TERM

WFT

The reference wave function is obtained by carrying out a small CI calculation with several determinants. The orbitals may also be optimized (CASSCF). Requires a guess based upon "chemical intuition."

DFT

Correlation energy due to quasi-degeneracies, often associated with making and breaking bonds.

WFT methods are much better established than DFT methods for including static correlation.

IDEA!

Include dynamic correlation by using DFT to calculate the diagonal elements.

Include static correlation by using WFT to calculate the off-diagonal elements.

$$
\begin{vmatrix}
E[i\bar{i}] & 0 & 0 & 0 & 0 & B \\
0 & E[a\bar{i}] & A & 0 & 0 & 0 \\
0 & A & E[i\bar{a}] & 0 & 0 & 0 \\
0 & 0 & 0 & E[ia] & 0 & 0 \\
0 & 0 & 0 & 0 & E[\bar{a}\bar{i}] & 0 \\
B & 0 & 0 & 0 & 0 & E[a\bar{a}]
\end{vmatrix}
\begin{vmatrix}
C_0 \\
C_i^a \\
C_{\bar{i}}^{\bar{a}} \\
C_{\bar{i}}^a \\
C_i^{\bar{a}} \\
C_{i\bar{i}}^{a\bar{a}}
\end{vmatrix}
= E
\begin{vmatrix}
C_0 \\
C_i^a \\
C_{\bar{i}}^{\bar{a}} \\
C_{\bar{i}}^a \\
C_i^{\bar{a}} \\
C_{i\bar{i}}^{a\bar{a}}
\end{vmatrix}
$$

Problem: The three triplet states are no longer degenerate!

$$\Psi_{0,0}=\frac{1}{\sqrt{2}}\left(\left|a\,\bar{i}\right|+\left|i\,\bar{a}\right|\right)$$

$$E_S=\left\langle\Psi_{0,0}\middle|\hat{H}\middle|\Psi_{0,0}\right\rangle=E\left[a\,\bar{i}\right]+A$$

$$\Psi_{1,+1}=\left|i\,a\right|$$

$$E_T=E\left[ia\right]$$

$$\Psi_{1,0}=\frac{1}{\sqrt{2}}\left(\left|a\,\bar{i}\right|+\left|i\,\bar{a}\right|\right)$$

$$E_T=\left\langle\Psi_{1,0}\middle|\hat{H}\middle|\Psi_{1,0}\right\rangle=E\left[a\,\bar{i}\right]-A$$

$$\Psi_{1,-1}=\left|\bar{i}\,\bar{a}\right|$$

Solving the three equations on the RHS gives

$$A=E\left[a\,\bar{i}\right]-E\left[ia\right]\neq\left(ai\middle|\middle|ai\right)\qquad\text{(except in WFT)}$$

Try to answer the question by developing diagrams for MS-DFT.
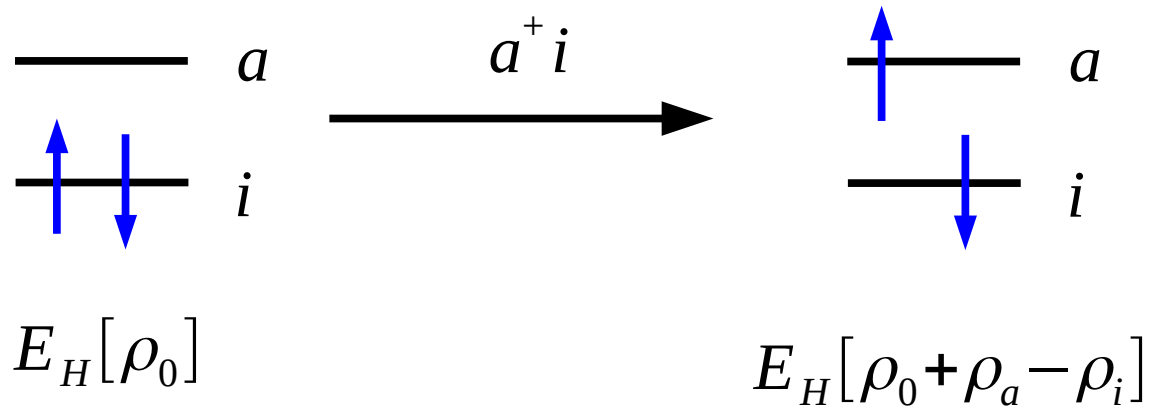
Expect:

Self-interaction (SI) terms that cancel in WFT but not in DFT.

Exchange diagrams will have to be transformed into direct diagrams.

These diagrams *might* also help us make and educated guess as to how DFT can be used to estimate off-diagonal CI elements *without* the use of symmetry.
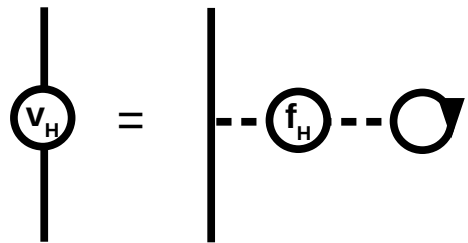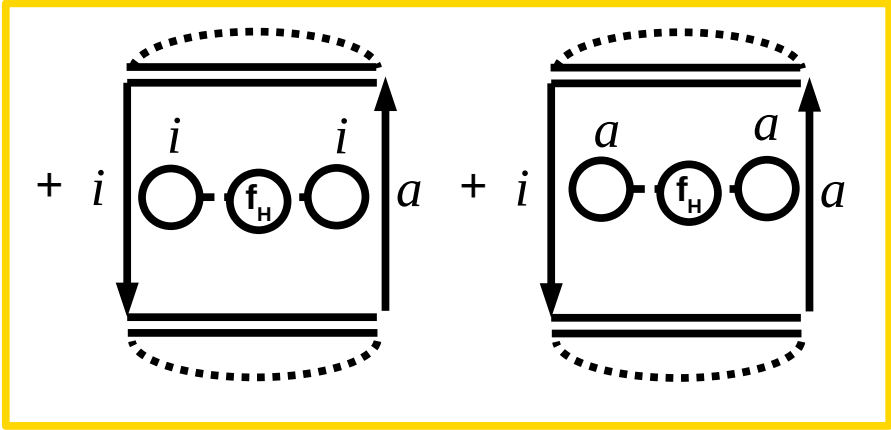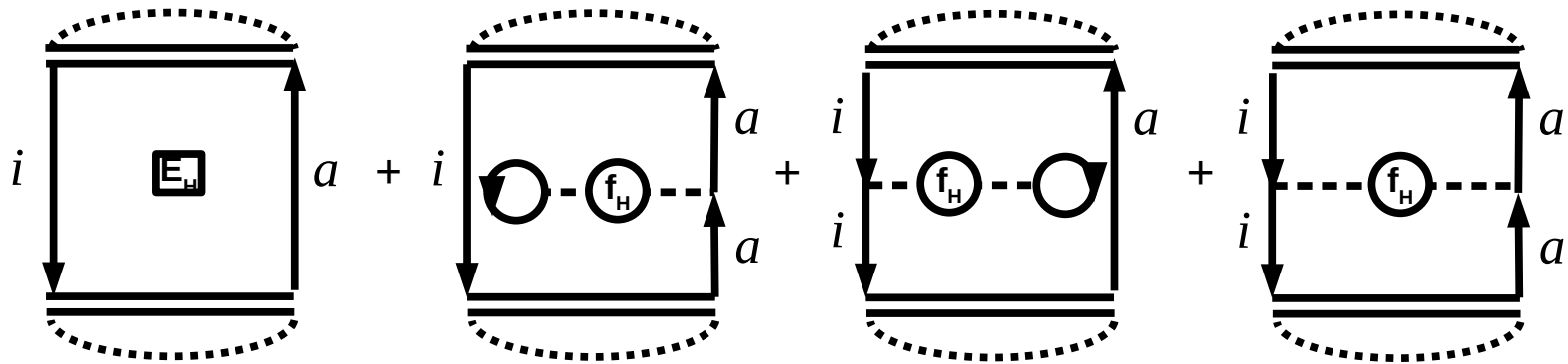
$$E_H[\rho_0] \qquad\qquad E_H[\rho_0 + \rho_a - \rho_i]$$

$$E_H[\rho_0 + \rho_a - \rho_i] = \frac{1}{2} \int \int \big(\rho_0(1) + \rho_a(1) - \rho_i(1)\big) \frac{1}{r_{1,2}} \big(\rho_0(2) + \rho_a(2) - \rho_i(2)\big) d1\, d2$$

$$= E_H[\rho_0] + \int v_H[\rho_0](1)\rho_a(1)\, d1 - \int v_H[\rho_0](1)\rho_i(1)\, d1 - (ii|f_H|aa)$$

$$+\frac{1}{2}(ii|f_H ii) + \frac{1}{2}(aa|f_H|aa)$$

$$E_H[\rho_0+\rho_a-\rho_i]=E_H[\rho_0]+\int v_H[\rho_0](1)\rho_a(1)d1-\int v_H[\rho_0](1)\rho_i(1)d1-(ii|f_H|aa)$$

$$+\frac{1}{2}(ii|f_H ii)+\frac{1}{2}(aa|f_H|aa)$$
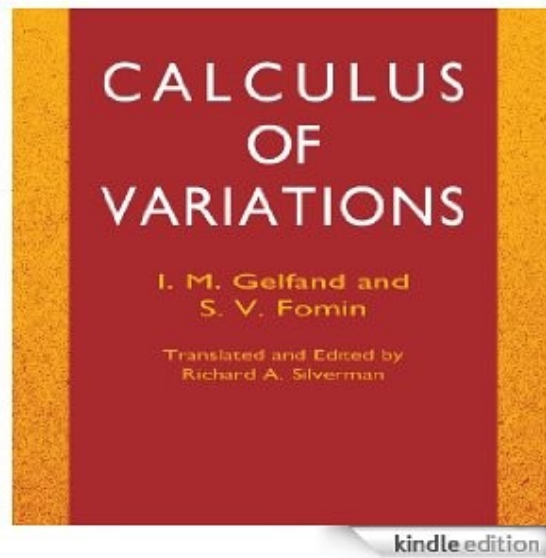
Multivariable calculus

$$\vec{f} = \begin{pmatrix} f_1 \\ f_2 \\ \vdots \end{pmatrix} \quad \text{(1a)}$$

$$dF(\vec{f}) = \sum_i \frac{\partial F}{\partial f_i} df_i \quad \text{(2a)}$$

Variational calculus

$$f = f(x) \quad \text{(1b)}$$

$$\delta F[f] = \int \frac{\delta F}{\delta f(x)} \delta f(x) \, dx \quad \text{2b)}$$

CALCULUS OF VARIATIONS

I. M. Gelfand and S. V. Fomin

Translated and Edited by Richard A. Silverman

kindle edition

Prentice-Hall 1963
McGraw Hill 1968
Dover 1974
… now in e-book format

$$E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}+\rho_a-\rho_i]=E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}]+\int \frac{\delta E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}]}{\delta\rho_0^{\uparrow}(1)}\rho_a(1)\,d1-\int \frac{\delta E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}]}{\delta\rho_0^{\uparrow}}(1)\rho_i(1)\,d1$$

$$-\int\int \rho_i(1)\frac{\delta^2 E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}]}{\delta\rho_0^{\uparrow}(1)\,\delta\rho_0^{\uparrow}(2)}\rho_a(2)\,d1\,d2$$

$$+\frac{1}{2}\int\int \rho_a(1)\frac{\delta^2 E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}]}{\delta\rho_0^{\uparrow}(1)\,\delta\rho_0^{\uparrow}(2)}\rho_a(2)\,d1\,d2+\frac{1}{2}\int\int \rho_a(1)\frac{\delta^2 E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}]}{\delta\rho_0^{\uparrow}(1)\,\delta\rho_0^{\uparrow}(2)}\rho_a(2)\,d1\,d2$$
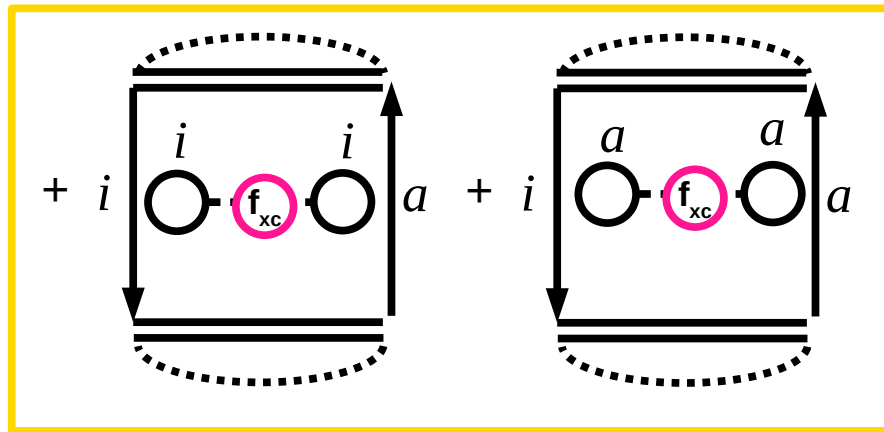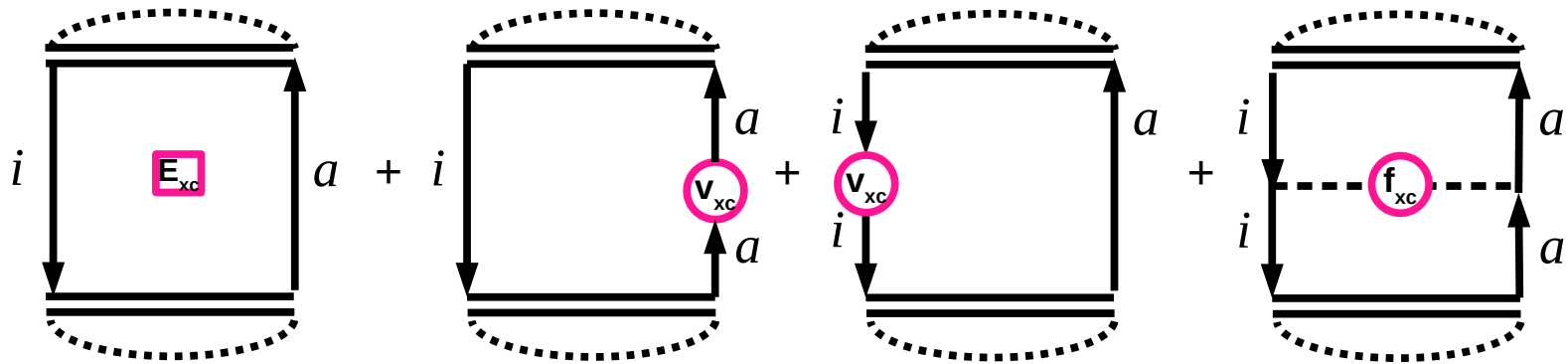
$$+\text{higher order terms (HOT)}$$

$$E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}+\rho_a-\rho_i]=E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}]+\int v_{xc}^{\uparrow}[\rho_0^{\uparrow},\rho_0^{\downarrow}](1)\rho_a(1)\,d1-\int v_{xc}^{\uparrow}[\rho_0^{\uparrow},\rho_0^{\downarrow}](1)\rho_i(1)\,d1$$

$$-(ii|f_{xc}^{\uparrow,\uparrow}[\rho_0^{\uparrow},\rho_0^{\downarrow}]|aa)+\frac{1}{2}(ii|f_{xc}^{\uparrow,\uparrow}[\rho_0^{\uparrow},\rho_0^{\downarrow}]|ii)+\frac{1}{2}(aa|f_{xc}^{\uparrow,\uparrow}[\rho_0^{\uparrow},\rho_0^{\downarrow}]|aa)$$

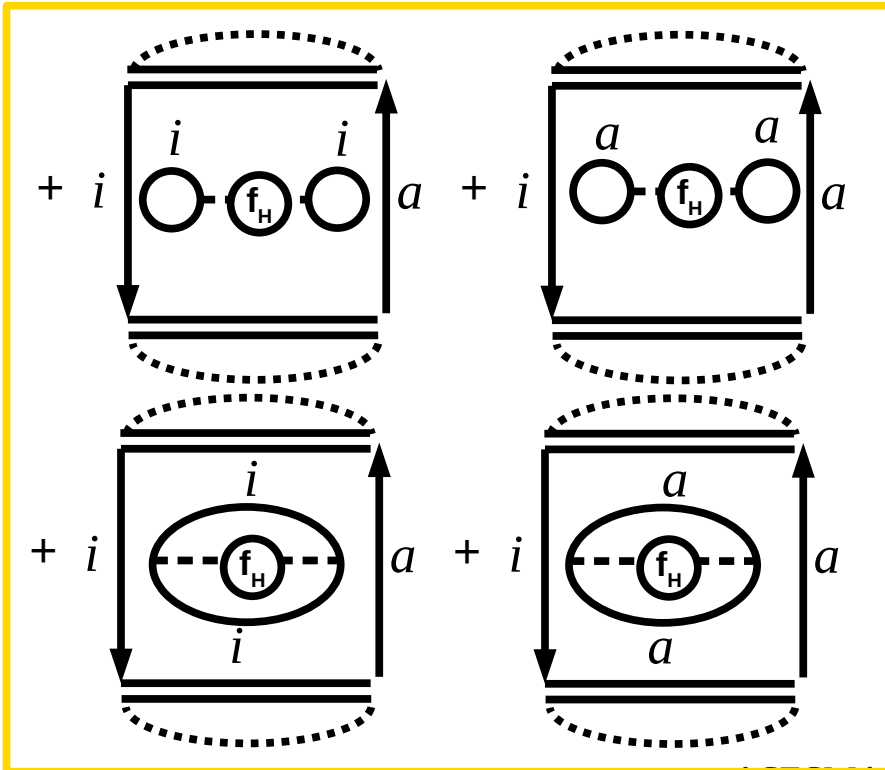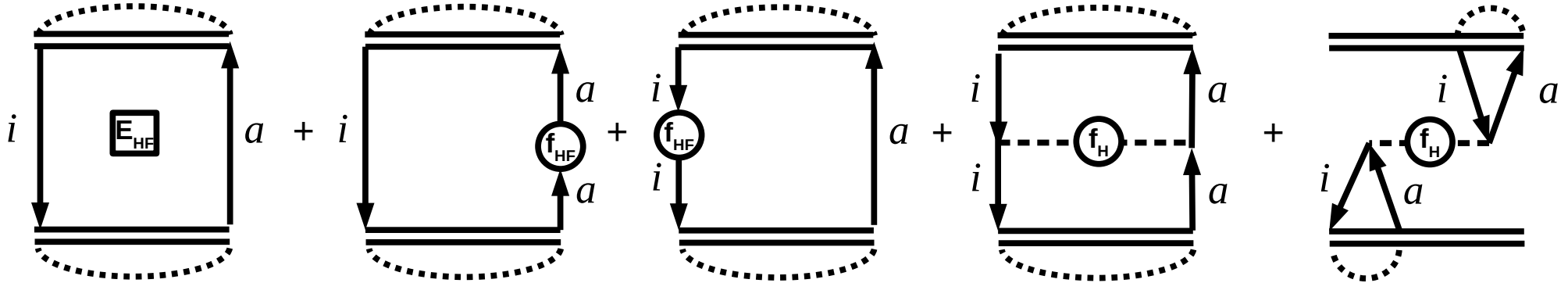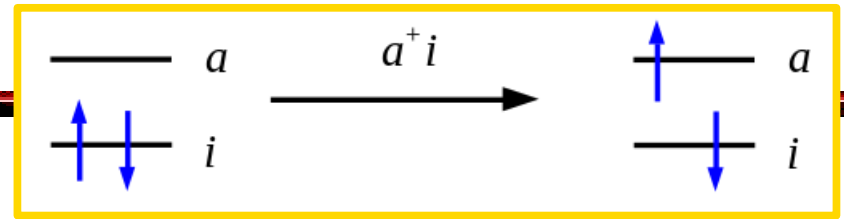$$E_{xc}[\rho_0^{\uparrow},\rho_0^{\downarrow}+\rho_a-\rho_i]=E_{xc}+\int v_{xc}^{\uparrow}\rho_a-\int v_{xc}^{\uparrow}\rho_i-(ii|f_{xc}^{\uparrow,\uparrow}|aa)+\frac{1}{2}(ii|f_{xc}^{\uparrow,\uparrow}|ii)+\frac{1}{2}(aa|f_{xc}^{\uparrow,\uparrow}|aa)$$

$$E_{xc}[\rho_0^{\uparrow}, \rho_0^{\downarrow} + \rho_a - \rho_i] = E_{xc} + \int v_{xc}^{\uparrow} \rho_a - \int v_{xc}^{\uparrow} \rho_i - (i\,i|f_{xc}^{\uparrow,\uparrow}|a\,a) + \frac{1}{2}(i\,i|f_{xc}^{\uparrow,\uparrow}|i\,i) + \frac{1}{2}(a\,a|f_{xc}^{\uparrow,\uparrow}|a\,a)$$
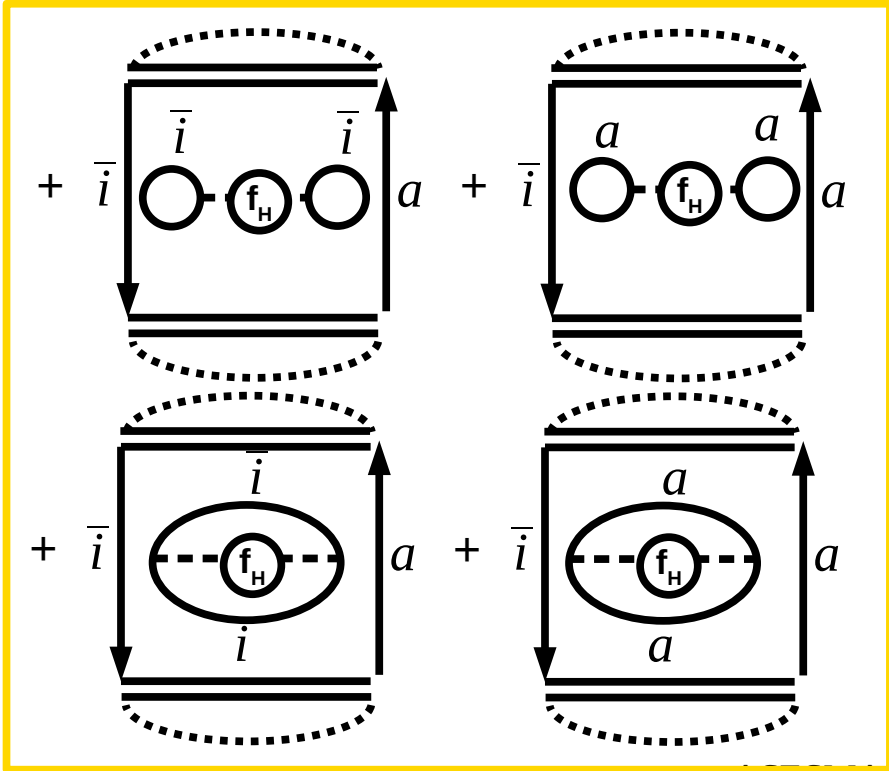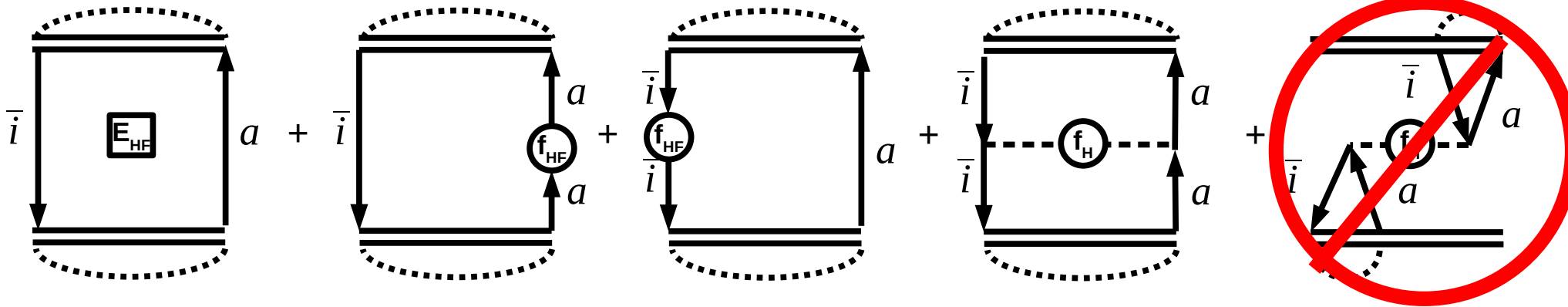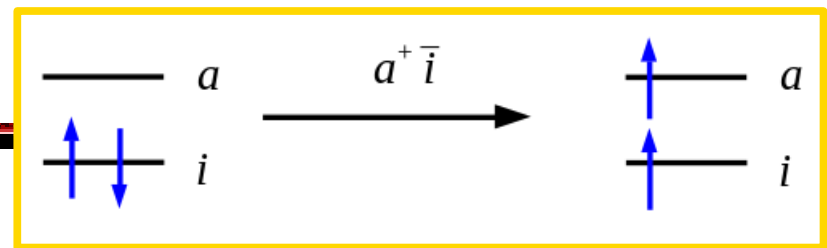
Self-interaction (SI) terms that cancel in WFT.

Self-interaction (SI) terms that cancel in WFT.

$$A = E[g\bar{u}] - E[gu]$$

$$A = \quad\quad\quad - \quad\quad\quad = (ia|f_H|ia)$$

$$E_S - E_0 = \epsilon_u - \epsilon_g - (gg|f_H|uu) + 2(gu|f_H|ug)$$

$$E[g\bar{u}] - E_0 = \epsilon_u - \epsilon_g - (gg|f_H|uu) + (gu|f_H|ug)$$

$$E_T - E_0 = \epsilon_u - \epsilon_g - (gg|f_H|uu)$$

Self-interaction (SI) terms that do not exactly cancel in DFT.

Self-interaction (SI) terms that do not exactly cancel in DFT.

$A = E[g\bar{u}] - E[gu]$

$$A = \quad = (ii|f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\downarrow,\uparrow}|aa)$$

$$E_S - E_0 = \epsilon_u - \epsilon_g + \frac{1}{2}(uu - gg|f_H + f_{xc}^{\uparrow,\uparrow}|uu - gg) - (gg|f_{xc}^{\uparrow,\uparrow} + f_{xc}^{\downarrow,\uparrow}|uu)$$

$$E[g\bar{u}] - E_0 = \epsilon_u - \epsilon_g + \frac{1}{2}(uu - gg|f_H + f_{xc}^{\uparrow,\uparrow}|uu - gg)$$

$$E_T - E_0 = \epsilon_u - \epsilon_g + \frac{1}{2}(uu - gg|f_H + f_{xc}^{\uparrow,\uparrow}|uu - gg) - (gg|f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\downarrow,\uparrow}|uu)$$

M.E. Casida, F. Gutierrez, J. Guan, F.-X. Gadea, D.R. Salahub, and J.-P. Daudey, *J. Chem. Phys.* **113**, 7062 (2000).
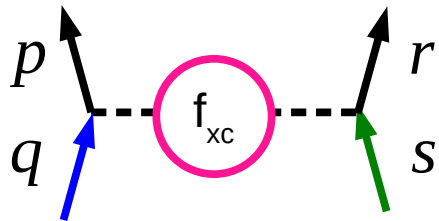
$$(pq|f_{xc}^{\uparrow,\uparrow}|rs) \rightarrow -(ps|f_H|rq)$$
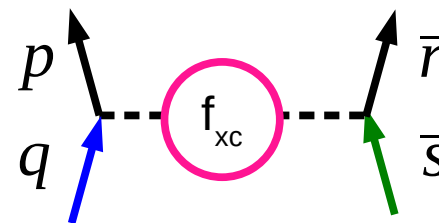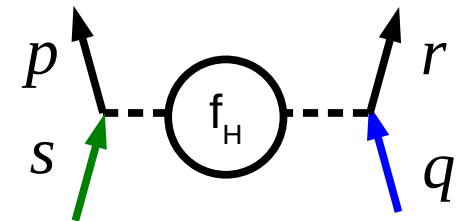
$$(pq|f_{xc}^{\uparrow,\downarrow}|rs) \rightarrow 0$$
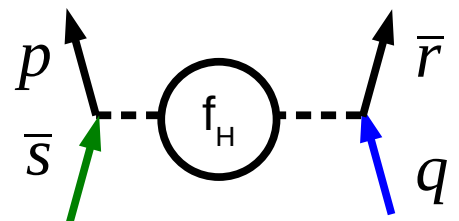
But we can only *guess* the reverse (WFT → DFT) direction!

I. INTRODUCTION
II. SECOND QUANTIZATION
III. SPIN COUPLING
IV. DISSOCIATION
V. DYNAMIC AND STATIC CORRELATION
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VIII. UNIFYING MS- AND TD-DFT
IX. CONCLUSION

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

The EOM

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

has excitation-type solutions

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

and de-excitation-type solutions

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

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

Let us seek a solution of the form

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

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

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

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

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

gives us

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

with

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

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

ASESMA, Kigali, 2023.06.21

excitation

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

corresponding de-excitation

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

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

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

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

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

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

* two-orbital two-electron model.

TD-DFT

$$\omega_T = \epsilon_a - \epsilon_i + \left(ia \left| f_{xc}^{\uparrow,\uparrow} - f_{xc}^{\uparrow,\downarrow} \right| ai \right) \qquad (1)$$

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

$$\left(pq \left| f_{xc}^{\uparrow,\uparrow} \right| rs \right) \rightarrow - \left(ps \left| f_H \right| rq \right) \quad (3) \qquad \left(pq \left| f_{xc}^{\uparrow,\downarrow} \right| rs \right) \rightarrow 0 \quad (4)$$

TD-HF

$$\omega_T = \epsilon_a - \epsilon_i + 2 \left(ai \left| f_H \right| ia \right) - \left(aa \left| f_H \right| ii \right) \qquad (5)$$

$$\omega_S = \epsilon_a - \epsilon_i + 2 \left(ai \left| f_H \right| ia \right) - \left(aa \left| f_H \right| ii \right) \qquad (6)$$

This suggests to me that
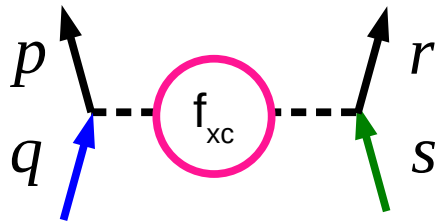
$$(pq|f_{xc}^{\uparrow,\uparrow}|rs) \approx -(ps|f_H|rq)$$
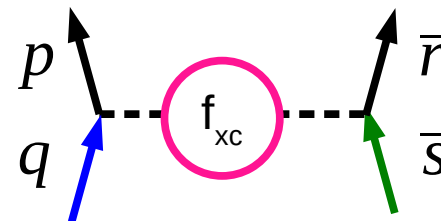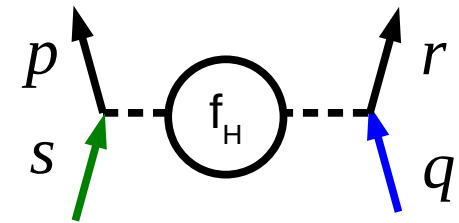
$$(pq|f_{xc}^{\uparrow,\downarrow}|rs) \approx 0$$
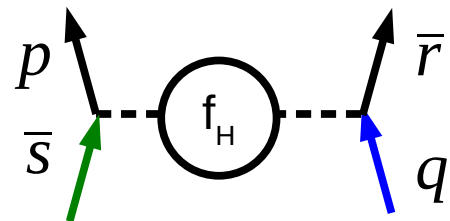
DIFFERENT FORMALISMS GIVING SIMILAR ANSWERS … WHY?

MS-DFT

?
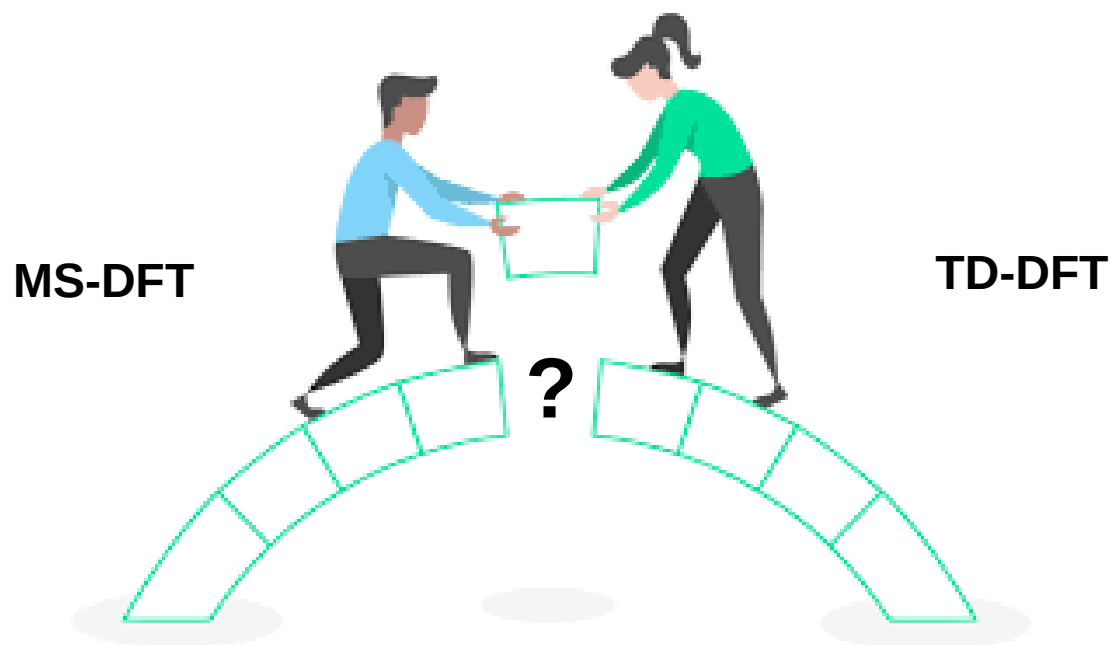
TD-DFT

Can TD-DFT be seen as a particular type of MS-DFT (ΔSCF) calculation?

(This is you & me.)

P.S. Finding links between seemingly unrelated things is really cool!

(13)

HOW DOES IT COME ABOUT THAT ∆SCF-DFT AND TDDFT ARE SO SIMILAR?

PERTURBATIVE APPROACH TO ∆SCF

Ψ_1, E_1

$$\Psi_\lambda = |\sqrt{1-\lambda^2}\,\psi_i + \lambda e^{i\alpha}\psi_a, \bar{\psi}_i|$$
$$= \sqrt{1-\lambda^2}\,\Psi_0 + \lambda e^{i\alpha}\Psi_1 \rightarrow \begin{cases} \Psi_0 \;;\; \lambda=0 \\ e^{i\alpha}\Psi_1 \;;\; \lambda=1 \end{cases}$$

λ

$$E_\lambda = \langle \Psi_\lambda | \hat{H} | \Psi_\lambda \rangle$$
$$= (1-\lambda^2)\langle \Psi_0 | \hat{H} | \Psi_0 \rangle + \lambda^2 \langle \Psi_1 | \hat{H} | \Psi_1 \rangle$$
$$= (1-\lambda^2) E_0 + \lambda^2 E_1 \rightarrow \begin{cases} E_0 \;;\; \lambda=0 \\ E_1 \;;\; \lambda=1 \end{cases}$$

Ψ_0, E_0

77

PERTURBATIVE APPROACH TO ΔSCF ⑭

EXPECT

$$\omega_\alpha = \lim_{\lambda \to 0} \frac{E_\lambda^* - E_0}{\lambda^2}$$

TO BE INDEPENDENT OF α AND TO EQUAL $\omega^{\Delta SCF}$

FIND

RESPONSE THEORY ANSWER, ω, IS GIVEN BY

$$\omega^2 = \omega_R \, \omega_I$$

WHERE

$$\omega_R = \omega_\alpha \big|_{\alpha = 0}$$

$$\omega_I = \omega_\alpha \big|_{\alpha = \pi/2}$$

78

MULTILEVEL TREATMENT (STABILITY ANALYSIS)

$$\psi_r' = e^{i\lambda \hat{Q}}\psi_r$$

$$\hat{Q} = \hat{R} + i\,\hat{I}$$

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

$$\underline{\underline{\Omega}}_R \qquad\qquad \underline{\underline{\Omega}}_I$$

$$\underline{\underline{\Omega}}_R\,\underline{\underline{\Omega}}_I\,\vec{Z} = \omega^2\,\vec{Z}$$

10 YRS. LATER

[ZSK+09]

On the relation between time-dependent and variational density functional theory approaches for the determination of excitation energies and transition moments.

Tom Ziegler,[1,a)] Michael Seth,[1] Mykhaylo Krykunov,[1] Jochen Autschbach,[2] and Fan Wang[3]

[1]Department of Chemistry, University of Calgary, University Drive 2500, Calgary, AB T2N-1N4, Canada
[2]Department of Chemistry, State University of New York at Buffalo, 312 Natural Sciences Complex, Buffalo, New York 14260-3000, USA
[3]College of Chemistry, Sichuan University Chengdu, Box No. 75, Sichuan 610064, People's Republic of China

It is shown that it is possible to derive the basic eigenvalue equation of adiabatic time-dependent density functional theory within the Tamm–Dancoff approximation (TD-DFT/TD) from a variational principle. The variational principle is applied to the regular Kohn–Sham formulation of DFT energy expression for a single Slater determinant and leads to the same energy spectrum as TD-DFT/TD. It is further shown that this variational approach affords the same electric and magnetic transition moments as TD-DFT/TD. The variational scheme can also be applied without the Tamm–Dancoff approximation. Practical implementations of TD-DFT are limited to second order response theory which introduces errors in transition energies for charge transfer and Rydberg excitations. It is indicated that higher order terms can be incorporated into the variational approach. It is also discussed how the current variational method is related to traditional DFT schemes based on variational principles such as ΔSCF-DFT, and how they can be combined. © 2009 American Institute of Physics. [DOI: 10.1063/1.3114988]

$$\psi_i'(1) = \psi_i(1) + \sum_a^{\text{vir}} U_{ai}\psi_a(1) - \frac{1}{2}\sum_a^{\text{vir}}\sum_k^{\text{occ}} U_{ai}U_{ak}^*\psi_k(1)$$

$$+ O^{(3)}[U]. \tag{12}$$

$$E_{\text{KS}}[\rho^0 + \Delta\rho'] - E_{\text{KS}}[\rho^0] = \Delta E^{\text{KS}}[\Delta\rho'] + O^{(3)}[E_{\text{HF}}(U)]$$

$$= \frac{1}{2}(U^* \; U)\begin{pmatrix} \mathbf{A}^{\text{KS}} & \mathbf{B}^{\text{KS}} \\ \mathbf{B}^{\text{KS}} & \mathbf{A}^{\text{KS}} \end{pmatrix}\begin{pmatrix} U \\ U^* \end{pmatrix}$$

$$+ O^{(3)}[U]. \tag{14}$$

$$\begin{pmatrix} \mathbf{A}^{\text{KS}} - \lambda & \mathbf{B}^{\text{KS}} \\ \mathbf{B}^{\text{KS}*} & \mathbf{A}^{\text{KS}*} - \lambda \end{pmatrix}\begin{pmatrix} U \\ U^* \end{pmatrix} = 0 \tag{30}$$

With $\mathbf{A}^{KS}$, B^{KS}, and λ all real, it is readily shown that Eq. (28) only is stationary with respect to a general variations, Eq. (29), if $U^{(I)}$ is either completely imaginary with $U^{(I)} = U^{(I)}_{im}$ or completely real with $U^{(I)} = U^{(I)}_R$.

In the first case the requirement of Eq. (29) reduces to the equation

$$(A^{KS} - B^{KS})U^{(I)}_{im} = \lambda_I U^{(I)}_{im}. \tag{32}$$

For pure density functionals $(A^{KS} - B^{KS})$ is a diagonal matrix with $(A^{KS} - B^{KS})_{ai,ai} = \varepsilon_a - \varepsilon_i$. Thus, for pure functionals Eq. (32) would afford $\lambda_I = \varepsilon_a - \varepsilon_i$ with the corresponding eigenvector $U^{(I)}$ containing the single element $U_{ai} = i$. We shall reject this set of solutions.

For $U^{(I)} = U^{(I)}_R$ we obtain the equation

$$(A^{KS} + B^{KS})U^{(I)} = \lambda_I U^{(I)}, \tag{33}$$

where we for the sake of economy has omitted the subscript R in $U^{(I)}_R$ with the understanding that all elements of $U^{(I)}$ are

I think there may be a problem here but I am happy to see that **[ZSK+09]** have understood the need to take a separate look at the real and imaginary parts.
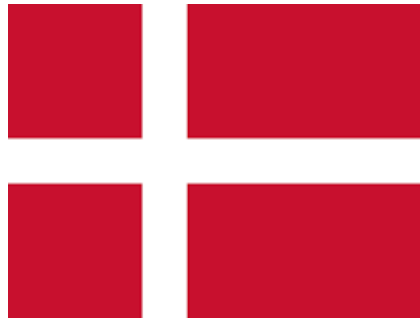
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Tom Ziegler   1945-2015

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⚙ Centos 🔷 Wiki ⊕ Emploi du temps ⊕ Docume... https://www.scm.com/doc/ADF/Input/Excitation_energies.html#cv-n-dft-constricted-variational-dft -deMon2k users' guide »

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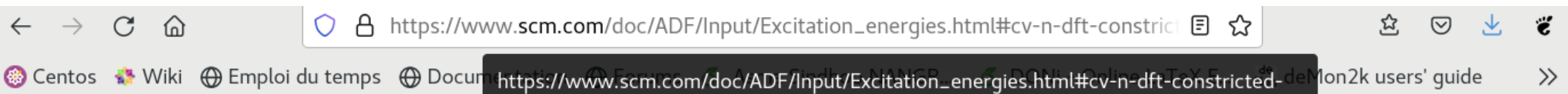
Applications   Products   Support   About us   Free trial

CV(n)-DFT: Constricted Variational DFT

HDA: Hybrid Diagonal Approximation

TD-DFT+TB, TDA-DFT+TB

sTDA, sTDDFT

CD spectra

MCD

> Analysis

Excited state (geometry) optimizations

Vibrationally resolved electronic spectra

(Hyper-)Polarizabilities, ORD, magnetizabilities, Verdet constants

Ligand Field and Density Functional Theory (LFDFT)

CV(n)-DFT: Constricted Variational DFT

In the constricted nth order variational density functional method (CV(n)-DFT) [19] [6] [20] the occupied excited state orbitals are allowed to relax in response to the change of both the Coulomb and exchange-correlation potential in going from the ground state to the excited state. This theory is not time-dependent nor is it based on response theory. It is instead variational in nature and has been termed constricted variational DFT or CV(n)-DFT.

Due to bugs in older versions it is important to use ADF2016.105 or later. In ADF2017 the relaxation density is a bit differently calculated than in ADF2016, which will slightly modify the results compared to ADF2016. In ADF2017 singlet-triplet excitations are added [21] There have been different working equations implemented in different modified versions of ADF. In ADF2016 and ADF2017 all CV-DFT excitation energies are calculated consistently, this is why some energies may differ from previously published values.

CV(n)-DFT requires an all electron basis set.

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PEDAGOGICAL

Failure of NIVR when there are quasidegeracies (open-shell, bond making/breaking)

Utility of 2nd quantization and diagrammatic techniques in WFT

Static vs dynamic correlation

Spin mulitiplets & CI for correct bond making/breaking

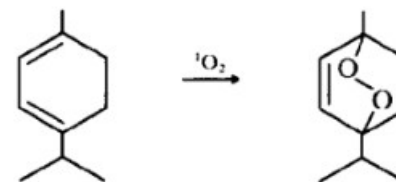MS-DFT, TD-DFT, and CV-DFT

RESEARCH

Diagrammatic analysis of MS-DFT

Because static correlation is needed to describe reactions such as this

THANK YOU

ASANTE

MURAKOZE

شكرا

MERCI